



**LEAD-FREE BISMUTH-BASED PEROVSKITE SATURABLE
ABSORBER FOR MODE-LOCKED FIBER LASER**

By

MAISARAH BINTI MANSOR

**Thesis Submitted to the School of Graduate Studies, Universiti Putra
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March 2024

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Perovskite single crystals, with their low defect density and absence of grain boundaries akin to top-quality silicon, offer exciting possibilities. Lead-based perovskite has shown promise in fiber lasers, but environmental and health concerns drive the search for lead-free alternatives with similar properties. This study introduces methylammonium bismuth bromide (MBB) as a lead-free alternative for saturable absorbers (SAs). MBB single crystals were synthesized with optimal results achieved at specific precursor ratios 2:3, and 3:3 of MaBr:BiBr.

MBB/PDMS composites were formed using different solvents, with MBB/PDMS: HEX and MBB/PDMS: TOL maintaining MBB perovskite's properties. These composites were deposited on optical fibers to fabricate SAs, exhibiting nonlinear properties. Characterization revealed transmission loss of 4.20 dB, saturation intensity (I_{sat}) of 200.03 MW/cm², and modulation

depth (MD) of 9.75 % for MBB/PDMS: HEX-SA. Meanwhile, MBB/PDMS: TOL-SA featured transmission loss of 3.58 dB, I_{sat} of 900.00 MW/cm², and MD of 19.30 % The SAs were incorporated into a ring cavity erbium-doped fiber laser (EDFL) and successfully generated stable ultrashort pulses pulse width (T_{pulse}) of 942.8 fs and 942.1 fs, respectively.

Long term stability test of the SA was then performed for MBB/PDMS: HEX-SA with higher SNR value (65.4 dB) compared to its counterpart. Stability tests under different lighting conditions were conducted for 16 weeks, comparing packaged (SA-WP) and unpackaged (SA-WOP) SAs. SA-WOP exhibited greater transmission loss deviation (1.00 dB vs. 0.79 dB) and greater mode-locked threshold deviation (50% at week 7 vs. 9% at week 14). An increase in MD by 6.00 % after 16 weeks attributed to light-induced perovskite bandgap decrease was observed for SA-WOP, while SA-WP displayed consistent decrease in MD by 4.65% due to regular perovskite degradation, which aligned with the observed pulse width deviation of 6.48% and 2.79% in the autocorrelation traces respectively.

This investigation offers insights for optimizing fabrication and packaging of lead-free bismuth-based perovskite SAs for fiber lasers and other applications.

Keywords: Bismuth-based perovskite, fiber laser, saturable absorber mode-locked fiber laser

SDG: GOAL 3: Good Health and Well-Being, GOAL 9: Industry, Innovation and Infrastructure

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**BISMUTH BERASASKAN PEROVSKITE BEBAS PLUMBUM
PENYERAP TEPU UNTUK OPERASI LASER TERKUNCI MOD**

Oleh

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Kristal tunggal perovskite, dengan ketumpatan kecacatan yang rendah dan ketiadaan sempadan bijian yang serupa dengan silikon berkualiti tinggi, menawarkan kemungkinan yang menarik. Perovskite berasaskan plumbum telah menunjukkan kesan yang terbaik dalam laser gentian, tetapi kebimbangan terhadap alam sekitar dan kesihatan mendorong pencarian alternatif yang bebas plumbum dengan sifat yang serupa. Kajian ini memperkenalkan methylammonium bismuth bromide (MBB) sebagai alternatif bebas plumbum untuk penyerap tepu. Kristal tunggal MBB telah disintesis dengan hasil yang optimum dicapai pada nisbah prekursor 2:3, dan 3:3 daripada $\text{MaBr}:\text{BiBr}$

Komposit MBB/PDMS telah dibentuk menggunakan pelarut yang berbeza, MBB/PDMS: HEX dan MBB/PDMS: TOL mengekalkan sifat perovskite MBB. Komposit ini didepositkan pada gentian optik untuk menghasilkan SA, mempamerkan sifat tak linear. Pencirian mendedahkan kehilangan penghantaran sebanyak 4.20 dB, keamatan tepu (I_{sat}) 200.03 MW/cm², dan kedalaman modulasi (MD) sebanyak 9.75 % untuk MBB/PDMS: HEX-SA. Sementara itu, MBB/PDMS: TOL-SA memaparkan kehilangan penghantaran sebanyak 3.58 dB, I_{sat} sebanyak 900.00 MW/cm², dan MD sebanyak 19.30 %. Penyerap tepu telah digabungkan ke dalam rongga cincin laser gentian berasaskan erbium dan berjaya menghasilkan denyutan yang stabil (τ_{pulse}) iaitu 942.8 fs dan 942.1 fs.

Ujian kestabilan jangka panjang penyerap tepu kemudiannya dilakukan untuk MBB/PDMS: HEX-SA kerana mempunyai nilai SNR yang lebih tinggi (65.4 dB) berbanding yang lain. Ujian kestabilan di bawah keadaan pencahayaan yang berbeza telah dijalankan selama 16 minggu, membandingkan penyerap tepu yang dibungkus (SA-WP) dan tidak dibungkus (SA-WOP). SA-WOP mempamerkan sisihan kehilangan penghantaran yang lebih besar (1.00 dB berbanding 0.79 dB) dan sisihan ambang terkunci mod yang lebih besar (50 % pada minggu ke-7 berbanding 9 % pada minggu ke-14). Peningkatan MD sebanyak 6.00% selepas 16 minggu disebabkan oleh penurunan celah jalur perovskite kesan daripada cahaya telah diperhatikan untuk SA-WOP, manakala SA-WP menunjukkan penurunan yang konsisten dalam MD sebanyak 4.65 % disebabkan oleh degradasi perovskit biasa, yang sejajar dengan lebar nadi yang diperhatikan. sisihan sebanyak 6.48% dan 2.79%

dalam surih autokorelasi.

Penyiasatan ini menawarkan pandangan untuk mengoptimumkan fabrikasi dan pembungkusan penyerap tepu perovskite berasaskan bismut tanpa plumbum untuk laser gentian dan aplikasi lain.

Kata Kunci: Bismuth berasaskan perovskite, laser gentian, penyerap tepu, operasi laser terkunci mod

SDG: MATLAMAT 3: Kesihatan Baik dan Kesejahteraan, MATLAMAT 9: Industri, Inovasi dan Infrastruktur

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depicting the relationship of average T_{pulse} and TBP for each week over 4-hours duration.



LIST OF ABBREVIATIONS

0D	0-Dimensional
2D	Two-Dimensional
3D	Three-Dimensional
AOM	Acoustic-Optic Modulator
ASE	Amplified Spontaneous Emission
AVC	Anti-Solvent Vapour-Assisted Crystallisation
BP	Black Phosphorus
BPF	Bandpass Filter
CB	Conduction Band
CFL	Compact Fluorescent Lamp
CNT	Carbon Nanotubes
CS	Conventional Soliton
DMA	N,N-Dimethylacetamide
DMF	N,N-Dimethylformamide
EDFA	Erbium-doped Fiber Amplifier
EDFL	Erbium-doped Fiber Laser
EDX	Energy Dispersive X-ray
EQE	External Quantum Efficiency
FESEM	Field Emission Scanning Electron Microscopy
FWHM	Full Widths Half Maximum
FWM	Four-Wave Mixing
GVD	Group Velocity Dispersion

HCVD	Hybrid Chemical Vapour Deposition
HOIPs	Hybrid Organic-Inorganic Perovskites
ISI	Intersymbol Interference
JCPDS	Powder Diffraction Standards
JDOS	Joint Density of States
LD	Laser Diode
LED	Light Emitting Diodes
LFHP	Lead-Free Halide Perovskite
LPE	Liquid-Phase Exfoliation
ME	Mechanical Exfoliation
MLFL	Mode-Locked Fiber Laser
MQW	Multiple Quantum Well
NLO	Nonlinear Optical
OC	Optical Coupler
OPM	Optical Power Meter
OSA	Optical Spectrum Analyzer
PC	Polarization Controller
PDL	Polarization Dependent Loss
PDMS	Polydimethylsiloxane
PLD	Pulse Laser Deposition
PLQY	Photoluminescence Quantum Yields
PLS	Pulsed Laser Source
PMMA	Polymethyl Methacrylate
PQD	Phosphorene Quantum Dot

PTFE	Polytetrafluoroethylene
PVA	Polyvinyl Alcohol
RBW	Resolution Bandwidth
SA	Saturable Absorber
SBS	Stimulated Brillouin-Scattering
SD	Standard Deviation
SESAM	Semiconductor Saturable Absorber Mirror
SNR	Signal to Noise Ratio
SPM	Self-Phase Modulation
TBP	Time Bandwidth Product
TE	Transverse Electric
TI	Topological Insulators
TM	Transverse Magnetic
TSSG	Top-Seeded Solution-Growth
UV-Vis-NIR	Ultraviolet-Visible-Near Infrared
VB	Valence Band
VBW	Video Bandwidth
VOA	Variable Optical Attenuator
WDM	Wavelength Division Multiplexing
XPM	Cross-Phase Modulation
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Overview

Pulsed lasers have evolved into one of the most versatile tools used in science and engineering and proven to be indispensable as they transform many fields. For example, their short and highly energetic pulses are used in the transmission of information over long distances, which has helped to propel the information age. Meanwhile in manufacturing, pulse lasers are used to deliver massive amounts of energy to extremely small areas for cleaning, printing, and cutting while the short duration pulses have enabled high-speed imaging for physical characterization of materials. There are three basic methods for producing pulsed sources: Q-switching, gain switching, and mode locking. The focus of this thesis will be on mode-locked fiber lasers (MLFLs).

MLFLs are primarily intended to produce ultra-short duration light pulses and can achieve pulse widths of a few femtoseconds [1] and peak powers in the kW range [2]. Ultra-short and high-power pulses have many applications, including observing chemical reactions on extremely short time scales using soft x-rays with wavelengths ranging from 4 to 40 nm. Micromachining with short ultraviolet (UV) wavelengths in the 300 nm range can attain very fine feature sizes via photochemical reactions, whereas laser ablation processes use a variety of wavelengths ranging from the UV to 10.6 μm CO₂ lasers.

Medical imaging has also made extensive use of MLFLs, whose typical wavelength applications range from visible to 900 nm, or near infrared (NIR). Terahertz generation has used ultra-short pulses, as has Doppler free precision spectroscopy, which both use a wide range of IR frequencies. High repetition rate MLFLs are widely used in high-capacity telecommunication and optical communications systems, as well as photonic switching devices that operate in the telecom C-band, which is centered at 1550 nm.

There are two types of MLFLs; actively and passively mode-locked fiber lasers. Active MLFLs use active modulation of light within a laser cavity to generate pulsed output, whereas passive MLFLs use the nonlinearity property of low-dimensional materials known as saturable absorption to attain mode-locking. Saturable absorbers (SA) are nonlinear optical devices featuring intensity dependence. The optical absorption of this device decreases with increasing input light intensity. While they are occasionally used in optical regeneration schemes [3], all optical switching [4], optical pulse shaping, and noise suppression [5], they are mostly used as passive components in MLFLs due to their simplicity. The understanding of SAs can be enhanced by picturing a basic two-state system involving a ground state and an excited state. When subjected to low optical excitation, carriers get induced to transverse the band gap, moving from valence band to the conduction band. Following this, the carrier generally reverts to the ground state through thermalization at a constant rate. Yet, if the optical excitation reaches a certain intensity, a substantial temporary population of carriers gathers in the conduction band. In this scenario, the material could reach a saturation point due to reduction in

ground state carriers caused by the high optical excitation. In theory, any material can demonstrate saturable absorption as long as it has the ability to tolerate heat accumulation throughout the thermalization process.

Mocker and Collins reported mode-locking with a SA for the first time in 1965 [6] using a rhodamine-based organic dye. Organic dyes were the dominant SA medium used in MLFLs until the late 1980s, but they had several limitations. Dyes have wavelength limitations and are typically only effective in the visible and near-infrared ranges. Low damage thresholds are also an issue in light sensitive organic dyes, resulting in power constraints and short device lifetimes. Dyes are also frequently highly toxic; this, combined with the need to replace dye cells on a regular basis, makes them particularly difficult to work with. Advances in semiconductor growth processes and band gap engineering led to the development of the semiconductor saturable absorber mirror (SESAM) in the early 1990s [7]. These devices use multiple quantum well (MQW) or quantum dot structures, which allow for precise band gap control, thermalization processes in the 10 to 100 of fs range, and can be robustly designed for long device lifetimes. SESAMs can be fabricated to operate in the NIR up to the 1550 nm C-band for telecom applications, depending on the semiconductor material used and the device geometry. Individual SESAMs can also be tunable over 100 nm. However, the disadvantages of SESAMs are the long recovery time (~picosecond level), narrowband operation (<100 nm), complicated fabrication and low damage threshold [8]. Carbon nanotubes (CNTs) have demonstrated excellent nonlinear optical properties among emerging materials [9]–[12]. However, the nonlinear response of CNTs is

affected by their diameters and chirality, which can cause CNTs to fail to work at the desired lasing wavelength and increase non-saturable losses [13]. With the advent of two-dimensional (2D) atomic crystals such as graphene [14], [15] topological insulators (TIs) [16], [17], transition-metal dichalcogenides [18], [19] and black phosphorus (BP) [20], [21] have demonstrated tremendous potential in broadband nonlinear optical responses and applications in ultrafast photonics. Although the nonlinear materials mentioned above can be used to modulate laser systems, the optical community is still on the hunt for low-cost nonlinear materials with simple fabrication method, broadband response, tunable nonlinear modulation depth, low saturation intensity, and high damage threshold.

In this regard, it is of research interest to investigate new functional materials as a mode-locker with desired properties. In recent years, hybrid organic-inorganic perovskites, photosensitive semiconductor crystals with the structural formula ABX_3 , where A, B, and X are organic and inorganic ions, have gotten a lot of attention for low-cost and high-performance optoelectronic devices [22]–[25]. The fundamental optoelectronic properties of perovskite and their applications have been extensively studied [22]–[24] and recent years have seen extremely rapid progress in perovskite solar cells with energy conversion efficiencies exceeding 20% [26]. This material is regarded important in many applications such as photodetectors [27], light-emitting diodes [28], random lasers [29], and other applications [30], [31].

1.2 Problem Statement

Perovskite single crystals bring forth exciting possibilities due to its low defect density and absence of grain boundaries which are comparable to the best performing quality of silicon [32]–[35]. The properties of single crystals, such as high carrier mobility [32], [36], [37], long carrier diffusion lengths, and long carrier lifetimes [33], [34], [38], make them advantageous in solar cells [38]–[41], photodetectors (PDs) [42]–[44], light emitting diodes (LEDs), and lasers [45]–[47]. These studies demonstrate that perovskite single crystals are promising building blocks for photoelectric conversion applications. In the field of fiber lasers, cesium lead bromide (CsPbBr_3) perovskite was employed as nanosheet-based SA to generate mode-locked pulses at 1 μm [48] with modulation depth of 13.1%, and was also reported to possess a modulation depth of 2.5% in the form of nanocrystal-based SA [49]. Both works prove it is desirable choice to be efficient SA candidate's materials for fiber lasers. However, there are some environmental concerns and health risks about using lead-based perovskite in large-scale applications due to possible lead contamination from leakage of damaged or disposed devices [50]–[52]. To date, researchers are now exploring alternatives to replace lead in perovskite-based applications. Recently, researchers are looking into a promising lead-free alternative for light absorber in optoelectronic applications. The new material of methylammonium bismuth iodide ($\text{MA}_3\text{Bi}_2\text{Br}_9$) with contain environment friendly and chemically stable bismuth (Bi^{3+})-based and has $6s^2$ valence electronic configuration similar to Pb^{2+} making it a potential replacement [23].

Additionally, the widely used fabrication process of SA in which single crystals are mixed in with a certain solvent before added to a polymer matrix is bound to affect the properties of the single crystal depending on its polarity [53]. A comprehensive report on the varied effects of commonly available solvents of different polarity classes (i.e., polar protic, polar aprotic, and non-polar) on perovskite single crystal properties for SA fabrication is also nonexistent. Therefore, it is fundamental to investigate this effect to determine the condition and properties of the perovskite single crystals before and after the SA fabrication process to gain insights on optimization of perovskite-based SA for prospective applications.

Despite the outstanding photoelectric and optoelectronic properties of perovskite, the instability of this material in the presence of environmental elements, such as light, oxygen, heat, and moisture, limits its full potential for many applications [54]–[56]. In particular, previous study shows methylammonium (MA) lead triiodide (MAPbI_3) perovskite immediately decomposes into MA, HI and PbI_2 in a humid environment which would require proper encapsulation via a waterproof coating or composite that would not impede its performance [57]. Perovskites have also shown minimal instability in indoor condition under regular visible light LED exposure and but accelerated degradation in outdoor condition under visible and UV light exposure [56], [58]–[60]. Therefore, different types of environmental exposure can induce different degradation pathways, thus it is important to examine the degradation of the perovskite samples under each condition to have a full assessment of the stability of the material. However, the effects of ambient

indoor lighting towards the performance of perovskite-based SAs in generating ultrashort pulse in fiber laser systems remains to be investigated.

1.3 Research Aim and Objectives

The overall aim of this investigation is to synthesize a lead-free halide-based perovskite; methylammonium bismuth bromide, $\text{MA}_3\text{Bi}_2\text{Br}_9$ (MBB) to replace lead-based perovskites in optical applications, specifically in the fabrication of tapered fiber-based SAs. The role of different solvent classes in the fabrication process of the SA and its relation to the SA properties and functional performance in generating optical pulses in erbium-doped fiber laser (EDFL) cavity is analyzed. The fabricated SA samples were also evaluated for its degradation under ambient light for long term operation and its impact towards pulse performance stability.

The overall aim can be achieved through the following objectives:

- i. To synthesize lead-free MBB perovskite single crystals via slow evaporation method by precursor ratio variation.
- ii. To evaluate the effect of different solvent classes in the fabrication process of MBB perovskite polydimethylsiloxane (PDMS) on the SA properties.

- iii. To investigate the functionality of the fabricated MBB/PDMS-SAs in erbium-doped fiber cavity for ultrashort pulse laser generation.
- iv. To characterize the degradation of MBB/PDMS-SA in the presence of ambient indoor lighting and assess its impact towards pulse performance stability.

1.4 Research Scope

This research focuses on the two highlighted subsets in Figure 1.1. The first subset is the use of a ring-type Erbium-Doped Fiber Laser (EDFL) setup for ultrashort pulse fiber laser generation. Ring-type EDFLs are chosen because their mechanism for ultrashort pulse fiber laser were well understood. The second subset is the use of passive mode-locking based on real SAs. Real SAs allow for greater control of pulse performance against environmental changes compared to artificial SAs. A tapered fiber is chosen as the substrate for the real SAs because it promotes high nonlinearity and yields a strong evanescent field for light-matter interaction at the tapered region. In this work, bismuth-based halide perovskite is synthesized and fabricated as SA by spin coating the perovskite-polymer onto the tapered fiber. The fabrication process of SA was performed with various solvent classes to determine the solvent effect on perovskite properties. Finally, the optical performance of the fabricated perovskite-based SA was observed and analyzed in the presence of environmental elements such as ambient light. A bismuth-based halide

perovskite-PDMS tapered fiber SA will be evaluated for generating a stable mode-locked pulse laser in the C-band wavelength region.

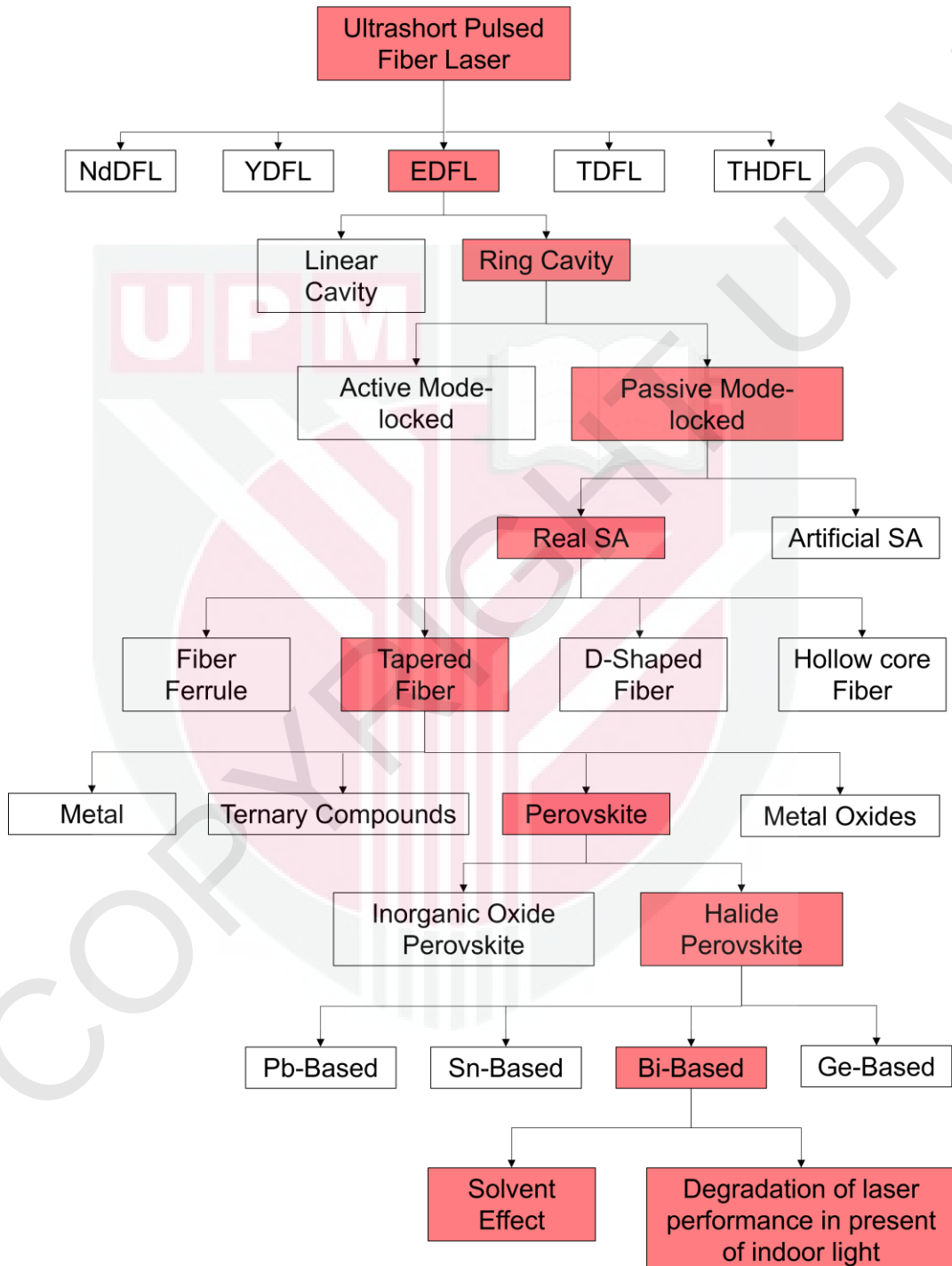


Figure 1.1 : Scope of Work

1.5 Organization of Thesis

Chapter 1 provides background information on lasers and an overview of mode-locked fiber lasers. It also discusses the latest trends in passive mode-locking fiber laser SA fabrication, the motivation for this study, and the research objectives and scope of work

Chapter 2 discusses the optical properties of perovskite and its synthesis methods based on different applications usage. Additionally, the experimental and theoretical of ultrashort pulse fiber lasers, including the working principle of lasers, the effects of pulse propagation in optical fibers, soliton formation, and SA fabrication techniques for mode-locked fiber lasers. The reported perovskite material synthesis and fabrication techniques of halide perovskite-based SAs for ultrashort pulse generation are summarized.

Chapter 3 elaborates on the synthesis of single crystal bismuth-based halide perovskite using slow evaporation method by varied BiBr_3 molar ratio, for which the formation of the single crystals in the solvent liquid is explained in detail.

Chapter 4 describes how to fabricate a bismuth-based halide perovskite-based SA and its mode-locking performance in an erbium-doped fiber laser (EDFL) cavity. The solvents used to prepare the perovskite composite are varied, and the SA is embedded on a tapered fiber to generate femtosecond pulses. All the findings are discussed and analyzed.

Chapter 5 elaborates the degradation of perovskite SA in the presence of ambient indoor lighting and compare with other perovskite SA without any exposure to UV light in term of laser performance.

Chapter 6 summarizes the key findings of this research and suggests directions for future work.



CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter begins with an overview of perovskites featuring outstanding hybrid organic-inorganic characteristic and the instability and toxicity of lead-based perovskites. The alternative lead-free halide perovskites are discussed extensively including the different growing techniques in thin film and single crystals with their usage in different optoelectronic applications. In order to generate ultrashort pulses, it starts with development of pulse fiber lasers generation. Next, fiber characteristics that affect pulse propagation, including nonlinear effect and dispersion effects are discussed. A general description of self-phase modulation and the insight of soliton are noted. The implementation of fiber-based SA, and recent studies related with halide perovskite as SA is also elaborated in this chapter.

2.2 Hybrid Organic-Inorganic Perovskites (HOIPs)

Hybrid organic-inorganic perovskites (HOIPs) are solution-processable materials that contain earth-abundant elements while exhibiting remarkable semiconducting and light-absorption characteristics [61]. In HOIPs, the A-site is occupied by an organic cation (typically MA and FA). The B-site created with the Group 14 elements Ge, Sn, Bi, and Pb, along with a halogen Cl, Br, and I

on X-site, are the most important. Because the organic ion's valence state is +1, the B cation needs to adopt the +2 or +3 state. Figure 2.1 shows the crystal structure of perovskites and the ideal ABX_3 perovskite structure is made up of layers of AX_3 atoms arranged in a cubic close-packed structure, with the B cations filling in the octahedral gaps between the layers. This creates a three-dimensional (3D) network of BX_6 octahedra connected at the corners.

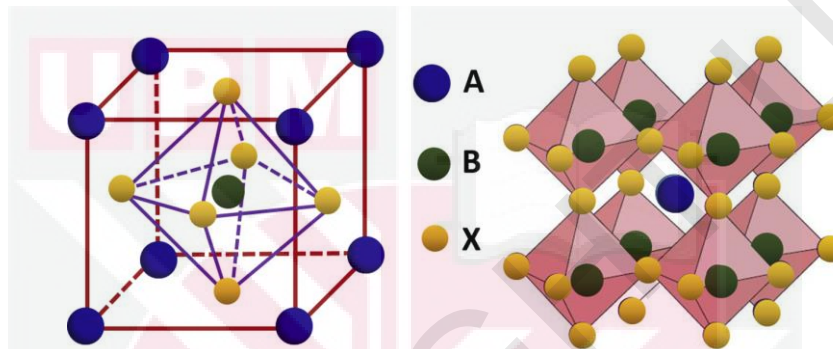


Figure 2.1 : Crystal structure of perovskites with chemical formula of ABX_3 [62]

2.2.1 Exceptional Properties of Hybrid Lead Halide Perovskite and Their Origin

The excellent performance and adaptability of lead halide perovskites attributed to their suitable bandgap [63], large absorption coefficient, low exciton binding energies [64], long electron and hole diffusion lengths [65] and high mobilities [66], [67], and absence of deep defects in the band gap. The primary cause for these results is related to the peculiar orbital properties of the Pb^{2+} cation [68]. At 450 nm, the absorption coefficient of $CH_3NH_3PbI_3$ is approximately $2 \times 10^5 \text{ cm}^{-1}$, which is greater than that of most common semiconductors [69].

Perovskites have strong optical absorption properties from the visible to the near infrared (IR) region due to their high optical absorption coefficient. This makes them excellent light absorbers for solar cells and photodetectors [70], [71], [72]. Figure 2.2 compares the effective absorption coefficient of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film (the most commonly used perovskite) to various materials. $\text{CH}_3\text{NH}_3\text{PbI}_3$ has a light absorption coefficient that is comparable to or higher than other materials above its bandgap of 1.57 eV. Just below the bandgap, there is a sharp shoulder followed by a near-ideal exponential trend towards lower energies. Furthermore, the Urbach energy determined from the slope of the exponential component of the curve is around 15 meV, while amorphous silicon (a-Si) has a value of 40-45 meV. This shows that the structural disorder in this class of materials is quite low [70].

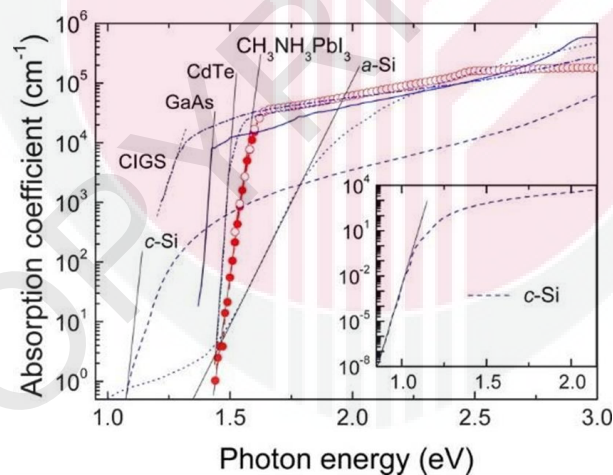


Figure 2.2 : Optical absorption coefficient of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ in comparison with other materials. (Taken from [70]).

The optical absorption of a material is strongly dependent on its electronic structure. In the 1st generation solar cell absorber made from silicon (Si), the optical absorption is from the Si p orbital and s orbital. Nevertheless, since Si

is an indirect bandgap semiconductor, the absorber layer required is two orders more compared to a direct bandgap material, increasing its cost significantly. The 2nd generation (GaAs) and 3rd generation of halide perovskite (methylammonium lead iodide (MAPbI_3)) both have direct bandgaps and thus have stronger optical absorption than of Si. In lead halide perovskites, the I p to Pb p transitions are particularly favourable because the I p orbitals are strongly localized on the I atoms and the Pb p orbitals are strongly localized on the Pb atoms. Furthermore, the Pb s to Pb p transition is an intra-atomic transition, which means that it does not require the electron to move between different atoms. This makes the Pb s to Pb p transition more likely to occur than an inter-atomic transition, such as an s to p transition illustrated in Figure 2.3 [73].

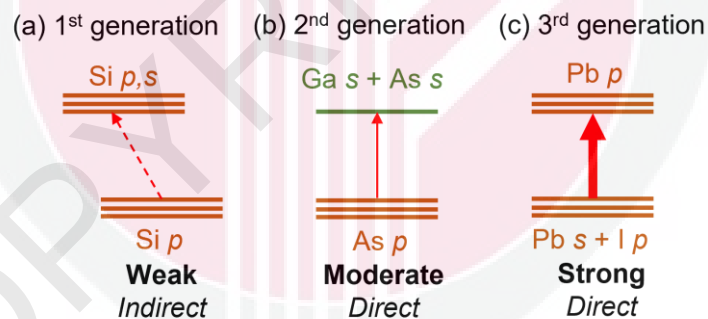


Figure 2.3 : The schematic optical absorption of (a) 1st generation, (b) 2nd generation, and (c) 3rd generation of halide perovskite solar cell absorbers [73].

One of the most attractive features of perovskites is their tunable bandgap, which makes them ideal for tandem solar cells. The bandgap of the most common perovskite, MAPbI_3 , is around 1.57 eV. For example, the bandgap of the material can be slightly tuned by adjusting the A-site cation. When the A-

site cation decreases from FA to MA to Cs, the bandgap of the material increases from 1.48 eV to 1.57 eV to 1.73 eV [74]. The bandgap of the material is also significantly affected by changing the metal cation from Pb to Sn [28]. For example, MAPbI₃ has a bandgap of 1.57 eV and MASnI₃ has a bandgap of 1.35 eV, the bandgap of the alloyed perovskite MAPb_{0.5}Sn_{0.5}I₃ is significantly lower at 1.17 eV [75]. Perovskites can also be used as light emitters in LEDs and lasers. The emission spectrum of perovskite LEDs and lasers can be tuned across the visible and near-infrared regions using the same technique as for light absorbers. The emission wavelength of all-inorganic perovskite CsPbX₃, where X is Cl, Br, or I, or a mixture of these halides (Cl:Br or Br:I), cover the entire visible range from 400 to 780 nm which makes perovskites promising materials for full-color displays and lighting applications [76], [77], [78]. All-inorganic perovskite CsPbX₃ (X = Cl, Br, and I) also shows a property of tunable wavelength, high photoluminescence quantum yields (PLQYs around 90%) and narrow full widths at half maximum (FWHMs ~20 nm). This makes it a promising material for full-color displays with BT2020 standard [79], [80], [81].

2.2.2 Instability and Toxicity of Lead (Pb²⁺)

Despite all of the amazing properties of lead (Pb)-based perovskite as an absorber, lead toxicity is a major concern for commercial usage. The main reason for the toxicity of perovskite solar cells is the presence of lead, which is harmful to the environment and raises concerns about their long-term viability. Lead is a common component in hazardous materials, such as

cadmium, which are now used in commercial photovoltaic applications. However, lead's high solubility in water and ease of entering the environment make it potentially more dangerous. The problem is exacerbated by the material's poor stability in humid environments. A potential failure of the encapsulation of a perovskite solar cell could release Pb^{2+} ions into the soil and groundwater. Long-term damage will occur to air, land and water once lead enters the environment by rainwater and also have negative consequences for human health [82], [83].

Lead exposure is especially dangerous for children, with a 70% chance of absorption. In adults, the risk is much lower, with less than 20% absorption. Figure 2.4 shows images from the US Department of Health and Human Services that summarize the likely sources of lead exposure in children [84]. Lead poisoning can go unnoticed, but can cause learning disabilities, behavioral problems, deformed bones, slow growth, seizures, coma, and even death. This is a major barrier to the commercialization of perovskites [82]. As a result, eliminating lead from perovskites is a top priority for researchers.

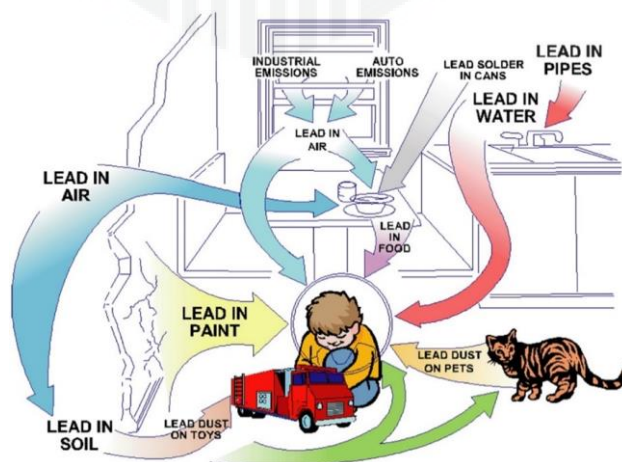


Figure 2.4 : Environmental sources of childhood lead exposure [84]

2.3 Alternative Lead-Free Halide Perovskite (LFHP)

Over the years, researchers have tried a variety of ways to make perovskites safer, including reducing lead leakage [85], [86], replacing lead partially or completely to reduce its effects [87], [88], and finding other materials that can serve the same role as lead [89], [90]. However, the most sustainable solution is to develop lead-free halide perovskites (LFHPs), which have recently received a lot of attention [91].

The study on LFHPs is still in its early stages and has a long way to go before it can be realised. Pb^{2+} , which is toxic, can be replaced with less hazardous metal ions. These alternatives include divalent ions like tin (Sn^{2+}) or germanium (Ge^{2+}), as well as trivalent ions like bismuth (Bi^{3+}) or antimony (Sb^{3+}). In terms of electrical properties similar to Pb^{2+} , Sn^{2+} and Ge^{2+} are the most promising. The primary criteria in the quest for novel materials include suitable oxidation states, ionic sizes, the presence of ns^2 electrons, and a connected lattice, which resulted in the defect tolerant properties exhibited in lead halide perovskites.

2.3.1 Tin (Sn) based Halide Perovskites

Recent experiments have shown that Sn^{2+} based perovskites have direct bandgaps between 0.75 eV and 1.3 eV [92]. Tin has an electrical configuration $[\text{Kr}] 4\text{d}^{10} 5\text{s}^2 5\text{p}^2$ (Kr, krypton) that is similar to lead, and hence the most likely replacement. Tin-based perovskites exhibit optoelectronic features similar to

lead-based, such as small exciton binding energy, high charge carrier mobility, and high light absorption [93]. These characteristics make Sn-based perovskites suitable for other optoelectronic applications. The earliest study on Sn-based perovskites in solar cells was on $\text{CH}_3\text{NH}_3\text{SnI}_3$, which had a 6.4% efficiency [94]. $\text{CH}_3\text{NH}_3\text{SnI}_3$ [95] microcrystals also had grown directly on D-shaped as saturable absorbers for generating mode-locked pulses in fiber lasers with an energy efficiency of 5.6%.

Sn, on the other hand, differs from lead in fundamental atomic characteristics. Despite the promises of Sn^{2+} -based perovskites, the material was exceedingly unstable in air due to oxidation of +2 Sn to +4 states (Equation 2.1) and in the presence of oxygen (Equation 2.2), resulting in high system instability and so limiting their application [96], [97], [98]. The presence of +4 Sn caused variable self-doping of the material. Recombination with these self-doped carriers reduced diffusion lengths to 30 nm and mobility to $1.6 \text{ cm}^2/\text{Vs}$, both of which are much lower than MAPbI_3 .



In 2016, Jellicoe et al. synthesized an all inorganic CsSnX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) nanocrystals investigating their spectral tunability via quantum confinement effects and anionic composition control [99]. They demonstrated that by changing the halides from Cl to Br, the bandgap could be tuned from visible to

near-IR region. Unfortunately, because to the dynamic character of ligand absorption and desorption processes, most colloidal Sn-based nanocrystals tend to precipitate over time, up to two weeks [100]. Furthermore, when Sn-based nanocrystals were exposed to ambient conditions, Sn^{2+} quickly converted to Sn^{4+} , resulting in decomposition of nanocrystals. Moreover, due to Sn instability, synthesizing Sn-based single crystals in an ambient atmosphere is difficult.

2.3.2 Germanium (Ge) based Halide Perovskites

Ge was also explored as a viable candidate to make perovskites due to its superior optoelectronic characteristics [101], [102], [103], [104]. Ge^{2+} -based LFHPs showed a power conversion efficiency (PCE) of about 0.11% (for CsGeI_3) and 0.2% (for MAGeI_3) [102]. In the ambient environment, Ge^{2+} also undergoes rapid oxidation to Ge^{4+} , resulting in severe device instability. The problem is exacerbated by its low solubility in polar solvents, which makes proper film formation difficult.

The majority of lead alternative research has been concentrated on Sn or Ge. The inert pair effect, which is responsible for the stability of the +2 state of lead, is known to decrease as we move up in the group. As a result, Sn^{2+} and Ge^{2+} are extremely unstable and oxidize to +4 ions. These +4 ions can behave as traps, causing recombination and restricting performance. Zeng et al. showed that it is possible to tune the bandgap of perovskite materials by mixing Ge and Sn and the bandgap of these mixed-composition perovskites can vary from 0.9

eV to 3.15 eV [105]. $\text{RbSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$, for example, is projected to have a maximum PCE up to 25% [105]. The inclusion of Ge in Sn-based perovskites also helps to reduce the number of defects in the material. This is because Ge and Sn have a synergistic effect [96], [106]. Compositional engineering methods have been used to obtain longer carrier lifetimes, and a record PCE of 7.9% was recently announced [106] but Ge^{2+} based perovskites cannot function on their own.

2.3.3 Antimony (Sb) based Halide Perovskites

Other feasible possibilities include Sb^{3+} , which has a similar electronic structure to Pb^{2+} . It was predicted that the existence of ns^2 electrons would provide them with lead's defect tolerant characteristic. Sb-based perovskites, also known as $\text{A}_3\text{Sb}_2\text{X}_9$ compounds, have a dimer structure is formed by two perovskite units that are fused together at a common octahedron or a layered structure is formed by stacking perovskite units on top of each other which are being investigated for usage in photovoltaic applications. Hebig et al. used solution technique to synthesize $\text{MA}_3\text{Sb}_2\text{I}_9$ perovskite with promising optoelectronic characteristics. Sb-based perovskites have wide bandgaps and low film quality, which has resulted in poor photovoltaic performance when used as absorbers in solar cells [107]. Some of these limitations have been addressed to some extent by adding hydroiodic acid (HI) to $\text{A}_3\text{Sb}_2\text{I}_9$ during solution preparation and optimizing the synthesis procedures [108], [109]. However, Sb-based halide perovskites known as “defect perovskites,” and indeed there are high contents of deep-level defects in the $\text{A}_3\text{B}_2\text{X}_9$ structure

that restricting photovoltaic performance [110]. To achieve good performance with these kinds of compounds, rigorous control over stoichiometry employing optimal manufacturing conditions would be required.

2.3.4 Bismuth (Bi) based Halide Perovskites

Researchers have discovered that Bi is a more stable and non-toxic alternative to Pb in perovskite solar cells. Bi has a similar electronic structure and ionic radius to Pb, and it can substitute for Pb^{2+} in the general formula $\text{A}_3\text{Bi}_2\text{X}_9$ [111]. Recently, Bi-based perovskite are promising candidates for lead-free halide perovskites (LFHPs) [112], [113], [114]. Some of the earliest studies synthesized $\text{MA}_3\text{Bi}_2\text{I}_9$ and $\text{Cs}_3\text{Bi}_2\text{I}_9$ as absorbers for optoelectronic devices [113], [114]. The study of $\text{Cs}_3\text{Bi}_2\text{I}_9$ as an absorber in solar cells began steadily, with initial PCE of around 1.09% [113]. This poor performance is likely due to the wide bandgap (around 2 eV) of the absorber [115]. Researchers have since attempted to improve the photovoltaic performance of $\text{MA}_3\text{Bi}_2\text{I}_9$ and $\text{Cs}_3\text{Bi}_2\text{I}_9$ through by bandgap engineering via doping [116], or by varying the stoichiometries of the precursors in the solution [117]. This resulted in significantly better device performance and laid the door for continued study into these materials and their derivatives. Despite poor photovoltaic performance, these materials demonstrated remarkable ambient stability at 50-60% relative humidity.

Ahmad et al. proposed a two-step method for producing stable $\text{MA}_3\text{Bi}_2\text{I}_9$ films with enhanced morphology and surface coverage, which achieved a power

conversion efficiency (PCE) of 0.41% [118]. Another effective method was the vapor-assisted solution process, which produced highly uniform thin films of $\text{MA}_3\text{Bi}_2\text{I}_9$ [119]. Researchers made a significant breakthrough when they used $\text{CH}_3\text{NH}_3\text{I}$ vapor treatment to obtain $\text{MA}_3\text{Bi}_2\text{I}_9$ films from as-deposited BiI_3 films. This modified approach produced absorbers with a reported PCE of about 3.17% [119]. Zhu et al. tuned the photovoltaic properties of silver bismuth iodide (ABI) perovskites by changing the $\text{AgI}:\text{BiI}_3$ precursor ratios in the solution. This resulted in crystallization in different space groups and structures, namely $\text{Fd-}3\text{m}$ hexagonal when the $\text{AgI}:\text{BiI}_3$ ratio is 1:2 and $\text{R}3\text{m}$ hexagonal when the $\text{AgI}:\text{BiI}_3$ ratio is 2:1 [120], [121]. For $\text{R}3\text{m}$ -based absorbers, the highest PCEs achieved were 2.1% [120].

2.4 Degradation of Emerging Perovskite Material

Moisture, light, heat, and oxygen are the most significant elements that degrade perovskite, as shown in Figure 2.5. These forces destroy perovskites by a number of mechanisms such as hydration, decomposition, polymorphic transformation, and oxidation. While the degradation of Pb-based hybrid perovskites has been extensively explored in recent years, knowledge of the degradation of the perovskites are very limited [122], [123], [124], [125].

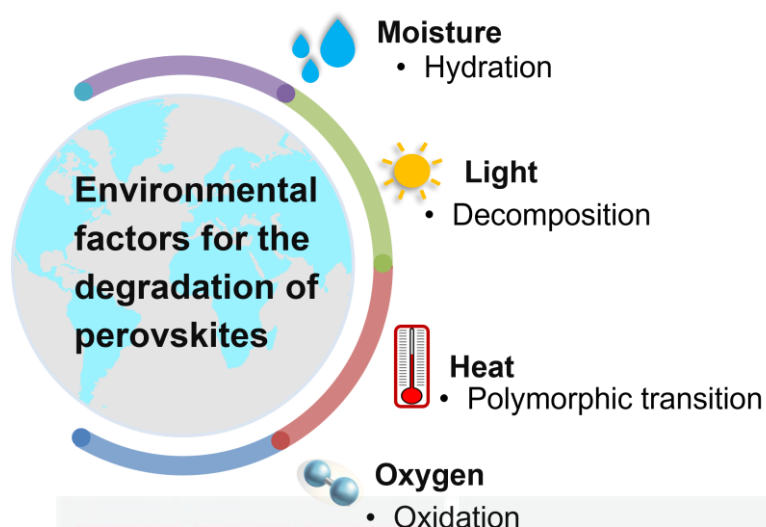


Figure 2.5 : Environmental factors that are responsible for the degradation of perovskite materials.

CsSnI_3 , a Pb-free perovskite material as discussed earlier in Section 2.3.1 with 1.3 eV optical bandgap, relatively strong carrier mobility, and high thermal stability due to its all-inorganic nature and strong covalent/ionic bonding in the crystal structure. However, when exposed to air, CsSnI_3 'black' phase rapidly transforms to CsSnI_3 'yellow' polymorph. Meanwhile, in the presence of oxygen, Sn^{2+} in CsSnI_3 can be particularly vulnerable to oxidation to Sn^{4+} , changing it to Cs_2SnI_6 [126], [127], [128]. Furthermore, it is probable that moisture in the environment infiltrates CsSnI_3 perovskite thin films, generating hydrates and eventually decomposing CsSnI_3 to metal halides. These degradation pathways may occur concurrently, resulting in a fast drop in PCE of the thin film. In cases where the ambient was erratic, high-PCE perovskite thin films based on Sn-containing organic-inorganic halide perovskites, MASnI_3 or FASnI_3 exhibited degradation within minutes when not encapsulated. Furthermore, the stability and degradation of several other Pb-free perovskite candidates, such as CsGeI_3 , $\text{CsSn}_x\text{Ge}_{1-x}\text{I}_3$, $\text{Cs}_2\text{TiI}_{6-x}\text{Br}_x$, and

$\text{Cs}_2\text{AgBiBr}_6$, have received little attention [103], [105], [129]. Their resistance to major environmental elements (moisture, light, heat, and oxygen) and probable degradation mechanisms have not been adequately established, which will be a rich topic of research. The investigation of the stability of these emerging perovskites will result in significant scientific discoveries that will guide the development of new Pb-free, stable perovskites single crystals.

2.5 Synthesis of Perovskite

2.5.1 Growth of Perovskite Thin Film via Deposition Techniques

Figure 2.6 shows two different methods for spin-coating perovskite on substrates: one-step and two-step coating. In the one-step coating process, a solution of perovskite containing $\text{CH}_3\text{NH}_3\text{I}/\text{PbI}_2$ (in a 1:1 molar ratio) in N,N-dimethylacetamide (DMA) is spin-coated onto a mesoporous TiO_2 layer. In the two-step coating process, firstly a spin coated solution of PbI_2 in N,N-dimethylformamide (DMF) onto the substrate. This PbI_2 layer is then transformed into perovskite by spin-coating a solution of $\text{CH}_3\text{NH}_3\text{I}$ onto it using either dip-coating [130] or spin-coating [131]. In the early days of perovskite solar cells, researchers realized that it was difficult to control the nucleation and crystallization of the perovskite layer in the one-step coating method. This led to a lot of research into developing better methods. The two-step spin-coating method is a well-defined method because the process is quantitatively controlled. This is in contrast to the dip-coating method, which is less controlled.

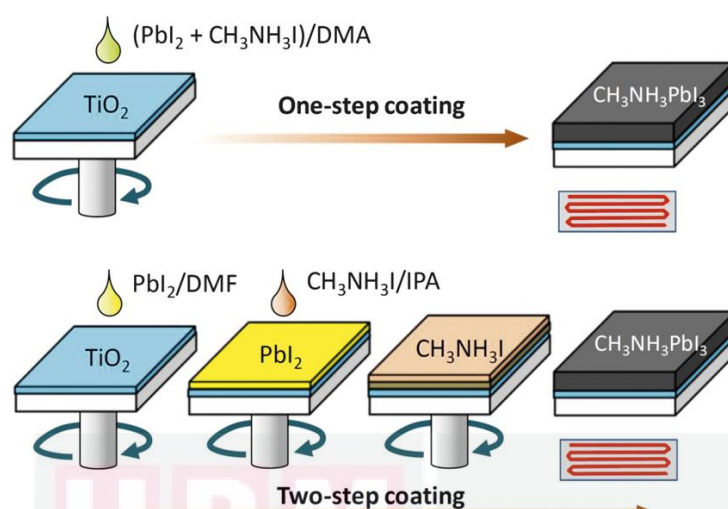


Figure 2.6 : Schematic of perovskite thin film growth using solution process methods: (a) one-step coating method and (b) two-step coating method [132], [133]

The second deposition method which is thermal evaporation method is a unique method to deposit perovskite materials without the use of any solvent [134]. Figure 2.8 shows a dual-source thermal evaporation system. In this system, MAI and PbX_2 are evaporated simultaneously at high vacuum from two separate sources onto rotating substrates. This method can produce perovskite films with better morphology and higher surface coverage than films deposited using the conventional one-step solution process (without the use of any treatment) by controlling the deposition rates and times for the two sources. This method may coat homogenous perovskite films over large substrates surfaces of sizes of $1\ \mu\text{m}$ and beyond. This method, however, has certain drawbacks. It is frequently challenging to achieve the correct compositions of the final perovskite films by balancing the organic and inorganic rates. Furthermore, the organic salt may not be thermally stable up to the temperatures required for evaporation in some circumstances, rendering

this technique impractical for a number of systems. Nonetheless, this approach has been found to have efficiency of up to 20% [135]. It is emphasized that increasing the number of sources can increase the complexity of perovskite [136].

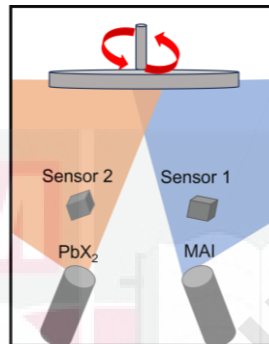


Figure 2.7 : Setup of the machine for perovskite thin film growth by dual-source thermal evaporation [134]

Another innovative way to deposit perovskite films is to use a vapor-assisted solution process (VASP) [137]. In this method, an inorganic film (PbI_2) is deposited on the substrate using either a solution process or single-source thermal evaporation then the inorganic film is converted into perovskite by exposing it to organic vapour (MAI) (see Figure 2.8 (a)). This method produces a more uniform perovskite film with grain sizes as small as a micron. This technology was later improved into a more scalable variant called hybrid chemical vapor deposition (HCVD) [138]. The HCVD process begins with PbI_2 films deposited by single-source thermal evaporation. The films are placed in a tube furnace with a low-temperature central zone, where a flow of MAI vapor from the high-temperature zone reacts with the PbI_2 films to form perovskite films (see Figure 2.8 (b)). This method has consistent results due to better

control of pressure, gas flow rate, and substrate temperature with multiple zones.

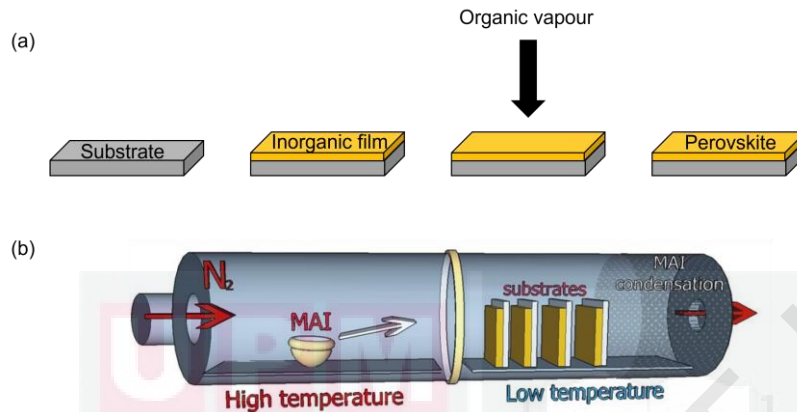


Figure 2.8 : (a) Vapour assisted perovskite deposition method [137], and (b) Hybrid chemical vapour deposition method – HVCD [138], [139]

2.5.2 Growth of Perovskite Single Crystals

Apart from perovskite thin film growth via deposition techniques, other techniques have been developed to grow perovskites in its single crystal form. One of the methods is the inverse temperature crystallization (ITC) which involves heating a perovskite precursor in suitable solvents to a predetermined temperature in order to induce fast crystallization of perovskite single crystals (Figure 2.9 (a)). Since crystallization in some organic solvents occurs through inverse solubility, the ITC method is highly sensitive to solution temperature, and the resulting growth process is a balance between dissolution and precipitation. Nucleation occurs at some point after the solution reaches the supersaturation stage, followed by crystal growth. A suitable solvent must be chosen in order to grow a highly crystalline single crystal. Polarity, viscosity, and coordination capabilities of the solvents used to dissolve the perovskite

single crystals are crucial [140]. This method was initially utilized to create single-crystal MAPbX_3 perovskites. However, it is still difficult to use a single solvent for both precursor materials for synthesizing mixed-halide perovskites.

The second method is the slow evaporation crystallization, which is the most basic and widely used method for synthesizing single crystals via solution-assisted growth in ambient conditions. The evaporating solution is made by combining two or more precursor in a certain solvent. By draining the solvent, such systems can easily become supersaturated. To achieve the best crystallization results, it is important to choose solvents with moderate solubility, as supersaturated solutions can lead to the formation of very small crystals. Figure 2.9 (b) depicts the solvent evaporation procedure schematically. The solvent evaporated faster during the crystallization process by heating, which appears to be similar to the ITC method. However, the solvent evaporation method by heating reduces the solubility of the perovskite precursor more than the ITC method.

The third method for creating single crystal perovskites is anti-solvent vapor-assisted crystallization (AVC). In this method, an anti-solvent is slowly diffused into a solution containing perovskite precursor, which causes the perovskite to crystallize into single crystals (see Figure 2.9 (c)). When the anti-solvent is introduced to the saturated precursor solution, the solute's solubility rapidly decreases, resulting in precipitation; thus, the antisolvent loading speed is a significant element in solubility change [141], [142], [143], [144], [145]. Shi et al. [142] used anti-solvent vapor-assisted crystallization to create high-quality

millimeter-sized MAPbBr_3 and MAPbI_3 single crystals. Because this process is not impacted by temperature fluctuations, temperature-induced phase transitions do not occur, resulting in crystals with a highly ordered lattice arrangement and smoother surfaces than those created by the ITC method.

The last method to be discussed is the top-seeded solution-growth (TSSG) strategy. In this method, a temperature gradient between the top and bottom of a supersaturated perovskite solution creates enough convective transport of perovskite from the bottom to the top of the container to grow large single crystals (see Figure 2.9(d)). The single crystals were formed by dissolving small seed crystals at the bottom of the solution due to the temperature difference between the bottom and top of the solution, which caused supersaturation. For the first time, [146] has generated mass high quality hybrid tin iodide perovskite single crystals using the TSSG approach. The temperature-lowering approach is straightforward, practical, and appropriate for the formation of high-quality large-size single crystal perovskites. However, it is not suitable for low solubility materials at high temperature

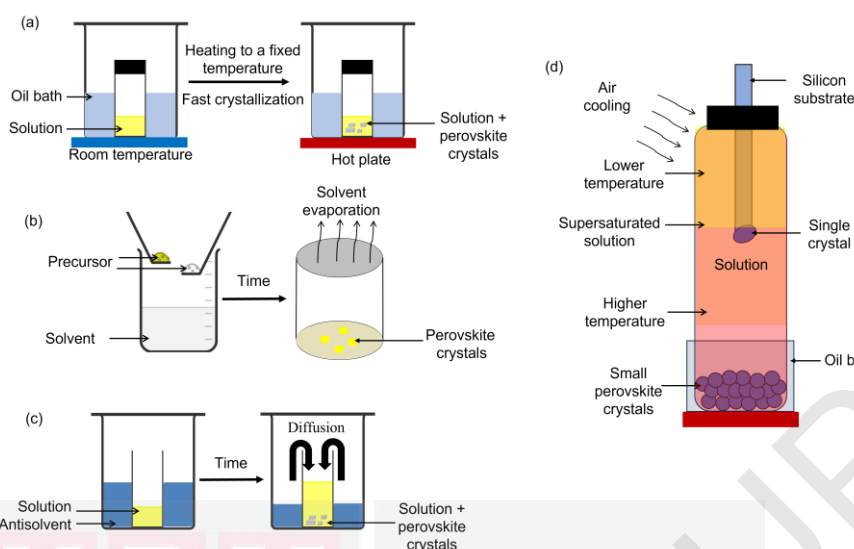


Figure 2.9 : (a) Growth of perovskite single crystals via (a) inverse temperature crystallization – ITC, (b) slow evaporation crystallization, (c) anti-solvent vapour-assisted crystallization – AVC, and (d) top-seeded solution-growth – TSSG.

2.6 Halide Perovskite in Optoelectronic Applications

This section highlights halide perovskite in a variety of applications, including solar cells, photodetectors, light-emitting diodes (LEDs), lasers, and flexible electronics. These technologies are grouped based on device type and latest research findings.

2.6.1 Solar cells

Chen et al. [147] who achieved a significantly high efficiency of 17.8% by using ITC method to grow MAPbI_3 single crystals free of pinholes and grain boundaries for use as an active layer in solar cells. Alsalloum et al. reported the second highest efficiency of 21.9% for MAPbI_3 -based single crystal, which demonstrated bench-level progress within a few years [148]. However, single

crystal solar cells have yet surpassed the Shockley-Queisser (S-Q) limit of efficiency around 31.64% for a 1.5 eV bandgap semiconductor [149], [150]. The Shockley-Queisser limit describes the maximum solar energy conversion efficiency feasible for a particular material and is used to assess emerging photovoltaic technology [151]. Despite the challenges of thickness control and solution-growth conditions compatible with devices, a few groups of researchers are leading the development of single-crystal-based perovskite solar cells.

2.6.2 Photodetectors

Perovskite is also a fantastic material for photodetectors. High carrier mobility and low trap density result in a fast response time and high external quantum efficiency (EQE), which are essential for photodetectors [152], [153], X-ray detectors [145], [154], and γ -ray detector [155]. Liu et al. [156] used high-quality MAPbBr₃ single crystals to manufacture imaging sensor applications due to its superior optoelectronic properties. The superior performance criteria of homogeneity, high detectivity, fast response, and long-term stability outperformed silicon or InGaAs. Pan et al reported the usage of Cs₂AgBiBr₆ single crystals in the fabrication of x-ray detectors for the first time in 2017 [157]. The detector had a high sensitivity of $105 \mu\text{C Gy}_{\text{air}}^{-1}\text{cm}^{-2}$ and a low detection limit of $59.7 \text{ nGy}_{\text{air}} \text{ s}^{-1}$ under 5 V. The Ag⁺/Bi³⁺ disordering had resulting poor structural stability on the Cs₂AgBiBr₆ double perovskite, resulting in poor photoelectric characteristics. Zhuang et al [158] also successfully fabricated a (NH₄)₃Bi₂I₉ single-crystal x-ray detector and the

devices had a high sensitivity ($8.2 \times 10^3 \mu\text{C Gy}_{\text{air}}^{-1}\text{cm}^{-2}$) and a low detection limit ($55 \text{ nGy}_{\text{air}} \text{ s}^{-1}$). Zhang et al. [159] used a nucleation-controlled solution approach to synthesize large-sized $\text{Cs}_3\text{Bi}_2\text{I}_9$ single crystals in 2020. Refining the precursor solution allows the nucleation-controlled approach to be realised. The sensitivity of the detector based on the $\text{Cs}_3\text{Bi}_2\text{I}_9$ single crystal was $1146.7 \mu\text{C Gy}_{\text{air}}^{-1}\text{cm}^{-2}$.

2.6.3 Light Emitting Diodes (LEDs)

Perovskite-based LEDs are ideal candidates for next-generation lighting technology due to high photoluminescence quantum yield (PLQY) (~100%), narrow bandwidth (<20 nm), and easy wavelength tuning across the entire visible light spectrum (400 to 800 nm) [160], [161], [162]. Over the last five years, the EQE of perovskite LEDs has improved from 0.1% to more than 20%, promising tremendous potential [163]. Recent advances in perovskite LEDs have been based on 3D perovskites, 2D or semi-two-2D perovskites, and perovskite nanocrystals. Single-crystalline perovskite microplatelets are a type of 3D perovskite crystal that can be used to create single-crystalline LEDs. Chen et al. [164] fabricated a simple LED based on MAPbBr_3 microplatelets with an ITO anode on glass and an Au cathode film.

2.6.4 Lasers

The strong absorption of perovskite has sparked research into the nonlinear optical response of perovskites. They have been frequently used in pulsed

laser generation due to its broadband nonlinear optical (NLO) features and ultrafast response. Kalanoor et al [165] recently discovered third-order optical nonlinearities in methylammonium lead iodide thin films, attributing the highly nonlinear intensity-dependent refractive index to free-carrier concentration changes and the Pauli blocking effect. At 532 nm, S. Mirershadi et al. revealed the large third-order nonlinear response of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ [166]. Zhang et al. [167] discovered that organic-inorganic halide perovskites ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$) as an SA have a large nonlinear refractive index that is several orders of magnitude greater than silicon. Hong et al. reported an all-fiber laser operating in the C- and L-bands utilising $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$ perovskite crystallites as a SA in 2018, demonstrating the potentials of hybrid organic-inorganic perovskite in nonlinear photonics over a broad spectral range [168]. However, there are some environmental problems and health risks associated with using lead-based materials on a broad scale due to the possibility of lead contamination caused by leaking from damaged devices. For the first time in 2018, Bao et al demonstrate that the lead-free organic-inorganic perovskite $\text{CH}_3\text{NH}_3\text{SnI}_3$ perovskite can be an effective material choice for ultrafast optical applications [95]. These progresses suggest the potential of perovskites to be applied in ultrafast photonic device.

2.7 Overview of Fiber Laser

Fiber technology is maturing, and the most recent significant change is that fiber lasers are increasingly becoming well-developed tools for industrial applications. Fiber lasers were proposed and explored as a possible laser

design soon after Maiman's first presentation of the practical laser in 1960 [169]. Many researchers have been captivated by optical fiber's capacity to confine light and propagate it around bends and loops. Rare-earth ion doped optical fibers, such as erbium, ytterbium, thulium, neodymium, or holmium, have been widely employed as gain mediums in fiber lasers. These rare-earth doped fiber lasers produce an extremely narrow infrared beam laser output with exceptional high beam quality and optical-to-optical efficiency. Because these rare-earth elements are optically active, they can absorb light at one wavelength while emitting light at another [170]. Erbium ions in erbium-doped optical fiber, for example, can absorb light at 980 and 1480 nm and re-emit it in the 1550 nm telecommunications range via stimulated or spontaneous emission. The advent of rare-earth doped fiber has paved the way for the development of many new active devices, such as those capable of generating ultrashort pulses, which have numerous applications.

2.7.1 Erbium-doped Fiber Laser (EDFL)

Due to its broad-spectrum range in tens of nanometers and anomalous fiber dispersion in 1.55-micron region, EDF is chosen as a gain medium for ultrashort pulse generation in this thesis. [171]. Anomalous dispersion and nonlinearity in optical fibers can work together to create self-stable pulses that are ideal for wavelength division multiplexing (WDM) networks, which are used in telecommunications [172], [173].

The energy-level diagram and numerous energy-level transition processes of these Er^{3+} ions in silica fibers are depicted in Figure 2.10. Metastable level; $^4\text{I}_{13/2}$ level and the pump level; $^4\text{I}_{11/2}$ are the two principal levels for telecommunication applications. The term metastable refers to the fact that transitions from this state to the ground state; $^4\text{I}_{15/2}$ level have very long lifetimes in comparison to the lifetimes of the states that lead to this level. When a photon of light is absorbed by an Er^{3+} ion, the ion is excited to $^4\text{I}_{11/2}$ or $^4\text{I}_{13/2}$ levels, depending on the wavelength of the photon. In this experiment, the erbium ions are excited by 980 nm photons from a laser diode. The excited ions then undergo a non-radiative decay to $^4\text{I}_{13/2}$ level, which can remain in a stimulated state for a relatively long time (lifetime ~ 10 ms). During this decay, the extra energy is released as phonons, or more precisely, mechanical vibrations in the fiber. The ability to stay stimulated for a long time is essential, as it determines the quantum efficiency of the device. If it relaxes too quickly, it requires more photons to keep it stimulated, meaning that the amplifier demands a larger input pump [173].

Erbium can also be excited by pump photons at 1480 nm (energy level $^4\text{I}_{13/2}$). In the absence of an externally stimulated photon flux, some of the ions in the $^4\text{I}_{13/2}$ level can decay back to the $^4\text{I}_{15/2}$ level, which is known as spontaneous emission. When energy is pumped into the system, it excites the atoms to a higher energy level. These atoms can then emit photons of the same wavelength and energy as the pump photons. When a flux of signal photons with energies corresponding to the bandgap energy between the $^4\text{I}_{13/2}$ level and the $^4\text{I}_{15/2}$ level passes through the device, two further types of transitions occur.

First, some of the external photons will be absorbed by ions in the ground state, raising them to the $^4I_{13/2}$ level as stimulated absorption. Second, a signal photon causes an excited ion to drop to the ground state, generating a new photon with the same energy, wave vector (direction of travel), and polarization as the incoming signal photon. Because of the widths of the $^4I_{13/2}$ and $^4I_{15/2}$ levels, substantial quantities of stimulated emissions can occur in the 1530–1560-nm range. After 1560 nm, the gain rapidly drops until it hits 0 dB (unity gain) at 1616 nm [174].

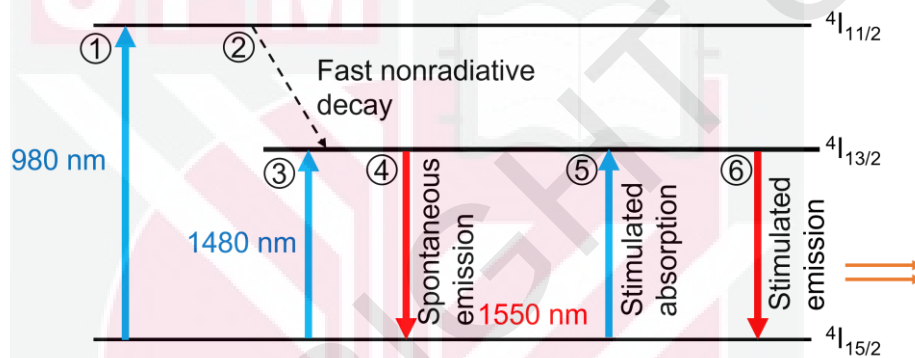


Figure 2.10 : Energy-level diagrams

2.8 Ultrashort Pulse Fiber Laser

Q-switching and mode-locking are two techniques that can be used to generate short pulses of light from fiber lasers. These lasers have a wide range of applications in material processing, medical applications, and scientific research.

2.8.1 Q-Switching

Q-switching is a way to create short pulses of light with high energy by changing the quality factor (Q-factor) of a laser cavity. The Q-factor is a measure of how much light is lost from the cavity during each round trip. Q-switched lasers have a much lower repetition rate which means the number of pulses emitted per second than the time it takes for light to make a round trip in the cavity. This is because the Q-factor is reduced during the pulse generation process. One way to implement Q-switching is to insert an optical loss modulator into the laser cavity. The optical loss modulator can be used to quickly change the Q-factor of the cavity. When the Q-factor is high, light builds up in the cavity. When the Q-factor is reduced, the light in the cavity is emitted as a pulse. The Q-factor of a laser cavity can be mathematically described as Equation 2.3.

$$Q = 2\pi\nu\tau_c \quad (2.3)$$

This equation shows that the Q-factor is proportional to the energy stored in the cavity as 2π times the number of oscillations of the electric field of a light wave, ν , during a duration equal to the cavity lifespan, τ_c [175].

When the loss in the laser cavity is low (high Q-factor), the output power increases rapidly because the gain is much greater than the loss. This causes the gain medium to saturate, which means that it can no longer amplify light as effectively. This causes the power to drop and a pulse to form. By

repeatedly changing the loss in the cavity, a train of pulses can be generated as shown in Figure 2.11. This is called Q-switching. The device that changes the loss in the cavity is called the loss modulator. The loss modulator can be an active device, for example electronic shutter, or a passive device, such as a SA. A SA is a material that absorbs light less strongly at high intensities. This means that the loss modulator can work without the need for any external power source. Passive Q-switching is simpler than active Q-switching, but it has the disadvantage that the repetition rate and pulse duration of the laser become dependent on the power of the laser. At kHz repetition rates, a Q-switched fiber laser can typically produce microsecond to nanosecond pulses.

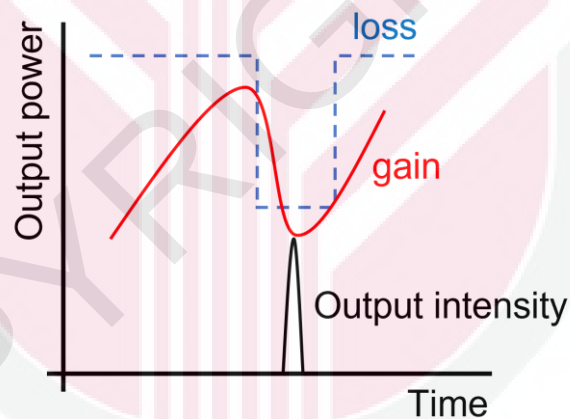


Figure 2.11 : The gain and loss of the laser cavity changed over time.

2.8.2 Mode-Locking

Mode-locking technique was proposed for the first time in 1964 [176]. When a laser works, it oscillates synchronously over all of the laser cavity's resonant frequencies as long as the gain exceeds the cavity losses. These resonance frequencies comprise the laser's set of longitudinal modes [177]. Each

longitudinal mode of a cavity resonator has a specific bandwidth or frequency range. This bandwidth is determined by the physical characteristics of the cavity, such as its length and shape. The bandwidth of a longitudinal mode is typically much smaller than the frequency difference between two adjacent longitudinal modes. We can think of longitudinal modes as ideal plane waves, as shown in Equation 2.4.

$$E_j(t) = E_j \exp[i(\omega_j t + \phi_j)] \quad (2.4)$$

E_j is the amplitude of electrical field, ω_j is the frequency, ϕ_j is the phase of the j^{th} longitude mode, respectively.

The laser cavity incorporates either an active element (an optical modulator) or a nonlinear passive element (SA) to accomplish mode-locking. The primary function of these active and passive components is to generate an initial ultrashort pulse that circulates in the laser resonator. The circulation pulse is impacted by numerous factors in the steady condition. The pulse repetition rate is the same as the resonator round-trip time (usually several nanoseconds) in the case of a single circulating pulse, but the pulse length is substantially smaller (generally between 30 fs and 30 ps).

Figure 2.12 depicts the sum of the oscilloscope train following phase locking by three longitudinal modes in the laser cavity: E_A , E_B , and E_C . When the phases of numerous longitudinal modes in the laser cavity are locked, a periodic constructive interference occurs, which appears as a pulse with a

pulse separation equal to the repetition rate. This method produces pulses with extremely tiny pulse widths (picoseconds to femtoseconds). The shorter the circulation pulse, the greater the number of resonance modes [177].

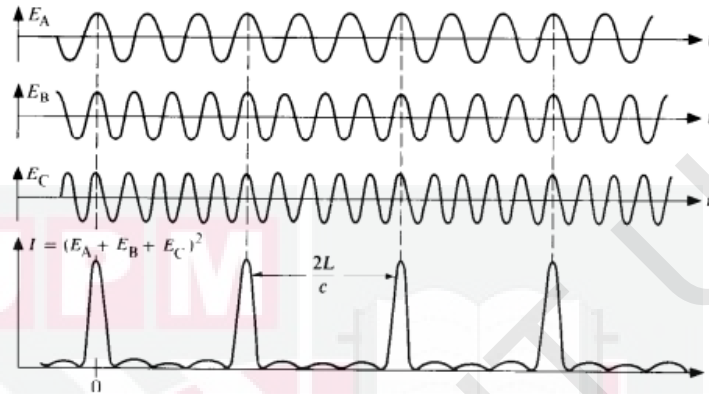


Figure 2.12 : Phase-locking process [178]

2.8.2.1 Active Mode-Locking

Active optical modulation uses an external signal to control an optical modulator, which changes the phase or frequency of the light. The most common types of optical modulators are acousto-optic (AOM) and electro-optic devices. The modulator will cause the amplitude of each longitudinal mode to change. When the modulation frequency is an integer multiple of the laser cavity frequency, the laser can be mode-locked and the output pulse train can be synchronized to the modulation signal. Harmonic active mode-locking can generate pulse trains with repetition rates that are over 1000 times higher than the fundamental laser frequency, reaching up to tens of gigahertz. To stabilize the output, a spectral filter, typically a bandpass filter (BPF), is always required. Lasers that are actively mode-locked can be ideal pulse sources for optical

communication systems. It is not, however, an ideal method for generating pulses with pulse widths less than a few picoseconds. This problem is caused by a limiting factor caused by the modulation electronics' speed.

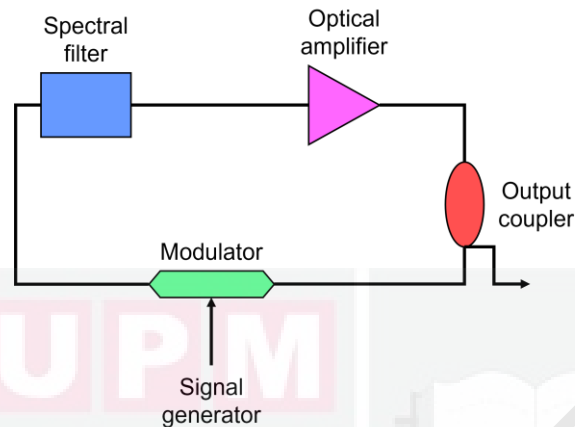


Figure 2.13 : Schematic setup of an active mode-locked laser

Setting the modulation frequency close to the laser cavity round-trip time allows a single pulse to extract the maximum net gain from the laser cavity (Figure 2.14). This requires the modes to develop a precise phase relationship, which is achieved by the sidebands generated from each running mode (due to the modulation signal) being injected into the neighboring modes of the running mode. This leads to synchronization and locking of the neighboring modes, and eventually to global phase locking, which results in a single oscillating pulse that contains all the energy of the cavity.

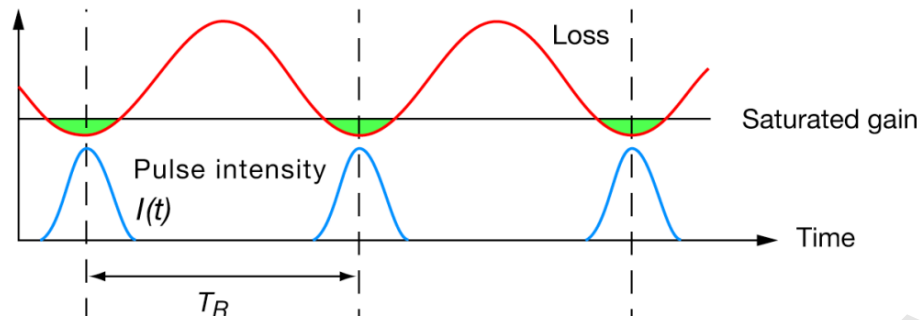


Figure 2.14 : Temporal evolution of gain and loss of an active mode-locking [179]

2.8.2.2 Passive Mode-Locking

Passive mode locking is a technique for generating ultrashort laser pulses without using an external signal. It is often used in high-power flash-pumped lasers and continuous-wave (CW) mode-locked lasers to produce the shortest possible pulses. However, passive mode locking can be more difficult to control and characterize than active mode locking, and it is often less susceptible to basic analytical methods.

The main process in almost all passive mode-locking is pulse shortening, which is achieved by using a SA placed inside the laser cavity, as shown in Figure 2.15. A SA is a type of optical device that has different transmission depending on the intensity of the light passing through it. For passive mode-locking, a SA should ideally absorb low-intensity light but transmit high-intensity light. This provides "positive feedback" to the laser cavity, causing more light of higher intensity to be transmitted. As a result, it can be used to achieve self-amplitude modulation of the light in the laser cavity. The SA

introduces some loss to the intra-cavity laser radiation and is integrated into a fiber laser cavity to generate ultrashort pulses.

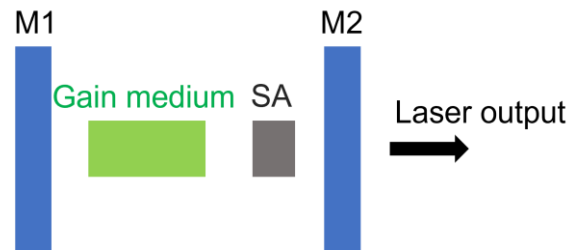


Figure 2.15 : Schematic setup of a passively mode-locked laser with a saturable absorber (SA) mirror (M1 and M2).

The majority of the SAs are made of a semiconductor material, which provides the saturable absorption effect due to resonant nonlinearities involving carrier transitions from the valance to conduction band. Figure 2.16 depicts the entire process of the SA in particle form based on a two-level model. As the diagram shows, electrons in the ground state of the lower energy level (or valence band, E_1) can absorb photons if the photons have the same energy as the difference between the two levels. The electrons can then be excited to the higher energy level (or conduction band, E_2) if there is no other electron at the higher energy level.

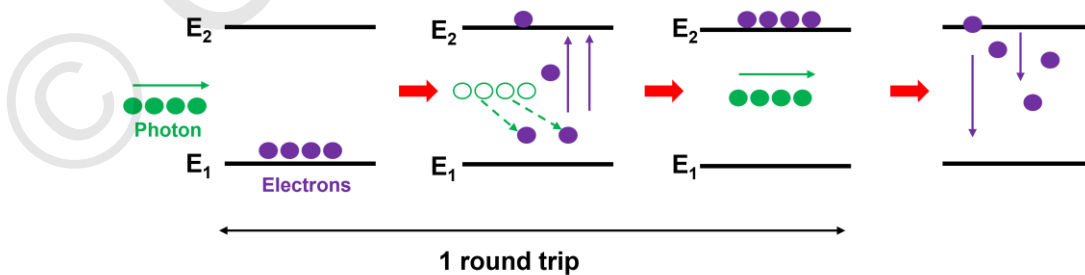


Figure 2.16 : Mechanism of SA based on a two-level model in particle form.

In direct gap materials, the absorption and refractive index can change significantly at wavelengths near the bandgap energy when the light intensity is high. This is called saturable absorption. Band-filling is the main cause of saturable absorption. When the material is strongly illuminated, the energy states at the edges of the conduction and valence bands become filled, preventing further absorption as the intensity increases. This is because no two electrons can occupy the same state. When the intensity is high enough, the material becomes transparent to light at photon energies just above the band edge. This mechanism, known as Pauli blocking or phase space filling, was predicted in 1969 [180]. As electrons fill the higher energy state (E_2), the material is unable to absorb further photons. As a result, the absorption becomes saturated, and light can pass through the material without being absorbed. After a certain amount of time (the electron lifetime), the electrons in the higher energy state decay back to the ground state, and the process repeats itself.

According to this simple model, the nonlinear optical properties of a SA are directly related to the intensity of the incident light as shown in Equation 2.5 [181], [182], [183].

$$\alpha(I) = \frac{\alpha_s}{(1 + I/I_{sat})} + \alpha_{ns} \quad (2.5)$$

Where $\alpha(I)$ is the absorption coefficient, α_{ns} is the modulation depth, α_{ns} is non-saturable loss, I is the laser power intensity and I_{sat} is the saturation intensity, a phenomenological parameter, at which α decreases to a half of its

value at low incident intensity $\alpha(I_{sat}) = \alpha_s/2$). The saturation intensity is a crucial parameter in determining saturable absorber performance. Figure 2.17 depicts the nonlinear relationship between the absorption coefficient and the incident light intensity. Because of this nonlinear relationship, the SA device can be employed in passive mode-locking for ultrashort pulse laser production.

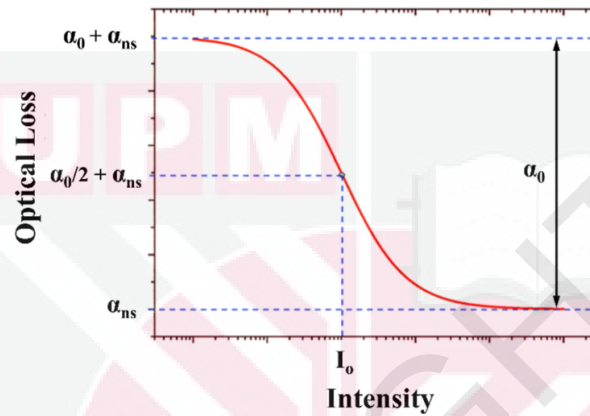


Figure 2.17 : Nonlinear optical profile of the absorption coefficient of a two-level system as a function of the incident light intensity [184]

The temporal evolution of gain and loss of a passive mode-locking inside the laser cavity is depicted in Figure 2.18. A SA absorbs more light at low intensities than at high intensities. This is why the loss is very high for low intensity laser light and significantly smaller for a short pulse with high intensity. The high intensity at the peak of the pulse saturates the absorber more strongly than its low intensity wings, which results in loss modulation with a short pulse. This causes loss modulation, with a fast-initial loss saturation (loss reduction) determined by the pulse width and typically slow recovery, depending on the specific mechanism of the absorption process in the SA. In effect, the circulating pulse saturates the laser gain to just enough to compensate for the

pulse's losses, but any other circulating low-intensity light experiences more loss than gain and hence dies out during subsequent round trips.

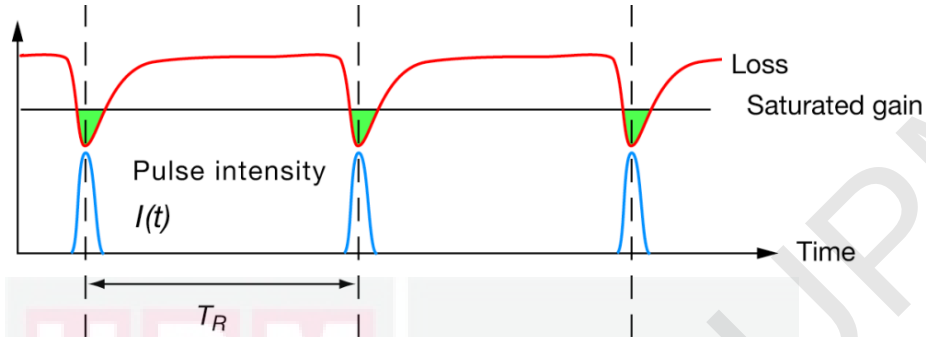


Figure 2.18 : Temporal evolution of gain and loss of a passive mode-locking inside the laser cavity [179]

2.9 Propagation of Optical Pulses in a Fiber

Light can be transmitted inside the fiber due to the difference in refractive indices between the core and cladding. The core's refractive index must always be greater than the claddings. The presence of an angle of incidence that allows total internal reflection to occur can be explained by the modal theory [185]. Light propagating through an optical fiber can be described by Maxwell's equations, which govern the behavior of electromagnetic fields [186]. Any pulse of light that experiences time dispersion in an optical fiber, especially in the linear regime, will broaden and may cause intersymbol interference (ISI). This can severely limit the bandwidth of the information that can be transmitted.

The optical Kerr effect influences pulse propagation in the nonlinear regime. In the Nonlinear Dispersive Regime, pulse propagation is determined by both the

Self-Phase Modulation (SPM) and the group velocity dispersion (GVD) [187]. The SPM effect is opposite to the GVD in the anomalous dispersion zone, giving particularly intriguing pulse propagation because it does not alter throughout fiber transmission. These pulses are known as soliton. The dispersion phenomenon, SPM, and soliton formation are briefly covered in this section.

2.9.1 Dispersion

From Equation 2.6, light travels through free space at the speed of light, c and light travels slower through a material than it does through a vacuum because of the interaction between the light's electromagnetic field and the material's electrons. This slowing down of light is called chromatic dispersion. The word "chromatic" means that the amount of slowing down depends on the color, or wavelength, of the light. The refractive index, n , of a material is a measure of how much light slows down in the material.

$$v_m = \frac{c}{n} \quad (2.6)$$

Light of different wavelengths travels through a material at different speeds because the interaction of the electromagnetic field with the material depends on the wavelength. This property is known as material dispersion, and it is defined as Equation 2.7.

$$D_M(\lambda) = \frac{\lambda}{n} \frac{d^2 n}{d\lambda^2} \quad (2.7)$$

Material dispersion is a property of materials where the refractive index, n , changes depending on the wavelength of light. This is important for the propagation of laser pulses. If a laser pulse had only one wavelength component, it would pass through the material without changing its shape. However, laser pulses typically have a range of wavelengths, which can cause the pulse to spread out over time as it propagates through the material. In practice, a pulse is made up of a variety of frequencies. The wider the range of frequencies in a laser pulse, the shorter the pulse will be in duration. However, different frequencies travel at different speeds, so the pulse will become distorted as it travels through a material. This causes the pulse width to broaden.

Aside from material dispersion, light is also subjected to dispersion induced by the optical fiber's structure. Light moves more slowly in the core and more quickly in the cladding. The overall speed is determined by the proportion of power transferred between the core and the cladding. The more the power in the cladding, the longer the wavelength. As a result of the different power distribution in the core and cladding, different colors of light travel at different speeds. It is referred to as waveguide dispersion and is defined as Equation 2.8.

$$D_w(\lambda) = \frac{n_2(\lambda)\Delta}{c\lambda} V \frac{d^2(Vb)}{dV^2} \quad (2.8)$$

Where $n_2(\lambda)$ is the refractive index of the fiber core, Δ is the difference in refractive index, b is the normalized propagation constant, and V is the

normalized frequency. The total chromatic dispersion of a fiber is the sum of the material dispersion and the waveguide dispersion as shown in Equation 2.9.

$$D(\lambda) = D_M(\lambda) + D_W(\lambda) \quad (2.9)$$

Chromatic dispersion is a very important factor in the propagation of pulses through optical fibers. The propagation of a laser pulse through a fiber is described by a mode propagation constant, β . Because the frequencies of time-limited pulses are concentrated around the central frequency, ω_0 the mode propagation constant, β can be expanded in a Taylor series around the center frequency, ω_0 as shown in Equation 2.10 and 2.11.

$$\begin{aligned} B(\omega) &= \frac{n(\omega)\omega}{c} \\ &= \beta_0 + \beta_1(\omega - \omega_0) + \frac{1}{2}\beta_2(\omega - \omega_0)^2 \\ &\quad + \dots \end{aligned} \quad (2.10)$$

where

$$\beta_m = \left(\frac{d^m \beta}{d\omega^m} \right)_{\omega=\omega_0} \quad (m = 0, 1, 2, \dots) \quad (2.11)$$

The pulse envelope moves at the group velocity $v_g = 1/\beta_1$ while the parameter β_2 is responsible for pulse broadening. β_2 is also known as GVD

and is related to the chromatic dispersion parameter, D . The β_1 and β_2 parameters are defined as Equation 2.12 and 2.13.

$$\beta_1 = \frac{1}{v_g} = \frac{n_g}{c} = \frac{1}{c} \left(n + \omega \frac{dn}{d\omega} \right) \left[\frac{ps}{km} \right] \quad (2.12)$$

$$\beta_2 = \frac{1}{c} \left(2 \frac{dn}{d\omega} + \omega \frac{d^2n}{d\omega^2} \right) \left[\frac{ps^2}{km} \right] \quad (2.13)$$

Where v_g is the group velocity of the pulse and n_g is the group refractive index. Thus, β_1 is the reciprocal of the group velocity, and β_2 quantifies the pulse broadening caused by not all of its components propagating at the same velocity. This is known as GVD Higher orders of dispersion are also defined; however, higher order dispersion is frequently required in cases of extreme spectral broadening, such as the supercontinuum generation process which is not the focus of this thesis.

For $\beta_2 > 0$, the fiber has normal dispersion and for $\beta_2 < 0$, it has anomalous dispersion. In the normal dispersion regime, shorter wavelengths of light travel slower than longer wavelengths through an optical fiber. The opposite is true in the anomalous dispersion regime. Dispersion spreads out light pulses over time, which reduces their intensity and can cause adjacent pulses to overlap. This can lead to errors in fiber optic communication systems. However, the combination of dispersion and the SPM effect can also lead to the formation of optical solitons, which are stable pulses of light that keep their shape as they travel through a fiber.

2.9.2 Nonlinear Effect

Nonlinear effect phenomena occur from the linear interaction between a material's polarization response and the electric component of an applied electro-magnetic field [188]. An optical nonlinearity is defined as the relationship between the dipole moment per unit volume, or polarization, $\tilde{P}(t)$ of a material system and the strength, $\tilde{E}(t)$ of an applied optical field [189]. Positive charges tend to travel in the opposite direction of electrons when an external, E field is applied to the material. This interaction results in charge separation, which gives rise to dipole moments within the material. These dipoles oscillate at the same frequency (ω) as the incident light when subjected to an electric field. Material polarization is caused by the sum of all the microscopic dipoles of the medium oscillating with time. The induced polarization is proportional to the field strength and can be expressed as Equation 2.14 [189].

$$\tilde{P}(t) = \epsilon_0 \chi^{(1)} \tilde{E}(t) \quad (2.14)$$

Where ϵ_0 is the vacuum permittivity and the proportionality constant $\chi^{(1)}$ is known as the linear susceptibility. In this scenario, $\chi^{(1)}$ is frequency dependent and so directly related to the linear refractive index, but it is not amplitude dependent, implying that the frequency of light does not change as it passes through matter. At large intensities, $\tilde{P}(t)$ is a nonlinear function of $\tilde{E}(t)$ whereas, at low intensities, the interaction is a linear function. So, for materials with nonlinear characteristics, in which the polarization given by the

Equation 2.14 is no longer valid, $\tilde{P}(t)$ must be written in a more general form, as a power series of $\tilde{E}(t)$ as shown in Equation 2.15.

$$\begin{aligned}\tilde{P}(t) &= \epsilon_0[\chi^{(1)}\tilde{E}^1(t) + \chi^{(2)}\tilde{E}^2(t) + \chi^{(3)}\tilde{E}^3(t) + \dots] \\ &= \tilde{P}^{(1)}(t) + \tilde{P}^{(2)}(t) + \tilde{P}^{(3)}(t) + \dots.\end{aligned}\tag{2.15}$$

Where the values of $\chi^{(2)}$ and $\chi^{(3)}$ are known as the second- and third-order nonlinear optical susceptibilities, respectively. Assumed from Equation 2.14 and 2.15 that the polarization at time t is solely determined by the instantaneous value of the electric field intensity. Noncentrosymmetric crystals (crystals without inversion symmetry) are the only ones that can have second-order nonlinear optical interactions. Referred to $\tilde{P}^{(2)}(t) = \epsilon_0\chi^{(2)}\tilde{E}^2(t)$ as the second-order nonlinear polarization and to $\tilde{P}^{(3)}(t) = \epsilon_0\chi^{(3)}\tilde{E}^3(t)$ as the third-order nonlinear polarization. Third-order nonlinear effects in optical fiber occur due to either the intensity dependence of the silica glass medium refractive index or to an inelastic-scattering phenomena known as Kerr nonlinearity, which may be represented as Equation 2.16.

$$n = n_0 + n_2|E|^2\tag{2.16}$$

Where n_0 represents the linear refractive index, n_2 represents the nonlinear index coefficient, and $|E|^2$ represents the optical intensity in the fiber. SPM, cross-phase modulation (XPM), and four-wave mixing (FWM) are three important nonlinear optical effects that occur in silica glass when the refractive index of the material changes depending on the intensity of light. Stimulated

Brillouin scattering (SBS) and stimulated Raman scattering (SRS) are two other nonlinear optical effects that can occur in silica glass at high power levels, but these effects involve inelastic scattering, meaning that the energy of the photons is changed. Only SPM nonlinear effect will be discussed in this thesis.

2.9.3 Self-Phase Modulation (SPM)

The refractive index of an optical fiber changes with both wavelength and the intensity of the light propagating through it. This is because the interaction of light with the electrons in the material increases nonlinearly with light intensity. As a result, high-intensity light travels slower than low-intensity light, and the refractive index of the fiber increases with light intensity. This property is best described as nonlinear refraction as shown in Equation 2.17.

$$n_{eff} = n_l + n_{nl}I \quad (2.17)$$

The effective refractive index is n_{eff} , the linear refractive index is n_l , the nonlinear refractive index is n_{nl} , and the light intensity inside the fiber is I .

SPM is a major effect of nonlinearity in silica fibers that can significantly impact pulse propagation. The refractive index of the fiber depends on the intensity of the light when light travels through a silica fiber. This means that different refractive indices can cause the pulse to shift in phase. The shape of the pulse will remain unchanged, but the phase shift can lead to a number of effects,

such as pulse broadening and spectral broadening. The nonlinear phase constant ϕ_{nl} introduced by an $E = E_0 \cos(\omega t - kz)$ field across a fiber length, L as shown in Equation 2.18 [190].

$$\phi_{nl} = \frac{2\pi}{\lambda} n_{eff} L \quad (2.18)$$

Where λ is the pulse laser's operating wavelength in fiber of n_{eff} over a distance L through an optical fiber specified as shown in Equation 2.19

$$L = \frac{(1 - \exp(-\alpha L))}{\alpha} \quad (2.19)$$

When an optical pulse passes through a fiber, the higher intensity part faces a higher refractive index of the fiber than the lower intensity part. As a result, the leading edge of a pulse will encounter a positive refractive index gradient ($+dn/dt$), resulting in red shift, while the trailing edge will experience a negative refractive index gradient ($-dn/dt$), resulting in blue shift as seen in Figure 2.19 [190].

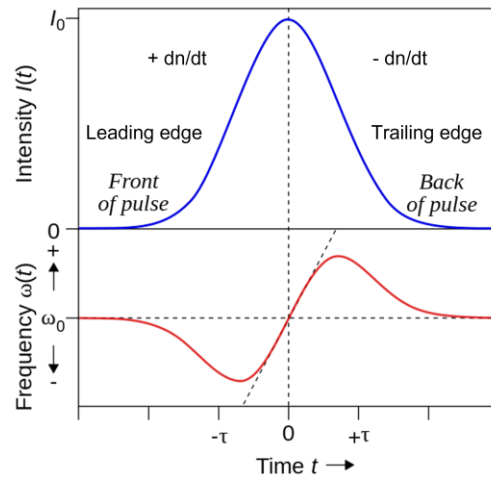


Figure 2.19 : Pulse broadening due to SPM [191]

If the intensity changes over time, the wave is temporally modulated, and the phase ϕ as well. This change in phase, ϕ_{nl} in time, is accountable for the shift in frequency spectrum, which is represented by Equation 2.20.

$$\delta\omega = \frac{d\phi_{nl}}{dt} \quad (2.20)$$

The temporal dependence of $\delta\omega$ is specified to frequency chirping. The chirping phenomenon happens along the temporal pulse profile, with ϕ_{nl} increasing as the length of the interaction fiber increases. This refers to the generation of a new instantaneous frequency at $\omega_0 + \delta\omega(t)$ as the pulse propagates inside a fiber, causing the pulse's spectrum to broaden. The SPM phenomenon can also be exploited in pulse compression. The red-shifted leading edge of the pulse travels slower and goes towards the centre of the pulse in the wavelength range when chromatic dispersion is positive. Similarly, the blue shifted trailing edge travels faster and goes towards the pulse's centre.

SPM causes the pulses to narrow in the time domain and which translates to broadening in the optical spectrum [192], [193].

2.9.4 Soliton

Positive GVD and SPM lead the similar redistribution of the spectral component, but enhances the pulse spreading in time or pulse broadening [194]. However, negative GVD and positive SPM values compensate each other instead, leading to the formation of soliton. Negative dispersion causes the high carrier frequency of the wave packet travel faster than the low carrier frequency part, giving a chance for the high frequency of the leading parts of the SPM packets to catch up with the pulse due to the negative dispersion, while the low frequency packets are in contrast case [195]. The solitons are able to propagate undistorted over long distance and stay unaffected even after collision with each other [194].

Solitons are an important application of the SPM concept. Consider a pulse laser operating in an anomalous dispersion regime $\beta_2 < 0$. SPM resulted in lower frequency (longer wavelength) components at the pulse's leading edge and higher frequency (shorter wavelength) components at the pulse's trailing edge. Lower frequency (longer wavelength) components travel slower than higher frequency (shorter wavelength) components in the anomalous dispersion regime. As a result of the anomalous dispersion, the leading edge of the pulse slows down while the trailing edge accelerates. SPM effectively compensates for pulse broadening and undoes laser-induced dispersion. If the

pulse is shaped in such a way that the effects of SPM and GVD cancel each other out, the pulse will propagate undistorted due to mutual compensation of dispersion and SPM. This solitary wave pulse is referred to as a soliton. Because a soliton pulse does not broaden during propagation, it has enormous potential for use in ultrahigh bandwidth optical communication systems.

One way to better understand the balanced interaction between nonlinearity and dispersion is through characteristic length. The nonlinear characteristic length, L_{nl} in the optical fiber can be described as Equation 2.21.

$$L_{nl} = \frac{1}{\gamma P_p} \quad (2.21)$$

Where P_p is the peak power of the pulse, γ is the nonlinear coefficient of the fiber and the characteristic length for dispersion, L_d as shown in Equation 2.22.

$$L_d = \frac{(t/1.763)^2}{\beta_2} \quad (2.22)$$

In fiber cavity where the condition $L_{nl} > L_d$, nonlinearity dominates and causes pulse distortion. When $L_d > L_{nl}$, dispersion dominates and results in temporal broadening of the pulse. To form a fundamental soliton, L_{nl} and L_d must be equal as shown in Equation 2.23 [194].

$$N^2 = \frac{L_d}{L_{nl}} = 1 \quad (2.23)$$

where the parameter N is referred to as the soliton order. A typical soliton pulse laser has narrow sidebands observable on both the left and right sides of the soliton spectrum (Figure 2.20). These sidebands are known as Kelly sidebands. Kelly sidebands form as a result of the soliton being impacted by periodic perturbations in the cavity during one roundtrip. These disturbances are represented by amplification in the gain fiber and by losses coming from, for example, the output coupler, free-space coupling sections, and splices. Following such a perturbation, the soliton reshapes itself by depleting excessive energy into a dispersive wave that copropagating with the soliton [196]. In general, such a dispersive wave would have no effect on the soliton's propagation. However, when the relative phase per roundtrip between the dispersive wave and the soliton is an integer multiple of 2π , both interfere constructively, resulting in a visible superposition in the optical spectrum [197].

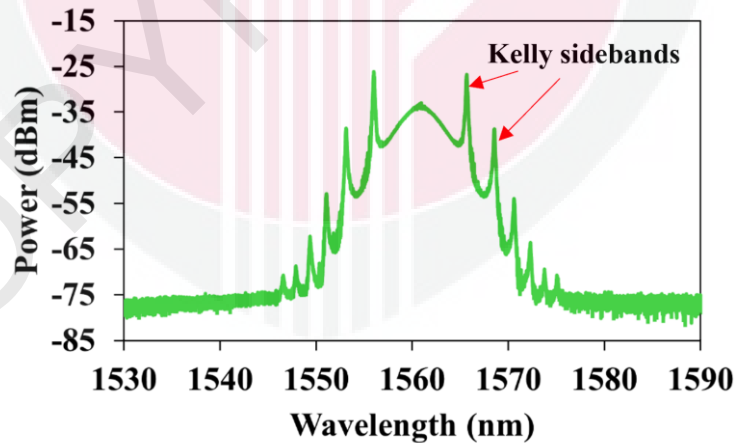


Figure 2.20 : Output spectrum of soliton pulse laser

2.10 Different types of SAs on Mode-Locked Fiber Lasers

Many technologies and optical materials, such as fiber ferrules, tapered fiber (microfiber), and D-shaped optical fiber, have been used to create high-performance SA for pulse generation in fiber lasers. Passive mode-locking techniques based on SAs are a popular choice for generating soliton pulses in fiber lasers due to their compactness, simplicity, and design flexibility [198], [199].

2.10.1 Fiber Ferrule SA

Fiber ferrule SA are one of the simplest and quickest ways to passively mode-lock fiber laser cavities. They are made by depositing a nonlinear optical material in between two fiber ferrules that are joined by a fiber ferrule connector (see Figure 2.21 (b)). The most common methods for preparing nonlinear optical materials for fiber ferrule SAs are liquid-phase exfoliation (LPE), chemical vapor deposition (CVD), and mechanical exfoliation (ME) [200], [201], [202], [203]. The CVD method is suitable for producing high-quality thin films without the need of a polymer matrix. However, in order to achieve good quality deposition, this method demands precise control of furnace temperature and duration [204] making the synthesis process more complicated [205], [206]. Additionally, the etching process using this method is challenging because it requires the use of hazardous solutions and polymers [207].

Liquid-phase exfoliation (LPE) is a simple and inexpensive way in order to make high-quality 2D SA materials. Some of the nonlinear optical materials that can be used to create SAs via LPE include molybdenum disulfide (MoS_2), tungsten disulfide (WS_2), and black phosphorus crystal. LPE involves mixing the material with a solvent (usually alcohol) and sonicating it for a certain time. Then, followed by centrifugation with precise rotational parameters to break up particle aggregation. After the procedure, precipitation is formed and collected. The collected material is then transferred to the surface of the fiber ferrule. Figure 2.21 (a) shows a fiber ferrule SA with a thin film attached to the end of the ferrule [208], [209].

ME is another method for preparing nanosized nonlinear optical materials. One example is the P-type Bi_2Te_3 topological insulator. Proper precaution needs to be taken into account when the produced nanoparticle is deposited on the end of the fiber ferrule in order to reduce thickness and loss caused by beam divergence between two single mode fiber connections [210]. However, this fiber ferrule SA structure is vulnerable to physical damage caused by direct physical contact between fiber ferrules or thermal damage caused by high energy pulse interaction with SA material within the limited interaction length. Thermal damage, in particular, causes pulse breaking, restricting high power applications [211].

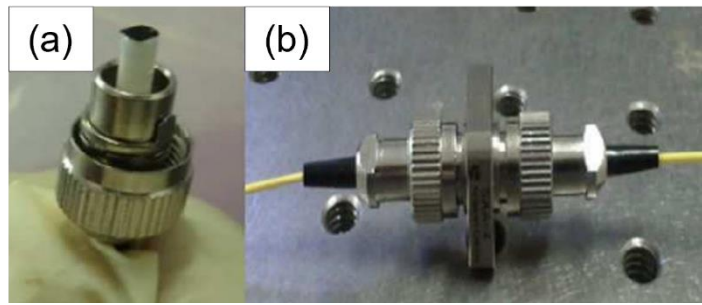


Figure 2.21 : (a) and (b) Material attached on the fiber ferrule [212]

2.10.2 Tapered Fiber SA

Tapered fiber SA are made by coating a tapered fiber with a layer of micro- or nano-sized optical material. In general, research has study that the waist diameter of the tapered fiber must be small enough to ensure efficient interaction between the evanescent wave and the optical material surrounding the fiber waist. Tapered fiber improves the optical damage threshold by dissipating heat more effectively due to its long nonlinear interaction length [213], [214] [215].

There are many ways to make tapered fiber SAs but the most common are pulse laser deposition (PLD) and optical deposition. PLD is a well-known advanced fabrication technique for creating thin films. It works by focusing a high-intensity laser beam onto a target material in a vacuum chamber, which vaporizes the material and creates a plasma. The plasma is then deposited onto a substrate, which is in this case the tapered fiber. The thickness can be controlled by adjusting the PLD parameters, in term of the laser energy, time of deposition, temperature, vacuum pressure, and deposition area. As a result, PLD gradually grows the coated material on the surface of the tapered fiber's

waist. The thin coating is placed directly on the surface of the waist region on tapered fiber, which makes the SA very robust and suitable for packaging. Additionally, the deposition techniques suitable for multiple tapered fibers simultaneously, making it suitable for low-cost mass manufacturing. Topological insulators (Bi_2Te_3 and Sb_2Te_3) and WS_2 are examples of successful materials utilized for SA tapered fiber via the PLD process [216], [217], [218].

Tapered fiber SA can also be made by optically depositing a thin film of material on the surface of the waist region of tapered fiber. For example, this method is used to create phosphorene quantum dot (PQD) tapered fiber SAs. The process begins with the preparation of the PQD material using liquid-phase exfoliation, which involves sonicating bulk powdered PQD powder. The PQD is then deposited on the tapered fiber by an optical deposition process. The PQD solution from the synthesis process is dropped onto waist region of tapered fiber that placed on a quartz plate. The optical deposition process is started with a 980 nm continuous wave laser with an optical power of 60 mW. The optical power of the applied light and the deposition time can be used to adjust the depth of PQD deposition on the tapered fiber [219]. Tapered fibers are fragile and have high evanescent optical loss due to their small core size. [220]. This is why it is important to carefully fabricate tapered fibers with low insertion loss to avoid scattering and ensure precise deposition of SA material [221]. Figure 2.22 illustrate the deposited material on the tapered fiber.

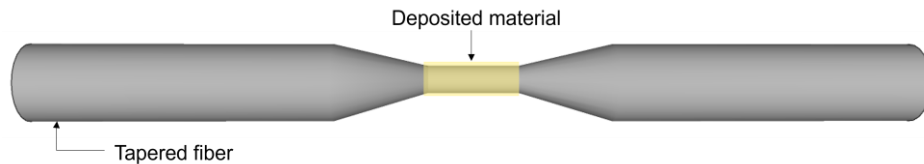


Figure 2.22 : Deposited material on tapered fiber

2.10.3 D-Shaped Fiber SA

D-shaped fiber is a proposed alternative to tapered fiber for SA. Similar principle with tapered fiber SAs based on interaction of evanescent wave with the deposited SA material benefitting on higher thermal damage. D-shaped fiber is prepared by polishing single-mode fiber to achieve good uniformity and low surface roughness. This is typically done using a mechanical polishing machine. The fiber is polished against a rotating polishing wheel until the desired surface quality is achieved [222], [223]. Graphene is one of the most commonly used materials for D-shaped fiber SAs, according to published research. Figure 2.23 shows a cross section of a coated D-shaped fiber made of SA material [224], [225], [226].

D-shaped fiber has a lower evanescent wave intensity interacting with the SA material than fiber ferrule SA. This means that the interaction between the evanescent wave and the SA material is weaker in a D-shaped fiber SA, which results in higher output power [227]. D-shaped fiber is also more resilient than tapered fiber [228]. However, D-shaped fiber SAs have the limitation of generating polarization dependent loss (PDL) based on transverse electric (TE) and transverse magnetic (TM) polarizations. The PDL generated by D-

shaped fiber SAs is typically low, typically less than 1 dB. This is because the interaction between the evanescent wave of the guided mode and the SA material is weak [229], [230]. PDL causes instability in SA performance, which requires precise control of the polarization state.

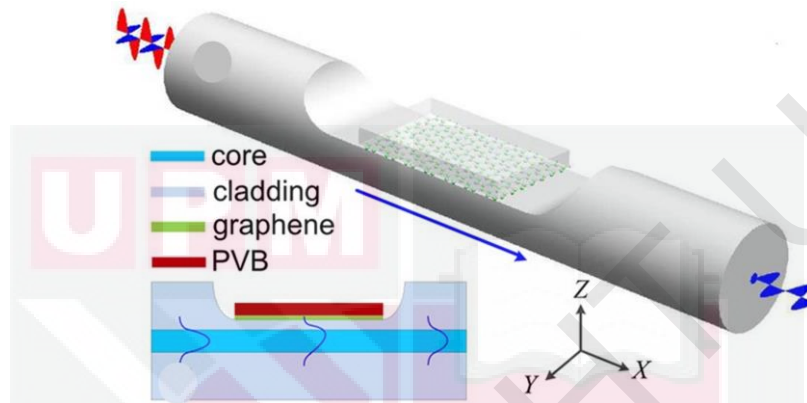


Figure 2.23 : Cross section of the coated D-shaped fiber [231]

2.11 Performance of Perovskite with Mode-Locked Pulsed Fiber Laser

Critical review on the ultrashort pulse generation based on halide perovskite based-SAs are summarized in Table 2.1. The importance of this critical review is to highlight the synthesis technique, SA fabrication techniques, laser type, and pulse duration. Majority of SAs in this category were fabricated through sandwiching method in which perovskite thin film is placed on fiber ferrule [49], [232], [233], [234]. For Q-switching pulse laser operation in EDFL cavity, this type of fabrication managed to reach 5.96 μs pulse duration at a center wavelength of about 1560 [233]. While for mode locking, the fiber laser was able to generate 492 fs, 922 fs and 950 fs laser pulses that are located at 1569.5, 1562.0 and 1558.8 nm, respectively [232]. Dissipative soliton was

obtained for CsPbBr₃ at center wavelength of 1600 nm with an edge-to-edge bandwidth of 4.5 nm and the pulse duration can be compressed from 14.4 ps to 1.046 ps with additional 25 m single mode fiber [49]. MAPbI₃ was incorporated into a ring laser cavity operating at 1064 nm by using YDF laser type and the output pulse has a pulse duration of 931 ps [234]. The weakness of this SA type has been discussed earlier. On the other hand, there are another method to deposit SA in order to fabricate SA. For example, The SA has been prepared by pressing high quality CH₃NH₃PbI₃ film onto the D-shaped fiber [235], and growth of CH₃NH₃SnI₃ micro sheet by solution method and deposited onto a D-shaped fiber [95] with achievement of shortest pulse duration at 1.13 ps and 1.77 ns, respectively. Furthermore, the operation of these halide perovskite SAs at differing wavelength bands show the promising potential of the SA for broadband operation as well. No investigation has been made on the use of halide perovskite-based polymer composites on tapered fiber.

Previous studies exhibited that halide perovskite is a suitable SA for nanosecond pulse generation in high-power solid-state lasers. CH₃NH₃PbI₃ film was used in application as a pulsed modulator in solid-state lasers at 1.06 μm [167]. Also, in another work, CH₃NH₃PbI₃-SA was applied for passively Q-switched Nd:YAG laser and the pulse duration was 192 ns. MAPbBr₃ was successfully embedded in mesoporous SiO₂ thin film and was employed as a SA to generate a Q-switched pulsed laser at 1.06 μm [236]. The latest work shows that the corresponding pulse width of CsPbBr₃ nanoplatelets was 69 ns and indicate its potential applications in optical communication, laser pulses

and nonlinear optics [237]. In general, solid-state lasers are large in size and easily disturbed by external factors such as vibration and temperature changes, leading to stability issues and higher maintenance costs. However, they have high output peak power, good beam quality, and high signal-to-noise ratio. In this thesis, one of the focuses are to integrate halide perovskite tapered fiber SAs in fiber lasers. Fiber laser features a compact structure, stable performance, and are not easily disturbed by external factors, making them easy to operate and maintain.

Despite the successful works on halide perovskite-based SAs, it has some environmental issues as a result of the use of a highly toxic heavy material (lead), as well as serious stability issue in moisture and UV irradiation. It becomes the researchers' social responsibility to find an alternative material to lead that does not impair the photo conversion efficiency of the semiconductor. In order to avoid lead pollution, lead should be replaced with elements that have similar properties.

Table 2.1: Material synthesis and fabrication techniques of halide perovskite-based SAs for ultrashort pulse generation.

No.	Halide Perovskite	Synthesis Technique	SA Fabrication	Laser Type	Pulse Duration	Year	Ref.
1.	CH ₃ NH ₃ PbI ₃ film	Solution processing and spin coating of perovskite solution on polyethylene substrate	Pressing of perovskite film on D-shaped fiber	EDF	1.13 ps	2018	[235]
2.	CsPbBr ₃ nanocrystal film	Solution-processing	Drop-casting of colloidal perovskite solution on gold mirror	YDF	216 ps	2016	[48]
3.	CsPbBr ₃ quantum dots	Solution-processing	Deposition of nanocrystals on fiber ferrule end-facet via light pressure	EDF	14.4 ps	2018	[49]
4.	CH ₃ NH ₃ SnI ₃ microsheet	Solution-processing	Growth of crystals on D-shaped fiber by deposition of reaction solution	YDF	1.77 ns	2018	[95]
5.	MAPbI ₃ nanosheet	Solution processing and vapor phase conversion	All-dry transfer of single nanosheet perovskite onto fiber ferrule end-facet	YDF	931 ps	2017	[234]
6.	CH ₃ NH ₃ PbI ₃ film	Solution processing	Drop cast of precursor solution onto glass and annealing	YDF	919 ns	2017	[238]
7.	CH ₃ NH ₃ PbI ₃ film	Solution processing	Spin-coating on quartz substrate	EDF	661 fs	2017	[239]
8.	(C ₆ H ₅ C ₂ H ₄ NH ₃) ₂ PbI ₄ film	Solution processing	Deposition the perovskite film on a side-polished fiber using spin coating	EDF	381 fs	2018	[168]

Table 2.1: Continued

9.	2D $\text{PEA}_2\text{PbBr}_4$ film	Solution processing	Perovskite film sandwiched between two fiber connectors of fiber ferrule	EDF	492 fs	2022	[232]
	Quasi-2D $\text{PEA}_2(\text{CsPbBr}_3)_n\text{-PbBr}_4$				922 fs		
	3D CsPbBr_3				950 fs		
10.	CsPbBr_3 nanocrystal film	Hot injection method	Perovskite film sandwiched between two fiber connectors of fiber ferrule	EDF	5.96 μs	2022	[233]
11.	$\text{CH}_3\text{NH}_3\text{PbI}_3$ film	Sequential deposition method	Spin coating thin film on a glass substrate	Nd:YGG	305 ns	2016	[167]
12.	$\text{CH}_3\text{NH}_3\text{PbI}_3$ film	-	Spin-coating on quartz substrate	Nd:YAG	192 ns	2019	[240]
13.	CsPbBr_3 nanoplatelets	Lateral growth with self-assembling arrangement	Spin-coating on quartz substrate	Nd:YVO	69 ns	2023	[237]
14.	MAPbBr_3 quantum dots	Spin-coating perovskite in mesoporous SiO_2 thin films	Embedded perovskite- mSiO_2 thin films as SA	Nd:YVO ₄	686 ns	2021	[236]
15.	CsPbBr_3 nanocrystal film	-	Drop coating toluene liquid on a gold mirror and dried at room temperature	Tm-doped double - clad fiber	24.2 ps	2019	[241]

2.12 Summary

To summarize, this chapter have four main parts which are the fundamentals of hybrid organic-inorganic perovskite, its instability and toxicity of lead (Pb^{2+}), single crystal perovskite in optoelectronic applications and the fundamental study of the pulse laser propagation in fiber cavity. It is important to understand the optical properties of the perovskite and its instability and toxicity of lead. This toxicity issue considered a major concern which is the toxicity of the dissolvable lead content in these materials presents a critical concern for future commercial development. It is also important to understand the fundamental of the soliton generation, and the choices of the fiber type SA available.

CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF METHYLAMMONIUM BISMUTH BROMIDE $\text{MA}_3\text{Bi}_2\text{Br}_9$ (MBB) PEROVSKITE SINGLE CRYSTAL

3.1 Introduction

This chapter describes the procedures, materials, and tools for the synthesis of methylammonium bromide, MABr precursor salt, the synthesis of methylammonium bismuth bromide, MBB perovskite single crystals, and both their material characterizations. The chapter begins by detailing the procedure to synthesize MABr precursor salt. Upon successful synthesis of the precursor salt, different precursor ratios were tested for the growth of MBB perovskite single crystals using slow evaporation method. The synthesized single crystal samples were characterized to validate successful material synthesis using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) analysis. UV-visible-Near-infrared (UV-Vis-NIR) spectroscopy analysis was performed for sample absorbance characterization. The flow chart of the methodology for this chapter is illustrated in Figure 3.1.

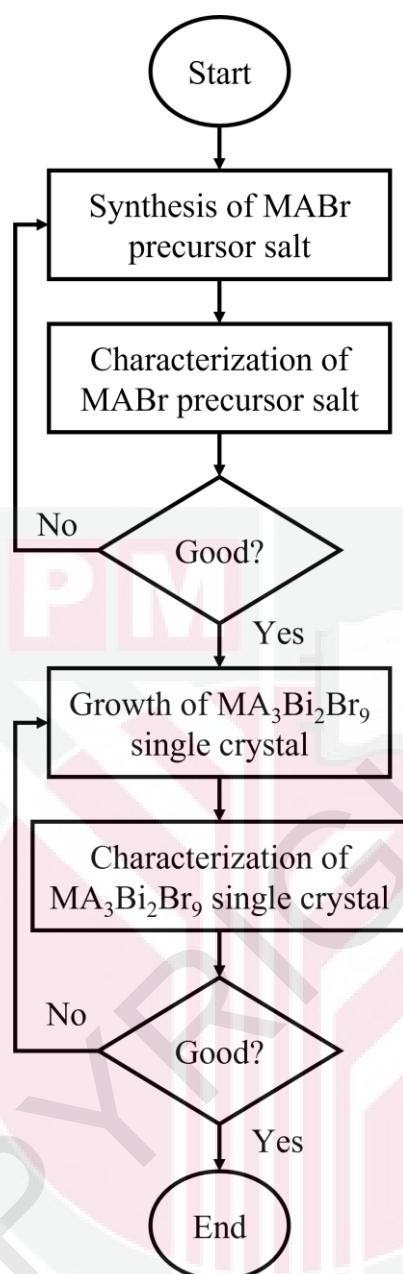


Figure 3.1 : Flow chart of the methodology.

3.2 Synthesis and Characterization of Methylammonium Bromide $\text{CH}_3\text{NH}_3\text{Br}$ (MABr) Precursor Salt

All materials used for MABr precursor salt synthesis were purchased and used as received without further purification. The materials include hydrobromic acid (HBr, 57 wt. % in water, distilled, stabilized, 99.95%), methylamines (CH_3NH_2 ,

33 wt. % in absolute ethanol), and diethyl ether (EMSURE ACS) were all purchased from Merck. Figure 3.2 shows the schematic diagram of the MABr precursor salt synthesis. The process began by reacting 30 mL of CH_3NH_2 and 23 mL of HBr as presented in chemical reaction Equation 3.1. Both CH_3NH_2 and HBr are volatile and exist as gas phase at room temperature, so this reaction was performed on one-neck round-bottom flask with constant stirring for 2 hours at (0°C) in ice bath, then homogenous transparent MABr solution was obtained [242]

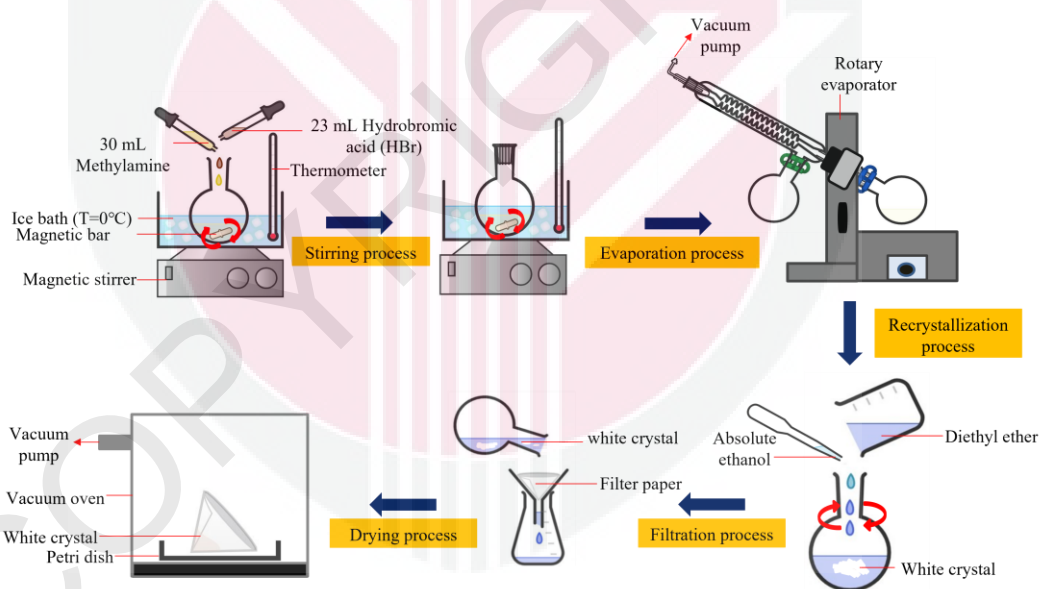


Figure 3.2 : The synthesis of MABr precursor salt.

The constant stirring condition provided kinetic energy to accelerate the acid-base reaction. The acid-base reaction is exothermic which releases energy in the form of heat to the surroundings, and therefore needs a cooling system

provided by the ice bath. After that, the product was placed in a rotary evaporator for 15 minutes, for solvent removal by evaporation. The rotary evaporator settings were 95 mbar, 400 rotation per minute and 60°C for the pressure, rotation speed, and temperature of the water bath, respectively. A yellowish precipitate was obtained after evaporation process and further purification process needed for the next step until white and crystalline salt appeared [242]. To purify the precipitate, it was dissolved in absolute ethanol and washed around three times using diethyl ether to remove the residual reagents. The diethyl ether was used as its good solvent for amine and the acid, but a poor solvent for salts as salts have very low solubility in it [243]. Diethyl ether also a hazardous chemical that vaporizes quickly at ambient temperature. The white and crystalline salt was appeared in solution after purification process, then the product was filtered with Whatman 40 filter paper (8-micron pore size) and dried in a vacuum oven at 60°C for 24 hours. Figure 3.3 (a) shows the photograph image in vial of white and crystalline salt obtained after the product was dried in the final process. After the drying process, the salt was stored in a desiccator at a pressure of -0.05 MPa. Vacuum desiccators are used to protect powder salt from reacting with water vapor from humid air. The physical appearance of MABr powder was assessed using an optical microscope as shown in Figure 3.3 (b).

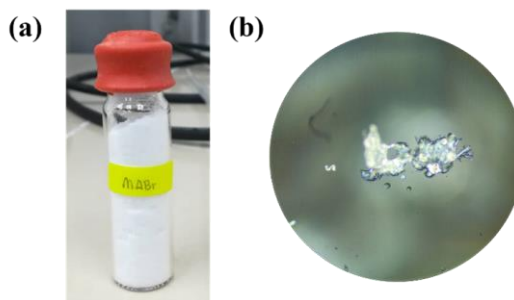


Figure 3.3 : Synthesized MABr powder salt (a) powder in vial and its (b) optical microscope image.

3.2.1 X-Ray Diffraction (XRD) Analysis

The phase formation of as-synthesized MABr precursor salt powder is confirmed by XRD method using a Bruker AXS D8 diffractometer with Cu-K α radiation at $\lambda = 1.54 \text{ \AA}$. The scan was performed from 5° to 70° . Figure 3.4 shows the powder XRD patterns of the MABr precursor salt and the characterization results match well with previous findings indicating high purity of the MABr powder [244]. The similar phase identification of the XRD pattern characterization and the reference code of Joint Committee on Powder Diffraction Standards (JCPDS) database in reference code of JCPDS 00-010-0699 indexing the MABr compound were also verified. Based on the analysis, the MABr precursor salt has a tetragonal structure with lattice parameters of $a=b=4.82 \text{ \AA}$ and $c=8.78 \text{ \AA}$. Meanwhile, the α , β and γ are 90.000° . The typical peaks at 2θ with 10.03° , 20.18° , 20.93° , 27.19° , 27.39° , 30.48° , 33.18° , 35.79° , 37.15° , 38.59° , 40.51° , 45.30° , 46.77° , 48.83° , 51.97° , and 59.06° were ascribed to (001), (002), (101), (110), (102), (111), (003), (112), (103), (200), (201), (113), (004), (212), (203), (005), and (115) planes, respectively which

indicate the tetragonal phase of the MABr powder. In addition, sharp XRD peaks further reveal the tetragonal MABr powder's phase purity.

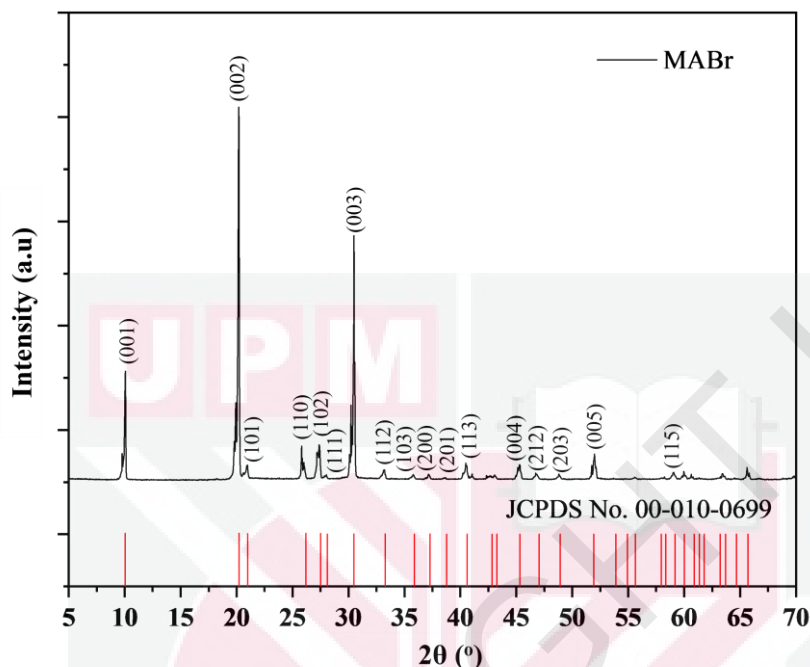


Figure 3.4 : XRD pattern of synthesized MABr precursor salt powder.

3.2.2 Field Emission Scanning Electron Microscope (FESEM) and Energy Dispersive X-Ray (EDX) Analysis

The FESEM-EDX image (JEOL JSM-7600F) were used to analyze the morphology of the surface and the elemental composition of synthesized MABr powder are shown in Figure 3.5. Upon examination of the image in Figure 3.5 (a), the FESEM image of 100 x magnification reveal that the synthesized MABr salt shows nonuniform aggregation morphologies that are irregular in shape, a typical characteristic of the MABr organic compound [245]. Then, MABr powder was further examined using EDX to check its elemental composition. The EDX results in Figure 3.5 (b) shows that the Carbon (C), nitrogen (N) and

bromine (Br) powder elements were considered to exist on the MABr with 29.57 wt%, 26.35 wt% and 44.08 wt% respectively.

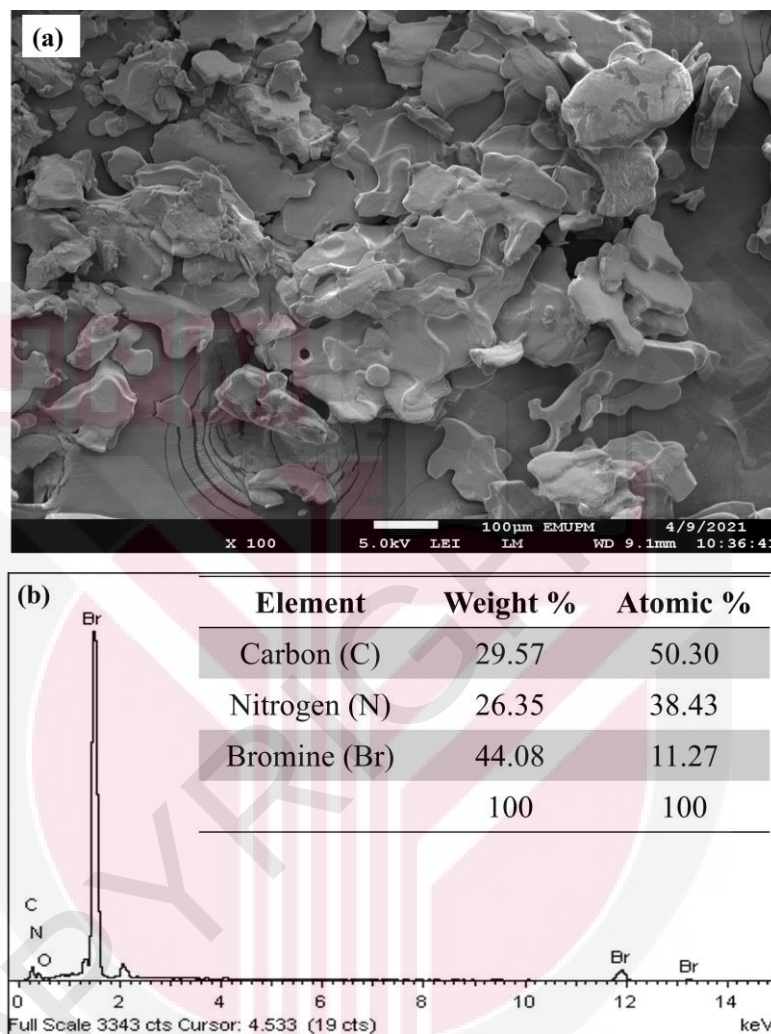


Figure 3.5 : (a) FESEM image and (b) EDX analysis of the synthesized MABr precursor salt powder.

3.2.3 UV-Vis-NIR Spectroscopy Analysis

The UV–Vis-NIR absorbance of MABr powder ranging from 250 nm to 2000 nm was obtained using Shimadzu UV-2600 spectrophotometer. Figure 3.6 (a) depicts the strong and broad absorption spectra obtained in the visible range

between 350 and 650 nm as denoted in shaded region A, indicating the MABr powder's light harvesting property. Additionally, the clear absorption edge of MABr powder was observed at nearly 650 nm, which is consistent with prior reported studies [246]. For near-infrared laser application, the absorption of as-synthesized MABr precursor salt at long wavelength was also investigated. Our result in Figure 3.6 (a) shows broad absorption from 1500 nm to 1950 nm at shaded region B. The origin of this absorption can be speculated from different synthesis environment such as pressure, temperature, humidity, pH and other factors. Hence, this preliminary result will be beneficial for our future perovskite-SA pulse laser application in future work.

The bandgap of MABr powder was estimated through Tauc plot as shown in Figure 3.6 (b). This plot is derived from the UV-Vis-NIR absorption spectrum, where the optical density (O.D.) of absorbance is converted to $(\alpha h\nu)^{1/r}$ for the y-coordinates. In this conversion, the absorption coefficient, α , of the material is related to the optical density by dividing the optical density by the thickness of the material, or by using previously reported values of α for the material. The absorption coefficient is then multiplied by the energy of light in eV and raised to the power of $1/r$, where the value of r is determined by the type of semiconductor studied, and if the transition is allowed or forbidden [247]. Allowed transitions most likely take place when angular momentum, energy, and linear momentum are conserved, resulting in direct transitions induced by a single photon process. On the other hand, when these quantum quantities are not conserved, forbidden transitions occur, which are transitions between states that require other interactions with additional particles involved, such as

photons or phonons, and are less likely to occur. Here, $r = 1/2$ for direct band gap semiconductors with allowed transitions, $r = 3/2$ for direct band gap semiconductors with forbidden transitions, $r = 2$ for indirect band gap semiconductors with allowed transitions, and $r = 3$ for indirect band gap semiconductors with forbidden transitions. Therefore, $r = 1/2$ for MABr is chosen for the Tauc plot, as it is a direct band gap semiconductor with allowed transition. Band-to-band transitions are often used to estimate the optical band gap. The x-coordinates in the Tauc plot are simply the wavelength converted to energy of incident light by the relationship shown in Equation 3.2 [242].

$$E_g \text{ (eV)} = 1237.5/\lambda \quad (3.2)$$

where E_g is the bandgap of the material in eV and λ is the wavelength of the absorption edge curve. When these are plotted together, the Tauc plot is formed. By extrapolating the linear region of the $(\alpha h\nu)^2$ to the energy-axis ($h\nu$) intercept as shown in Figure 3.6 (b), E_g is established. Here, the E_g of MABr powder was estimated at 1.88 eV.

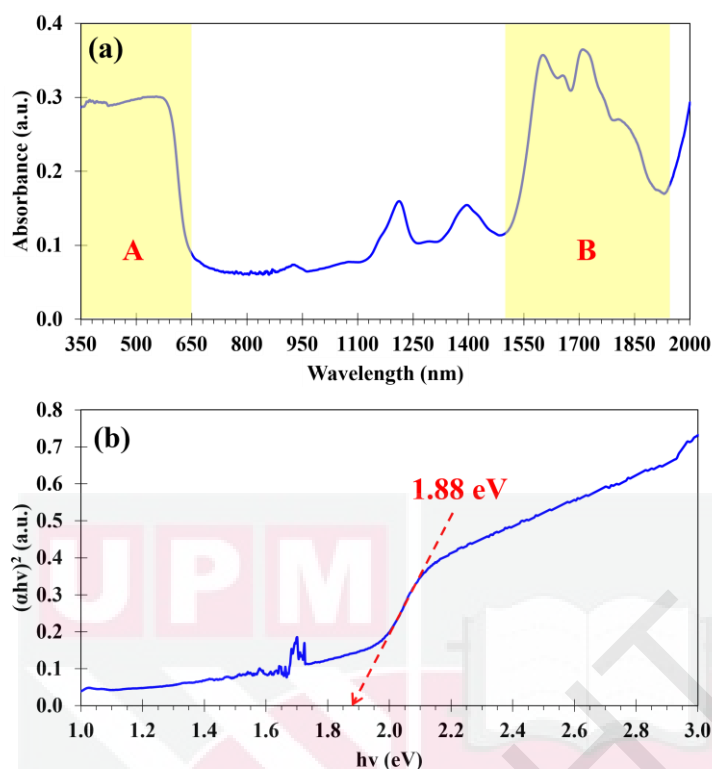


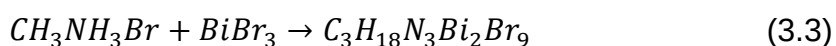
Figure 3.6 : (a) UV-Vis-NIR optical absorption spectrum and (b) Tauc plot of synthesized MABr precursor salt powder

3.3 General Growth and Characterization of MBB Single Crystal

All MBB single crystals studied in this work were synthesized as part of this work. All materials used for MBB single crystal synthesis were purchased and used as received. The materials include MABr as synthesized in Section 3.2 and bismuth tribromide (BiBr_3 , $\geq 98\%$, Sigma-Aldrich). Solvent used for crystal growth solutions include anhydrous methanol for analysis (Supelco, max. 0.003% H_2O) were used without further purification.

All single crystals in this work were grown using slow evaporation method and this method had been reported in many previous studies for synthesis MBB

single crystal [248], [249], [250]. In this method, when the solvent evaporates, the concentration of the solution reaches the critical concentration and becomes supersaturating, solute colloid begins to nucleate and grow into crystal. First, the stoichiometric mixture of 3 mmol (0.12 g) of MABr and 2 mmol (0.40 g) of BiBr₃ was dissolved in 15 mL anhydrous methanol (CH₃OH). The precursor solution was magnetically stirred using magnetic bar at room temperature until the solution has fully dissolved. Then, the solution is filtered using 0.05 µm polytetrafluoroethylene (PTFE) filter. Once filtered, the solution is placed in a petri dish and sealed with parafilm and punctured with needles to control the rate of crystalline growth. Then, the petri dish was kept at room temperature and the solution is gradually evaporated to promote crystallization for crystal growth over the course of 4 days. As shown in Figure 3.7, the schematic representation of crystal growth process. Once all the solution had been completely evaporated, the crystals are stored in a desiccator under vacuum condition to avoid any environmental effects from ambient air conditions, and the desiccator was stored in dark room to avoid any adverse effects from prolonged exposure to light during storage. Figure 3.8 depicts the variety of single crystals grown after 4 days the solution were evaporated in petri dish. This process is presented in chemical reaction Equation 3.3.



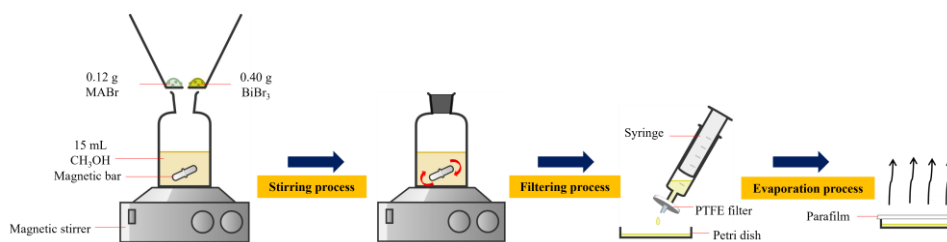


Figure 3.7 : Schematic representation of crystal growth process via slow evaporation method.

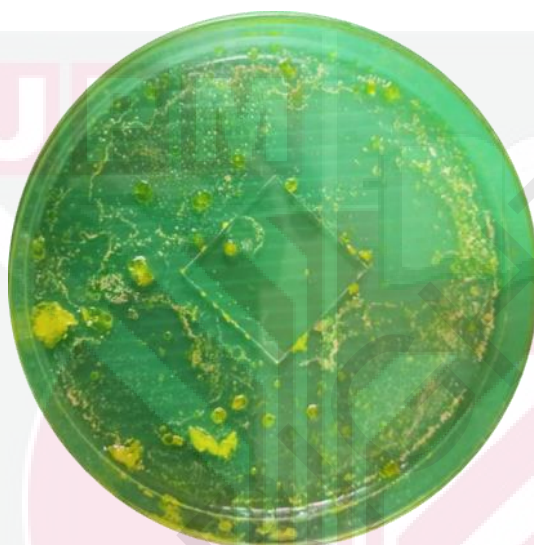


Figure 3.8 : Photograph image of single crystals grown in a petri dish.

Diverse single-crystal shapes can be achieved by effectively managing the thermodynamics and kinetics of nucleation and growth. According to classical nucleation theory shown in Equation 3.4 [251], the nucleation of a single crystal is initiated when the concentration of the solute is sufficiently higher than the solid solubility or in supersaturated state. This is achieved by overcoming the Gibbs total free energy (ΔG_T) which is the sum of surface free energy (ΔG_s), and bulk free energy (ΔG_v). The surface free energy ΔG_s is the free energy between the particle surface and the bulk of the particle, which is proportional to r^2 , while bulk free energy ΔG_v is the free energy between a very large particle

and the solute in solution, which is proportional to r^3 and negative when the solution is in supersaturated state.

$$\Delta G_T = \Delta G_V + \Delta G_S = -\frac{4}{3}\pi \frac{r^3}{V} \Delta\mu + 4\pi r^2 \sigma \quad (3.4)$$

where r , V , $\Delta\mu$, and σ represent the radius of the nucleus, the volume of each nucleus or molecule, the difference in the free energy of the system between its final and initial states, and the surface free energy, respectively. $\Delta\mu$ can also be thermodynamically expressed as Equation 3.5.

$$\Delta\mu = kT \ln S \quad (3.5)$$

where k , T , and S refer to the Boltzmann constant, absolute temperature, and supersaturation ratio, respectively. Specifically for solution-based growth methods, supersaturation can be initiated by regulating the temperature, by adjusting the evaporating solvents, or by introducing poor solubility solvent into the solution [252], [253], [254]. Meanwhile, factors such as temperature, different solvent, evaporation rate, concentration, and pressure play substantial impact on packing arrangements, morphologies and properties even though the molecular structures are the same [255], [256]. Due to the slow self-assembly process, a solvent with high boiling point is generally preferable for the ordered molecular packing arrangements. Meanwhile, high solubility may hinder precipitation until only a small amount of solution remains, resulting in polycrystals, whereas low solubility solvents are unlikely to yield

crystals or large crystals. A fast evaporation rate (high temperature and low boiling point) may also result in clusters along the contact line [257]. Furthermore, He et al. [258] shows different concentration of solution were also another important factor which is platelet-shaped α -C6-DBTDT were obtained at concentration of chlorobenzene solution (5.0 mg mL^{-1}), whereas micro ribbon-shaped β -C6-DBTDT were obtained at concentration of chlorobenzene solution (0.3 mg mL^{-1}). Park et al. also discovered a crystal shape is heavily influenced by the geometry of the solvent as pseudo-3D (carbon tetrachloride (CCl_4)) solvents guide C_{60} molecules to self-assemble into p2D hexagonal disc structures, whereas p2D (mesitylene, m-dichlorobenzene, and m-xylene) and p1D (n-hexane) solvents produce p1D C_{60} wire and p0D C_{60} dot structures, respectively [259].

Figure 3.9 shows the photographs observations by using optical microscope of MBB crystal morphologies grown via slow evaporation method. It's worth noting that the MBB crystals are yellow in colour and growth in variety of shape. Different crystal shapes forms are frequently caused by intrinsic crystallographic structures and preferred growth directions [260]. From previous report, a similar shape is observed for the MBB crystals in Figure 3.9 (a) which are generally formed as hexagonal shape [248], [261]. It is also found that in Figure 3.9 (b), some of them formed square shape was observed. While most of them are generally formed as irregular shapes and stacked together as shown in Figure 3.9 (c) as it might happened due to the different temperature during growing process in room temperature for an extended period of time [260], [262]. Solution-based crystal growth based on slow

evaporation method has proven advantageous due to the simple, low-cost, and quick yield technique.

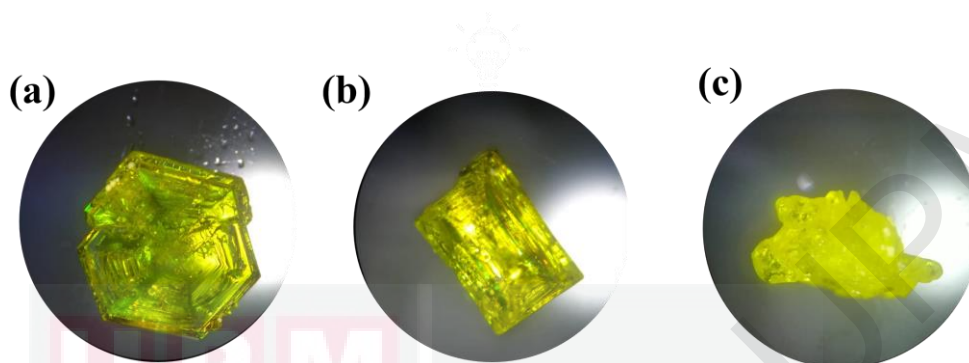


Figure 3.9 : Different shapes of MBB single crystals grown via slow evaporation method; (a) hexagonal, (b) square, and (c) other shape.

3.3.1 XRD Analysis

XRD analysis with Cu K α radiation was used to characterize our MBB single crystals to determine the crystal structure and phases. To perform this characterization, the MBB single crystal has to be grinded into fine powder. In order to make sure that the samples are free from residues or inclusion of starting materials MABr and BiBr₃, the XRD from the reactant samples was also measured and is included in Figure 3.10 (a)-(c). Careful examination confirms that there is no crystalline residue from either MABr and BiBr₃ in the final crystal products. All the samples are not only pure in composition, but also in crystalline phases. Powder XRD crystallographic analysis reveals that the crystal structure of all three different shape in MBB perovskite belongs to the hexagonal system at room temperature. The peaks of the three shapes were indexed and matched with the JCPDS 00-044-1927 reference code and

consistent with previous literature [261]. Metal halide octahedra layers are visible in the structure, and the voids between the layers are filled with MA^+ . Six metal halide octahedra surround one MA^+ group [248], [263].

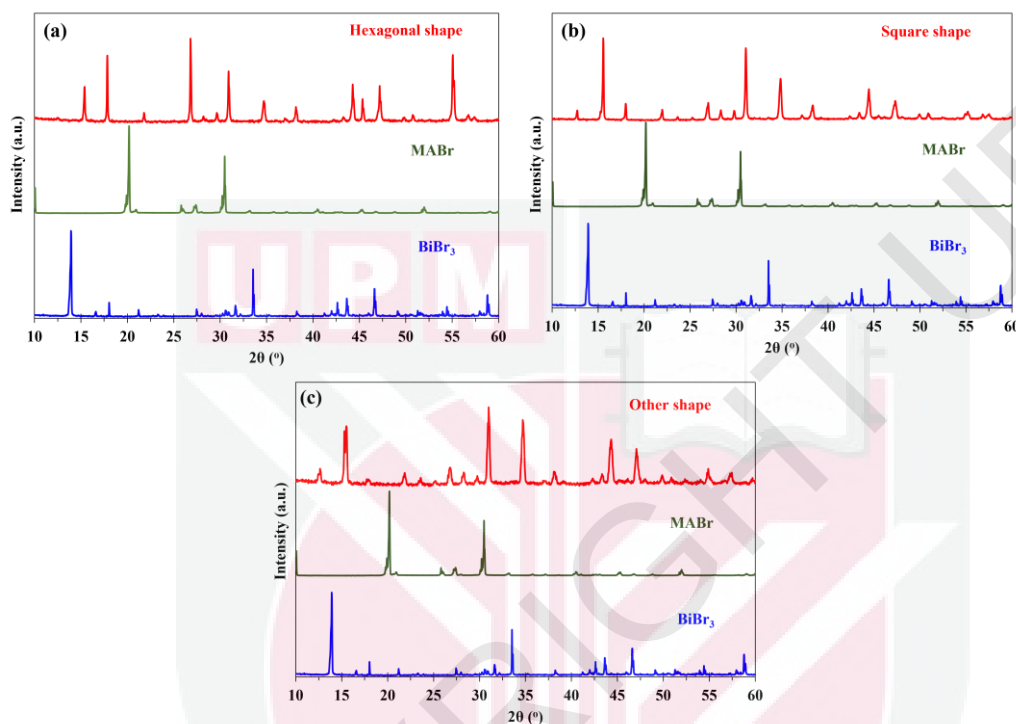


Figure 3.10 : Powder XRD pattern of MBB single crystal; (a) hexagonal shape, (b) square shape, and (c) other shape.

For comparison, XRD patterns of the three different crystal shapes (hexagonal, square and other) are shown and compared in Figure 3.11. The similarities in peak positions between the three different shapes indicate that the as-grown MBB single crystals have the same pattern and phase. The dominant peaks in MBB powder were observed for three different shapes are at $2\theta = 15.28^\circ$, 26.73° , 30.84° , and 34.61° corresponding to lattice planes of (101), (003), (202) and (113), respectively. However, the intensity peaks of the three different shapes differ, which could be due to a variety of factors. For instance,

if a crystal structure has more atoms in a specific plane, it may show a higher intensity in the XRD pattern because more counts accumulate in this orientation [264]. Different atomic planes have different atomic densities per unit area of the plane, resulting in a different amount of scatterers, different scattering density, which translates to different intensity peaks in the XRD. In other words, peak intensities in an XRD will vary because the intensity is proportional to the number of scatterers per unit area of a given atomic plane [265]. The intensity of the peak typically decreases as the plane's indices increase, indicating higher angles in the pattern. Figure 3.11 shows that the dominant peak for the hexagonal shape is (003), whereas the dominant peaks for the square and other shapes are (101) and (202), respectively. Another possible reason for the differing highest intensity peaks is due to texture in some directions of the measured crystal [266]. Other reasons could be the measurement geometry setup or the intrinsic properties of the crystal [20].

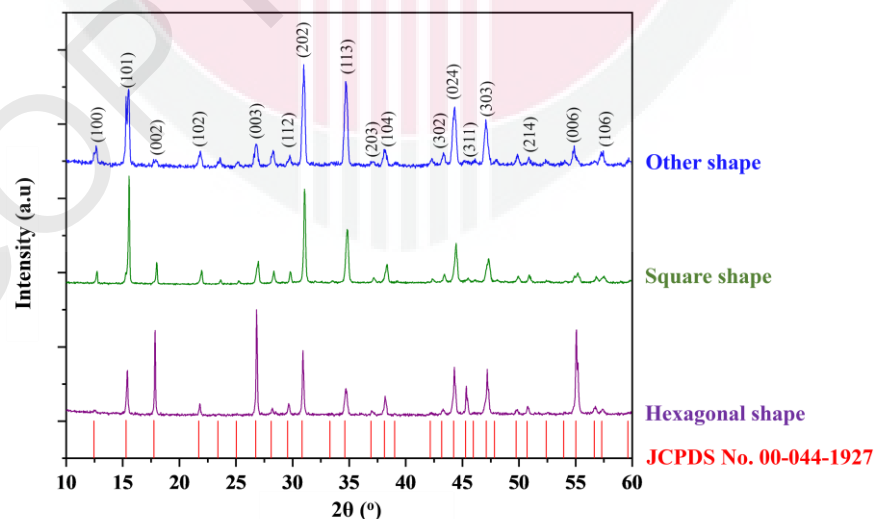


Figure 3.11 : The powder XRD comparison of MBB single crystal; hexagonal shape, square shape, and other shape.

Table 3.1: Crystallographic Data for MBB single crystal.

Chemical Formula	$C_3H_{18}Bi_2Br_9N_3$
Wavelength, Å	CuK α ($\lambda=1.5418$ Å)
Crystal System	Hexagonal
Lattice type	P
Space group name	P-3m1
Space group number	164
Z	1
Lattice parameters	
a, Å	8.2120
b, Å	8.2120
c, Å	10.0089
α , deg	90.0000
β , deg	90.0000
γ , deg	120.0000

Where a, b, c, unit-cell parameters; α , β , γ , unit-cell angles; Z, number of formula units in the unit cell. The crystallographic data in Table 3.1 shows that MBB belongs to hexagonal crystal family with trigonal crystal system and space group of P-3m1. The unit cell in this lattice has a hexagonal shape with three equal sides of three 120 degrees angles between them. The letter P indicates a primitive lattice type where only 1 atom exist per unit cell, while m in the space group symbol indicates presence of 3 mirror planes that intersect at 60 degrees angle which define the lattice symmetry. The negative sign in

the space group indicates the lattice also exhibits inversion symmetry. Unit cell parameters and angles are $a = b = 8.2120 \text{ \AA}$, $c = 10.0089 \text{ \AA}$, and $\alpha = \beta = 90.00^\circ$, and $\gamma = 120.00^\circ$, respectively.

3.3.2 UV-Vis-NIR Spectroscopy Analysis

The optical properties of MBB crystal powder in three different shapes (hexagonal, square and other) were investigated using UV-Vis-NIR spectrometers. The MBB perovskite is yellow in colour shows the strong broadband absorption at about 490 nm as shown in Figure 3.12 (a), which is slightly redshift from the value reported before [263], [267]. This is happened due to increase of precursor concentration on MBB single crystals preparation [268]. The corresponding bandgaps of MBB perovskite in three different shapes were determined on the basis of the tauc plot by plotting $(\alpha h\nu)^{1/r}$ with respect to $h\nu$ in Figure 3.12 (b) by the crossing points of the prolonged tangent of the absorption edge to the photon energy axis. As all three different shape kinds of MBB perovskite are direct-bandgap semiconductor materials, the r value is $\frac{1}{2}$ [269]. The estimated direct bandgap, E_g of the MBB perovskite were 2.57 eV, 2.53 eV and 2.58 eV for hexagonal, square and other shape, respectively. The wide bandgap of perovskite for three shapes around ~ 2.5 eV is consistent to previous reported works in [248]. Additionally, Figure 3.12 (a) also presents broad absorption of MBB perovskite at longer wavelengths between 1500 nm to 1950 nm. Absorption in the near-infrared offers potential optical applications in the communication channel.

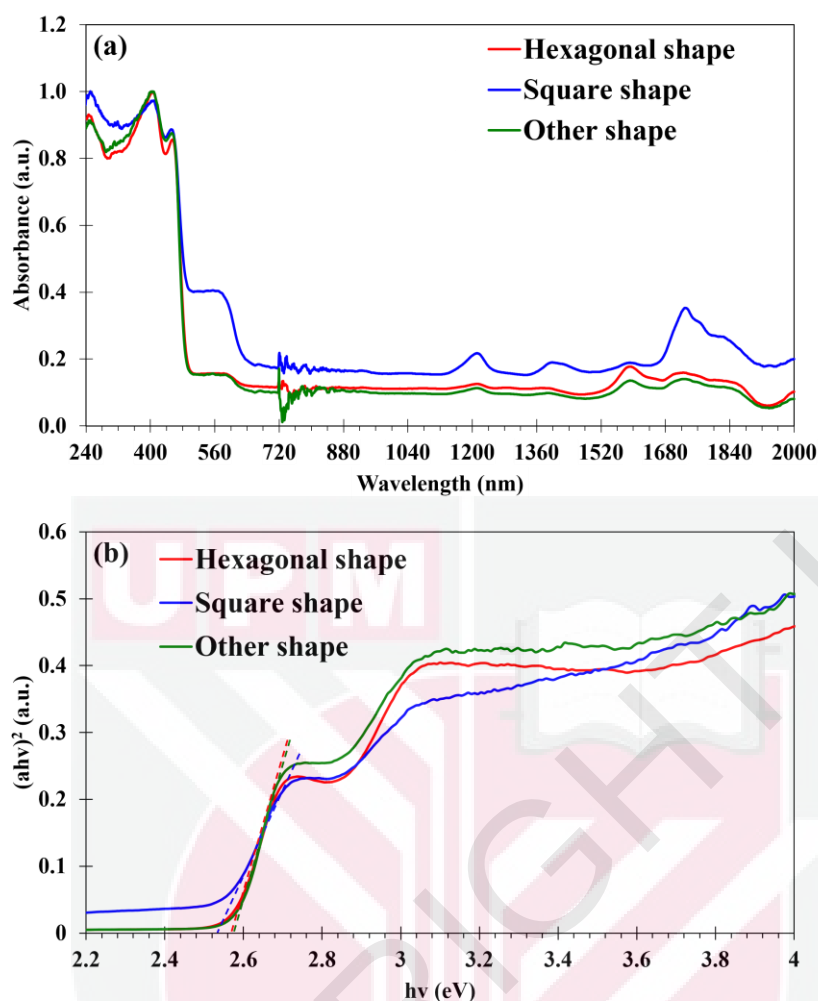


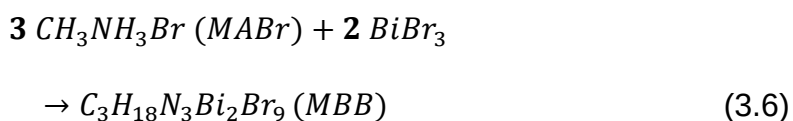
Figure 3.12 : (a) UV-Vis-NIR absorption spectrum (b) Tauc plot from an absorbance to calculate band gap of MBB single crystal; hexagonal shape, square shape, and other shape.

3.4 Precursor Ratio Effect on MBB Single Crystal Growth

The next parameter investigated in the perovskite crystal growth is the amount and the molar ratio of precursors in solution. Numerous papers in the literature mention the usage of various precursor quantities, but seldom go into depth about why the quantity and ratios of precursors significantly affect the crystalline quality [260], [262]. From the previous report, Wei et al [270] reported with more MABr in growing high-quality MAPbBr₃ single crystals and

yield better crystals are needed in order to achieve a large charge carrier mobility (μ)-charge carrier lifetime (τ) product ($\mu\tau$ -product) [270]. An alternative to lead to constitute in perovskite would be bismuth, Bi^{3+} because it is isoelectronic (has similar electronic structure) with Pb^{2+} and is more stable than Sn^{2+} [271]. Bismuth is also lower in toxicity than lead according to materials safety data sheet. However, there are no reports on the effects of precursor ratio for bismuth-based perovskite material yet. In this section, MBB single crystals will be grown with various precursor molar ratios of MABr to BiBr_3 including 3:1, 3:2, 3:3, and 3:4, using anhydrous methanol as the solution solvent via slow evaporation method as described previously in Section 3.3.

Figures 3.13 presents the photographs of crystals formed by different molar ratio precursor composition. In Figure 3.13 (a), a few white-colored deposits (red arrows) in the top-view image for a 3:1 molar ratio of MABr: BiBr_3 suggests that there was an excess of MABr precursor in the synthesis, and it did not react completely with the BiBr_3 precursor. This phenomenon indicates that there may have been unreacted or partially reacted MABr in the mixture. In a chemical reaction, it's essential to have the correct stoichiometric ratio of reactants to ensure complete reaction and the formation of the desired product. Equation 3.6 shows the balanced equation from synthesis reaction for MBB perovskite.



From the standard balanced equation of Equation 3.6, it shows that 3 moles of MABr reacts with 2 moles of BiBr_3 forming 1 mole of MBB. Because of that, as shown in Figure 3.13 (b), the crystals of 3:2 molar ratio allow complete single crystals growth with similar grain size. Moreover, 3:3 molar ratio also allows for complete single crystal growth, however the crystal grain size of 3:3 molar ratio showed irregular and smaller than 3:2 molar ratio as depicted in Figure 3.13 (c) indicating that the nucleation and growth of the MBB perovskite single crystals is random. Increasing the amount of BiBr_3 in the perovskite precursor increases the number and coverage of crystal grains, but decreases their size. This suggests that a high molar ratio of BiBr_3 can retard the growth of crystalline grains while enhancing the amount of nucleation [272]. Moreover, we found that the shape of the MBB crystals were induced from Figure 3.13 (b) different from Figure 3.9 even though similar molar ratio of 3:2 was used. This is due to uncontrollable temperature throughout the growing process, as temperature is a critical concern in the slow evaporation method [260], [262]. On the other hand, incomplete crystal growth is exhibited for 3:4 molar ratio, where the saturated solution did not evaporate completely, leading to wet condition (red arrows) and unfinished growing process of single crystal even after a month as shown in Figure 3.13 (d). The concentration of the precursor MABr: BiBr_3 is at its highest in a saturated solution. When a solution is supersaturated (3:4 molar ratio), an excess of BiBr_3 is present that cannot dissolve in the solvent at the prevailing conditions. This excess BiBr_3 may go undissolved and impede the growth of well-defined single crystals. Therefore, 3:4 molar ratio of MABr to BiBr_3 is not suitable for further characterization.

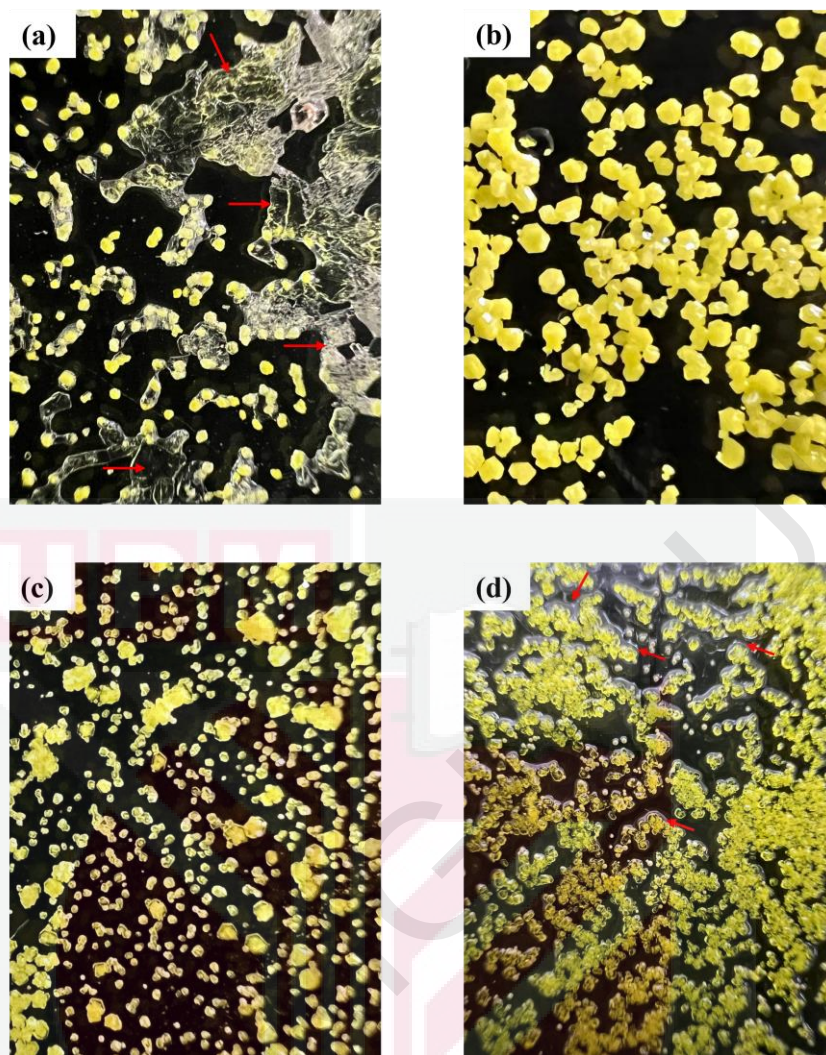


Figure 3.13 : The photograph of single crystals obtained with different molar ratio of MABr:BiBr₃ (a) 3:1, (b) 3:2 and (c) 3:3 (d) 3:4.

3.4.1 Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscopy (SEM) are carried out to image the nanocrystals and to provide direct evidence for variation of sizes with molar ratio. The SEM images, EDX spectra, and particle size distributions of the MBB single crystals with different precursor molar ratios are presented in Figure 3.14. The single crystals were characterized by SEM images as shown in Figure 3.14 (a)(d)(g). The single crystals for the three different molar ratios showed irregular grain

shapes and different grain sizes. All samples tended to agglomerate, or clump together, due to surface interactions and magnetic forces between the particles. To further characterize the variation in crystal size, the grain crystal size distribution was calculated for each molar ratio (Figure 3.14 (b)(e)(h)). The quantitative analysis for the SEM images using lognormal distribution model revealed that the average particle sizes of the samples were of 8.47 ± 2.65 , 4.09 ± 1.22 , and $3.09 \pm 0.82 \mu\text{m}$ for the respective 3:1, 3:2, 3:3 molar ratios samples, confirming the reduction of crystal size concomitant with the increase of BiBr_3 ratio precursor and proved the photograph images observed from Figure 3.13. The quantity and coverage of crystal grains increase as the BiBr_3 content of the perovskite precursor increased, whereas the size decreased. As the concentration of the precursor increases, so does the level of supersaturation in the solution. Supersaturation occurs when the concentration of a precursor surpasses its equilibrium solubility. Supersaturation increases the driving force for nucleation and crystal growth [272].

Figure 3.14 (c)(f)(i) shows EDX characterization of the samples and the existence of the Br, Bi and C atoms were confirmed. The weight percentage of the Br contents in molar ratio $\text{MABr}:\text{BiBr}_3$ of 3:1, 3:2 and 3:3 was 49.81, 36.43 and 52.46 wt%, respectively, whereas weight percentage of the Bi contents were 26.52, 19.14 and 31.68 wt%, respectively. Gold (Au) was also detected from this analysis due to the sputtering process which is typical before an analysis is performed to prevent charging of the surface, to promote the emission of secondary electrons so that the specimen conducts evenly, and to provide a homogeneous surface for analysis and imaging.

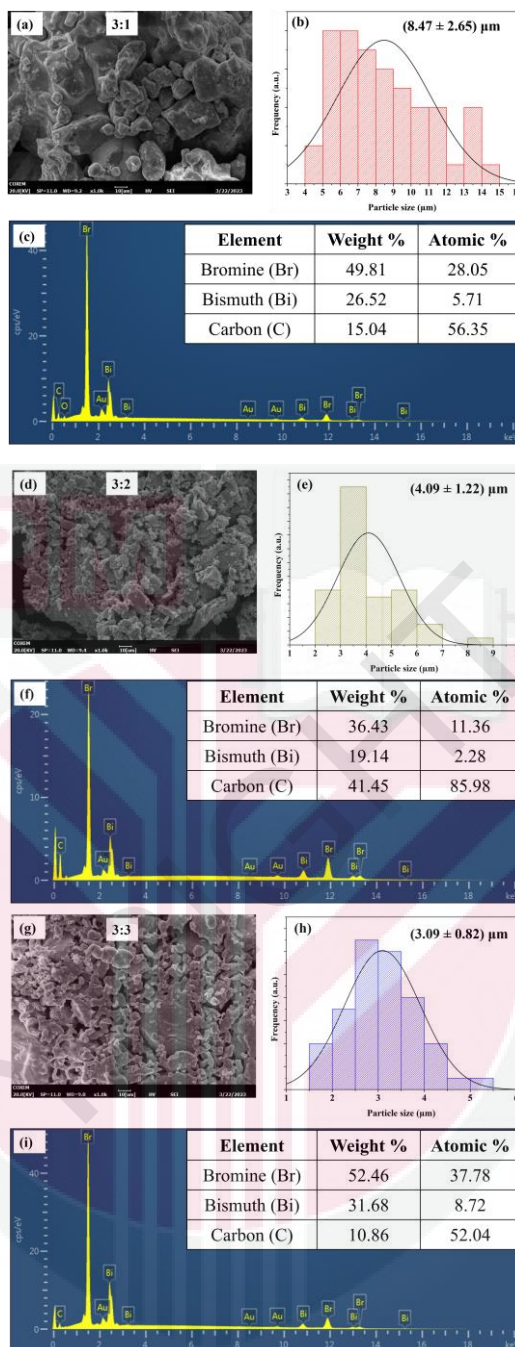


Figure 3.14: SEM images of MABr:BiBr₃ different molar ratios of (a) 3:1, (d) 3:2, and (g) 3:3, respectively. The corresponding size distribution is given on the right panel with MABr:BiBr₃ different molar ratios of (b) 3:1, (e) 3:2, and (h) 3:3, respectively. EDX spectra of MABr:BiBr₃ different molar ratios of (c) 3:1, (f) 3:2, and (i) 3:3, respectively. Inset: element percent composition.

3.4.2 UV-Vis NIR Spectroscopy Analysis

To further study the influence of MABr: BiBr₃ ratio on the optical properties of MBB single crystals, Figure 3.15 (a) shows the UV-Vis-NIR absorption of MBB single crystals with different molar ratios of MABr to BiBr₃; 3:1, 3:2, and 3:3 in the range from 200 nm to 2500 nm wavelength. Figure 3.15 (a) shows the UV-Vis-NIR absorption spectra with sharp absorption edges, whose blue shift is indicative of an enlargement of band gap energy and vice versa. As illustrated in Figure 3.15 (a), a gradual red-shift of absorption edge is observed with the increase of BiBr₃ in MABr: BiBr₃ ratio, which means a decrease of bandgap energy as shown in Figure 3.15 (b). This decrease can be attributed to the increase in bromine doping caused by the addition of BiBr₃. The increasing absorbance of MBB perovskite single crystals may be due to the increase in the absorbed area caused by the large coverage of grains [272]. Also, the absorbance of MBB perovskite single crystals is positively correlated with precursor concentration as the concentration increases, the absorption of the MBB perovskite single crystal increases [268]. Value of the bandgap (E_g) can be observed from the intercept of a tangent line to the linear part of the plot $(\alpha h\nu)^2$ versus $h\nu$ as shown in Figure 3.15 (b). Values of bandgap are deduced for the molar ratio of 3:1 was 2.74 eV, while for molar ratio of 3:2 and 3:3, the bandgap were 2.58 eV and 2.57 eV, respectively and which is bandgap for molar ratio of 3:2 and 3:3 match with previous reports [248], [263].

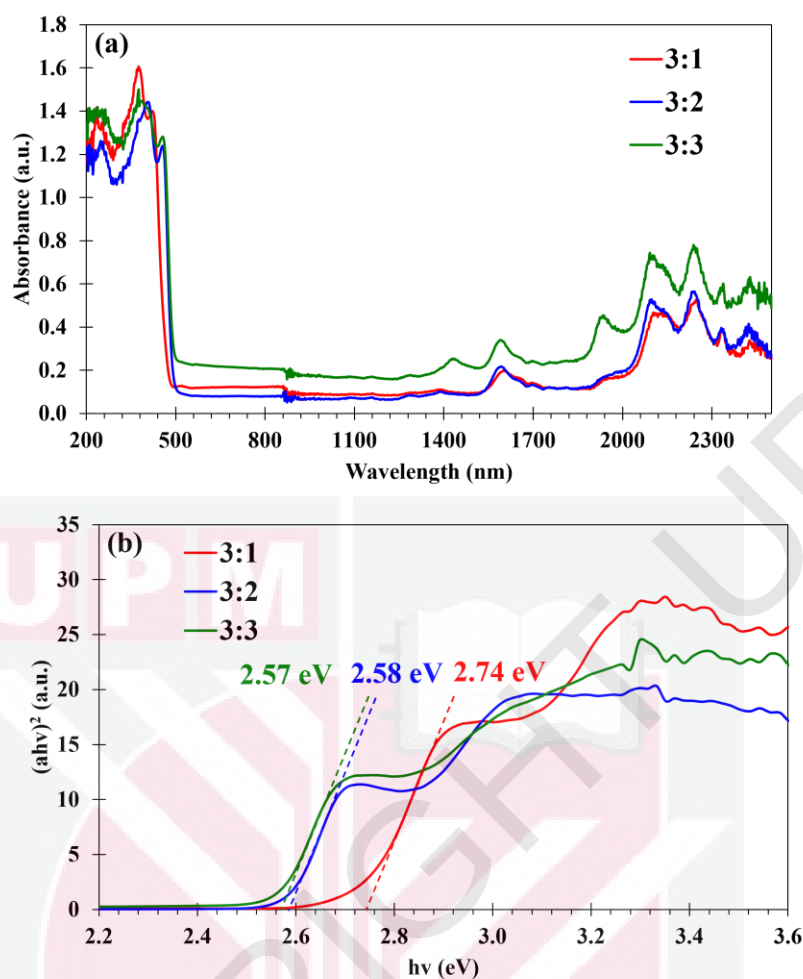


Figure 3.15 : (a) UV-Vis-NIR spectra and (b) the corresponding optical bandgap energies estimated using Tauc plot of MABr:BiBr₃ different molar ratios; 3:1, 3:2, and 3:3.

3.4.3 XRD Analysis

To characterize the quality of our as-grown single crystal and analyze the change in crystal structure, we applied the powder XRD test as shown in Figure 3.16. From Figure 3.16, it is revealed that the XRD pattern for molar ratios 3:2 and 3:3 is similar with previous references database without any impurity phases confirming the high crystallinity. Furthermore, the MBB crystals from molar ratio 3:2 and 3:3 belong to the hexagonal structure and

perfectly align to P-3m1 space group with the main characteristic peaks located at 15.3° , 30.8° and 34.6° assigned to (101), (202) and (113) planes, as reported in other literature [261]. The dominance of (101) peak indicates the preferred orientation of MBB perovskite growth is (100). With the increase of BiBr_3 molar ratio, the XRD peak intensity gradually increases, which is attributed to the addition of BiBr_3 enhancing the orientation growth of MBB perovskite. The XRD pattern of the molar ratio (3:1) is however different than the other two ratios indicate different in the crystal structure and composition of the synthesized perovskite material was observed, which validates the incomplete reaction of MABr with BiBr_3 . The XRD results demonstrated that molar ratio of MABr to BiBr_3 will directly influence the structure of crystal. Usually, the structure of crystal changes will also affect the optical properties of the MBB perovskite [273], [274].

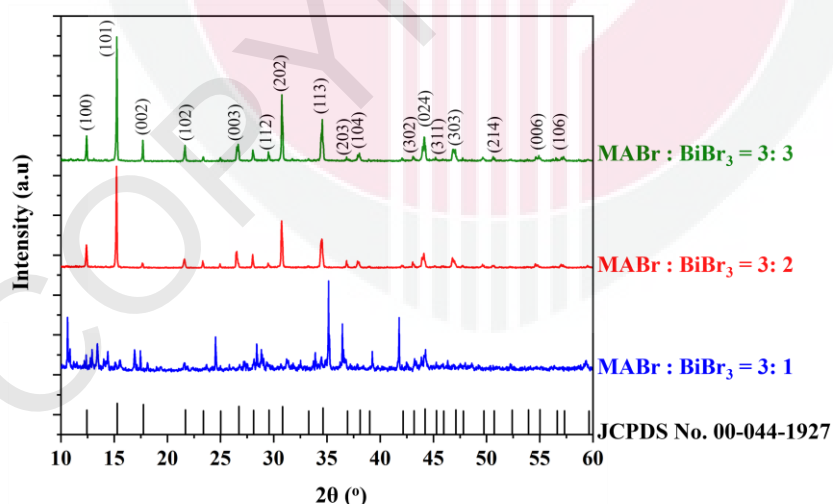


Figure 3.16: The XRD pattern for different molar ratio of $\text{MABr}:\text{BiBr}_3$; 3:1 (in blue), 3:2 (in red), and 3:3 (in green).

3.5 Summary

MBB single crystal perovskite was successfully synthesized using slow evaporation method. The formation of MBB single crystal was confirmed using the XRD and UV-Vis-NIR measurements. Different shapes of MBB perovskite were observed during slow evaporation method, however their structural and optical properties were similar. The molar ratio of MABr:BiBr₃ in the precursor solution was then manipulated and the effects on the growth of single crystals in terms of morphology, structure and optical properties of MBB perovskite were investigated. The experimental results showed that the morphology of the crystals changed with different molar ratio of BiBr₃ content. The XRD pattern of the molar ratio 3:1 presented incomplete reaction of MABr with the BiBr₃ during the crystal growth process. While for molar ratio 3:4, uncomplete evaporation was observed after a month indicate unsuitable molar ratio for further applications. Different optical properties were observed from the bandgap of the molar ratio 3:1 (2.74 eV) compared to molar ratio 3:2 and 3:3 of 2.58 eV and 2.57 eV, respectively. These findings shows that MABr: BiBr₃ molar ratio of 3:2 and 3:3 present complete growth of MBB perovskite and have similar properties in term of structural and optical from the previous reported work. These results are beneficial for our future MBB-SA pulse laser application in future work.

CHAPTER 4

FABRICATION AND CHARACTERIZATION OF MBB/PDMS SATURABLE ABSORBER (SA) FOR ULTRASHORT PULSE GENERATION

4.1 Introduction

This chapter focuses on the synthesis of MBB/PDMS tapered fiber-based SA for femtosecond pulse generation. The MBB/PDMS was first prepared with different polarity solvents and characterized using RAMAN and UV-visible-Near-infrared (UV-Vis-NIR) spectroscopy to investigate its optical properties. The fabrication of tapered fiber and its linear optical characterization were performed. Then, the MBB/PDMS was deposited onto tapered optical fiber to fabricate the SA. Finally, the pulse performance of the fabricated SAs were tested by integrating the SA in an erbium-doped fiber laser (EDFL) ring cavity. The mode-locking performance of the SAs prepared with different solvents were analyzed in terms of pulse width, repetition rate, signal-to-noise ratio, central wavelength and 3-dB spectral bandwidth. The main motivation of the research work in this chapter is to fabricate robust, low-cost tapered fiber SAs deposited with MBB composite for best generation of ultrashort pulses. The flow chart of the methodology in this chapter is illustrated in Figure 4.1.

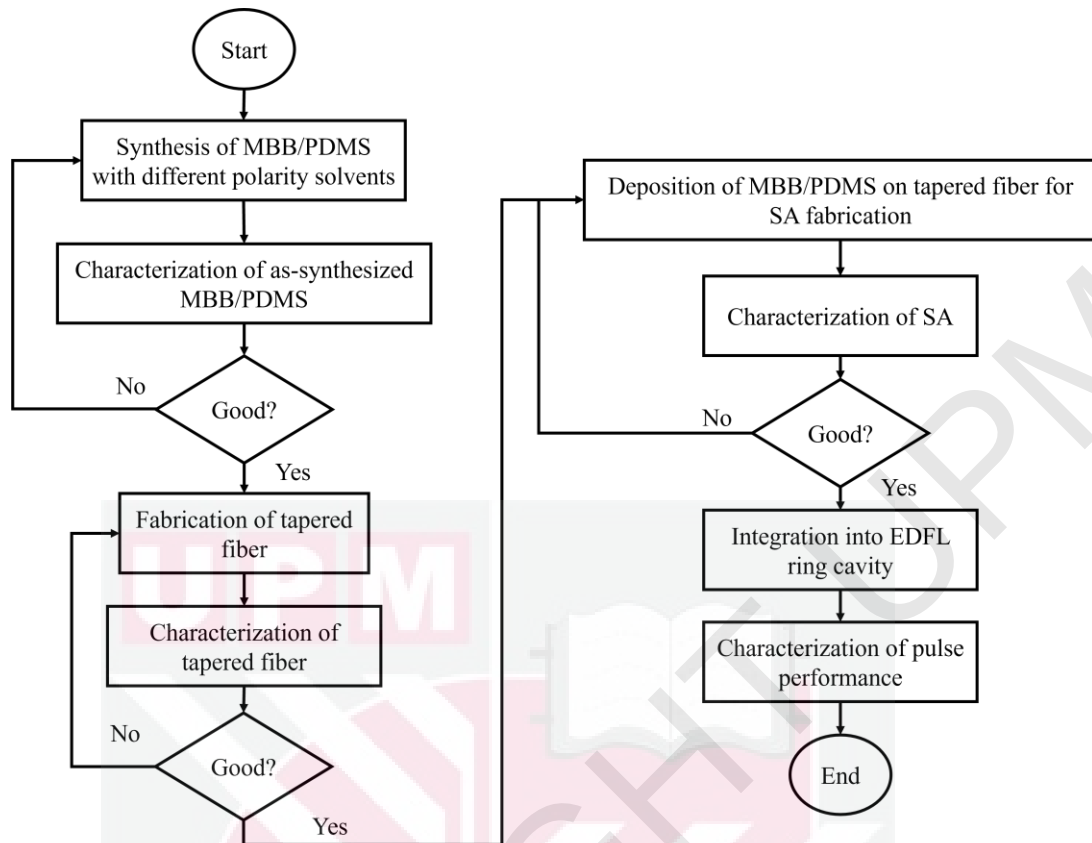


Figure 4.1: Flow chart of the methodology.

4.2 Preparation of MBB/PDMS and its Characterization

The preparation of MBB/PDMS is illustrated in Figure 4.2 by 2 mg of MBB crystal powder as synthesized from the chapter 3 previously was weighed and placed in a vial. The vial was then added with 1 ml of different solvents that were commonly available in the laboratory were employed in order to prepare the MBB/PDMS. These values were fixed to facilitate comparison between composite prepared by different solvents. Therefore, different types of commonly available solvents; in the category of non-polar solvents, polar aprotic solvents, and polar protic solvents were used to investigate its effect on the properties of MBB/PDMS which will be elaborated in the next section.

It is critical to understand the impact of the selected solvent in the preparation of MBB/PDMS.

Following that, a digital ultrasonic bath processor equipment (CJ-010S) was used to sonicate the mixture for half an hour. The sonication process resulted in either an even dispersion or complete dissolution of the MBB crystal powder in the selected solvent. After sonication, the MBB solution was added with 1.0 g of PDMS polymer (Sylgard® 184 Silicone Elastomer) and continuously stirred on a hot plate magnetic stirrer at ~500 revolution per minute (rpm) at 50 °C temperature for at least 24 hours to ensure complete evaporation of the solvent and to achieve homogeneous distribution of the MBB in the polymer matrix. This step is crucial to intercalate MBB into the PDMS matrix, forming a homogenous composite. The MBB/PDMS was then treated with 0.1 g of curing agent in 1:10 ratio of curing agent to polymer PDMS. The mixture was swirled for a while with a glass rod to ensure that the curing agent was completely mixed with the MBB/PDMS. Next, degassing process were performed as air bubbles were unavoidably incorporated into the MBB/PDMS from the entire process and this can be accomplished simply by allowing the MBB/PDMS to sit at room temperature for 1 hour. This final step completed the MBB/PDMS preparation.

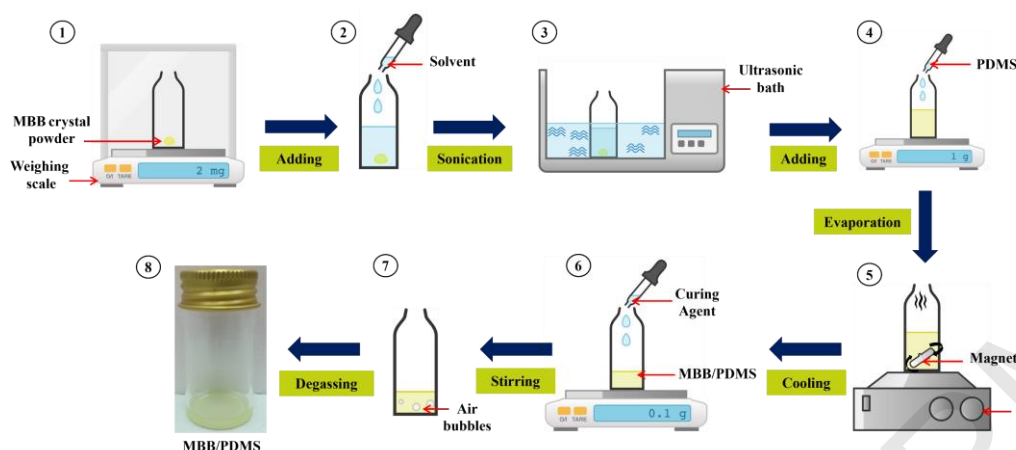


Figure 4.2: Preparation procedures of MBB/PDMS; (1) weighing of MBB crystal powder, (2) addition of solvent, (3) sonication of MBB solvent mixture, (4) addition of PDMS, (5) evaporation of solvent, (6) addition of curing agent, (7) degassing of MBB/PDMS, and (8) completion of MBB/PDMS preparation.

4.2.1 Effect of Solvent Compatibility on MBB/PDMS

When preparing MBB/PDMS, the choice of a solvent is critical. The selection of an appropriate solvent has a significant impact on whether or not the MBB perovskite retain its structure and properties when prepared as a composite. In step 2 from Figure 4.2, to investigate the solvent effect, the MBB perovskite single crystals were added in non-polar, protic polar, and aprotic polar solvents, and the resulting solution is as shown in Figure 4.3. Hexane (HEX), toluene (TOL), and chlorobenzene (PhCl) were chosen as the nonpolar solvents (labelled in red in Figure 4.3), isopropanol (ISO) and ethanol (EtOH) as polar protic solvents (labelled in blue in Figure 4.3), and tetrahydrofuran (THF), acetone (ACE), and acetonitrile (ACN) as the polar aprotic solvent (labelled in yellow in Figure 4.3). The solubility of perovskites in different solvents is related to its relative polarity (which is correlated to the dielectric constant or ϵ_r), in which more polar solvents have a stronger dipole moment

and, therefore, a greater ability to dissociate bonded species to cause dissolution. From Figure 4.4, as-synthesized MBB are dissolved in solvents (i.e., ACN, which are polar, with high dielectric constants, $\epsilon_r = 37.5$; relative polarity = 0.460). The dielectric constant of a solvent is a measure of how easily the solvent can be polarized. Polar solvents have a high dielectric constant, which means that they can be easily polarized by an external electric field. This makes polar solvents good at dissolving ionic compounds, such as MBB.

MBB are a class of materials with a general formula of ABX_3 ($MA_3Bi_2Br_9$), where MA and Bi are cations and Br is an anion. They are typically ionic compounds, with the cations and anions held together by strong electrostatic forces. In order for a MBB to dissolve in a solvent, the solvent molecules must be able to overcome the electrostatic forces between the cations and anions. Polar solvents are able to do this because they have a large dipole moment. The dipole moment of a solvent is a measure of how unevenly the electrical charge is distributed within the solvent molecule. Polar solvents have a large dipole moment because they have a positive and negative pole. The positive pole of a polar solvent molecule is attracted to the negative ions of the MBB, and the negative pole of a polar solvent molecule is attracted to the positive ions of the MBB. This attraction helps to weaken the electrostatic forces between the cations and anions, and allows the MBB to dissolve in the solvent.

Polar aprotic solvents, such as THF, ACE and ACN, are generally better at dissolving MBB than polar protic solvents, such as ISO and EtOH due to higher dielectric constant and are better at dissolving ionic compounds as shown in

Figure 4.3 and Figure 4.4. Polar aprotic solvents are typically used to fabricate perovskite solar cells, because they allow for the formation of high-quality perovskite films [275]. However, most polar aprotic solvents are toxic and environmentally hazardous [276]. While for as-synthesized MBB in solvents, such as HEX ($\epsilon_r = 1.88$; relative polarity = 0.009), which are typically non-polar and have low dielectric constants. MBB are ionic compounds, which means that they are made up of positively and negatively charged ions held together by electrostatic forces. Non-polar solvents, on the other hand, do not have a strong dipole moment and cannot overcome these electrostatic forces. As a result, MBB are insoluble in non-polar solvents. Non-polar solvents also have a low dielectric constant and cannot be easily polarized.



Figure 4.3: MBB crystal powder with different types of solvent; Hexane (HEX), toluene (TOL), chlorobenzene (PhCl), 2-propanol (ISO), ethanol (EtOH), tetrahydrofuran (THF), acetone (ACE), and acetonitrile (ACN) (word in red: non-polar; word in blue: polar protic; word in yellow: polar- aprotic).

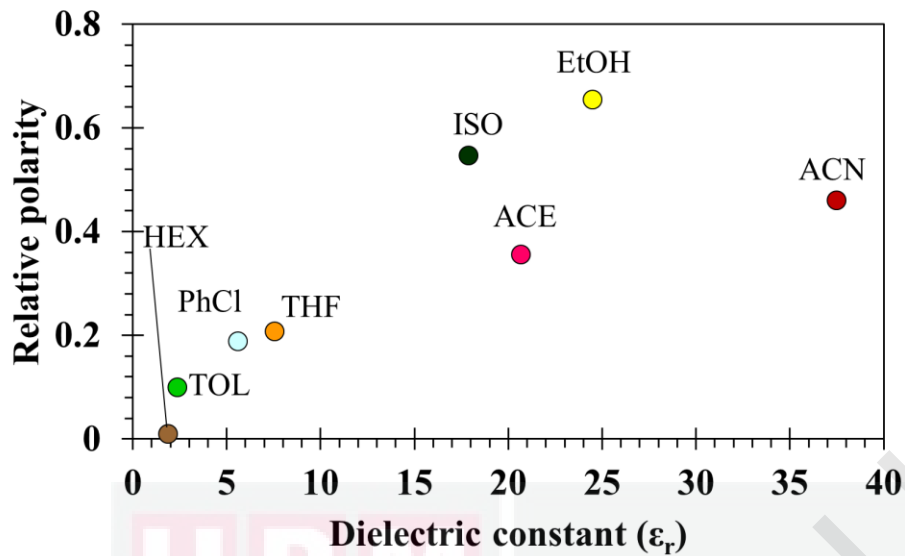


Figure 4.4: Relationship between relative polarity and dielectric constant of various solvents.

Next, after the MBB perovskite been sonicated using different solvent, PDMS polymer or better known as Sylgard® 184 Silicone Elastomer is used as protective coating material and mixed with the sonicated solution. The PDMS comes with two chemicals; base and curing agents that are mixed in 10:1 mass ratio. It has an empirical structure of $[(CH_3)_2Si-O]_n$, where n is the number of duplicate monomers. The appearance of PDMS is usually transparent with high viscosity, suitable to be molded into any shape. Major advantages of using PDMS are thermal stability, oxidation resistance, flexibility, and easy to mix with other materials to form composites. PDMS was chosen for its low absorption properties to form a composite with MBB to minimize the impact on nonlinear saturable performance [277]. These properties have made the PDMS polymer to become so useful in many applications such as, mechanical sensors [278] electronic components [279] biomedical devices [280] and photonics applications [281]. PDMS is low cost, simple to use, and has 1.3997

refractive index at 1554 nm, rendering it as an appropriate material for wave-guiding structure in SA device fabrication [282]. Besides that, PDMS is complement to tapered fiber as it strengthens the weak structure of waist and the cured form of PDMS composite allows the material inside stay and react with evanescent wave leaking by tapered fiber. In this work, the use of PDMS polymer secures the contact between tapered fiber and the nonlinear material, increases the lifetime of the fabricated SA by protecting both the tapered fiber and nonlinear material from external damages caused by environmental effects like vibration and humidity, and also protects the materials from direct exposure to impurities [283].

In step 5 from Figure 4.2, to determines the compatibility of solvents in the PDMS, one of the parameters that is able to give us such information is known as the solubility parameters. One of the solubility parameters is cohesive energy density; the energy associated with the intermolecular attractive interactions within a unit volume of material, or in other words the potential energy of the liquid divided by its volume. The solvent and polymer must have similar cohesive energy densities for them to be to be soluble, since this energy is required to overcome the molecular interactions of the solute. For materials like cross-linked polymers that cannot be dissolved, solubility is measured by how much they swell in a solvent. The more a polymer swells, the more soluble it is in the solvent. Cohesive energy density can be expressed in the Hildebrand solubility parameter value as the following: $\delta = c^{1/2} = (-\frac{U}{V})^{1/2}$ (cal^{1/2} cm^{-3/2}) [284]. The unit for δ is expressed as the square root of the cohesive energy density (cal^{1/2} cm^{-3/2}) or as the square root of the pressure

(MPa^{1/2}), where 1 cal^{1/2} cm^{-3/2} = 0.48888 MPa^{1/2}. The solubility parameter can be used to predict the swelling behavior of a polymer in a solvent without knowing any other information about the solvent. For a binary system, the Hildebrand-Scatchard equation relates the solubility parameters of nonpolar liquids to the enthalpy (internal energy) change on mixing them: $\Delta H_m = V_m(\delta_p - \delta_s)^2 \varphi_p \varphi_s$ where ΔH_m is the change in enthalpy of the mixture, V_m is the volume of the mixture, δ_p and δ_s is the solubility parameter of the polymer and the solvent, and φ_p and φ_s is the volume fraction of the polymer and the solvent in the mixture [284]. For swelling to occur in a polymer-solvent system, the free energy of mixing (the change in free energy that occurs when two or more substances are mixed) must be favorable, that is, $\Delta G_m < 0$. Since $\Delta G_m = \Delta H_m - T\Delta S_m$, and $\Delta H_m \propto (\delta_p - \delta_s)^2$, swelling is the greatest when $(\delta_p - \delta_s)^2$ is 0, where T is the temperature and ΔS_m is the change in swelling of the mixture [284].

Figure 4.5 shows the values of δ for a range of solvents often used in preparation of composite. Solvents that have a solubility parameter similar to that of PDMS, $\delta = 7.3 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ swell PDMS more than solvents that have a solubility parameter very different from that of PDMS. For example, ACN and ISO have almost identical solubility parameters $\delta = 11.9 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ but ISO swells PDMS much more than ACN. This difference is due to the different polarities of the two solvents. The solubility parameter can also be expressed by Hansen's total solubility parameter which is the sum of the dispersion forces, polar forces, and hydrogen-bonding forces within the material; [284]

that is, $\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$. Two solvents can have the same total solubility parameter, but the contributions of dispersion, polar, and hydrogen bonding forces to this value can be different. This means that two solvents with the same total solubility parameter but different contributions of these three forces may swell PDMS to different extents. The solvent with the contributions most similar to PDMS will swell PDMS the most.

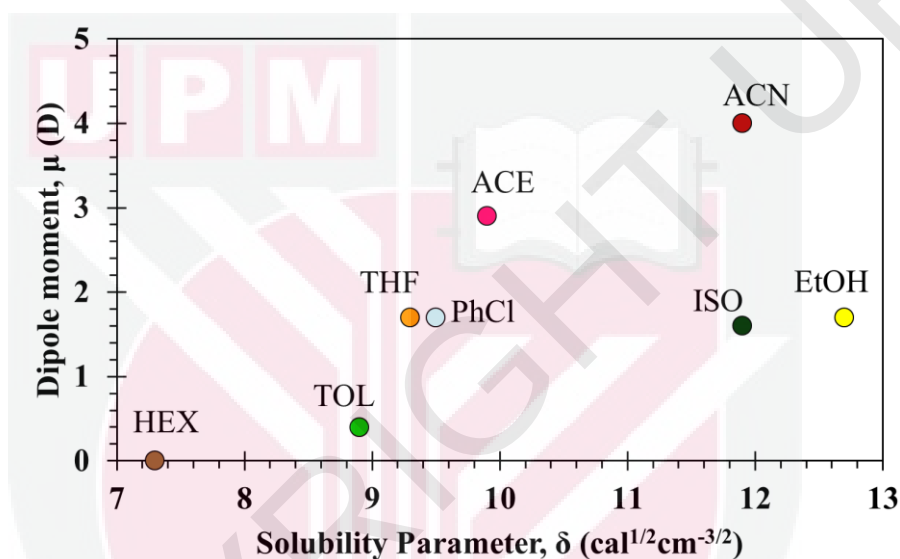


Figure 4.5: Relationship between dipole moment and solubility parameter of various solvents.

To help explain the trend in solubility, we consider the dipole moment of the solvent, μ (D), which represents the polar contributions. This is because μ is readily available for most materials. For example, in the case of ACN ($\mu = 4.0$ D) and ISO ($\mu = 1.6$ D), ISO has smaller polar contributions than ACN. PDMS has a low dipole moment ($\mu = \sim 0.6-0.9$ D) [285], which means it has lower polar contributions. This is why it is not surprising that ISO is more soluble in PDMS than ACN, as shown in Figure 4.6.

In the case of EtOH and ACN, these solvents generally have $\delta > 9.9 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ with moderate to high polar contributions ($\mu > 1.4 \text{ D}$). Due to the huge difference in polar contributions in comparison to PDMS, it can be expected that these solvents have extremely poor solubility with PDMS. This is validated in Figure 4.6, where these solvents exhibited agglomeration effect when mixed with PDMS (see EtOH and ACN). Therefore, it can be concluded that low solubility solvents are not suitable to be used in preparation of PDMS-based composites for saturable absorber fabrication.

Solvents with a solubility parameter in the range of $7.3 - 12.5 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ are generally considered to be high solubility solvents. In Figure 4.5, these solvents (HEX and TOL) tend to be non-polar, with $\mu \leq 1.0 \text{ D}$, with the exception of THF ($\mu = 1.7 \text{ D}$) that has $\mu = 1.0 \text{ D}$. The main contribution to the δ of these solvents is from dispersion forces. Meanwhile solvents for PhCl and ACE solvents have a solubility parameter ($9.5 < \delta < 9.9$) and dipole moment ($1.7 < \mu < 2.9$) that overlap with either the high or low solubility groups. These observations reemphasize the fact that the proportion of dispersion, polar, and hydrogen bonding forces for a particular solvent greatly influences its ability to swell PDMS. This happened as the swelling ratio, S in PhCl ($S = 1.22$) and ACE ($S = 1.06$) solvents is moderately low ($S = 1.22$), perhaps because both solvents have a lower contribution of dispersion forces to δ . This is validated in Figure 4.6, where these high solubility solvents mixed well with PDMS which is suitable to be used in preparation of PDMS-based composites for saturable absorber fabrication.

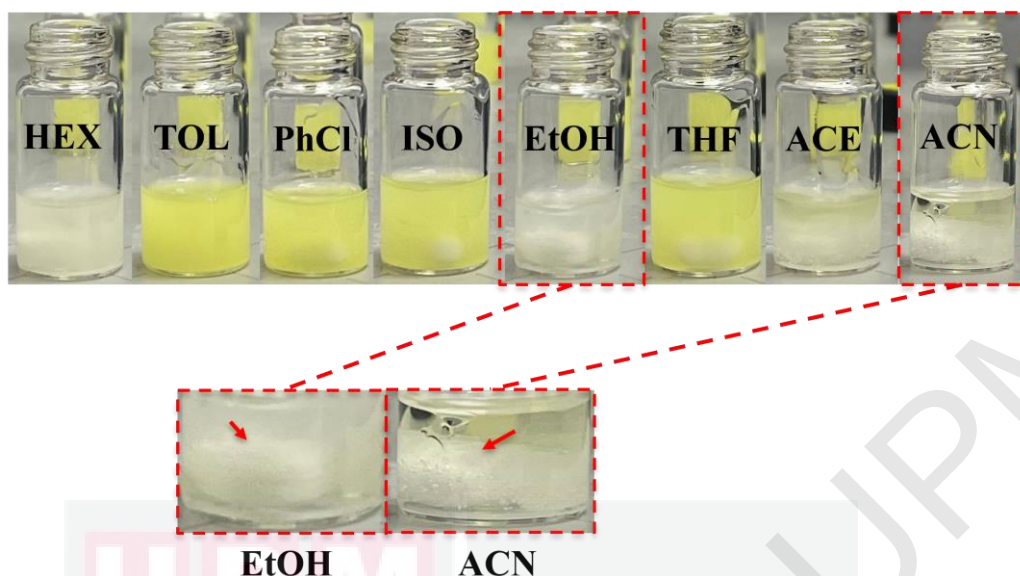


Figure 4.6: MBB perovskite solution with different types of solvent after adding PDMS polymer (box in red: EtOH and ACN solvents shows agglomeration).

Figure 4.7 shows the results of PDMS mixed with as-synthesized MBB perovskite solutions after curing process in step 8 from Figure 4.2. It can be observed that complete curing was achieved for all solvents except for THF. The result shows the presence of the hydrolysis product BiOBr, [286] a white color. This reaction proceeds according to the equation 4.1;



Hydrolysis of BiOBr can lead to the formation of a layer of water molecules on the surface of the BiOBr particles. This water layer can reduce the adhesion between the BiOBr particles and the PDMS polymer matrix, which can lead to debonding and failure of the composite. It should be noted that this reason would make complete curing of the composites unachievable as mentioned earlier for THF shown in Figure 4.7.

Upon the composite cured from using PhCl solvent, we find that the composite layer change from yellow to red was observed in Figure 4.7 (red arrow). The physical appearance of BiBr₃ powder is white to light yellow in colour. From the investigation, it reveals different colours in composite containing bromide salt are very common due to the existence of Bi-O or Bi-N bonds between the BiBr₃ and PhCl [287]. This is because these bonds can form different complexes with the bromide ions, which can absorb light at different wavelengths. It is important to note the Bi-O and Bi-N bonds that can form between BiBr₃ and PhCl are not stable and can decompose over time. This can lead to a change in the color of the final composite as observed in Figure 4.7. It also proves that the different solvents have a significant impact in the properties of perovskite composite, which plays an important role to the efficiency of many applications [288], [289].

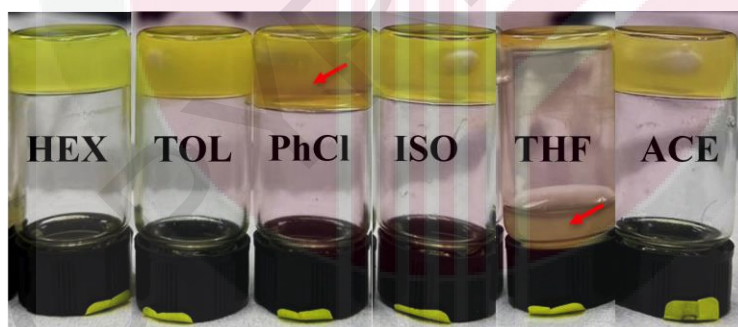


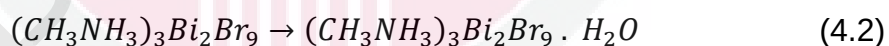
Figure 4.7: MBB/PDMS after curing process. THF did not achieve complete curing as white color appear while PhCl changed from yellow to red as indicated by the red arrow.

4.2.2 Degradation of MBB Single Crystal

The instability of MBB perovskite's sensitivity due to environmental factors such as oxygen and moisture, as well as structural changes when exposed to

illumination. The low electrostatic lattice energy of an ionic structure of halide perovskite in comparison to non-halide perovskite compounds is one factor that leads in an unstable halide perovskite [290]. Aside from environmental factors, the reaction medium referring to the polarity of the solvents, could affect the stability of the photocatalytic reaction environment.

MBB perovskite with organic ammonium ions at the A-site, such as MA^+ , have high chemical reactivity that is enhanced by polar surroundings of C-N or N-H bonding, which adversely affects the decomposition rate of halide perovskites at elevated temperatures. Polar surroundings, such as the presence of H_2O and $O_2.H_2O$, can have both advantageous and disadvantageous effects on perovskite. It is undeniable that preparing perovskite in the presence of humidity improves the performance of solar cells [291]. However, in most situations, it is clear that water plays a catalytic role in the degradation process, which accelerates perovskite decomposition (Equation 4.2).



Perovskite crystal is prone to hydration by first forming an intermediate monohydrate $MA_3Bi_2Br_9.H_2O$ structure [292], [293], [294]. Due to this reason further material characterizations were proceeded in next section with MBB/PDMS with HEX, TOL, ISO and ACE solvents.

4.2.3 Material Characterization of MBB/PDMS

4.2.3.1 UV-Vis-NIR Absorption Spectroscopy

The results from the previous section shows that MBB/PDMS sonicated with HEX, TOL, ISO and ACE solvents had been completely cured in the final step and was further proceeded by optical properties through UV-Vis-NIR Spectroscopy, which is technique used to analyze the absorbance capabilities of samples in 240–2200 nm wavelength range. The absorbance UV–Vis–NIR spectra of the MBB/PDMS prepared with different solvents are shown in Figure 4.8 (a). The absorbance of the as synthesized MBB single crystal and MBB/PDMS coincides with the desired 1.55 and 2 μm wavelength region for ultrashort pulse generation with erbium and thulium gain medium, respectively. Tabulated values of absorption edge and corresponding calculated optical bandgap are shown in Table 4.1. From Figure 4.8 (b), the absorption edge observed at around ~ 495 nm for MBB single crystal powder corresponding to optical bandgap of 2.57 eV and matches with the value given in the literature [295]. The absorption edge slightly decreases to 490 nm for MBB/PDMS: HEX and 470 nm for MBB/PDMS: ACE MBB/PDMS: TOL, respectively. This indicates an increase in optical bandgap of 2.62 eV for MBB/PDMS: HEX and 2.66 eV for MBB/PDMS: ACE MBB/PDMS: TOL, respectively. On the other hand, the absorption edge of MBB/PDMS: ISO increases compared to MBB single crystal with optical bandgap of 2.47 eV. It was observed that the calculated bandgap changes minimally.

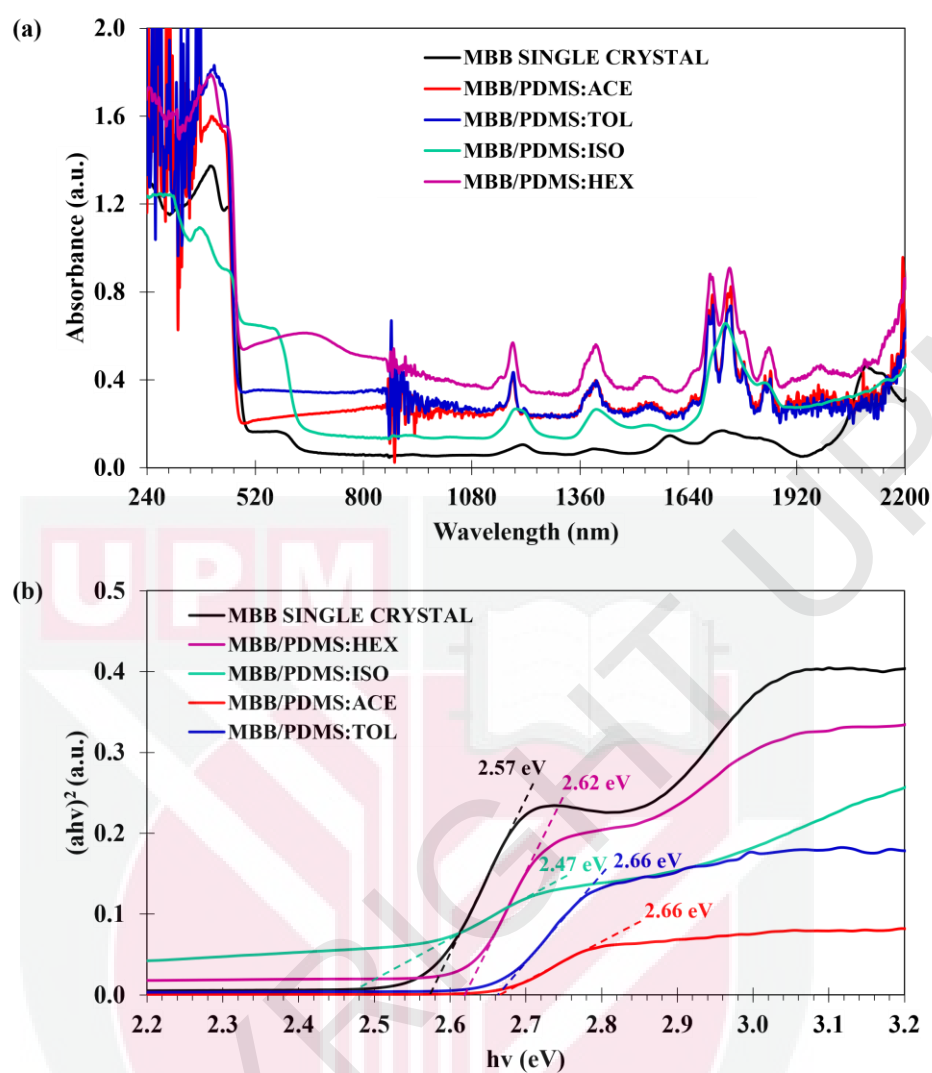


Figure 4.8: (a) UV-Vis-NIR spectra (b) Tauc plot of MBB/PDMS using different solvents

Table 4.1: Absorption edge and calculated bandgap for different solvents.

	Absorption edge (nm)	Calculated bandgap (eV)
MBB single crystal	495	2.57
MBB/PDMS: HEX	490	2.62
MBB/PDMS: ISO	635	2.47
MBB/PDMS: ACE	470	2.66
MBB/PDMS: TOL	470	2.66

When MBB perovskites are in contact with air, moisture, polar solvents, oxygen, and heat, they would result in undesirable phase transition and decomposition ($\text{MA}_3\text{Bi}_2\text{Br}_9 \rightarrow \text{MABr} + \text{BiBr}_3$) and alter the structural and optoelectronic properties of the perovskite materials [296]. Hence, it is ascertained that the ionic lattices of MBB perovskites under certain photocatalytic reaction conditions such as water or polar solvents are highly unstable.

4.2.3.2 Raman Spectroscopy

The MBB/PDMS sonicated with HEX, TOL, ISO and ACE solvents was also verified by characterization on Raman spectroscopy. We found assortment in literature in Raman band assignments for MBB perovskite single crystal material. Raman bands obtained in the present study and their assignment are tabulated in Table 4.2. The Raman spectrum for each MBB/PDMS prepared with different solvents together with MBB single crystal for reference are shown in the Figure 4.9. As illustrated in Figure 4.9 (a), the two Raman peaks from 125 to 225 cm^{-1} (yellow shaded region) are assigned to the Bi–Br stretching modes of MBB single crystal. No obvious discontinuity is observed in the Bi–Br stretching modes and it is suggested that the inorganic component of Bi and Br is negligibly affected from the preparation of MBB/PDMS.

Table 4.2: Different peaks in the Raman spectra found in the present study and its assignment.

	Observed peak position (cm ⁻¹)	Assignment
1	125-225	Bi-Br stretching
2	1435-1520	CH ₃ bending
3	1550-1640	NH ₃ bending
4	2940-3005	CH ₃ stretching

The Raman peaks of MBB single crystals in the range of 1435 to 1520 cm⁻¹. (red shaded region) represents CH₃ bending while 1550 to 1640 cm⁻¹ (blue shaded region) represents NH₃ bending as shown in Figure 4.9 (b). Missing of the peaks of CH₃ and NH₃ bending in the range 1400 to 1700 cm⁻¹ for MBB/PDMS: ACE and only missing peak of NH₃ bending for MBB/PDMS: ISO were marked by the asterisks symbol in Figure 4.9 (b), which correspond to the modes of organic part of the perovskite [297]. This indicates towards the dissolution of organic part of CH₃NH₃- BiBr₃ due to the solubility in polar ACE and ISO solvents. ISO and ACE as polar solvent can lead to the decomposition of the MBB structure. This is because the hydrogen atoms in ISO can form hydrogen bonds with the Br ions in the MBB structure. This can weaken the electrostatic forces between the cations and anions, and thus weakening CH₃NH₃...Br hydrogen bonding interaction which lead to the decomposition of the MBB [294], [298]. This shows by using ACE and ISO solvents, the MBB perovskite cannot retain its structure when added with PDMS polymer to form the MBB/PDMS. However, lower intensity of the Raman peak on MBB/PDMS:ISO was observed and similar with MBB/PDMS: HEX, further material characterization is required in the following section. Meanwhile, the detected vibrational modes at 2905 cm⁻¹ and 2965 cm⁻¹ are related to the

stretching bands of methyl group (CH_3) in the PDMS matrix [299] as shown in Figure 4.9 (c). For comparison, the peak in MBB single crystal (green shaded region) were presence for all solvents. The Raman peak intensity peak at 2905 cm^{-1} in Figure 4.9 (c) represents the methyl group in the PDMS matrix for MBB/PDMS: TOL is lower than in other samples because fewer molecules were detected in the sample during characterization process since the Raman peak intensity is affected by the quantity of molecules in the sample if the light source intensity and wavelength are kept constant. These findings suggest that only preparation of MBB/PDMS: HEX and MBB/PDMS: TOL were successful [249], [300]. Therefore, only MBB/PDMS: HEX and MBB/PDMS: TOL shows promising result by maintaining structural properties of MBB perovskite and proceeded with fabrication of SA.

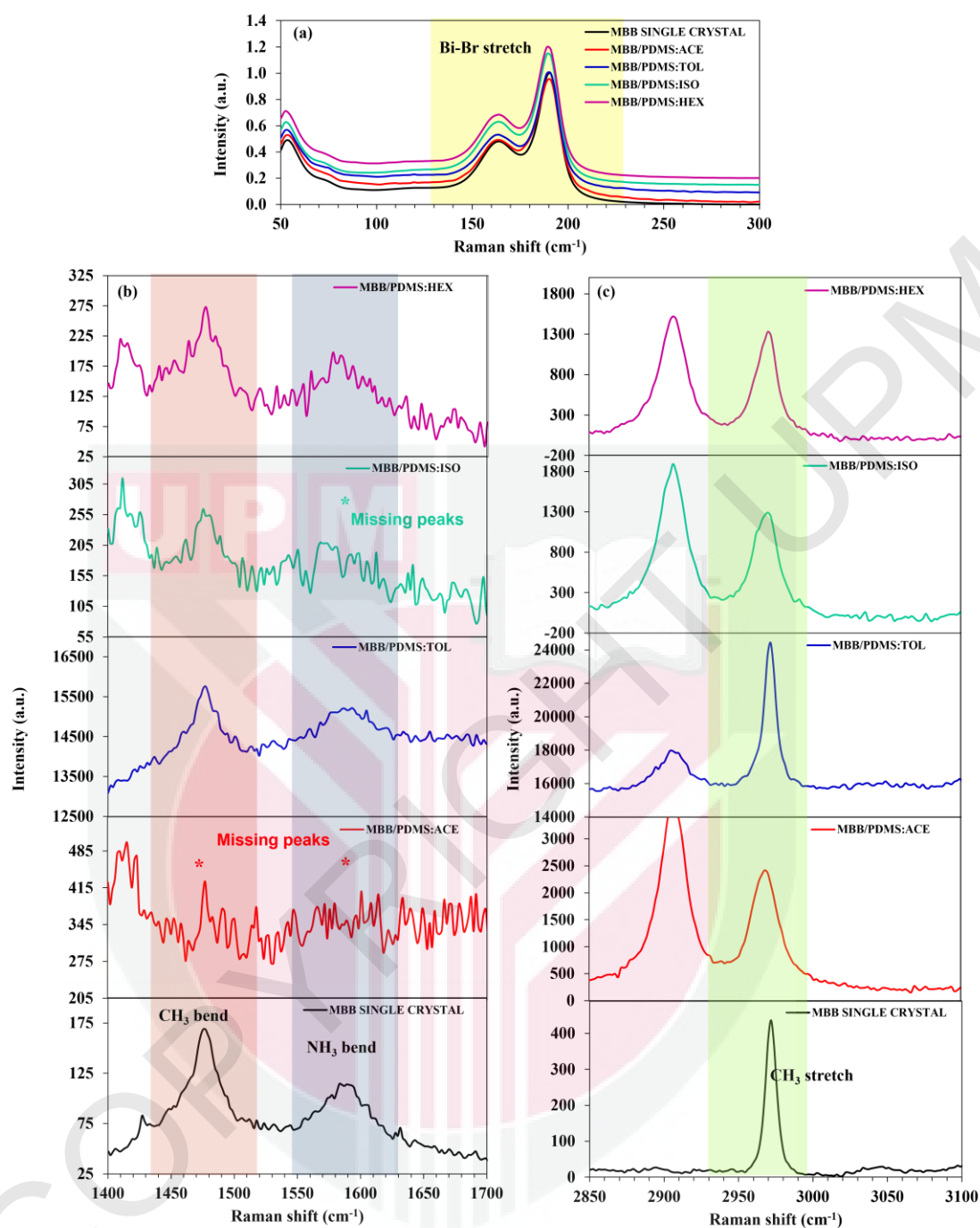


Figure 4.9: (a) Raman spectra of Bi-Br stretching modes (b) and (c) Evolutions of typical Raman modes from MA^+ cations (CH_3 bending, NH_3 bending, and CH_3 stretching) with different solvents.

4.3 Fabrication of SA

4.3.1 Fabrication of Tapered Fiber

The fabrication of saturable absorber (SA) begins with the preparation of tapered optical fiber. Vytran GPX-3400 automated glass processing workstation was employed to prepare tapered optical fibers as depicted in Figure 4.10. It incorporates a filament-based furnace that provides a stable high temperature heat source at about 3000 °C for consistency during a tapering process. The workstation also comes with two 125 μm fiber holding blocks for precise fiber positioning and clamping. This machine can fabricate fiber with high precision and repeatability. Throughout this research work, single-mode optical fibers (SMF-28) from Corning with a core diameter of $\sim 8.25 \mu\text{m}$ and a cladding diameter of 125 μm were used to prepare tapered fibers. Before placing the two ends of the SMF-28 fiber on the fiber holders at the workstation, a ~ 3 cm length section of the buffer jacket was removed and cleaned with alcohol. Then, the desired taper dimensions were set at a fixed taper pulling velocity of 0.50 mm/s and a filament power of 50 W using the graphical user interface on the computer screen. These settings remained constant throughout the experiment to ensure consistent tapered fiber shaping tailored to the desired profiles.

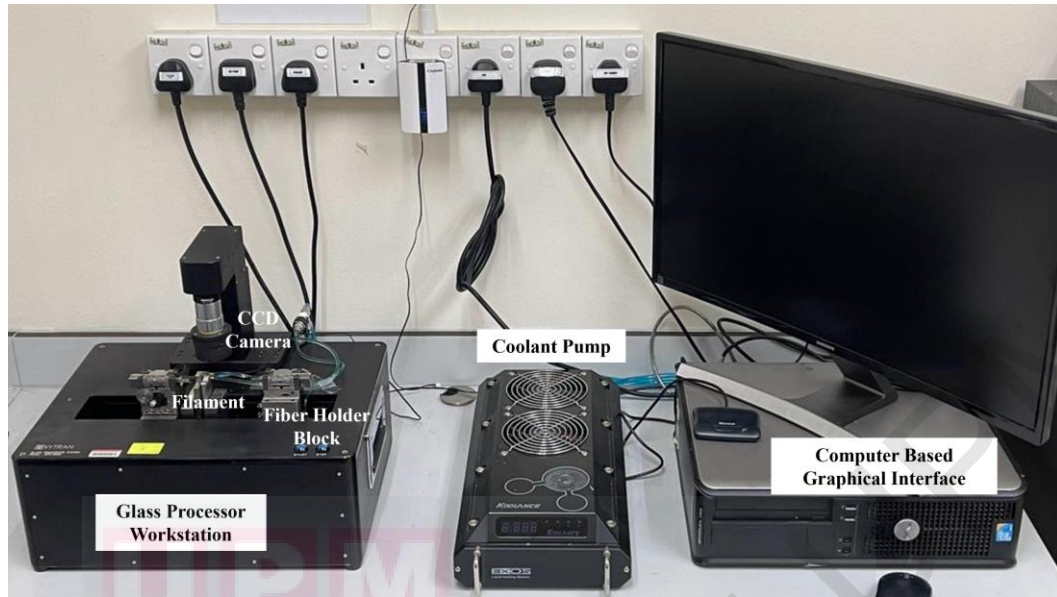


Figure 4.10: Vytran automated glass processor workstation.

A tapered fiber is formed when a short length of SMF-28 with a stripped section is pulled in opposite directions along its axial length while it is heated. This action produces a narrow taper waist diameter shaped together with two transition zones as illustrated in Figure 4.11. The taper angle, θ (theta) of the transition zones, is the critical parameter affecting the optical transmission behavior of a tapered fiber. If the taper angle is less than ~ 5 mrad, the taper is considered as adiabatic whereas when it exceeds ~ 5 mrad, it is termed as a non-adiabatic taper [301], [302]. In this experiment, an adiabatic taper is preferable to take advantage of the low propagation loss, strong and accessible evanescent field for light-matter interaction. Based on the reported literature, decreasing taper's waist diameter will create strong evanescent field thus facilitate the light-material interaction for pulse shortening [303]. However, the taper's waist diameter of less than $10\ \mu\text{m}$ was extremely fragile and difficult to handle, therefore the up and down transition taper regions were set as 30

mm, the waist length was fixed at 0.8 mm and the waist diameter was 10 μm [304]. It is observed that the up and down transition taper length, waist length, and waist diameter can be precisely controlled through this method, ensuring adiabaticity and uniformity.

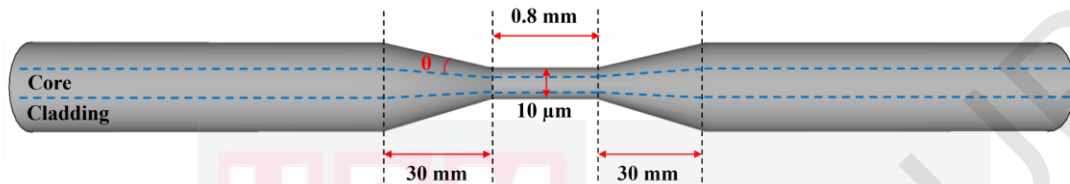


Figure 4.11: Schematic diagram of a tapered fiber.

4.3.2 Deposition of MBB/PDMS on Tapered Fiber

Following the preparation procedures of MBB/PDMS illustrated in Figure 4.2 of Section 4.2, the prepared MBB/PDMS was deposited on tapered optical fiber using spin coating technique. Spin coating was selected because it is a simple and effective method for depositing a uniform layer of material across the entire surface of a substrate. The thickness of the deposition is determined by the spin coater speed which is faster speed or higher rpm results in a thinner layer, and the other way round. In this work, a spin coater (TB616-SYSILE) was used and then to secure the tapered fiber and prevent it from breaking during the spin coating process, the tapered fiber was carefully placed on a flat surface substrate and secured with scotch tape on its ends. The spin coating process began by putting several drops of MBB/PDMS onto the center of the substrate that holds the tapered fiber as illustrated in Figure 4.12. Afterwards,

the substrate was accelerated to 4000 rpm for 300 seconds to obtain an effective thickness below $\sim 5\ \mu\text{m}$ for functional SA [305].

The spin coating process was repeated for few samples of tapered fiber with MBB/PDMS: HEX and MBB/PDMS: TOL. After the spin-coating process, a thin layer of MBB/PDMS was formed on the tapered fiber. Finally, the coated tapered fiber was placed in a dry cabinet to allow the coating to cure and stabilize the composite. This marks the completion of SA fabrication. The presence of deposited materials on the tapered fiber were validated by SEM and EDX in the next section.

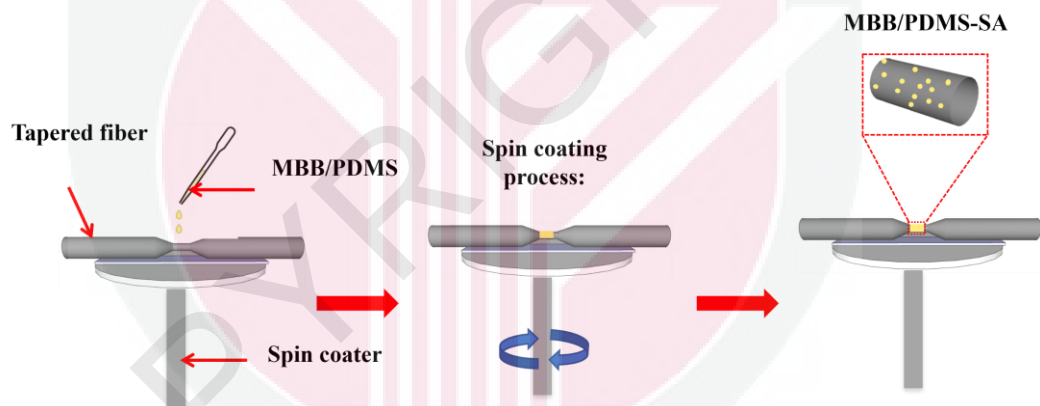


Figure 4.12. Depositing MBB/PDMS on tapered fiber using spin coating technique.

4.3.3 Material Characterization of SA

4.3.3.1 Micro-X-ray Fluorescence (μ -XRF)

Figure 4.13 (a) shows the distribution of Bi and Br elements in the MBB/PDMS: HEX coated on tapered fiber using micro-X-ray fluorescence (μ -XRF) (M4 Tornado Plus from Bruker). A uniform distribution of Bi and Br are observed throughout the PDMS composite. Figure 4.14 (a) shows the distribution of Bi and Br elements in the MBB/PDMS: TOL coated on tapered fiber, characterized using μ -XRF. Similar to Figure 4.13 (a), the Bi and Br elements show uniform distribution throughout the PDMS composite. Figure 4.13 and Figure 4.14 (b) and (c) shows the individual elemental mapping of Bi and Br with good homogeneous distribution on the tapered fiber. The detection range of μ -XRF is limited to elements between sodium (Na) and uranium (U) on the periodic table. Consequently, elements like hydrogen (H), nitrogen (N) and carbon (C) were not observed. Table 4.3 and Table 4.4 shows the atomic percentage of Bi (9.82% and 16.16%) and Br (90.09% and 84.24%) in the MBB perovskite ((CH₃NH₃)₃Bi₂Br₉) for MBB/PDMS: HEX and MBB/PDMS: TOL, respectively. These values correspond to Bi:Br ratios of close to 2:18 and 2:10, respectively. The observed Bi:Br ratios suggest that during SA fabrication, remaining bromide material reflects the percentage that hasn't undergone this process. The results indicate that nearly 50% and 10% of the bromide material in the MBB perovskite have been decrystallized for MBB/PDMS: HEX and MBB/PDMS: TOL, respectively.

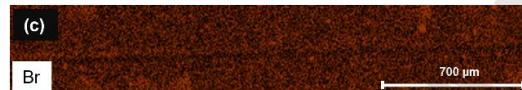
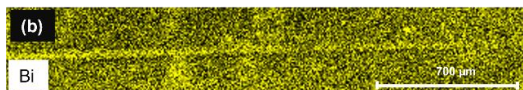
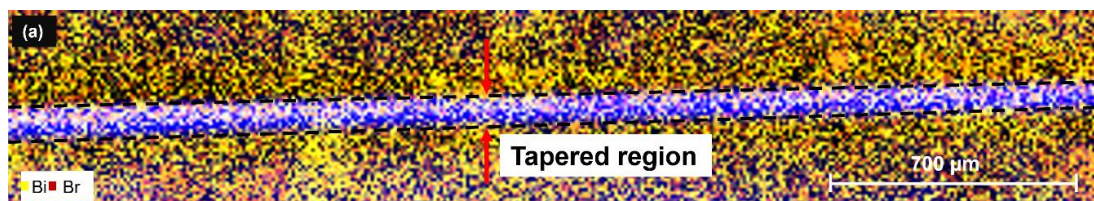


Figure 4.13: (a) μ -XRF top view, elemental mapping of (b) Bi, and (c) Br of MBB/PDMS: HEX-SA.

Table 4.3: Elemental percentage from the μ -XRF image of MBB/PDMS: HEX-SA.

Element	Weight percentage, (wt%)	Relative (wt%)	Atomic weights (g/mol)	Atomic percentage, (at%)
Bi	0.02	22.22	208.98	9.82
Br	0.07	77.78	79.90	90.09

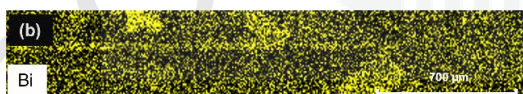
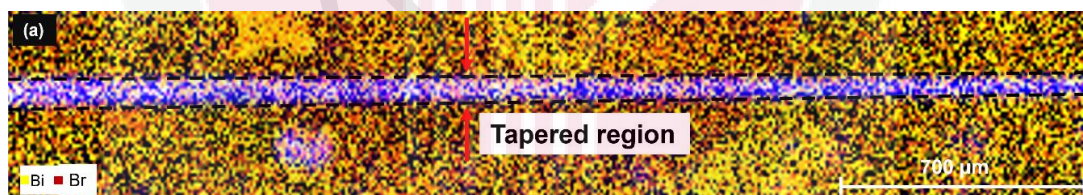


Figure 4.14: (a) μ -XRF top view, elemental mapping of (b) Bi and (c) Br of MBB/PDMS: TOL-SA.

Table 4.4: Elemental percentage from the μ -XRF image of MBB/PDMS: TOL-SA.

Element	Weight percentage, (wt%)	Relative (wt%)	Atomic weights (g/mol)	Atomic percentage, (at%)
Bi	0.01	33.33	208.98	16.16
Br	0.02	66.67	79.90	84.24

4.4 Optical Characterization of SA

Both MBB/PDMS: HEX-SA and MBB/PDMS: TOL-SA samples are then characterized for optical transmission loss and nonlinear saturable absorption properties.

4.4.1 Transmission Loss Measurement

The transmission loss after deposition of materials were measured using a broadband amplified spontaneous emission (ASE) source (Amonics, ALS-CL-17-B-SC). The reference spectrum, with resolution bandwidth of 0.02 nm and span of 1530 -1570 nm, was acquired by connecting the ASE source directly to the optical spectrum analyzer (OSA). Transmission loss of the bare tapered fiber was measured initially to be less than 1.0 dB before depositing both MBB/PDMS: HEX-SA and MBB/PDMS: TOL-SA. After that, the fabricated MBB/PDMS: HEX-SA was inserted between the ASE and OSA to sweep for a second spectrum. This process was repeated with fabricated MBB/PDMS: TOL-SA and the measurements are portrayed in Figure 4.15. The flat spectral

profile observed in depicts the adiabatic nature of the employed tapered fiber, where the main portion of propagating light resides within the fiber core and coupling to higher order modes at the transition region is negligible [306]. Transmission loss commonly increases after the deposition process owing to the surface deficiencies or impurities attachment to the tapered fiber surface [307], [308]. As shown in Figure 4.15, MBB/PDMS: HEX-SA has a transmission loss of 4.20 dB at 1560 nm wavelength region (green line), whereas MBB/PDMS: TOL-SA has transmission loss of 3.58 dB (purple line). The difference of ~ 0.62 dB between these two SAs suggested that the higher loss (MBB/PDMS: HEX-SA) could have been due to the existence of MBB/PDMS in the tapered fiber itself.

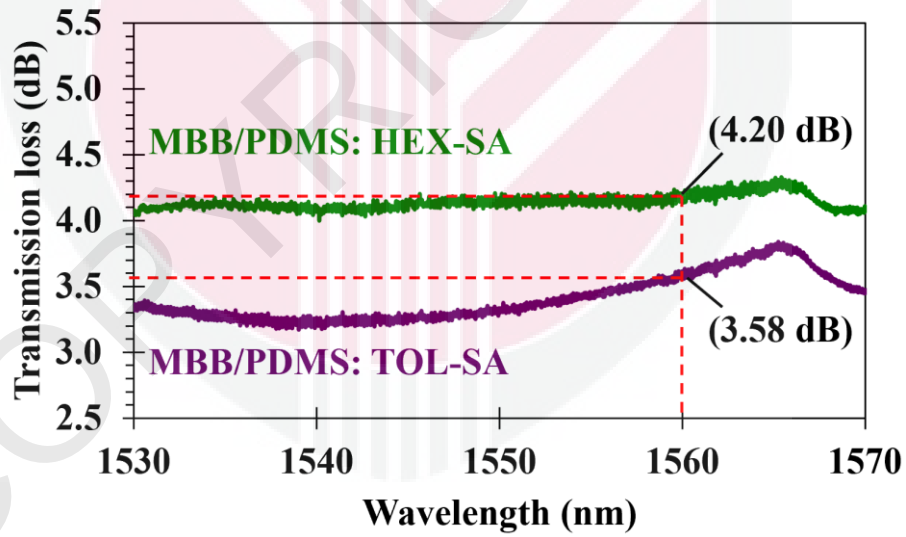


Figure 4.15: Transmission loss of (a) MBB/PDMS: HEX-SA and (b) MBB/PDMS: TOL-SA.

4.4.2 Nonlinear Saturable Absorption Properties

Before proceeding with the mode-locked laser performance testing, the nonlinear saturable absorption properties of both prepared SAs were characterized using the twin-balance setup in Figure 4.16. A pulsed laser source (PLS) (Menlo Systems M-Fiber model) at 1560 nm wavelength with 250 MHz repetition rate and 117 fs pulse duration was coupled to a variable optical attenuator (VOA) to attenuate the input optical power intensity. An isolator was inserted between PLS and VOA to circumvent back reflection of power into PLS. A 50:50 optical coupler (OC) was used to split the pump laser signal (PLS) into two equal parts. One part was used as a reference power measurement using an optical power meter (OPM 1), while the other part was used to measure the optical power that passed through the prepared sample arm (SA) using another optical power meter (OPM 2). The optical transmittance at one particular wavelength can be adjusted continuously by altering the input power. The relationship between optical transmission and input laser power could be well fit by Equation 4.3 [17];

$$T(I) = 1 - MD * \exp(-I/I_{sat}) - \alpha_{ns} \quad (4.3)$$

Where, $T(I)$ is the transmission rate, MD is the modulation depth, I is the input intensity of laser, I_{sat} is the saturation intensity, and α_{ns} is the non-saturable loss.

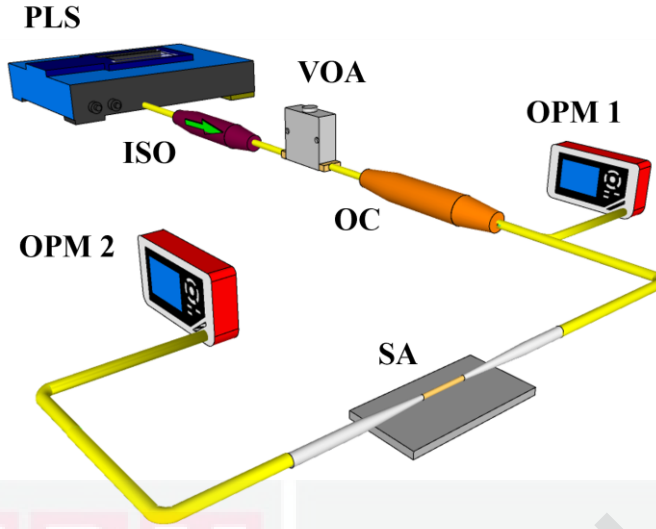


Figure 4.16: Nonlinear saturable absorption measurement setup using the twin detector method.

The MD of the fabricated MBB/PDMS: HEX-SA and MBB/PDMS: TOL-SA were determined to be 9.75 % and 19.30 % by referring to the discrepancy between the maximum and minimum transmission values. The occurrence can be justified by the mode-locked operation criterion, $E_p^2 > E_G E_{SA}(MD)$, in which the initiation of mode-locked generation appears to favour this criterion, where E_p is the single pulse energy, E_G is the gain fiber saturation energy, and E_{SA} is the SA saturation energy [309], [310]. In passively mode-locked lasers, large MD is desirable to achieve strong pulse formation and reliable self-starting ultrashort pulse [311]. The MD of MBB/PDMS: HEX-SA is significantly small compared to MBB/PDMS: TOL-SA, yet still able to function as a self-starting mode-locker because it fulfill the mode-locked criterion discussed earlier. A low value of I_{sat} means that mode-locked laser operation can be achieved at a low pump power, which typically results in a low mode-locked threshold [312]. From the transmission curve, MBB/PDMS: HEX-SA shows the I_{sat} and α_{ns} of

200.03 MW/cm² and 55.40 %, respectively. While for the MBB/PDMS: TOL-SA shows the I_{sat} and α_{ns} of 900.00 MW/cm² and 50.00 %, respectively. The α_{ns} is the constant linear loss level, which cannot be saturated during pulsed operation. It is highly desirable to fabricate SA with low α_{ns} to achieve highest possible laser output power and efficiency. The sonication of MBB single crystals to different solvents (HEX and TOL) might show different material distribution within the polymer matrix. When MBB is well dispersed in TOL solvent, it is distributed more evenly in the material, which reduces undesirable scattering losses. This improves the α_{ns} of the MBB/PDMS: TOL-SA [313].

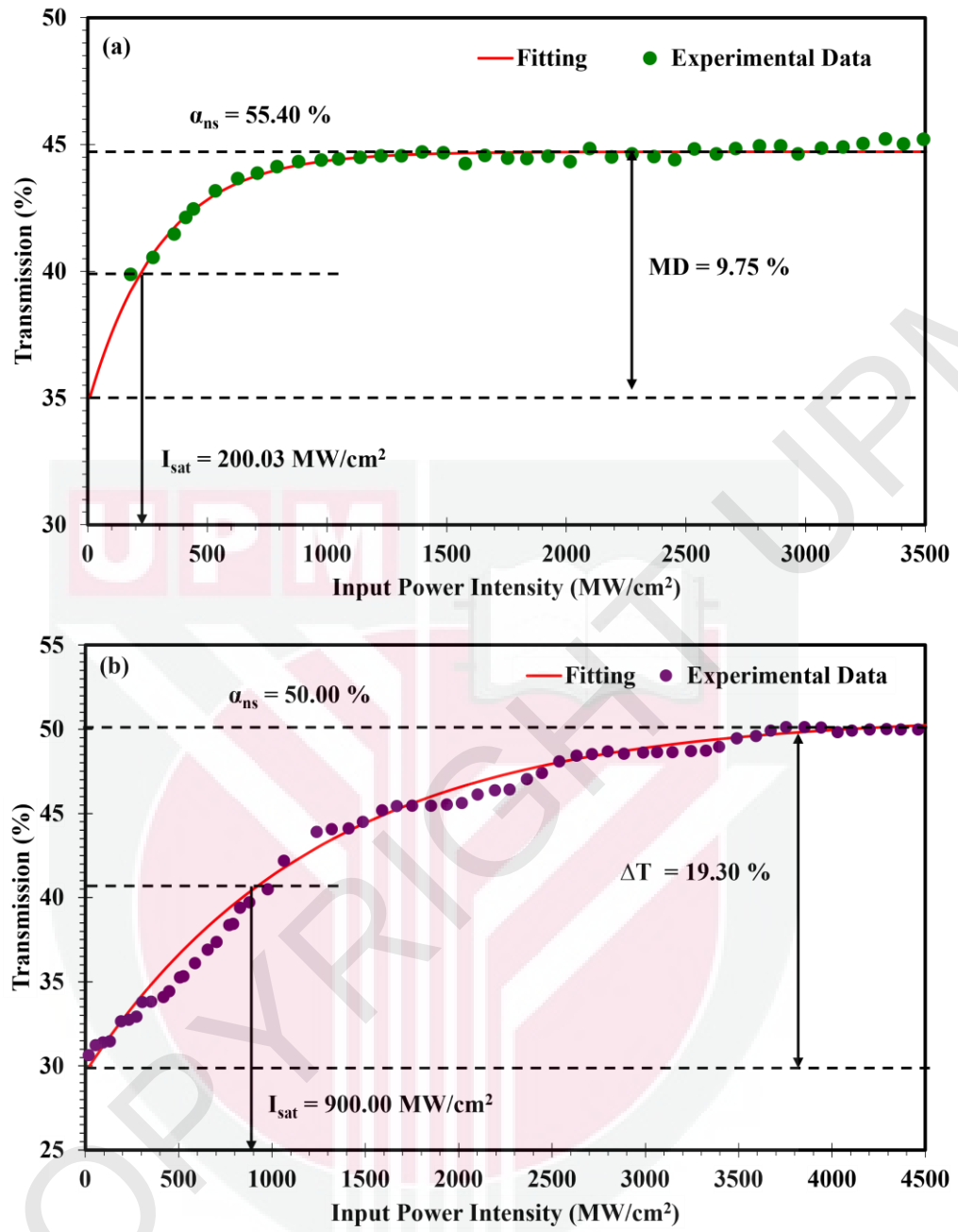


Figure 4.17: Nonlinear responses of (a) MBB/PDMS: HEX-SA and (b) MBB/PDMS: TOL-SA.

4.5 Mode-Locked Laser Cavity with Deposited MBB/PDMS-SA

The schematic diagram for the ring-cavity erbium-doped fiber laser (EDFL) to realize passive mode locked fiber laser (MLFL) is shown in Figure 4.18. The

ring cavity included an 0.5-meter-long erbium doped fiber (EDF, Leikki Er 80-8/125) as gain medium with 9.5 μm mode field diameter at 1550 nm, absorption of 80 dB/m at 1530 nm, and 0.13 numerical aperture was used. The cavity was forward-pumped by a 980 nm laser diode (LD) via a 980/1550 nm wavelength division multiplexer (WDM). An isolator (ISO) was spliced after the EDF to ensure light propagation remained in a clockwise direction and prevent any back-reflections from other optical devices that might perturb the lasing stability. The prepare SA, was inserted between ISO and 70/30 optical coupler (OC). The 70% coupler leg was rerouted back into the cavity which had a three-paddle polarization controller (PC) for a complete formation of ring cavity. PC was inserted to allow the adjustment of light polarization for optimum light-matter interaction in generation of optical pulses. On the other hand, 30% of the laser signal was extracted from the laser cavity for optical pulse performance analysis. For spectrum analysis, the 30% coupler end was connected to an additional 90/10 OC where Output 1 (10%) was connected to a Yokogawa AQ6370B optical spectrum analyzer (OSA) to analyze the power distribution over a wavelength span. The remaining 90% of the extracted signal was directed to an OPM (Thorlabs, PM100D, Thorlabs S302C) to measure the average output power, an oscilloscope (Tektronik TDS 3012C) via a 5GHz Thorlabs SIR5-FC InGaAs FC/PC-coupled photodetector to detect the pulse train, a radio-frequency (RF) spectrum analyzer (GW Instek GSP) to observe the RF frequency characteristics, and an autocorrelator (A.P.E. PulseCheck) to measure the pulse duration.

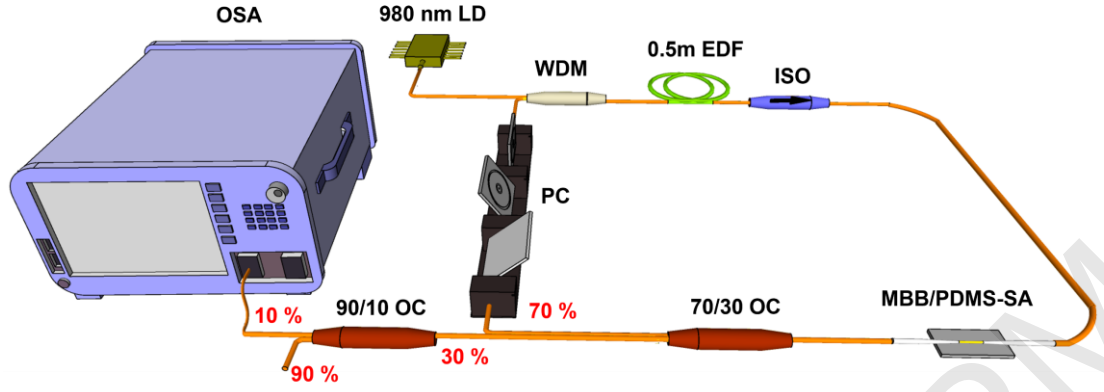


Figure 4.18: Ring cavity EDFL integrated with MBB/PDMS-SA.

4.5.1 Net Group Velocity Dispersion Calculation

The net GVD of the proposed MLFL was calculated to determine the operating pulse regime and its pulse characteristics. MLFL have been investigated to generate coherent ultrashort pulses in different dispersions regimes or net GVD values, comprising anomalous dispersion regime [314], dispersion-managed regime [315], and normal dispersion regime [316], [317]. In this research work, the scope of investigation was limited to the anomalous region only. The laser cavity comprised of three types of optical fibers which were Corning SMF-28, Corning Hi-1060 fiber, and Leikki Er 80-8/125 EDF. The dispersion coefficient, β_2 at 1550 nm was $-22 \text{ ps}^2/\text{km}$ for SMF-28, $-7 \text{ ps}^2/\text{km}$ for Hi-1060 SMF and $-19.5 \text{ ps}^2/\text{km}$ for Leikki Er 80-8/125 EDF. Therefore, the total GVD can be calculated based on the following Equation 4.4;

$$GVD_{net} = L_{SMF}\beta_{SMF} + L_{Hi-1060}\beta_{Hi-1060} + L_{EDF}\beta_{EDF} \quad (4.4)$$

where GVD_{net} is the total group velocity dispersion, L_{SMF} and β_{SMF} is the total length and the dispersion parameter for of the SMF-28 fiber, respectively. $L_{Hi-1060}$ and $\beta_{Hi-1060}$ is is the total length and the dispersion parameter for Hi-1060 fiber, respectively, while L_{EDF} and β_{EDF} is the total length and the dispersion parameter for gain medium length, Leikki EDF, respectively. Based on the length and fiber type used in the experiment, the estimated value of the GVD_{net} is -0.5422 as shown in Table 4.3. The value attained proves that the cavity setup was designed to operate in the anomalous dispersion ($GVD_{net} < 0$).

Table 4.5: Estimated GVD_{net} value for laser cavity setup.

Fiber Type	Length (m)	β_2 (ps ² /km)	Net GVD (ps ²)
SMF-28	23.88	-22.0	-0.5254
Hi-1060	1.0	-7.0	-0.0070
EDF	0.5	-19.5	-0.0098
			$GVD_{net} = -0.5422$

4.5.2 Optical Spectrum (OSA)

The optical spectrum with respect to pump power was measured using an OSA (AQ6370B, Yokogawa) with a resolution bandwidth of 0.02 nm. The optical spectrum was recorded with increasing pump power at an interval of around 5 mW up to a maximum of 250 mW. The optical spectrum's evolution to pump power for both MBB/PDMS: HEX-SA and MBB/PDMS: TOL-SA are shown in Figure. 4.19. Referring to Figure 4.19 (a) and (c), the Kelly sidebands were observed after mode-locked threshold until maximum pump power for both SAs. This is the main feature for conventional soliton mode-locked pulse in the

anomalous dispersion regime. Soliton pulses do not undergo any temporal or spatial change along the propagation distance due to the balance between SPM and chromatic dispersion. Noting that appearance of Kelly sidebands, indicating the pulse operating at conventional soliton (CS) in the anomalous dispersion regime [318], [319]. The optical spectrum for both SAs were observed at three distinct points which is at the CW laser threshold, the mode-locked threshold and the maximum pump power are illustrated in Figure 4.19 (b) and (d). At the beginning of mode-locking phase, the CW laser for both SAs was observed at the same pump power of 30 mW. As the pump power increased to 55 mW for MBB/PDMS: HEX-SA and 65 mW for MBB/PDMS: TOL-SA, stable mode-locked operation with an output spectrum of Kelly sidebands was formed (threshold mode-locking). Further increment of pump power had broadened the 3-dB bandwidth, with more peaks of Kelly sidebands, indicating the pulse operating at CS. The comparatively low pump power required for MBB/PDMS: HEX-SA to achieve mode-locked threshold is attributed to its low I_{sat} compared to MBB/PDMS: TOL-SA.

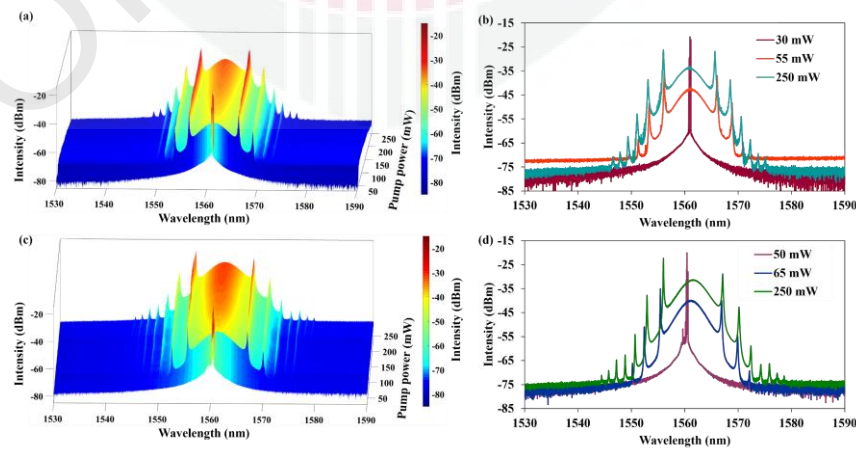


Figure 4.19: Optical spectrum evolution over pump power of (a)(b) MBB/PDMS: HEX-SA and (c)(d) MBB/PDMS: TOL-SA.

Figure 4.20 (a) and (c) illustrate the top view of optical spectrum which show the broadening effect of 3-dB bandwidth ($\Delta\lambda$) with the increment of pump power. Moreover, it could be observed that the central wavelength (λ_c) remained almost constant during pump power increment for both types of SAs. The spectral broadening of laser output is caused by SPM [320], which becomes more pronounced at higher pump powers. Figure 4.20 (b) and (d) illustrates the magnified view of the spectrum at the maximum pump powers to highlight the $\Delta\lambda$ and λ_c for both SAs. The MBB/PDMS: TOL-HEX possessed $\Delta\lambda$ of 3.23 nm while for MBB/PDMS: HEX-SA of 3.66 nm at maximum pump powers. Similarly, the λ_c of MBB/PDMS: HEX-SA and MBB/PDMS: TOL-SA were 1560.92 nm and 1561.53 nm, respectively. Based on the recorded optical spectra, no parasitic CW peaks were observed around the λ_c for both SAs, confirming stable passive MLFL was achieved.

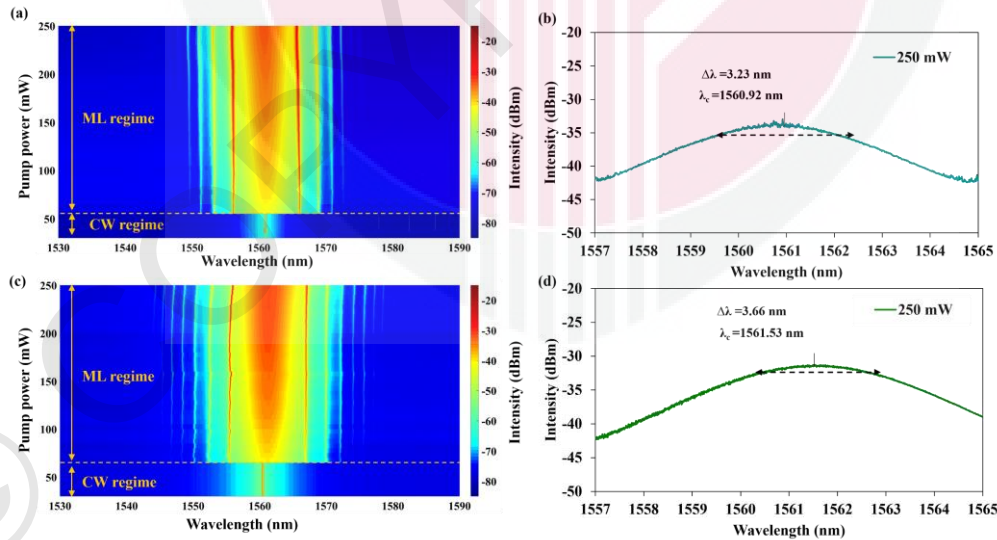


Figure 4.20: Top view of optical spectrum at different pump power (a) MBB/PDMS: HEX-SA and (c) MBB/PDMS: TOL-SA; spectrum at maximum pump power of 250 mW (b) MBB/PDMS: HEX-SA and (d) MBB/PDMS: TOL-SA.

4.5.3 Pulse Train

The pulse train was measured via photodetector (Thorlabs InGaAs, DET08CFC) connected to Tektronix (TD3012C) oscilloscope. The corresponding oscilloscope traces obtained at maximum pump power (250 mW) with both types of SAs are illustrated in Figure 4.21. Based on the experimental results, pulse trains from both SAs were attained at a fundamental repetition rate represents the time that corresponds to a cavity round-trip time per pulse and no sign of multiple pulse or q-switching within the pump power range. This indicates that the laser cavity was able to operate in the fundamental pulse regime and produced a stable pulse. Moreover, as illustrated in Figure 4.21, clean oscilloscope traces were recorded without any noise background, which only arises from periodic fluctuations of pulse energy in the cavity caused by the presence of harmonics or CW components [321]. This means that the SAs were able to produce stable mode-locked pulses. The fundamental pulse repetition rates of both SA were found to be about the same at ~8.05 MHz, which was expected because the cavity length was fixed throughout the experiment, as shown in Figure 4.21(a) and (b). The value corresponds to the cavity round-trip time of 124.2 ns is in agreement with the cavity length (L) and pulse propagation time (t) in the cavity as given by Equation 4.5, where n is the refractive index of fiber core (1.4682) and c is the speed of light.

$$t = \frac{Ln}{c} \quad (4.5)$$

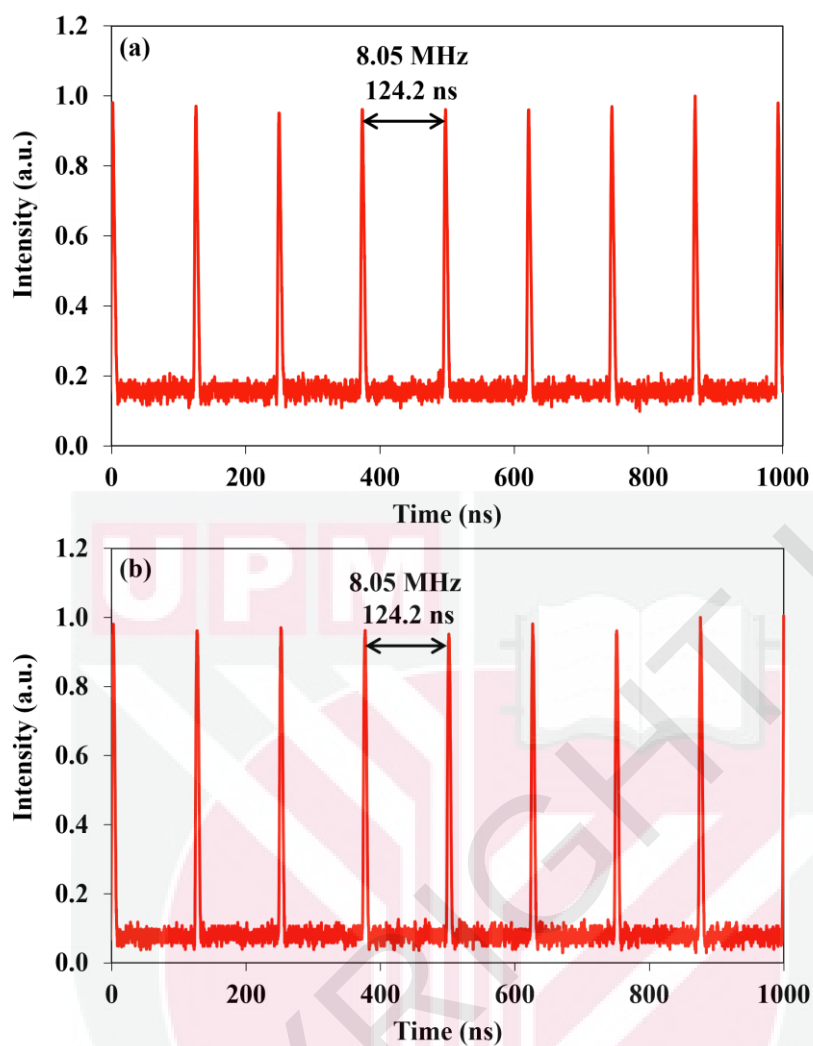


Figure 4.21: Oscilloscope traces of (a) MBB/PDMS: HEX-SA and (b) MBB/PDMS: TOL-SA.

4.5.4 Pulse Duration

The pulse duration was measured using an APE Pulse Check autocorrelator.

Figure 4.22 illustrates the experimental data measurement through autocorrelator and their corresponding squared hyperbolic secant (sech^2) fitting curve. Figure 4.22 (a) and (b) show the autocorrelation full width at half maximum (τ_{FWHM}), which is determined by a sech^2 function (red curve). This

indicates that soliton generation has occurred [322]. Based on the findings, output spectrum obtained with both types of SAs were fitted with the sech^2 profile, the characteristic of CS in net anomalous dispersion regime. Since the laser operates in the anomalous dispersion regime, the pulse shaping mechanism obeyed by the sech^2 profile function with decorrelation factor of 0.648 as represented by Equation 4.6 [322], [323];

$$\tau_{pulse} = 0.648 \times \tau_{FWHM} \quad (4.6)$$

These results on Figure 4.22 at maximum pump power of 250 mW indicate a well-fitted sech^2 fittings of experimental data having no indication of multiple pulses, harmonics or noise generation. The measured τ_{FWHM} was 1455.0 fs that corresponds to τ_{pulse} of 942.8 fs after decorrelation factor of 0.648 for MBB/PDMS: HEX-SA shown in Figure 4.22 (a). On the other hand, Figure 4.22 (b) shows τ_{pulse} of 942.1 fs, after decorrelation of 1454.0 fs τ_{FWHM} for MBB/PDMS: TOL-SA and there is no difference in τ_{pulse} for both SAs as the value difference is only ~ 0.7 fs.

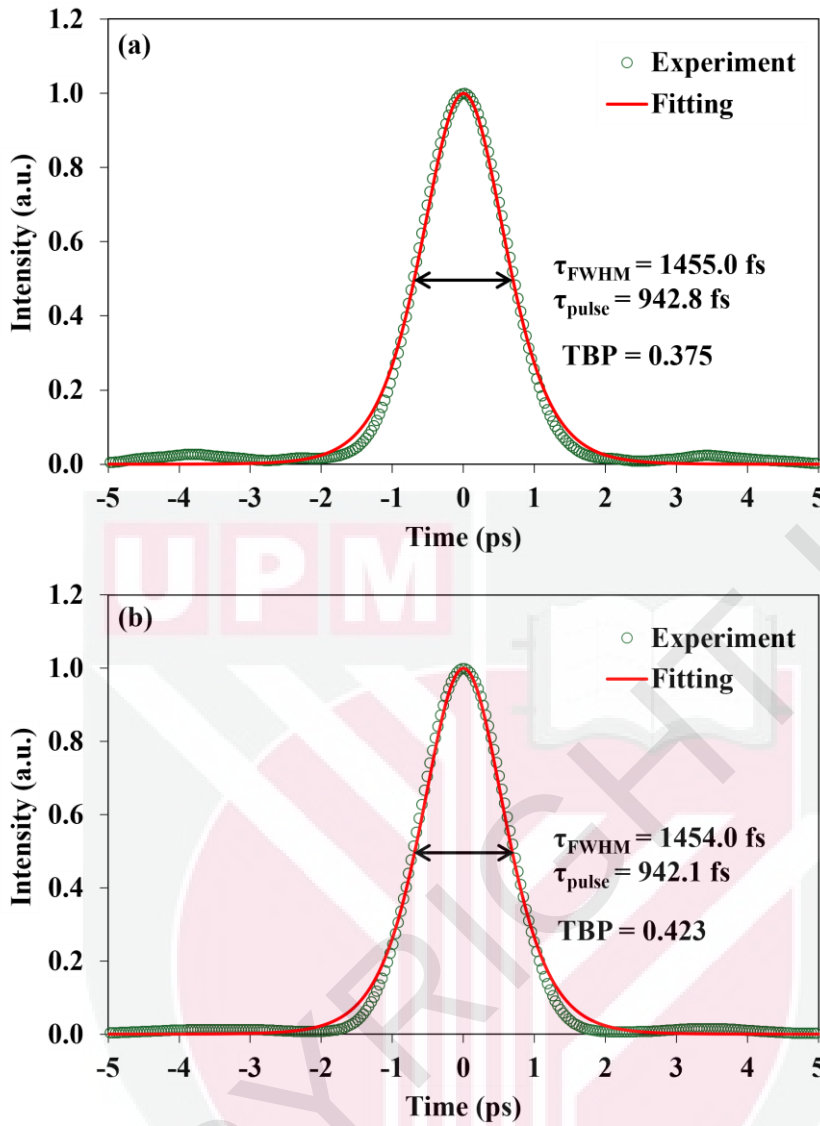


Figure 4.22: Autocorrelator trace and corresponding fittings of (a) MBB/PDMS: HEX-SA, and (b) MBB/PDMS: TOL-SA.

In the optical pulse analysis, another important parameter is the Time Bandwidth Product (TBP). TBP validates if the spectral profile of pulse is related to the theoretical limits of Fourier transform-limited pulse. It represents the product of temporal duration and spectral width in frequency domain, in which minimum TBP value determines the bandwidth-limited pulse. TBP is calculated from the $\Delta\lambda$, λ_c , and τ_{pulse} . The corresponding TBP can be calculated using Equation 4.7.

$$TBP = \Delta f \times \tau_{pulse}$$

$$\Delta f = \frac{\Delta\lambda \times c}{(\lambda_c)^2} \quad (4.7)$$

The minimum Fourier transform-limited pulse of sech^2 is 0.315. The aspect of pulse quality is determined by how close the product actual width and measured spectral width to the Fourier transform limited pulses, whereas chirp pulses have large values. As shown in Figure 4.22, the TBP calculated from the product of actual pulse width and spectral bandwidth at maximum pump power for MBB/PDMS: HEX-SA was 0.375 and for MBB/PDMS: TOL-SA was 0.423, respectively. These values indicate the pulses were slightly chirped compared to ideal transform limit of 0.315 [324]. Pulse chirping is due to the residual dispersion present in the cavity [325], which is explained as non-compensated high order dispersion [326]. Moreover, the chirped pulse with TBP less than 0.5 is considered a quality pulse.

4.5.5 Average Output Power and Pulse Energy

The average output power and pulse energy to the pump power increment for MBB/PDMS: HEX-SA and MBB/PDMS: TOL-SA SA are illustrated in Figure 4.23 (a) and (b). From the figure, the CW lasing threshold power is observed at 30 mW for both SAs, while the ML threshold power is attained at 55 mW and 65 mW for MBB/PDMS: HEX-SA and MBB/PDMS: TOL-SA, respectively. The average output power at a maximum pump power of MBB/PDMS: HEX-

SA and MBB/PDMS: TOL-SA were 8.05 and 11.33 mW, respectively. The corresponding slope efficiency from lasing threshold until the maximum pump power of MBB/PDMS: HEX-SA and MBB/PDMS: TOL-SA was calculated as 3.48% and 4.87%, respectively. The comparatively high power and efficiency of MBB/PDMS: TOL-SA are attributed to its low insertion loss. The pulse energy can be calculated from the average output power and repetition rate based on Equation 4.8 as follows;

$$E_p = \frac{P_{out}}{\Delta f} \quad (4.8)$$

where E_p is the pulse energy in unit Joule, P_{out} is the average output power in unit Watt and Δf is the pulse repetition rate in unit Hz. The evolution of pulse energy with respect to pump power for different SAs is depicted in Figure 4.23. The pulse energy can only be calculated when the cavity's mode-locked threshold is reached. The starting point of the symbol in the graph depicts the mode-locked threshold. The maximum pulse energy obtained with MBB/PDMS: HEX-SA 1.00 nJ and 1.41 nJ for MBB/PDMS: TOL-SA at maximum pump power. The slope efficiency of pulse energy calculated in the range of mode-locked threshold until maximum pump power for MBB/PDMS: HEX-SA was 0.0046 nJ/mW, whereas for MBB/PDMS: TOL-SA was 0.0065 nJ/mW.

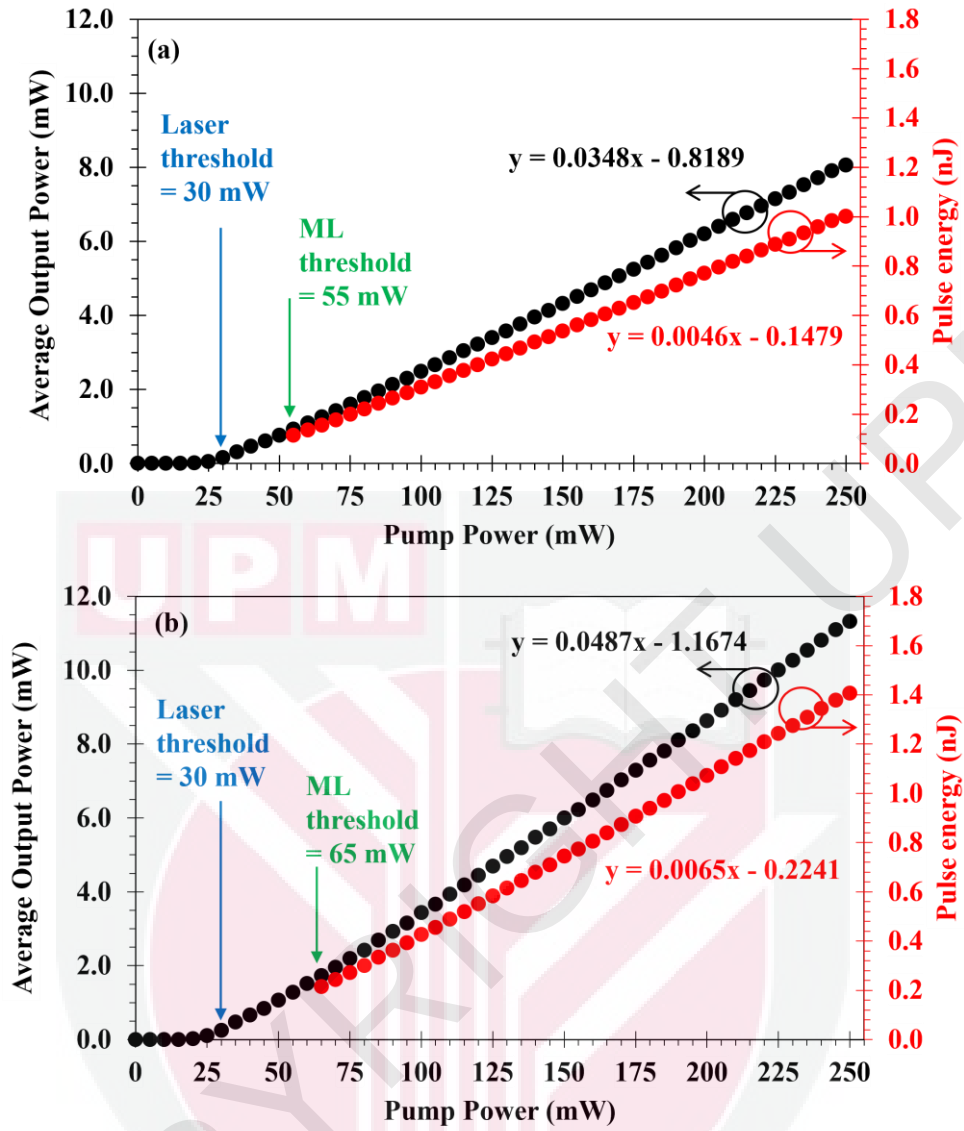


Figure 4.23: Average output power and pulse energy of (a) MBB/PDMS: HEX-SA and (b) MBB/PDMS: TOL-SA.

4.5.6 Pulse Stability

The pulse stability was evaluated by measuring its signal-to-noise ratio (SNR) through an electrical spectrum analyzer (GW Instek GSP-830). SNR is the contrast ratio between signal peak level to the background noise of the fundamental pulse frequency spectrum. In our work, the continuous RF

spectrum was recorded in 200 MHz span with RBW of 30 kHz. The measured SNRs for both SAs are shown in Figure 4.24. Based on the experimental data, the SNR of 65.4 and 59.8 dB were observed for MBB/PDMS: HEX-SA and MBB/PDMS: TOL-SA, respectively. From the previous studies, the generated pulse with SNR around 50 dB is considered stable [327], [328]. The RF measurement for both SAs was observed at the fundamental repetition rate of 8.05 MHz, confirming that the fabricated mode-locked laser is free from the multi-pulse operation and validating its stability [329].

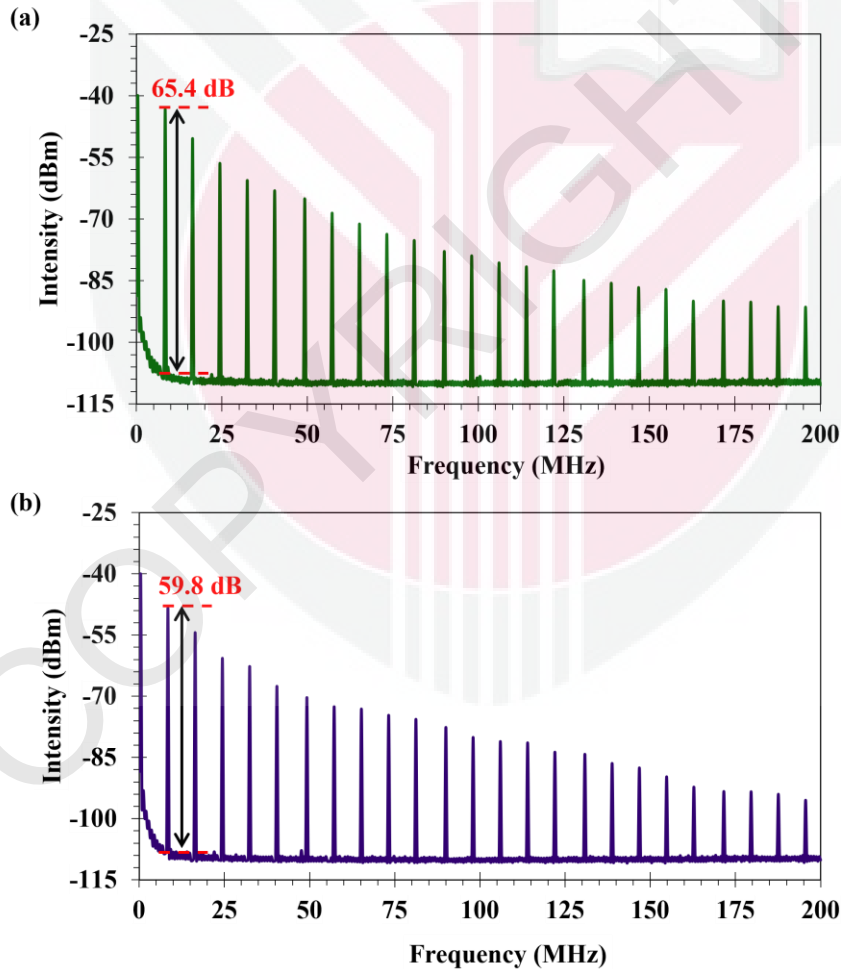


Figure 4.24: RF spectrums of MLFL of (a) MBB/PDMS: HEX-SA and (b) MBB/PDMS: TOL-SA.

To further validate the operational stability of the SAs, the MLFLs was operated for 4 hours with a spectrum recorded every 3 minutes inside the laboratory (relative humidity $57\pm5\%$ and temperature $22\pm4^\circ\text{C}$). The mode-locked spectrum at the maximum pump power is presented in Figures 4.25 (a) and (c) for MBB/PDMS: HEX-SA and MBB/PDMS: TOL-SA, respectively. From Figure 4.25 (b), MBB/PDMS: HEX-SA shows stable average λ_c at 1560.78 ± 0.11 nm and $\Delta\lambda$ at 3.28 ± 0.06 nm throughout the experiment. While for MBB/PDMS: TOL-SA also shows stable average λ_c at 1561.55 ± 0.12 nm and $\Delta\lambda$ at 3.77 ± 0.04 nm as shown in Figure 4.25 (d). Even though the experiments were performed in a regular laboratory environment, no significant changes were observed in the λ_c and $\Delta\lambda$ during the stability measurement for both SAs. The average values of λ_c and $\Delta\lambda$ and corresponding standard deviations (SD) for 4 hours are illustrated in Figures 4.25 (b) and (d). The cavity with both SAs had SD less than 0.2 nm for both λ_c and $\Delta\lambda$, which confirmed the stable operation of mode-locked fiber laser for 4 hours. This further justified that the cavity was not affected by periodic energy fluctuations in the cavity [321]. with the stability results together with high SNR implies that passive MLFL achieved through both SAs demonstrates quality pulse and stability.

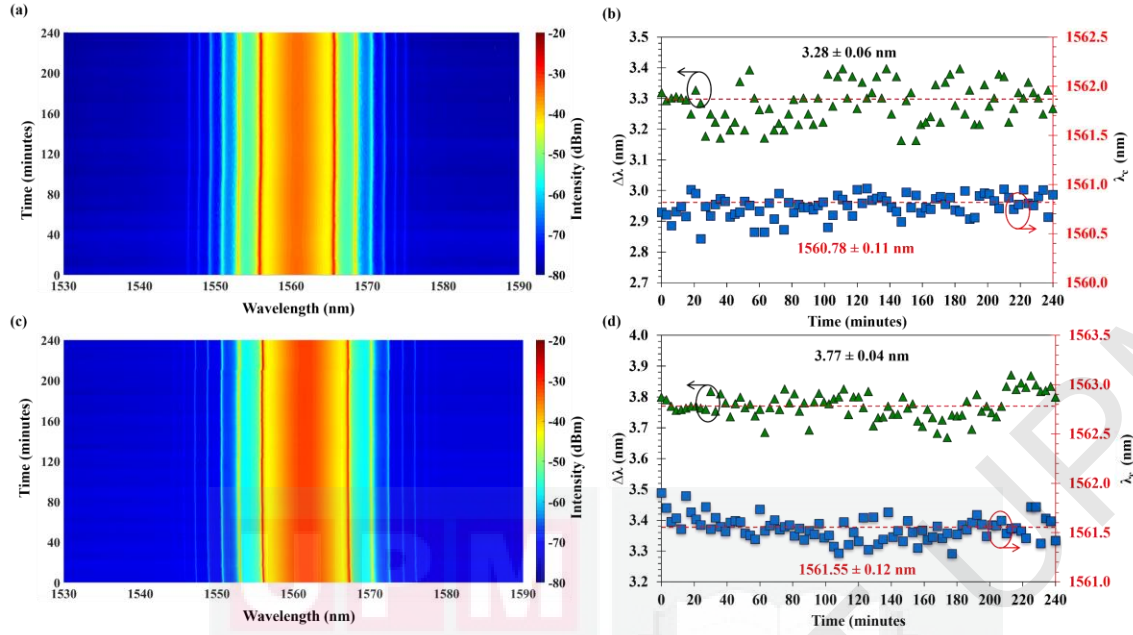


Figure 4.25: Stability spectrum evolution for 4-hours of (a) MBB/PDMS: HEX-SA and (c) MBB/PDMS: TOL-SA and evolution of $\Delta\lambda$ and λ_c during stability measurement for 4-hours of (b) MBB/PDMS: HEX-SA and (d) MBB/PDMS: TOL-SA.

The stability test was also conducted on the autocorrelation trace over 4 hours monitoring period for every 3 minutes and the results are presented in Figures 4.26 (a) and (c). The analyses of time domains are plotted in Figures 4.26 (b) and (d). From Figure 4.26 (b), MBB/PDMS: HEX-SA shows stable average T_{pulse} at 943.39 ± 13.87 fs and TBP at 0.381 ± 0.01 throughout the experiment. While for MBB/PDMS: TOL-SA also shows stable average T_{pulse} at 942.66 ± 18.31 fs and TBP at 0.437 ± 0.01 nm as shown in Figure 4.26 (d). From the findings, the generated pulse with lower SD across 4 hours monitoring period for MBB/PDMS: HEX-SA compared to MBB/PDMS: TOL-SA were observed, thus implying higher stable operation of MBB/PDMS: HEX-SA at ambient atmosphere.

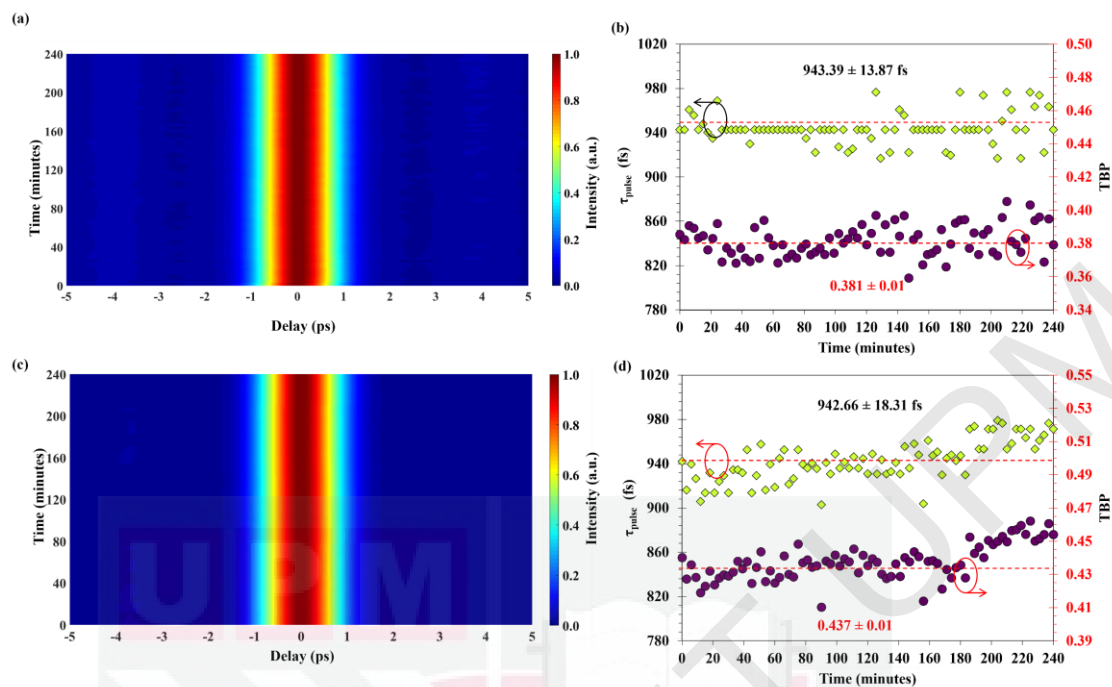


Figure 4.26: Stability evaluation of autocorrelation trace (a) MBB/PDMS: HEX-SA and (c) MBB/PDMS: TOL-SA and evolution of pulse width and TBP during stability measurement for 4-hours of (b) MBB/PDMS: HEX-SA and (d) MBB/PDMS: TOL-SA.

4.6 Summary

The process of fabrication MBB/PDMS using different solvent for SA fabrication was achieved by discussing the extrinsic effect during the fabrication process together with its material characterization were first discussed in this chapter. It was found that different solvents had different influences on maintaining MBB perovskite structure during the fabricated process of SA. MBB/PDMS: HEX-SA and MBB/PDMS: TOL-SA were the two SAs that were successfully fabricated while maintaining the structure of the perovskite. The both SAs was deposited on the tapered fiber surface via spin-coating technique. The SAs were then characterized for their transmission losses and nonlinear saturable absorption properties before integrated in

EDFL to test its mode-locking performance. The performance of both fabricated SAs were experimentally investigated as summarized in Table 4.4. The optical spectrum of both SAs exhibited Kelly sidebands, which proved the realization of the conventional soliton in a net anomalous dispersion regime. Similarly, clean oscilloscope traces were observed for both SAs at fundamental repetition rate, which is in agreement with the cavity round trip time. The CW laser threshold was obtained at the same pump power for both SAs and the mode-locked threshold for MBB/PDMS: HEX-SA was achieved at 55 mW while for MBB/PDMS: TOL-SA at 65 mW. The τ_{pulse} for both SAs was comparable. The SNR of 65.4 and 59.8 dB was obtained for MBB/PDMS: HEX-SA and MBB/PDMS: TOL-SA, respectively. The average output power and pulse energy of MBB/PDMS: TOL SA was larger compared to MBB/PDMS: HEX-SA. Similarly, the TBP values for both SAs indicated that the mode-locked pulse formed chirped pulses. The 4 hours operational stability in term of the spectrum and autocorrelation trace demonstrated a good performance with lower SD for MBB/PDMS: HEX-SA compared with MBB/PDMS: TOL-SA were observed.

Table 4.6: Summary of MLFL characteristics realized through MBB/PDMS based SA.

	MBB/PDMS: HEX-SA	MBB/PDMS: TOL-SA
Transmission loss (dB)	4.20	3.58
MD (%)	9.75	19.30
I_{sat} (MW/cm²)	200.03	900.00
α_{ns} (%)	55.40	50.00
λ_c (nm)	1560.92	1561.53
$\Delta\lambda$ (nm)	3.23	3.66
T_{pulse} (fs)	942.8	942.1
TBP	0.375	0.423
Repetition rate (MHz)	8.05	8.05
SNR (dB)	65.4	59.8
Average output power (mW)	8.05	11.33
Pulse energy (nJ)	1.00	1.41
ML_{threshold} (mW)	55	65

CHAPTER 5

EFFECTS OF AMBIENT INDOOR LIGHTING ON DEGRADATION OF MBB/PDMS-BASED SA TOWARDS LASER PULSE PERFORMANCE

5.1 Introduction

In the previous chapter, the MBB/PDMS prepared with different solvents were characterized, followed by the fabrication and characterization of MBB/PDMS-based SAs. Only MBB/PDMS: HEX and MBB/PDMS: TOL successfully fabricated while maintaining the structure of the perovskite. Moreover, both SAs were integrated into a fiber laser ring cavity and successfully generated mode-locked ultrashort pulses in the femtosecond range. Despite the better performance of the MBB/PDMS: TOL-SA being exhibited, it was decided to proceed with MBB/PDMS: HEX-SA due to the better stability exhibited by its SNR. A stable SA is preferred at this point for the 16 weeks stability test to be conducted for the next phase. SNR is one of the indicators on stability and quality of the generated pulses. A higher SNR provides greater resilience against environmental variation's, such as temperature fluctuations and vibrations, which leads to stable and well-defined pulses with minimal variations. During the 4 hour-stability observation for both SAs, lower standard deviation was observed for MBB/PDMS: HEX-SA compared to MBB/PDMS: TOL-SA. Therefore, MBB/PDMS: HEX-SA was chosen for further evaluation on its reliability and robustness in sustaining long periods of mode-locked operation. The flow chart of the methodology in this chapter is illustrated in Figure 5.1.

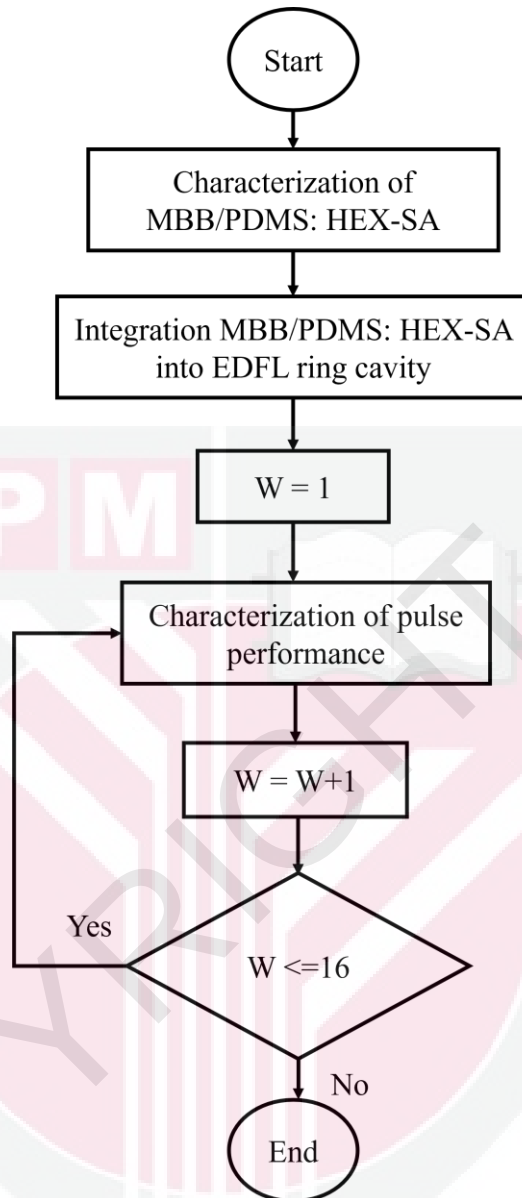


Figure 5.1: Flow chart of the methodology.

Perovskites devices have been used in enormous applications from indoor to outdoor environment but unfortunately these perovskite-based devices exhibit rapid degradation in their performance, which is keeping them away from being commercialized. There have been several reports and reviews on degradation phenomenon and stability in perovskite [330], [331]. The device's stability is

observed to be affected by a number of parameters such as humidity, light intensity, temperature, and electrical stress, and under actual weather conditions all of these parameters would work differently with arbitrary variation over time. Several research works attempted to overcome these by using various strategies to extend the shelf-life and long-term operability in various applications. For instance, composition engineering was used to substitute the organic component MA in MAPbBr_3 with cesium (Cs) to form CsPbBr_3 , making it completely inorganic and far more stable under ambient condition [332]. Waterproof perovskite lasers have also been demonstrated by encapsulating the perovskite with water-resistant polymer, growing the perovskite in quartz microcapillary through cast-capping method [333], [334], [335]. Hexagonal boron nitride flakes were also used to cap the perovskite crystal films for effective heat dissipation and to overcome the inherent vulnerability to moisture and polar solvents [333], [334], [335]. Chauhan et al. reported behavior of perovskite solar cells toward different open air environmental conditions. They found that perovskite solar cells stored outdoors degraded the most rapidly, followed by perovskite solar cell stored under compact fluorescent lamp (CFL) illumination and perovskite solar cell stored in the dark degraded the least [336]. Another study by Kim et al approached this issue by doping the perovskite solar cells with chlorine ions and found that it improved the performance with a maximum power density of $35.25 (231.78) \mu\text{W}/\text{cm}^2$, especially under 400 lux LED (halogen) illumination [337].

Several research works were conducted to show intriguing potential of perovskite as a new type of nonlinear optical material in ultrafast photonics

applications [234], [235], [238], [239]. Even the substitution of Cs to form CsPbBr₃ has also been shown to be an efficient SA for fiber laser [48], [49]. Among the research works, the degradation mechanisms in perovskite based-SA are not completely understood yet as it has been with perovskite solar cells, and it requires more detailed investigations. On top of that, long-term stability and sustainability evaluation of MLFL incorporating perovskite based-SA has remained elusive. Therefore, longer evaluation time is needed to validate the robustness, stability and reliability of the fabricated SA before it is truly market ready. This chapter shows the results regarding the degradation effect of MBB/PDMS: HEX-SA in different storage conditions (SA in packaging (SA-WP) versus SA without packaging (SA-WOP)) on the pulse performance of MLFL under CFL laboratory illumination. Therefore, the detailed mode-locked laser performance for both SAs were recorded up until week 16 under continuous illumination of CFL inside the laboratory.

5.2 Construction of Mode-Locked EDFL Cavities for Integration with MBB/PDMS: HEX-SAs

For degradation studies, two different MBB/PDMS: HEX-SA were prepared, where one in darkness (SA-WP) while the other was exposed to ambient lighting (SA-WOP) and were spliced into two different cavity fiber laser cavities that operating in anomalous dispersion regime where the first cavity fiber laser shown in Figure 5.2 (a) (we will call this as Cavity A) is the same cavity explained in Section 4.5, Figure 4.18. Meanwhile, the ring cavity fiber laser in Figure 5.2 (b) (we will call this as Cavity B) was constructed using 8-meter long Lucent HP980 EDF as gain medium and the cavity was forward-pumped by a

980 nm LD via a 980/1550 nm WDM. The Lucent HP980 erbium-doped fiber (EDF) has an absorption coefficient of 3.5 decibels per meter (dB/m) at a wavelength of 1530 nm and a mode field diameter of 6 μm . A standard 80/20 optical coupler (OC) splits the laser output into two parts, with 20% going to one port and 80% going to the other port. The 80% of the laser signal that goes to the other port propagates in the cavity towards the polarization controller (PC) to complete the ring loop. 99/1 OC and ISO were added to both ring cavities (indicated in red-dashed boxes) to monitor their respective intracavity power (power of light that is circulating inside an optical cavity) by monitoring the output power from OPM via back calculation denoted as P1 and P2, respectively.

The SA-WP was spliced into a fiber laser cavity between a 99/1 OC and an 70/30 OC as portrayed in Figure 5.2 (a) for Cavity A, while the SA-WOP was spliced into the fiber laser cavity between a 99/1 OC and an 80/20 OC as shown in Figure 5.2 (b) for Cavity B. Different cavities with different SAs (with and without packaging) were operated concurrently for 16 weeks to study and compare the pulse laser performance degradation under CFL illumination inside the laboratory while keeping the rest of the conditions relatively the same. The conditions that were fixed was the laboratory environment that the lasers were operating in, where under CFL illumination shows 260 ± 30 Lux measured by Yokogawa 510 Series Digital Lux Meters whereas relative humidity of $57 \pm 5\%$ and temperature $22 \pm 4^\circ\text{C}$ measured by Digital Temperature Humidity Meter HTC-1. The orange-dashed boxes shown in the

figure are pictures taken of the MBB/PDMS: HEX-SA devices with packaging and without packaging.

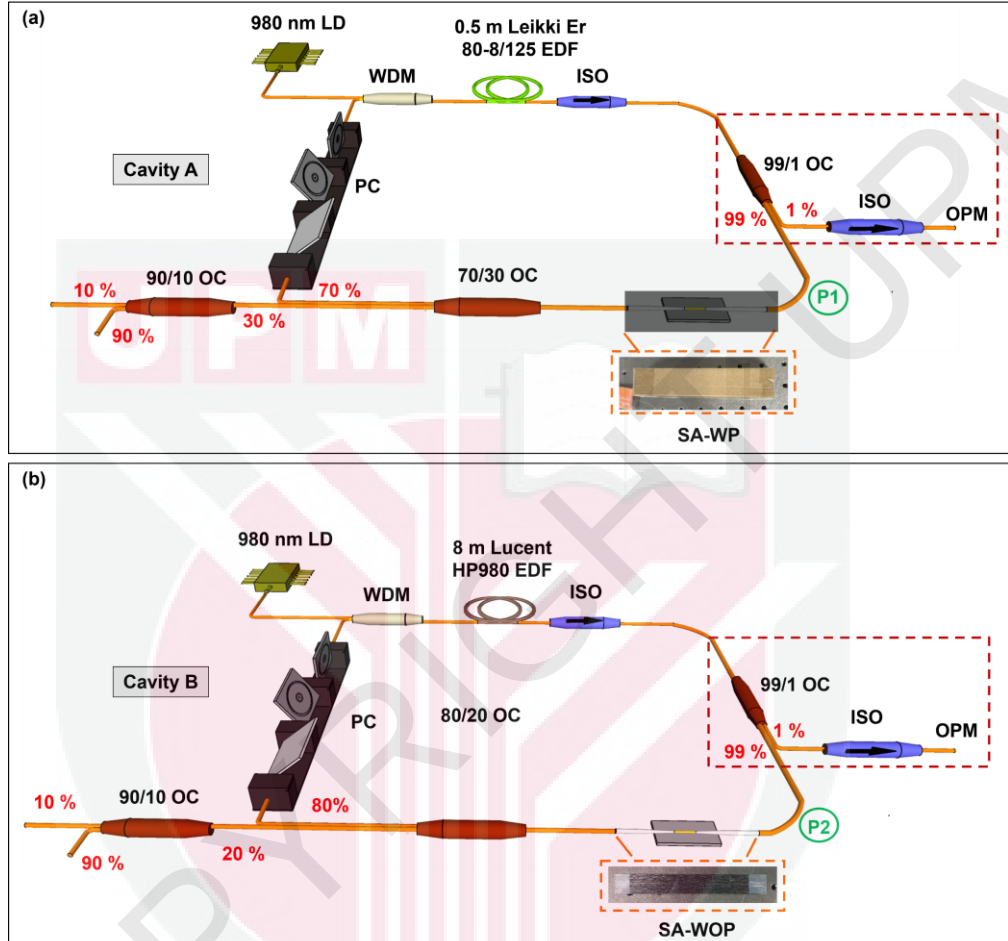


Figure 5.2: Mode-locked EDFL cavities integrated with (a) SA-WP and (b) SA-WOP.

Table 5.1 summarizes the parameters of Cavity A, while Table 5.2 summarizes that of Cavity B. In Table 5.1, the repetition rate of the fundamental pulse for Cavity A was found out to be at ~ 6.81 MHz. Subsequently, the measured period of the pulses was approximately 146.9 ns corresponding to a fundamental repetition rate of 6.81 MHz which matches well with total cavity length of ~ 30.02 m as given by Equation 4.6 in Chapter 4. The net group

velocity dispersion (GVD) for Cavity A is -0.644 ps^2 comprising of 0.5 m EDF, 28.52 m SMF-28, and 1 m Hi-1060, where the dispersion coefficient at 1550 nm are $-19.5 \text{ ps}^2/\text{km}$, $-22 \text{ ps}^2/\text{km}$ and $-7 \text{ ps}^2/\text{km}$, respectively. While in Table 5.2, Cavity B shows the repetition rate of the fundamental pulse to be 7.59 MHz with period between pulses of 131.7 ns matched the relation between the round-trip time, t and cavity length, L of 26.91 m. In fact, the repetition rate of generated pulses depends mainly on the cavity length [338]. Cavity B comprised of three types of optical fibers which were 17.91 m SMF-28, 1 m Hi-1060 fiber, and 8 m HP980 EDF. The dispersion coefficient at 1550 nm was $-22 \text{ ps}^2/\text{km}$ for SMF-28, $-7 \text{ ps}^2/\text{km}$ for Hi-1060 SMF and $23 \text{ ps}^2/\text{km}$ for HP980 EDF. Based on the length and fiber type used in the experiment, the estimated value of the net GVD is -0.217 ps^2 . The pump power of the 980 nm LD in Cavity A was gradually increased from 0 up to the maximum value of 250 mW and produced an intracavity power value, P_1 of 52.49 mW. In Cavity B, the pump power of the 980 nm LD was increased slowly until the intracavity power, P_2 was the same value as that of P_1 in Cavity A, at pump power of 153 mW. The value of intracavity power (P_1 and P_2) was monitored by output power utilizing OPM (shown in red-dashed boxes) and fixed throughout the experiment to ensure similar power of light circulating inside the cavity for different SAs in different cavities.

Table 5.1: Ring cavity erbium-doped fiber laser setup (EDF, Leikki Er 80-8/125).

Parameter	Value	Unit
Cavity length	30.02	m
Repetition rate	6.81	MHz
Net GVD	-0.644	ps ²
Leikki EDF length	0.5	m
P1 at pump power of 250 mW	52.49	mW

Table 5.2: Ring cavity erbium-doped fiber laser setup (EDF, Lucent HP980).

Parameter	Value	Unit
Cavity length	26.91	m
Repetition rate	7.59	MHz
Net GVD	-0.217	ps ²
Lucent EDF HP980 length	8.00	m
P2 at pump power of 153 mW	52.49	mW

As in the experiment, only 153 mW pump power is needed with 8 m of Lucent HP980 to achieve the same intracavity power with 250 mW pump power with only 0.5 m long Leikki Er 80-8/125. EDF plays a role as active gain medium for spontaneous emission and laser generation through stimulated emission with signal circulation in the laser resonator. There are two types of EDF; Leikki Er 80-8/125 & Lucent HP980 with different absorption coefficients used in this

work; 80.0 dB/m and 3.5 dB/m at 1530 nm. The absorption coefficient of an EDF is a measure of how much light is absorbed by the EDF material per unit length. The Lucent HP980 has a much lower absorption coefficient (3.5 dB/m) than the Leikki Er 80-8/125 (80.0 dB/m) at 1530 nm. For Lucent HP980, since it requires less pump power to achieve the same intracavity power than Leikki Er 80-8/125, less photons are generated through stimulated emission processes. Under this condition, less energy at the pump light (light that is used to excite the erbium ions in an erbium-doped fiber amplifier (EDFA)) is absorbed [339].

5.3 Characterization of MBB/PDMS: HEX-SA

5.3.1 Transmission Loss Measurement

Over the 16 weeks of observation, the optical transmission loss characterization was carried out for SA-WP and SA-WOP. Figure 5.3 (a) and (b) show the transmission loss of SA-WP and SA-WOP at 1560 nm for the initial week (Week 1, W1) and the last week of observation (Week 16, W16). From the results obtained, the SA-WP started off with a higher transmission loss of 4.19 dB compared to the SA-WOP of 2.89 dB. The higher transmission loss of SA-WP in Figure 5.3 (a) is suggested due to the greater quantity of MBB embedded in the composite that leads to greater scattering effect and large perturbation to the evanescent field, which resulted in increased in transmission loss. After 16 weeks, the transmission loss of SA-WP increased by 0.79 dB to a transmission loss of 4.98 dB at Week 16. Meanwhile, the

transmission loss of SA-WOP increased by 1.00 dB to 3.89 dB at Week 16. Degradation of the SAs is observed to occur in both samples but more so in the SA-WOP. Even though the PDMS polymer used in the composite is mainly waterproof, the microscopic porous structure of the polymer matrix would still allow minimal diffusion of moisture at a very slow rate and partially decompose the perovskite [340]. In addition, the higher illumination that was subjected to the SA-WOP exhibit higher range transmission loss between Week 1 and Week 16 in comparison to the SA-WP.

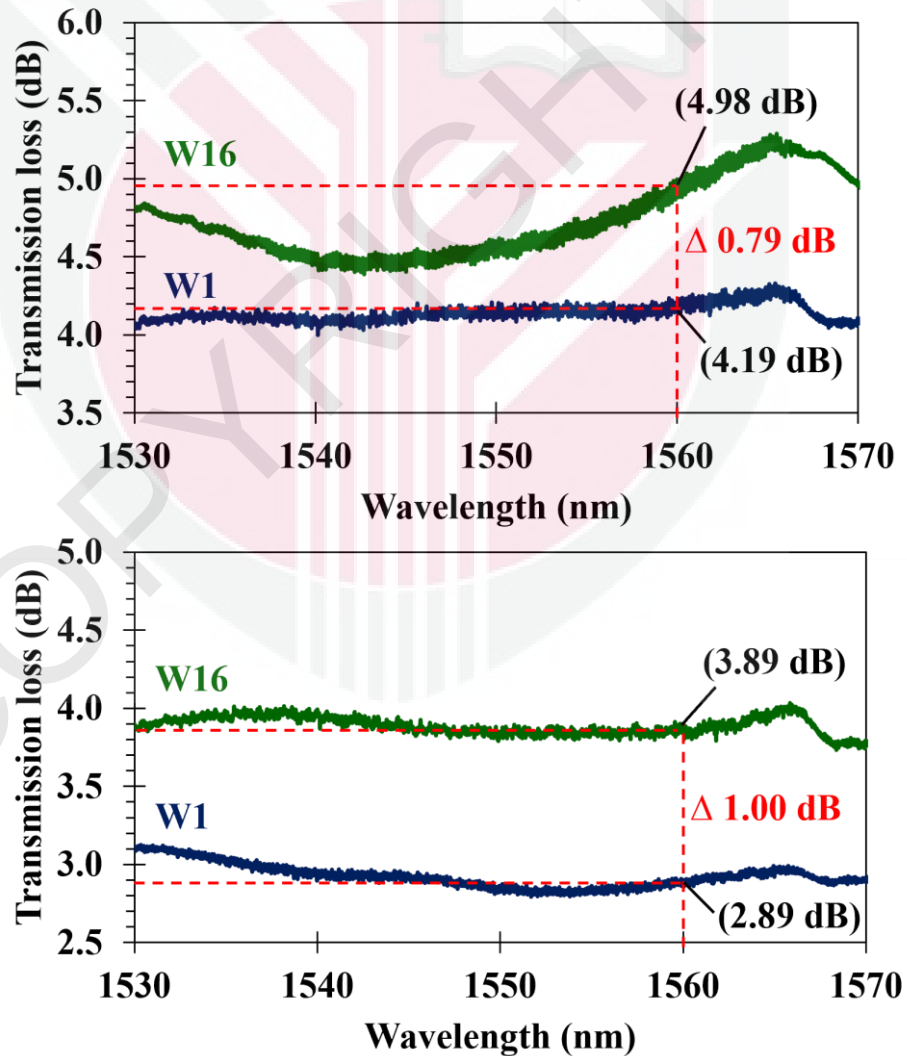


Figure 5.3: Transmission loss of (a) SA-WP and (b) SA-WOP.

5.3.2 Nonlinear Saturable Absorption Properties

Before testing the performance of the mode-locked laser, the saturable absorption properties of the two SA were characterized using the twin-balanced detector setup described in Figure 4.16 of Chapter 4. In this experiment, the powers were measured concurrently where the data were then fitted according to the Equation 4.4 [341]. In the experiment, the α_{ns} , I_{sat} and MD of MBB/PDMS: HEX-SAs with and without packaging were assessed from Week 1 to Week 16 respectively as shown in Figure 5.4. α_{ns} is a parameter that affects the cavity loss of a particular laser configuration. From this work, the α_{ns} value at 55.40 % and 49.90 % were achieved with SA-WP and SA-WOP at Week 1, respectively. α_{ns} is from the optical system or tapering loss that does not contribute to the saturable absorption process. The increment of α_{ns} for both SA-WP (68.30 %) and SA-WOP (60.30 %) was observed from Week 1 to Week 16. The trend is in good agreement with the increasing transmission loss of SA-WP and SA-WOP from Week 1 to Week 16 in Figure 5.3 discussed earlier. Meanwhile, the observation for I_{sat} for both SAs shows increasing pattern from 200.03 MW/cm² to 429.77 MW/cm² from Week 1 to Week 16 for SA-WP while 243.36 MW/cm² to 385.50 MW/cm² for SA-WOP. With I_{sat} increased, we can anticipate that the threshold of mode-locking ($ML_{threshold}$) operation in the cavity can be significantly increased [314], [342].

In terms of MD, SA-WP had decreased from 9.75 % (Figure 5.4 (a)) to 5.10 % (Figure 5.4 (c)) from Week 1 to Week 16 with the difference of 4.65 % due to regular degradation of perovskite. Meanwhile, the MD of SA-WOP increased

by 6.00 % from Week 1 of 5.40 % (Figure 5.4 (b)) to Week 16 of 11.40 % (Figure 5.4 (d)) due to light effect causes the perovskite bandgap to decrease. For fiber lasers working in negative GVD, the minimum value of MD was found to be around 2% [311]. In comparison to this, there is no maximum limit on MD. However, Hönninger et al. provides us a good guideline on this [343]. According to their guidelines, the product of saturation energy of laser gain material (E_G) and saturation energy of SA (E_{SA}), and modulation depth (MD) should be lower than energy inside the cavity (E_p) by $E_p^2 > E_G E_{SA} (MD)$. By satisfying this criterion, the laser will give mode locked pulses, otherwise Q-switched pulses will be achieved [343]. Increasing the MD beyond the Q-switched regime, the laser will only provide continuous wave laser and by increasing it further the laser will not work. In our work, even though different behavior of MD was observed after 16 weeks for SA-WP and SA-WOP, there are no Q-switched pulses achieved and both SAs still able to function as a self-starting mode-locker.

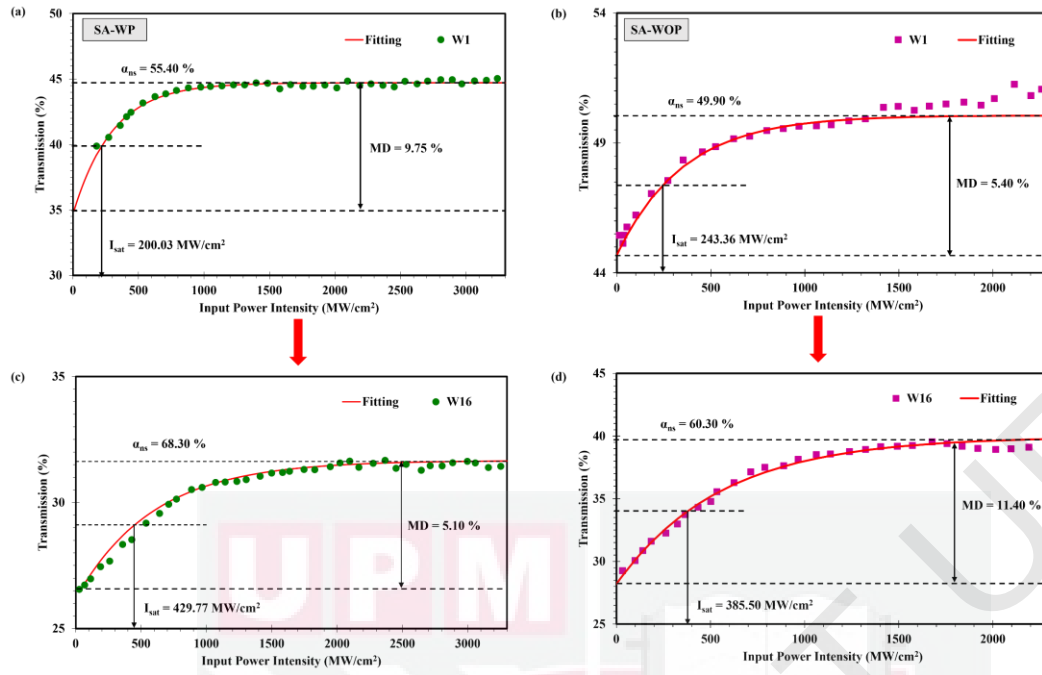


Figure 5.4: Nonlinear saturable absorption parameters of (a) SA-WP (Week 1), (b) SA-WOP (Week 1), (c) SA-WP (Week 16) and (d) SA-WOP (Week 16).

Table 5.3: Nonlinear saturable absorption parameters of SA-WP and SA-WOP.

SA-WP	α_{ns} (%)	MD (%)	T(I) (%)	I_{sat} (MW/cm ²)
W1	55.40	9.75	44.60	200.03
W16	68.30	5.10	31.70	429.77
SA-WOP				
W1	49.90	5.40	50.10	243.36
W16	60.30	11.40	39.70	385.50

5.4 Pulse Performance of Mode-Locked EDFL with MBB/PDMS: HEX- SA

5.4.1 SA-WP

The performance of the EDFL with SA-WP (Cavity A, see Figure 5.2 (a)) over 16 weeks was characterized where the pump power was fixed at 250 mW while the PC orientation was kept at the same angle. Figure 5.5 summarizes the optical spectra in terms of λ_c and $\Delta\lambda$ and the autocorrelator trace in terms of τ_{pulse} and TBP with respect to time in weeks.

The optical spectrum of the erbium-doped fiber laser (EDFL) was measured using an optical spectrum analyzer (OSA) with a resolution bandwidth of 0.02 nm and a wavelength range of 1530 to 1590 nm. The results in Figure 5.5 (a) show the presence of Kelly sidebands, which confirm that the EDFL is operating in a soliton regime [344]. The spectra in Figure 5.5 (a) also show a slight blue shift in the central wavelength (λ_c) over time. This can be attributed to the increased transmission loss shown in Figure 5.3 (a). Moreover, the output spectra were observed without signs of CW laser component indicating high stability of the mode-locked operation. Narrower $\Delta\lambda$ were observed over the week as shown in Figure 5.5 (a) and Figure 5.5 (c) plots linear trend line for λ_c and $\Delta\lambda$ with respect to time in weeks, yielding coefficient determination values of 0.612 and 0.142, respectively. In addition, λ_c and $\Delta\lambda$ decrease by approximately 0.0868 nm and 0.0334 nm for each week. Figure 5.5 (b) presents the τ_{FWHM} of the autocorrelator trace and fitted by the sech^2 function (red line curves) which corresponds to τ_{pulse} after decorrelation factor of

0.648. The sech^2 profile of the pulse further validates the soliton generation characteristic. The trend line of the τ_{pulse} in Figure 5.5 (d) demonstrated longer τ_{pulse} with the changes of 0.5653 fs/week with coefficient determination of 0.0242. The trendline observation shows that longer τ_{pulse} attained leading to a narrower $\Delta\lambda$ throughout the week, the relationship of the $\Delta\lambda$ and τ_{pulse} were depicted as Equation 5.1 [345];

$$\tau_{\text{pulse}} = \frac{\lambda^2}{c \cdot \Delta\lambda} \times 0.315 \quad (5.1)$$

Where c is the velocity of light in vacuum. The TBP calculated from the products of τ_{pulse} and $\Delta\lambda$ to be 0.479 of week 1 to 0.324 of week 16, this value of TBP is expected to decrease with decreasing MD (Figure 5.4, Table 5.4) as simulated by [311]. The trend line of the TBP in Figure 5.5 (d) demonstrated decrease changes of 0.0036/week with coefficient determination of 0.1359, respectively.

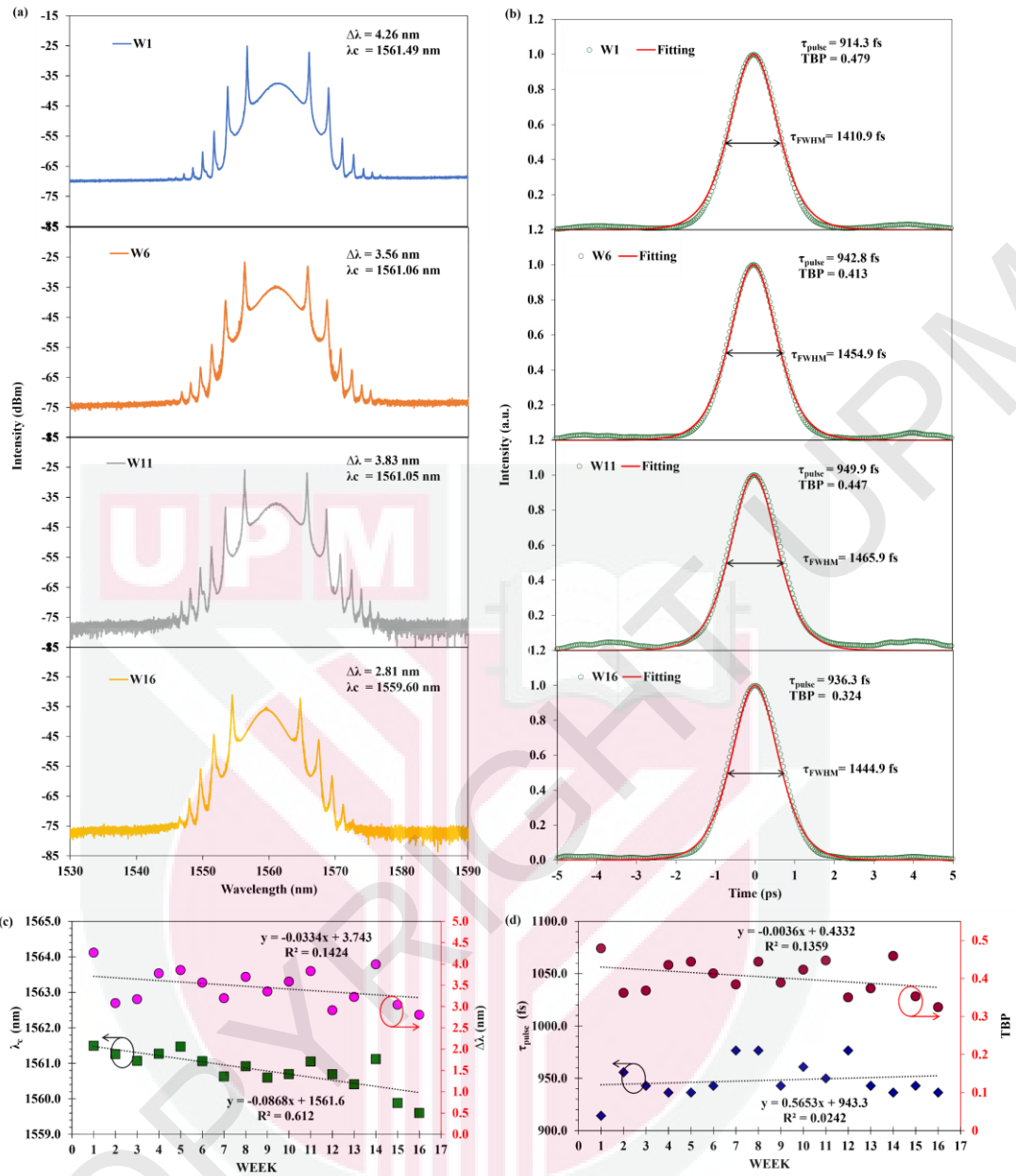


Figure 5.5: Performance of EDFL integrated with SA-WP; (a) optical spectra, (b) autocorrelator trace, and trend lines depicting the relationship of (c) λ_c and $\Delta\lambda$, and (d) τ_{pulse} and TBP as a function of time in weeks at maximum pump power.

Figure 5.6 summarizes the oscilloscope trace and SNR in RF spectra, and their relationship of with respect to time in weeks. The repetition rate of the fundamental pulse was found to be about the same at ~ 6.806 MHz as shown in Figure 5.6 (a), which is consistent with the measured total cavity length of 30.0 m. The almost constant pulse repetition rates also imply that the laser

maintains soliton mode-locked operation without switching to Q-switch operation. Figure 5.6 (c) presents the pulse repetition rate for each week, which exhibits a linear trend from 6.810 MHz in week 1 to 6.802 MHz in week 16. The difference in repetition rate is only 0.008 MHz which is insignificant. The trend line yields a coefficient determination value of 0.1437. Concurrently, the RF signals were captured with resolution bandwidth (RBW) of 30 kHz and video bandwidth (VBW) of 100 Hz. A high signal to noise ratios (SNR) of > 59 dB is illustrated in Figure 5.6 (b) confirming that the mode-locked laser is free from the multi-pulse operation and validating its stability [329]. The SNR recorded for each week shown in Figure 5.6 (d) revealed that the SNR remained relatively stable and fluctuated between 58.5 dB to 63 dB. with changes of 0.0124 dB/week.

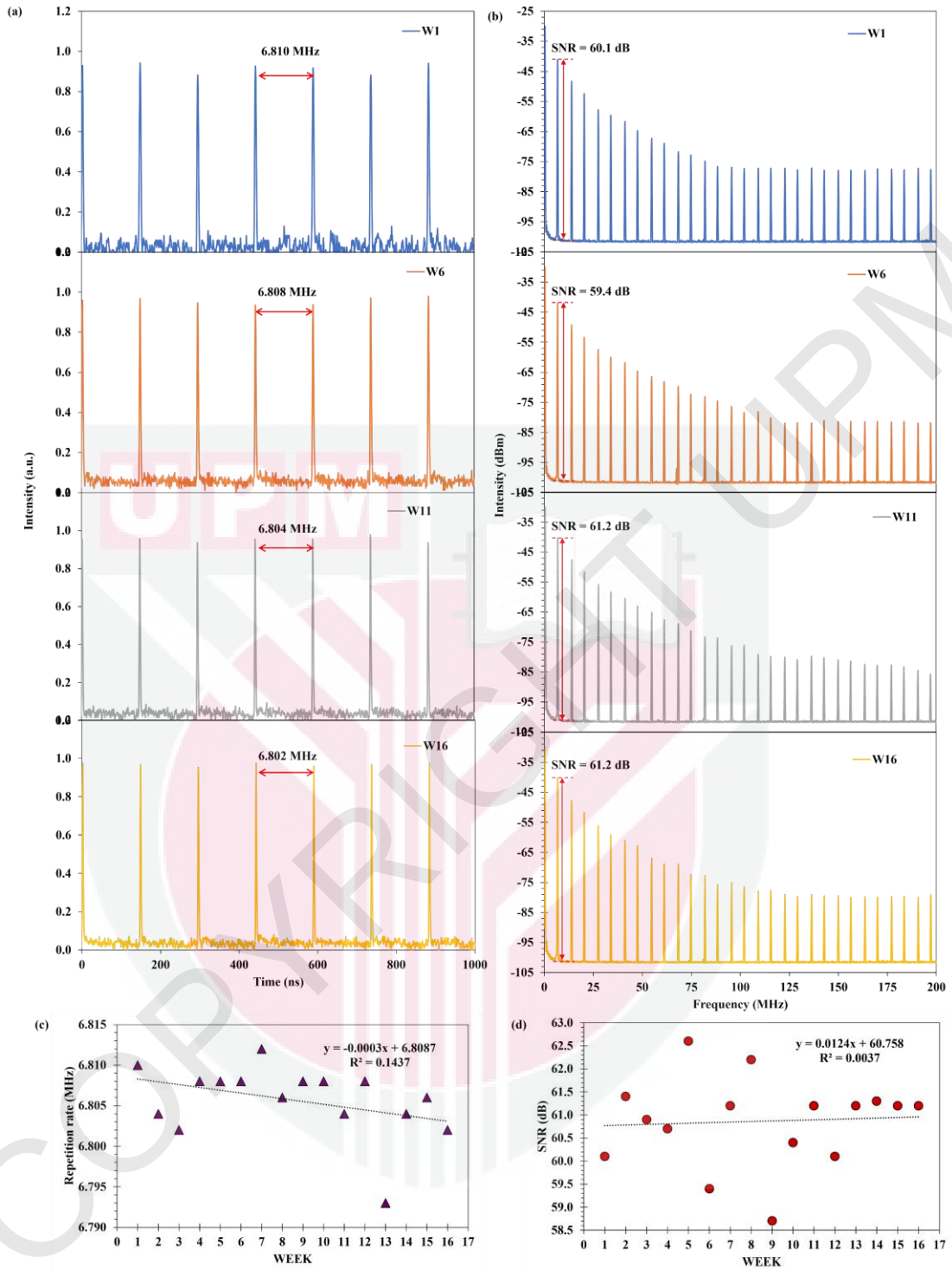


Figure 5.6: Performance of EDFL integrated with SA-WP; (a) oscilloscope trace, (b) RF spectra, and trend lines depicting the relationship of (c) repetition rate, and (d) SNR as a function of time in weeks at maximum pump power.

The lasing performance of the EDFL with SA-WP were investigated further by measuring its output power and mode-lock threshold as presented in Figure 5.7. The average output power decreased from Week 1 of 8.87 mW to Week 16 of 5.36 mW while the pulse energy decreased from Week 1 of 1.30 nJ to Week 16 of 0.79 nJ as shown in Figure 5.7 (a). The decrease in output power over time was due to the increase in transmission loss. The $ML_{\text{threshold}}$ recorded for each week is shown in Figure 5.7 (b) where the threshold was first realized at 55 mW pump power in Week 1 until Week 13, and then increased to 60 mW starting at Week 14 onwards with 9% deviation. Indeed, when the transmission loss increases, the amount of pump power needed to reach the $ML_{\text{threshold}}$ also increases [344]. This also coincides with the I_{sat} characteristics from week 1 (200.03 MW/cm²) increases to week 16 (429.77 MW/cm²) from Figure 5.4 (a) and (c) which justified the higher $ML_{\text{threshold}}$ obtained as shown in Figure 5.7 (b).

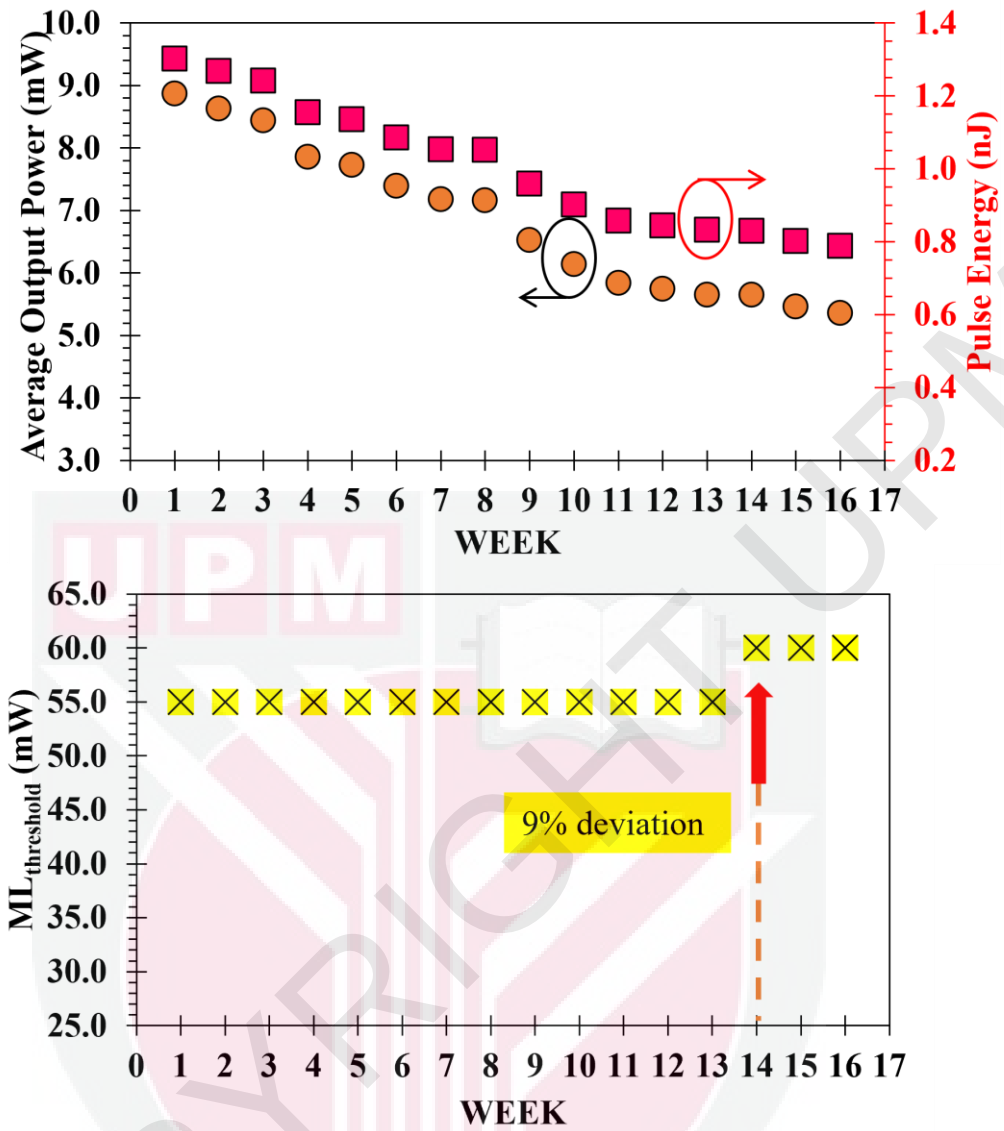


Figure 5.7: Performance of EDFL integrated with SA-WP; (a) average output power and pulse energy (b) mode-locked threshold as a function of time in weeks.

5.4.2 SA-WOP

The experimental work started by inserting SA-WOP into Cavity B (see Figure 5.2 (b)) and operated at maximum pump power of 153 mW and fixed PC orientation. Figure 5.8 summarizes the optical spectra in terms of λ_c and $\Delta\lambda$, and the autocorrelator trace in terms of τ_{pulse} and TBP with respect to time in

weeks. Similar to the SA-WP, a stable mode-locked operation with Kelly sidebands was observed in Figure 5.8 (a), indicating the pulse operation in soliton regime. As illustrated in Figure 5.8 (a), the blueshift in λ_c was caused by an increase in transmission loss over the week. Broader $\Delta\lambda$ were observed over time in Figure 5.8 (a) and corresponding trendline of λ_c and $\Delta\lambda$ for each week were plotted in Figure 5.8 (c). The value of λ_c was slightly blueshift by 0.0616 nm while $\Delta\lambda$ broaden by 0.0292 nm with coefficient determination values of 0.3389 and 0.1242, respectively. Meanwhile, Figures 5.7 (b) and (d) demonstrate the autocorrelation trace in terms of τ_{pulse} and TBP. Based on trendline observation in shows that shorter τ_{pulse} attained leading to a broader $\Delta\lambda$ throughout the week as depicted based on the Equation 5.1 [345]. The corresponding τ_{pulse} for each week are presented Figure 5.8 (d) and demonstrated changes of 1.3072 fs/week with coefficient determination of 0.0349. Interestingly, the TBP of the output pulses in SA-WOP was observed to increase from the trendline observation in Figure 5.8 (d) which is demonstrated slightly increase changes of 0.0024/week with coefficient determination of 0.0646, which is the value of transform-limited soliton pulses, as the MD increased (Figure 5.4, Table 5.3) [311]. The increase in the TBP indicates that the value of the optimum MD of the SA exists in order to generate transform-limited soliton pulses for the given cavity conditions of the cavity GVD and $\chi^{(3)}$ nonlinearity.

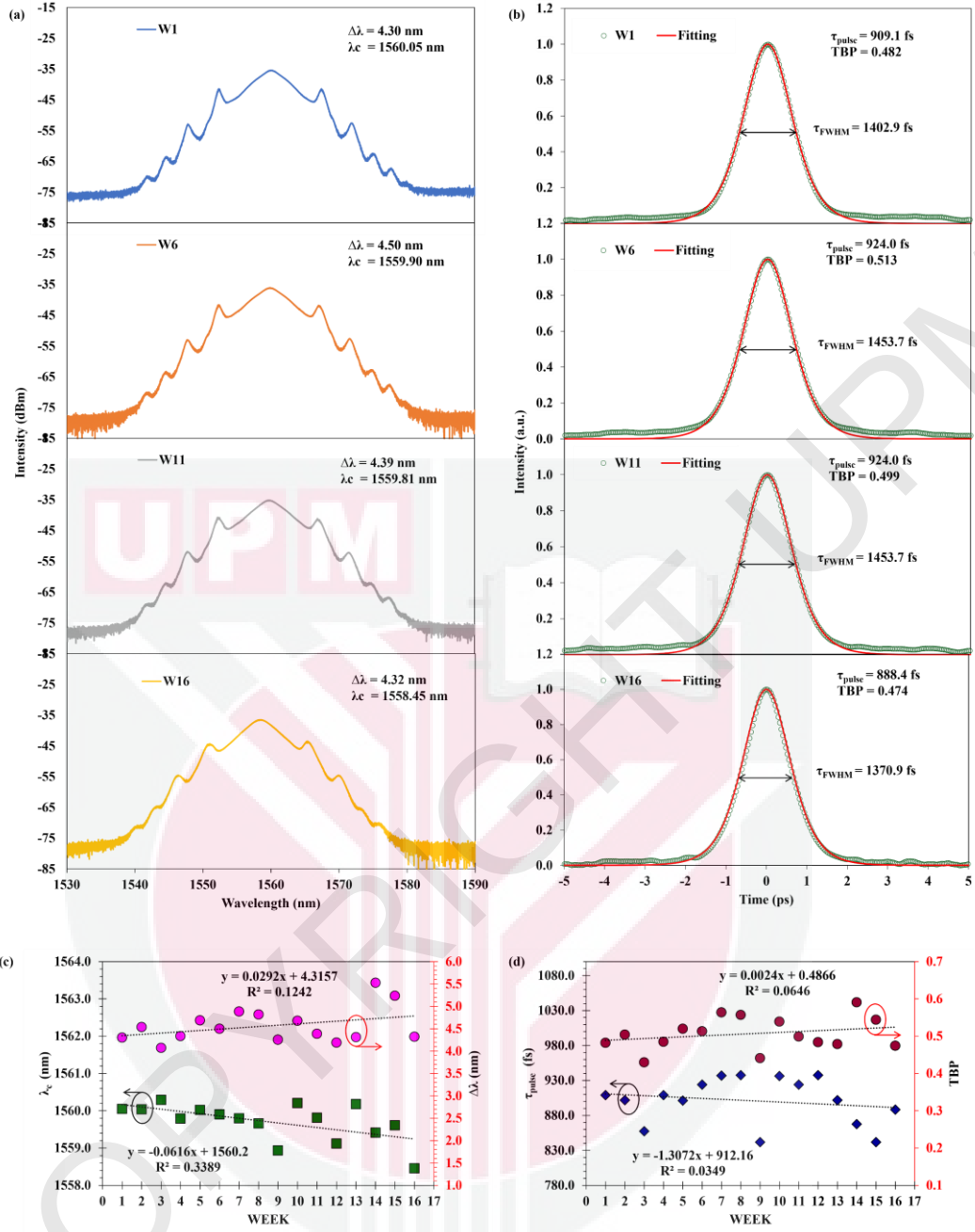


Figure 5.8: Performance of EDFL integrated with SA-WOP; (a) optical spectra, (b) autocorrelator trace, and trendlines depicting the relationship of (c) λ_c and $\Delta\lambda$ and (d) τ_{pulse} and TBP as a function of time in weeks at maximum pump power.

The fundamental pulse repetition rate was found to be about the same at ~ 7.755 MHz, as shown in Figure 5.9 (a). The pulse repetition rate matches the measured total cavity length of 26.9 m. Figure 5.9 (c) shows the corresponding

repetition rate for each week which displays minimal fluctuation between 7.752 MHz to 7.758 MHz, with a coefficient determination value of 0.1385. From Figure 5.9 (b), the average SNR value from Week 1 to Week 16 was 59.6 dB as was captured with resolution bandwidth (RBW) of 30 kHz and video bandwidth (VBW) of 100 Hz. The high SNR indicates that the MLFL operated with good stability since its SNR value is well over 50 dB [234]. No Q-switching was observed even when operating at the threshold pump power. The corresponding SNR measured for each week remained relatively stable with minimal fluctuation between 58.42 dB to 64.21 dB, as illustrated in Figure 5.9 (d) with changes of 0.0624 dB/week.

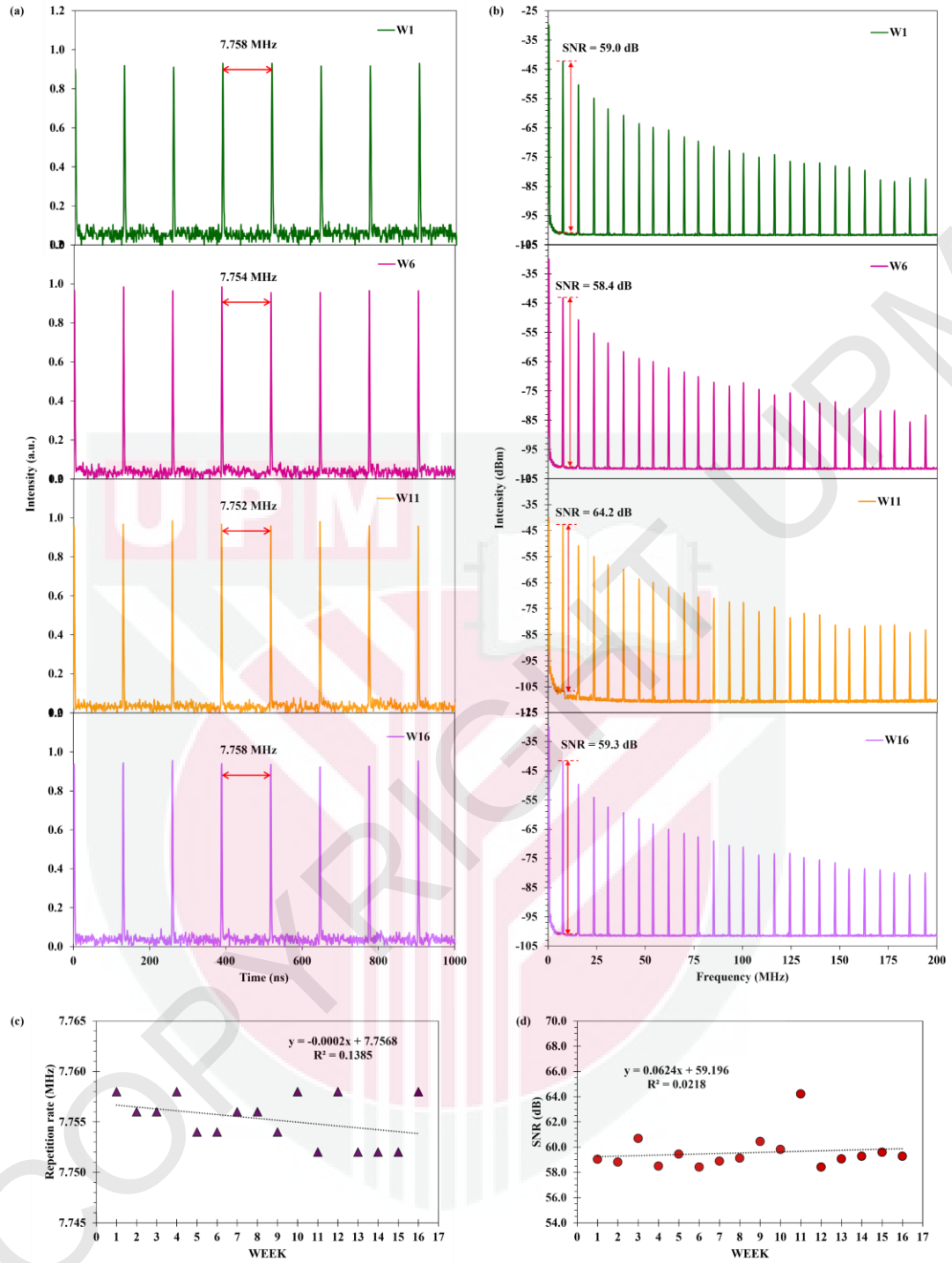


Figure 5.9: Performance of EDFL integrated with SA-WOP; (a) oscilloscope trace, (b) RF spectra, and trend lines depicting the relationship of (c) repetition rate, and (d) SNR as a function of time in weeks at maximum pump power.

The lasing performance of the SA-WOP were investigated further in terms of output power and $ML_{\text{threshold}}$. The average output power decreased from Week

1 of 5.93 mW to Week 16 of 3.24 mW as observed in Figure 5.10 (a). The pulse energy also followed the same decreasing trend over time from 0.76 nJ in Week 1 to 0.46 nJ in Week 16. The decrease in output power observed in Figure 5.10 (a) over time was caused by an increase in transmission loss shown in Figure 5.3 (b). From Figure 5.10 (b), the $ML_{threshold}$ was realized at 30 mW in Week 1 up to Week 6. The $ML_{threshold}$ then increased to 35 mW for Week 7 to Week 10. The $ML_{threshold}$ continued to increase to 40 mW in Week 11 to Week 14, and finally increased to 45 mW after Week 14 with 50% deviation. Similar with the observation shown in Figure 5.7, as transmission loss increases, so does the amount of pump power required to reach the $ML_{threshold}$ also increases. This also coincides with the I_{sat} characteristics from week 1 (243.36 MW/cm^2) increases to week 16 (385.50 MW/cm^2) from Figure 5.4 (b) and (d) which justified the higher $ML_{threshold}$ obtained as shown in Figure 5.10 (b).

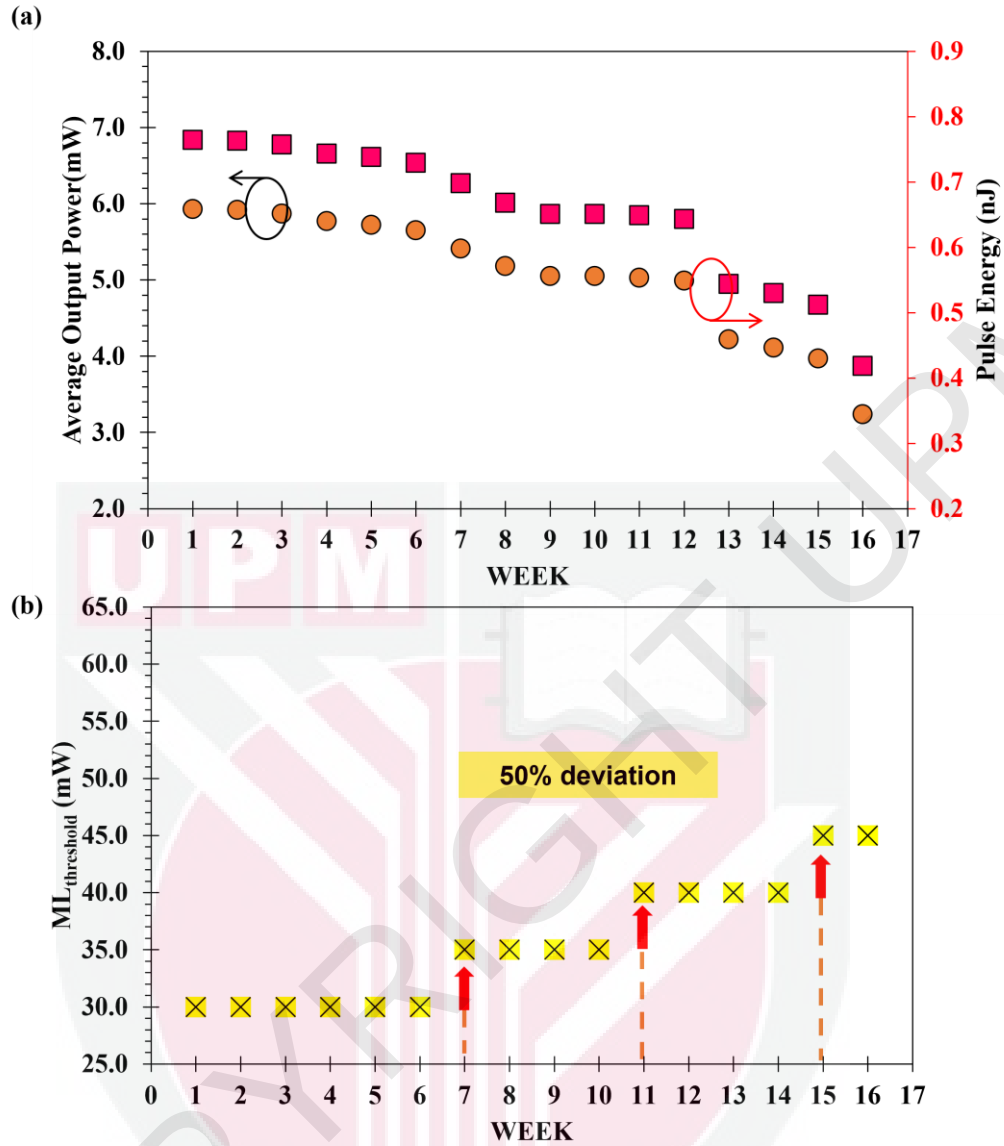


Figure 5.10: Performance of EDFL integrated with SA-WOP; (a) average output power and pulse energy (b) mode-locked threshold in 16 weeks.

5.4.3 Discussion

The lasing performance of SA-WP and SA-WOP for different week were presented in Section 5.4.1 and 5.4.2. The performance of both fabricated SAs were experimentally investigated after 16 weeks as summarized in Table 5.4. When the pump power was increased to 55 mW for SA-WP 30 mW for SA-WOP, the mode-locked spectrum was observed. The $ML_{threshold}$ was influenced

by the laser cavity loss and I_{sat} ; the optical intensity that it takes to reduce the absorption of the SA device by half. The comparatively lower pump power required for SA-WOP to achieve $ML_{\text{threshold}}$ is attributed to its lower transmission loss (2.92 dB) compared to SA-WP (4.14 dB). Over time, due to increases in transmission loss, both SAs with and without packaging show blue shifting λ_c in the laser output spectrum. Comparing between Week 1 to Week 16, the transmission loss in shorter wavelength becomes lower than the longer wavelength region. Therefore, the shorter wavelength component of the laser becomes relatively stronger than the longer wavelength component in the output, causing the blue shifting of the λ_c [346]. The formation of Kelly's sidebands in the optical spectrum for both SAs look symmetrical, confirming soliton operation in the anomalous dispersion regime [235]. This is owing to the phase matching of the linear and nonlinear dispersion phases, in which matching phase would appear as the small peak at both sides of the main peak.

Based on the findings, the autocorrelator traces obtained with both SAs with and without packaging were best fitted with the sech^2 profile without any presence of multiple pulses, harmonics or noise generation, indicating the characteristic of conventional soliton mode-locking in the net anomalous dispersion regime. Based on the Equation 5.1, the SA-WP showed longer τ_{pulse} from 914.3 fs in Week 1 to 936.3 fs in Week 16 (Figure 5.5 (b)) and the $\Delta\lambda$ would become narrower over time as expected as demonstrated by the trend line in Figure 5.5 (c). Meanwhile, the τ_{pulse} of SA-WOP showed shorter τ_{pulse} obtained from Week 1 (909.1 fs) to Week 16 (888.4 fs) in Figure 5.8 (b), which

is in agreement with the trend line of broader $\Delta\lambda$ generation over time as shown in Figure 5.8 (c). As observed in Week 1, the broader $\Delta\lambda$ and shorter τ_{pulse} in SA-WOP when the total cavity length lower (26.91 m), corresponding to the increment of the net GVD negative value (-0.217 ps²) compared with SA-WP with higher total cavity length (30.02 m) as decrement in the net GVD negative value gives narrower $\Delta\lambda$ and longer τ_{pulse} [347].

In general, the τ_{pulse} is inversely proportional to the MD of the SA as described in Equation 5.2 [348],

$$\tau_{\text{pulse}} \propto \left(\frac{2}{MD}\right)^\beta \quad (5.2)$$

Where β (>0) is an exponent. It can be seen that a larger MD facilitates the generation of short pulse, and vice versa. The MD of the SA-WP was 9.75 % in Week 1 and decreased to 5.10 % in Week 16 (see Table 5.3 in Section 5.3.2). Therefore, the τ_{pulse} would become longer over time as expected. This was clearly demonstrated by the trend line in Figure 5.5 (d). In contrast, the MD of the SA-WOP increased from 5.40 % in Week 1 to 11.40 % in Week 16, which is in agreement with the trend line of shorter τ_{pulse} generation over time. In addition, the τ_{pulse} of SA-WOP shows higher deviation of 6.48% compared to SA-WP of 2.79%.

As explained in Section 4.5.4, the minimum possible TBP for bandwidth-limited pulse for sech² shaped pulse is 0.315. The correlation between τ_{pulse} and $\Delta\lambda$ as expressed in Equation 4.8 determine whether the pulse is near the ideal

transform-limited pulses or heavily chirped. The chirp can be unfavorable merely because it would surmount the SPM-induced chirp and interrupt the exact balance between GVD and SPM effects which is important for soliton [194]. Based on the trendline of pulse τ_{pulse} as presented in Figure 5.5 (d) and Figure 5.8 (d), the variation is very minimal between 914.3 fs to 976.5 fs for SA-WP while for SA-WOP between 841.7 fs to 937.6 fs. Therefore, the main influence of TBP value was mainly determined by the $\Delta\lambda$.

It was observed that the TBP curves follow similar trends to the $\Delta\lambda$ as illustrated in Figure 5.5 (d) and Figure 5.8 (d). This shows that the dynamic nature of the optical spectrum will influence the TBP value if the τ_{pulse} is quite stable over the observation window. The corresponding TBP value of SA-WP decreases with decreasing MD, while value of TBP increasing as the MD increases for SA-WOP over the week. All the obtained TBP values for all observation weeks are slightly higher from the expected transform-limited sech^2 pulse of 0.315, which indicates minor chirping in the pulse due to residual dispersions in the laser cavity.

Based on the experimental results, pulse trains from both SA-WP and SA-WOP were attained at a fundamental repetition rate and no pulse breaking or instabilities. Moreover, as illustrated in Figure 5.6 (a) and Figure 5.9 (a), clean oscilloscope traces were recorded without any noise background, which can arise due to the periodic fluctuations of pulse energy in the cavity caused by the presence of harmonics or CW components [321]. Based on the experimental data, the average SNR for both SAs is comparable, with values

of 60.9 dB and 59.6 dB for SA-WP and SA-WOP as shown in Figure 5.6 (b) and Figure 5.9 (b)., respectively. Generated pulse with SNR greater than 50 dB is considered highly stable [235]. Although larger MD is often associated with better SNR, in this case, a larger MD is also associated with larger TBP value.

The evolution of average output power and pulse energy throughout the week for SA-WP and SA-WOP are illustrated in Figure 5.7 (a) and Figure 5.10 (a), respectively. Both SAs experience declining in output power over the time and was inferred due to the increasing transmission loss over time. The $ML_{threshold}$ recorded for each week is shown in Figure 5.7 (b) and Figure 5.10 (b), where the threshold SA-WP start increase at Week 14 with 9 % deviation while keep increasing start at Week 7 for SA-WOP with 50 % deviation than SA-WP This happened due to higher transmission loss observed on degradation effect of SA-WOP.

Table 5.4: Summary of MLFL characteristics of SA-WP and SA-WOP after 16 weeks.

	SA-WP	SA-WOP
Transmission loss (dB)	↑	↑
MD (%)	↓	↑
I_{sat} (MW/cm²)	↑	↑
α_{ns} (%)	↑	↑
λ_c (nm)	↓	↓
Δλ (nm)	↓	↑
T_{pulse} (fs)	↑	↓
TBP	↓	↑
Repetition rate (MHz)	↓	↓
SNR (dB)	↑	↑
Average output power (mW)	↓	↓
Pulse Energy (nJ)	↓	↓
ML_{threshold} (mW)	↑	↑

* ↑ = Increase, ↓ = Decrease

5.5 Stability Test of the Mode-Locked EDFL with MBB/PDMS: HEX-SA

5.5.1 SA-WP

The stability of a fiber laser is extremely crucial for industrial and scientific applications. Therefore, to examine the stability and reliability of the SA to sustain mode-locking operation, the stability performance test was performed at constant polarization state and pump power of 250 mW was carried out for each week, over 4-hour duration with 3-minute intervals in a laboratory environment. The results over 16 weeks are presented in Figure 5.11 and Figure 5.12. For discussion purposes, only Week 1 and Week 16 optical

spectral stability performance of the pulse laser are shown, while the rest of the weeks can be found in Appendix A. From the spectral evaluation as shown in Figure 5.11 (a) for Week 1 and Figure 5.11 (c) for Week 16, the λ_c and $\Delta\lambda$ are stable over 4-hour duration. In Week 1, the average λ_c is at 1561.49 ± 0.06 nm wavelength while the average $\Delta\lambda$ is at 4.04 nm with fluctuations of ± 0.09 nm as shown in Figures 5.10 (b). For Week 16, the average λ_c was at 1559.65 ± 0.03 , while the average $\Delta\lambda$ was at 2.98 ± 0.08 nm as shown in Figure 5.11 (d). The minimal different of standard deviation for λ_c and $\Delta\lambda$ in Week 1 and Week 16 indicates the higher stability of the mode-locked operation. In order to analyze the stability of the SA in proposed laser system, all λ_c and $\Delta\lambda$ data of 16 week were statistically analyzed as portrayed in Figure 5.11 (e). The trend line of the λ_c in Figure 5.11 (e), demonstrated a blueshift in λ_c of 0.088 nm/week with a coefficient determination of 0.6512 is exhibited due to increases in transmission loss, while the $\Delta\lambda$ narrowed by approximately 0.0254 nm from Week 1 to Week 16 with a coefficient determination of 0.0979. The mean of the average λ_c and $\Delta\lambda$ value are found to be 1560.835 nm and 3.489 nm with a standard deviation of 0.032 nm and 0.085 nm over 16 weeks, respectively. As shown in the Figure 5.11 (e), the error bars mark the variation range of the λ_c and $\Delta\lambda$ for each sampling week. From these findings, the maximum standard deviation for λ_c and $\Delta\lambda$ are 0.06 nm and 0.12 nm.

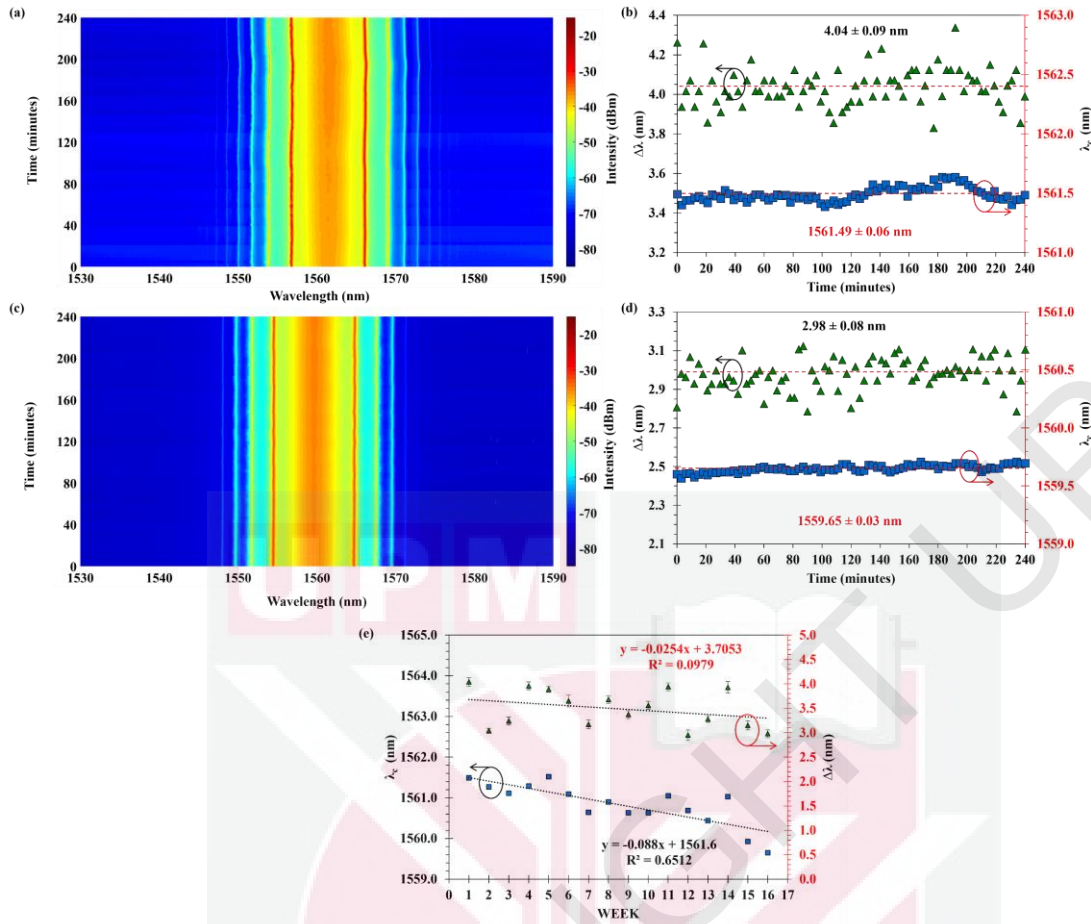


Figure 5.11: Stability performance of SA-WP; Week 1 (a) optical spectrum, (b) λ_c and $\Delta\lambda$, and W16 (c) optical spectrum, (d) λ_c and $\Delta\lambda$. (e) trend line depicting the relationship of average λ_c and $\Delta\lambda$ for each week over 4-hours duration.

The stability performance test was also carried out by acquiring the autocorrelation traces for each week, for a duration of 4 hours at 3 minutes intervals. The results are presented in Figures 5.11 (a) and (c) for Week 1 and Figures 5.11 (b) and (d) for Week 16, respectively. The stability results for the other weeks can be found in Appendix B. For Week 1, the average τ_{pulse} is 931.14 ± 8.94 fs and for TBP is 0.463 ± 0.01 as shown in Figure 5.12 (b). For Week 16, the average τ_{pulse} was calculated to be 964.15 ± 11.73 fs followed by average TBP of 0.354 ± 0.01 as shown in Figure 5.12 (d). In this analysis, the increases of standard deviation of τ_{pulse} between Week 1 (± 8.94 fs) and Week

16 (± 11.73 fs) around 2.79 fs was observed, however there are no difference of standard deviation in TBP value. These findings imply a small percentage of variation indicating the pulse operation is stable. Figure 5.12 (e) shows the average T_{pulse} and TBP for 4-hour duration over the week within the range of 931.14–965.43 fs and 0.341-0.463, respectively. In this analysis, the standard deviation is for T_{pulse} is varied between 5.58 and 16.00 fs and between 0.01 and 0.03 for TBP. From the analysis, the mean of the average T_{pulse} and TBP are about 946.71 ± 10.88 fs and 0.406 ± 0.01 . Figure 5.12 (e) also shows increasing linear trend of 0.9237 fs/week for average T_{pulse} and decreasing linear trend of 0.0036/week for average TBP over the 16 stability weeks observation, yielding coefficient determination values of 0.1469 and 0.0818, respectively.

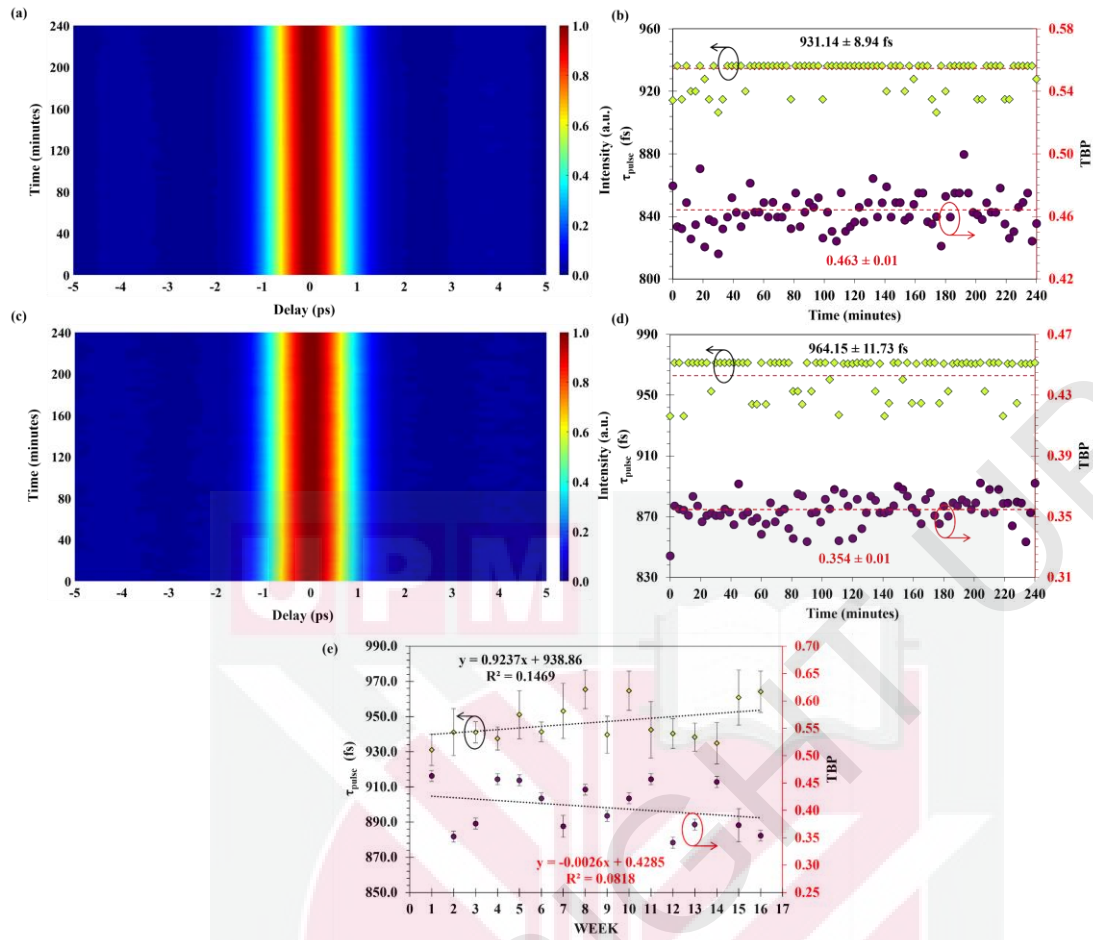


Figure 5.12: Stability performance of SA-WP; Week 1 (a) autocorrelator traces, (b) τ_{pulse} and TBP, and W16 (c) autocorrelator traces, (b) τ_{pulse} and TBP. (e) trend line depicting the relationship of average τ_{pulse} and TBP for each week over 4-hours duration.

5.5.2 SA-WOP

Then, same laser operational stability of the SA-WOP also for 4 hours recorded every 3 minutes for a duration of 16 weeks in a laboratory environment. The laser was operated at maximum pump power of 153 mW with fixed polarization state. The results for Week 1 and Week 16 are presented in Figure 5.13 and Figure 5.14, while the remaining stability tests for different weeks can be found in Appendix C. The optical spectra and corresponding λ_c and $\Delta\lambda$ as a function of time are as shown in Figures 5.12 (a) and (b) for Week 1 and Figure 5.13

(c) and (d) for Week 16, respectively. In Week 1, the average λ_c is 1560.09 ± 0.03 nm while the average $\Delta\lambda$ is at 4.32 nm with fluctuations of ± 0.04 nm as shown in Figure 5.13 (b). For Week 16, a highly stable average λ_c at 1555.50 ± 0.02 nm and $\Delta\lambda$ at 4.33 ± 0.03 nm was observed throughout the experiment as shown in Figure 5.13 (d). The observation also shows minimal different of standard deviation for λ_c and $\Delta\lambda$ in Week 1 and Week 16 indicates the higher stability of the mode-locked operation. Due to increasing in transmission loss after week 16, the trend line of the λ_c in Figure 5.13 (e) shows a blueshift in wavelength of 0.066 nm/week with a coefficient determination of 0.3807, while $\Delta\lambda$ broadens by approximately 0.033/week nm from Week 1 to Week 16 with a coefficient determination of 0.1764. The mean of the average λ_c and $\Delta\lambda$ value is found to be 1559.72 nm and 4.57 nm with a standard deviation of 0.05 nm and 0.08 nm over 16 weeks. The maximum standard deviation of λ_c and $\Delta\lambda$ were 0.14 nm and 0.45 nm, respectively.

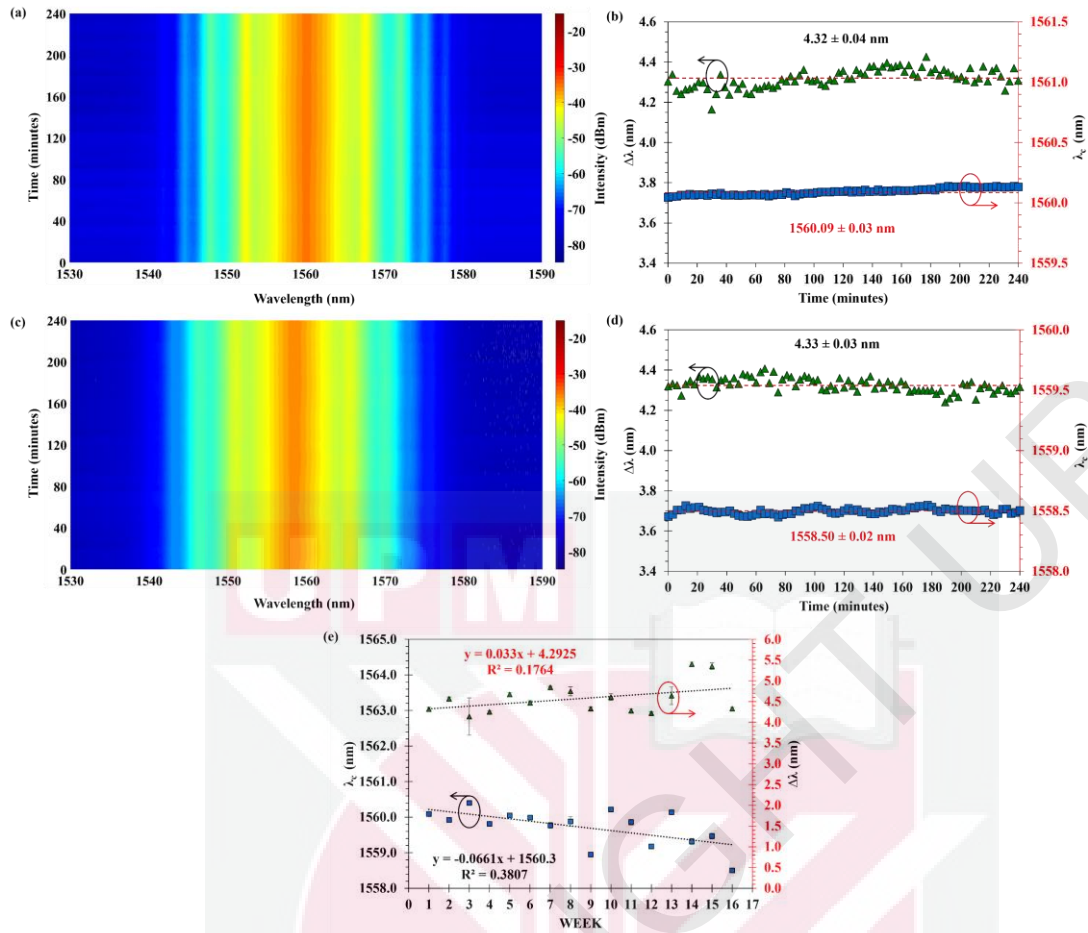


Figure 5.13: Stability performance of SA-WOP; Week 1 (a) optical spectrum, (b) λ_c and $\Delta\lambda$, and W16 (c) optical spectrum, (d) λ_c and $\Delta\lambda$. (e) trend line depicting the relationship of average λ_c and $\Delta\lambda$ throughout the week for each week over 4-hours duration.

The stability performance test for SA-WOP was also carried out by acquiring the autocorrelation traces of the soliton pulse was repeatedly recorded for every week, for a duration of 4 hours at 3 minutes intervals. The results are presented in Figures 5.13 (a) and (c) for Week 1 and Figures 5.13 (b) and (d) for Week 16, respectively. The stability results for the other weeks can be found in Appendix D. In Week 1, the average of τ_{pulse} is 914.01 ± 16.45 fs and the TBP is 0.486 ± 0.01 as shown in Figure 5.14 (b). In Week 16, the average τ_{pulse} is calculated to be 865.81 ± 21.04 fs followed by average TBP of 0.463 ± 0.01 nm as shown in Figure 5.14 (d). In this analysis, there are no difference

of standard deviation in TBP value of Week 1 and Week 16. From the observation, the standard deviation of τ_{pulse} already shows higher value in Week 1 (± 16.45 fs) and increasing to ± 21.04 fs in Week 16 which leads to higher difference in standard deviation of 4.59 fs between the two weeks. These findings imply a bigger percentage of variation indicating the pulse operation is slightly unstable. Figure 5.14 (e) shows the average T_{pulse} and TBP for 4-hour duration over the week within the range of 828.66–936.33 fs and 0.422–0.579, respectively. In this analysis, the standard deviation is for T_{pulse} is varied between 3.06 and 22.67 fs and between 0.01 and 0.03 for TBP. From the analysis, the mean of the average T_{pulse} and TBP are about 897.85 ± 15.34 fs and 0.506 ± 0.01 . Based on Figure 5.14 (e), a decreasing linear trend line of 2.0018 fs/week for the corresponding T_{pulse} and increasing linear trend of 0.0766/week for TBP, yielding a coefficient determination value of 0.0752 and 0.0766, respectively.

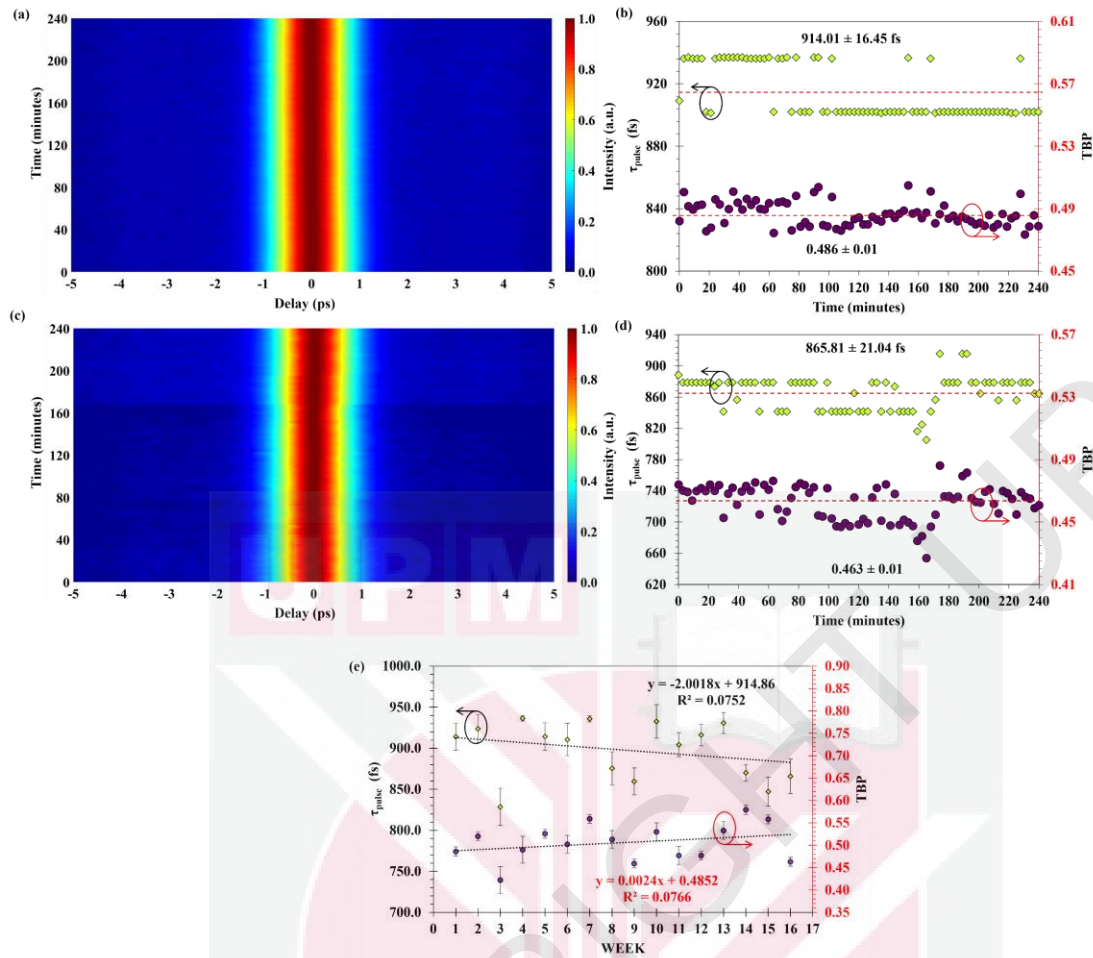


Figure 5.14: Stability performance of SA-WOP; Week 1 (a) autocorrelator traces, (b) τ_{pulse} and TBP, and W16 (c) autocorrelator traces, (b) τ_{pulse} and TBP. (e) trend line depicting the relationship of average τ_{pulse} and TBP for each week over 4-hours duration.

5.5.3 Discussion

The stability and reliability evaluation of both SA-WP and SA-WOP in mode-locked EDFL operation was conducted over 16 consecutive observation weeks for 4-hour duration in each week. Two important measurements were conducted, which were the optical spectra (Figure 5.11 and Figure 5.13) and autocorrelation traces (Figure 5.12 and Figure 5.14), Based on the experimental findings, both SA-WP and SA-WOP show excellent reliability for

mode-locked pulse generation. For SA-WP, the stability of λ_c ranged from 1559.650 to 1561.520 nm (Δ of 1.870 nm) and from 2.950 nm to 4.040 nm for the $\Delta\lambda$ (Δ of 1.090 nm), within the observation time for the 16 weeks. Then, for SA-WOP, the stability λ_c ranged from 1558.500 to 1560.400 nm (Δ of 1.900 nm) and from 4.140 nm to 5.400 nm for the $\Delta\lambda$ (Δ of 1.260 nm). The range of both SAs are almost similar despite the difference in ambient light exposure.

Furthermore, the stability observation of τ_{pulse} for SA-WP shows the τ_{pulse} ranged from 931.140 fs to 965.43 fs (Δ of 34.290 fs) and from 0.341 to 0.463 for the TBP (Δ of 0.122), within the observation time for the 16 weeks. Then, for SA-WOP, the τ_{pulse} ranged from 828.660 fs to 936.330 fs (Δ of 107.670 fs) and from 0.422 to 0.579 for the TBP (Δ of 0.157). The behavior of difference in ambient light exposure for SA-WP and SA-WOP shows higher different range in pulse operation was observed.

The coefficient of variation was then calculated and is defined as the ratio of standard deviation to average. The coefficient of variation values corresponding to the λ_c , $\Delta\lambda$, τ_{pulse} and TBP are tabulated in Table 5.5 for both SAs. The coefficient of variation of λ_c and $\Delta\lambda$ are 0.002 % and 2.436 % for SA-WP and 0.003 % and 1.837 % SA-WOP, respectively after 16 weeks of laser operation. The coefficient of variation of the $\Delta\lambda$ is higher for SA-WOP. Similar with TBP observation of SA-WP, the result shows smaller value of 2.956 % on coefficient of variation compared to SA-WOP of 3.162 %. All parameters are reasonably stable over the time period, indicating the good long-term stability of the mode-locking phenomenon. Meanwhile, the τ_{pulse} preserved with only

small coefficient of variation of 1.149 % from Week 1 to Week 16 for SA-WP compared to SA-WOP of 1.708 %. In addition, higher coefficient of variation is observed for SA-WOP which highlights the effect of ambient light exposure (illumination) deteriorates the PDMS encapsulated perovskite SA-WOP more than the SA-WP.

In general, it is widely known that perovskite solar cells applications exhibit lower stability under illumination than under dark conditions, even in the absence of moisture or oxygen decomposition [349]. The photodecomposition (photolysis) is believed to happen due to unreacted of PbI_2 crystals under continuous light illumination [350]. Schoonman suggested that photolysis of lead halide could explain the instability of hybrid perovskites [351]. As a result, the presence of PbI_2 crystals in films could be a source of perovskite instability. Therefore, photolysis of PbI_2 crystals in perovskite films occurred as predicted by Equation 5.3 [350];



Ultraviolet (UV) light particularly damages the perovskite materials because it has enough energy to break the bonds between the atoms in the perovskite crystal structure which leads to the formation of defects in the perovskite crystal structure. These defects can act as trapping centers for charge carriers, which can reduce the efficiency of the device [352]. Zhao et al. also speculate that under strong illumination, more ions tend to migrate toward device

because of the reduced energy barrier that causes irreversible degradation [353].

In our case, the inside laboratory conditions, such as humidity, temperature and illumination intensity, remained within a range with least variation, whereas the humidity, temperature and illumination intensity varied to a great extent outside the laboratory. Though the encapsulation provided some protection from the surrounding environment, which resulted in better stability, SA stored in dark (with packaging) exhibited higher stability, whereas SA-WOP exhibited lower stability. Minimal impact was observed for both SAs as the CFL spectrum has visible content and did not have both the UV and infra-red (IR) content. UV light exposure is more harmful compared to visible light exposure because UV light converts oxygen into ozone, which becomes more attacking to perovskite devices [354]. It is worth to note that the mode-locking operation remained stable even different storage condition (with and without packaging), with no pulse breaking or multiple pulses observed during the experiment.

Table 5.5: Coefficient of variation in stability test for SA-WP and SA-WOP.

SA	Λ_c (%)	$\Delta\Lambda$ (%)	T_{pulse} (%)	TBP (%)
SA-WP	0.002	2.436	1.149	2.956
SA-WOP	0.003	1.837	1.708	3.162

5.6 Summary

In the course of this investigation, two mode-locked EDFL cavities were constructed for the integration of MBB/PDMS: HEX-SAs. Two SA samples were prepared where the conditions for their performance evaluation were kept relatively similar except for the exposure to ambient lighting which was controlled by exposing the SA as it is versus packaging the other SA in a box. The SAs were employed in the different laser cavity setups but with similar intracavity powers as summarized in Table 5.1 and 5.2. The performance of both SAs were observed for 16 weeks. High humidity of the lab environment (based in Malaysia) affected both SAs where the transmission loss increased for each week. However, the higher illumination that was subjected to the SA-WOP caused the pulse performance to vary significantly in comparison to the SA-WP possibly due to the photolysis effect under continuous light illumination. This occurrence has been commonly reported for perovskite solar cells left to operate outdoor [352], [355]. The difference between the reported solar cells to our SAs is the encapsulation with PDMS which limits moisture from reacting aggressively with the perovskite crystal, extending its shelf life significantly.

We have also successfully demonstrated the stability and reliability both SA-WP and SA-WOP in mode-locked EDFL. Both fabricated SAs were tested for 4 hours continuous operation for each week over 16 weeks and the measured optical spectrum and autocorrelation trace was recorded and analyzed. In addition, the quality of optical spectrum and autocorrelation trace was also

monitored over 16 weeks and the coefficients of variation for both SAs were evaluated. These results presented good long-term stability of the mode-locking which proved encapsulation of perovskite with polymer PDMS was successful. However, the SA-WOP especially the T_{pulse} preserved higher coefficient of variation of 1.708 % compared to SA-WP of 1.149 % from Week 1 to Week 16. Up to date, there are no reports on studying the effect of degradation effect of MBB/PDMS: HEX-SA on SA performance for generating ultrashort pulses. Hence, to the best of our knowledge, this may be the first reporting on the impact ambient light exposure on MBB/PDMS: HEX-SA on the degradation of laser pulse performance.

CHAPTER 6

CONCLUSION, LIMITATION AND RECOMMENDATION FOR FUTURE WORK

6.1 Conclusion

This research focused on developing bismuth-based halide perovskite SA for ultrashort pulse generation. In this work, lead-free MBB perovskite single crystals were synthesized via a straightforward solution growth process known as slow evaporation method, where the precursor molar ratio $\text{MABr}:\text{BiBr}_3$ was varied (3:1, 3:2, 3:3), and the synthesized single crystals were characterized to determine the best quality perovskite single crystals. Characterization of the MBB single crystals showed broad absorption band covering from UV to NIR wavelength with 2θ dominant peaks at 26.8° and 55.1° which corresponds to lattice planes of (003) and (006) matched with the JCPDS 00-044-1927 reference code. Based on SEM and UV-Vis-NIR spectroscopy, molar ratio 3:1 exhibited incomplete growth of perovskite. Meanwhile, molar ratios 3:2 and 3:3 presented complete growths of average particle sizes within the range of 3-4 μm , with strong absorbance edge at 500 nm, indicative of similar bandgap properties. Based on these findings, lead-free MBB perovskite single crystals by variation of precursor ratio were synthesized via slow evaporation method. Once MBB single crystals were ready, they were mixed with PDMS with different solvent classes; non-polar, polar protic and polar aprotic through a simple solution preparation process in preparation of the perovskite composite to determine its effect on the fabricated SA properties. It was found polar

solvents, EtOH and ACN solvents are generally not compatible with PDMS which resulted in agglomeration effect and incompatible for SA fabrication. Non-polar solvent THF yielded uncured perovskite composite due to the formation of water molecules from BiOBr hydrolysis product of which can lead to debonding and composite failure. Non-polar solvent PhCl presented a cured composite which changed from yellow to red color indicating the existence of Bi-O or Bi-N bonds between the BiBr₃ and PhCl, resulting on instability and decomposition result over time. The effect of solvents on the composite formation depended on the reaction and cannot be predicted simply by its solvent class. The other four different solvents; HEX, TOL, ACE, and ISO were successful in the preparation of MBB/PDMS composite and were characterized by RAMAN spectroscopy in order to confirm the presence of materials functional groups in as-prepared samples. The RAMAN analysis confirmed only MBB/PDMS: TOL and MBB/PDMS: HEX retained all functional groups peaks. The result was also supported by UV-Vis-NIR characterizations which is both of MBB/PDMS: TOL and MBB/PDMS: HEX exhibit similar optical properties with reported MBB single crystals. Therefore, MBB/PDMS: HEX and MBB/PDMS: TOL were decorated on tapered fiber dimensions of 30 mm (up/down taper), 0.5 mm (waist length), and 10 μ m (waist diameter) for the fabrication of SAs and characterized. Both SAs present similar element of O, Si, Br and Bi were observed, which verifies the RAMAN analysis and indicate the successful deposition of MBB composite onto tapered fiber. The MD of MBB/PDMS: HEX-SA is significantly small compared to MBB/PDMS: TOL-SA, yet still able to function as a self-starting mode-locker because it fulfill the mode-locked criterion. Then, MBB/PDMS: HEX-SA presented low value of I_{sat}

indicative that a mode-locked laser operation can be easily attained at low pump power compared with MBB/PDMS: TOL-SA. The different value of α_{ns} of MBB/PDMS: HEX-SA and MBB/PDMS: TOL-SA were expected due to their transmission loss differences. Therefore, the effect of different solvent classes in the fabrication process of MBB/PDMS-based SA on its properties was evaluated.

Both MBB/PDMS: HEX-SA and MBB/PDMS: TOL-SA were integrated in net anomalous EDFLs operating at similar intracavity powers respectively, and successfully demonstrated by their SA functionality in generating mode-locked pulses. Table 1 present recent literatures that emphasize the suitability of ABX_3 structure of halide-based perovskite materials as SA devices. in comparison to our work that uses Bismuth (Bi) as a substitute to Pb in perovskite-based SAs. Unlike Lead (Pb)-based perovskites [235] [234] [238] [239], which are harmful to the environment [83], Bi-based perovskites pose a lower toxicity risk. Meanwhile, Tin (Sn)-based perovskites [95] degrade quickly due to oxidation [96]. Bi-based perovskites exhibit greater stability in air, making them more durable [111] that had been proved by Table 2 which is its long term continually working more than 16 weeks in an ambient environment. Technically speaking, the saturation intensity and modulation depth of any SA device is dependent on the SA fabrication. This includes the selection of taper parameters such as transition length, taper waist diameter and waist length, size and concentration of material, and material deposition method. However, due to the insufficient information of the reported literatures [95] [235] [234] [238] [239]. with regards to the aforementioned parameters, some parameters

are unable to be discussed. The similarity between drop-casting and spin-coating material/polymer composite is the random position of the attached material, which significantly affect the modulation depth. However, after the fabricated SAs underwent drying process, the mechanism of light propagation is different. Depositing material on the fiber ferrule resulted in low saturation intensity, as reported in [238] [239]. Previous works demonstrated that sandwiching thin film of MAPbI₃ with 280 nm thickness between fiber ferrules achieved low non-saturable loss of 22% [239] and 30% [238], respectively. The SAs of this thickness both have high modulation depth of 22.7% [238] and 27.8% [239], respectively, compared with a SA of similar material with only 25 nm thickness attaining a modulation depth of only 4.29% [234]. For thicker perovskite nanosheet, more light intensity is required to saturate it due to stronger absorption, thus the saturable absorption intensity is higher but the modulation depth is larger [234]. On the other hand, the PDMS used in this work is mainly to facilitate the light back-reflection after evanescent-wave interaction, minimize scattering effect and substantial coupling loss. In fact, the saturation intensity in material/polymer composite method in [234]. and our work are expected to be higher than [95] [235] [238] [239]. The main factor that influences this nonlinear parameter is material concentration in polymer matrix. In this work, the mass of MBB used was considerably low (2 mg), as compared to 1 g PDMS (MBB/PDMS ratio is 0.0002). As the excess MBB/PDMS on the tapered region was removed after spin-coating process, the final concentration of embedded MBB in PDMS matrix is expectably lower. On the other hand, considering weak evanescent waves that leaked at the silica core/PDMS interface and interacted with the embedded MBB within 0.8 mm waist length,

high light intensity is acquired to saturate the fabricated SA and function as mode-locker.

Table 6.1: SA fabrication methods of previously reported ABX_3 structure of halide-based perovskite materials as SA devices and their linear and nonlinear properties

Material	Precursor molar ratio	SA type	SA fabrication	MD (%)	I_{sat} (MW/cm ²)	α_{ns} (%)	Loss (dB)	Ref.
MASnI ₃	MAI : SnI ₂ (1:1)	DS F	Flake attachment	15.2	76.5	34.7	~1.85	[95]
MAPbI ₃	MABr : PbI ₂ (1:1)	DS F	Pressing on the D-shaped fiber	9.6	29	30.9	~1.61	[235]
MAPbI ₃	MAI : PbI ₂ (1:1)	FF	All-dry transfer process on polymer substrate	4.29	1600	-	-	[234]
MAPbI ₃	MAI : PbI ₂ (1:1)	FF	Dropped onto the glass substrate	22.7		~30	1.68	[238]
MAPbI ₃	MAI : PbI ₂ (1:1)	FF	Dropped onto end facet of the fiber ferrule	27.8	1.42	~22	~1.08	[239]
MA ₃ Bi ₂ Br ₉ /PDM S	MABr : BiBr ₃ (3:2)	TF	Spin-coated polymer composite	9.75	0.93	55.4	4.20	This Work

Note: FF: Fiber ferrule, TF: Tapered fiber

To further emphasize the contribution of this work, Table 2 summarizes previously reported pulse performances of halide-based perovskite SAs in fiber laser. As predicted by Hussain [356], the product of large modulation depth and saturation intensity in [238] yielded Q-switched pulse. Although Q-

switched pulse offers higher pulse energy (770 nJ) as compared to mode-locked pulses [95] [235] [234] [239], the pulse width is rather slow. In mode-locking regime, this work offers lower threshold condition of 55.0 mW than [95] [235] [234] [239] despite of its highest non-saturable loss. Although Q-switched pulse in [238] offers higher pulse energy as compared to soliton mode-locked pulses [95] [235] [234] [239], the pulse width in microsecond timescale is rather slow. From the literatures in Table 2, the highest pulse energy of 6.99 nJ was achieved by MASnI_3 -SA at the expense of slowest pulse width of 1150 ps [95]. The pulse width of 0.661 ps was recorded by MAPbI_3 -SA, achieved by the shortest cavity length that corresponded to 13.15 MHz repetition rate [239]. By using a slightly longer cavity length with 8.05 MHz repetition rate in this work, pulse width of 0.943 ps with tapered fiber based $\text{MA}_3\text{Bi}_2\text{Br}_9/\text{PDMS}$ -SA was achieved. This work demonstrates the significant improvement as compared to the other works reported especially in terms of mode-locked threshold power (55 mW) and pulse width (0.943 ps). Although the work reported in [95] [238] [239] shows high modulation depth of 15.2%, 22.7% and 27.8%, respectively compared to this work (9.75%), small modulation depth is sufficient to generate ultrashort pulse in the net anomalous dispersion regime [311]. This work demonstrates the higher output power of 8.05 mW, than ref. [235] [239] despite having higher transmission loss of 4.20 dB. Furthermore, the $\text{MA}_3\text{Bi}_2\text{Br}_9/\text{PDMS}$ -SA can get stable mode-locking output with a long term continually working more than 16 weeks in an ambient environment compared to ref. [95] [234] [239]. Furthermore, the presence of PDMS with hydrophobicity and viscous features assists in attaching materials on the substrate and providing mechanical supports. This approach protects the SA device from

external perturbations, extending its shelf-life. In short, the contribution of this work lies on the improvement of pulse performances in the halide-based perovskite as a whole while simultaneously offering a better performing substitute of Pb-based perovskite in SA application.

Table 6.2. Pulse performances of halide-based perovskite SA in fiber laser

Material	Laser type	QS/ML _{th} (mW)	Output power (mW)	Pulse width (ps)	Rep. rate (MHz)	Max. Pulse energy (nJ)	Stability (hour)	Ref.
MASnI ₃	ML	119.8	28.19	1150	4.03	~6.99	> 8	[95]
MAPbI ₃	ML	60	3.2	1.13	4	~0.8	-	[235]
MAPbI ₃	ML	319	15.71	603.3	4.08	3.85	7	[234]
MAPbI ₃	QS	2550	28	91900	0.036	770	-	[238]
MAPbI ₃	ML	70	1.7	0.661	13.15	0.13	> 8	[239]
MA ₃ Bi ₂ Br ₉ /PDM S	ML	55	8.05	0.943	8.05	1.00	Every 4 hour until 16 weeks	This Work

Noted: QS/ML_{th}: Q-switched/Mode-locked threshold power, QS: Q-switched, ML: Mode-locked

MBB/PDMS: HEX-SA was chosen for its better stability, as evidenced by its higher SNR, despite the MBB/PDMS: TOL-SA's better performance as better SNR more preferred for testing stability in this phase. For degradation investigations, the effect of ambient indoor lighting on MBB/PDMS: HEX-SA degradation and its impact towards laser pulse performances was investigated by employing two different operating conditions on the SA; SA-WP and SA-WOP for over 16 weeks. SA-WOP exhibited higher range transmission loss between Week 1 and Week 16 in comparison to SA-WP as expected due to

the exposure to ambient light. SA-WP showed longer τ_{pulse} attributed to the decrease of MD value between Week 1 to Week 16, which led to narrower $\Delta\lambda$. SA-WOP presented shorter τ_{pulse} which led to broader $\Delta\lambda$ due to the increase of MD between Week 1 to Week 16. TBP values obtained for both SAs in 16 weeks observation weeks are slightly higher from the expected transform-limited sech^2 pulse of 0.315, which indicates minor chirping in the pulse due to residual dispersions in the laser cavity. SA-WOP exhibited a greater decline in output power and pulse energy over the time compared to SA-WP. From the observation, the earlier changes in $M_{\text{Lthreshold}}$ were observed SA-WOP in Week 7 compared with SA-WP in Week 14. This is due to the accelerated degradation of SA-WOP as showed by the greater transmission loss over time. Note that, stability and reliability evaluation in sustaining mode-lock operation of SA-WP and SA-WOP was conducted for 4 hours over 16 consecutive observation weeks. These results presented good long-term stability of the mode-locking which proved encapsulation of perovskite with polymer PDMS to limit interaction with moisture was successful. Higher coefficient of variation was observed for SA-WOP which highlights the effect of ambient light exposure (illumination) that deteriorated the PDMS encapsulated perovskite SA-WOP more than the SA-WP which caused the pulse performance to vary significantly in comparison. This is possibly due to the photolysis effect under continuous light illumination. Based on the results, stability on laser performances of SA with and without packaging were significantly different, suggesting that impact ambient light exposure on degradation of laser pulse performance of SA. Therefore, the degradation of MBB/PDMS-SA in the

presence of ambient indoor lighting was characterized and its impact towards pulse performance stability was assessed.

6.2 Limitation of Work

There are three main limitations of this research work. Firstly, the effect of MBB single crystal properties for SA fabrication were limited to solvent tested only. Secondly, the research cavity design solely to demonstrate SA functionality only and further optimization of the cavity design is necessary for improved performance. Thirdly, the study did not investigate how polarization effect on MBB/PDMS based SA.

6.3 Recommendation for Future Work

As the investigation progressed, few ideas surfaced for future work. The recommendations are as follows;

- (a) Understanding the effect of polarization on MBB/PDMS based SA is crucial as polarization characteristics are very important for fabrication and application of optical devices
- (b) By replacing the EDF with other rare-earth doped fibers such as ytterbium- and thulium-doped fibers, different spectral bands with various pulse performance and phenomena can be obtained with an appropriate

selection of pump wavelengths. From that, ultrafast laser sources at various wavelengths can be fabricated to suit applications.

- (c) Single perovskite has the drawback of being unstable and resistant to environmental influences such as humidity, water, and temperature. Given their great structural stability, various inorganic double perovskites such as (Cs) and (K, Na, or Ag) based perovskites can be researched to overcome the instability difficulties.

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APPENDICES

Appendix A: Stability evaluation of optical spectrum of SA-WP in MLFL for different observation weeks

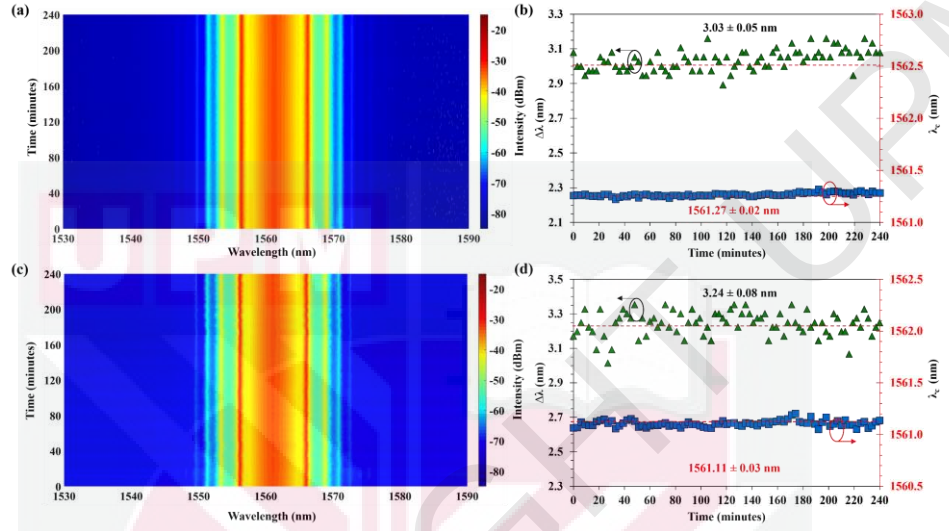


Figure A1: Stability evaluation of optical spectrum W2 (a) top view, (b) quantitative, W3 (c) top view and (d) quantitative.

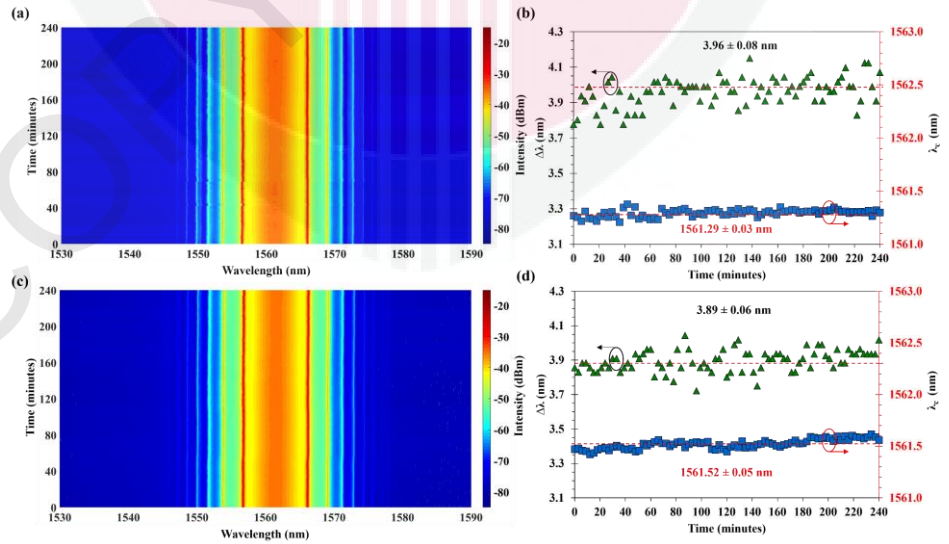


Figure A2: Stability evaluation of optical spectrum W4 (a) top view, (b) quantitative, W5 (c) top view and (d) quantitative.

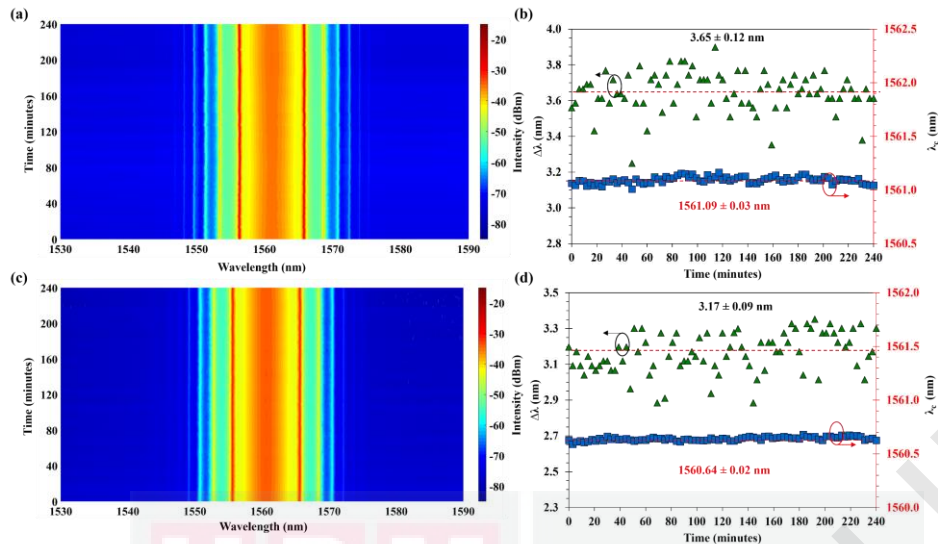


Figure A3: Stability evaluation of optical spectrum W6 (a) top view, (b) quantitative, W7 (c) top view and (d) quantitative.

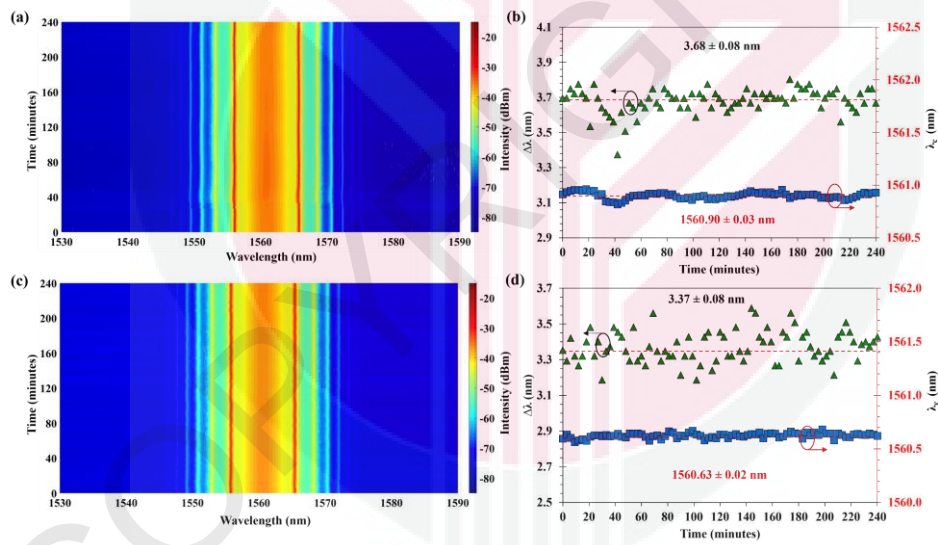


Figure A4: Stability evaluation of optical spectrum W8 (a) top view, (b) quantitative, W9 (c) top view and (d) quantitative.

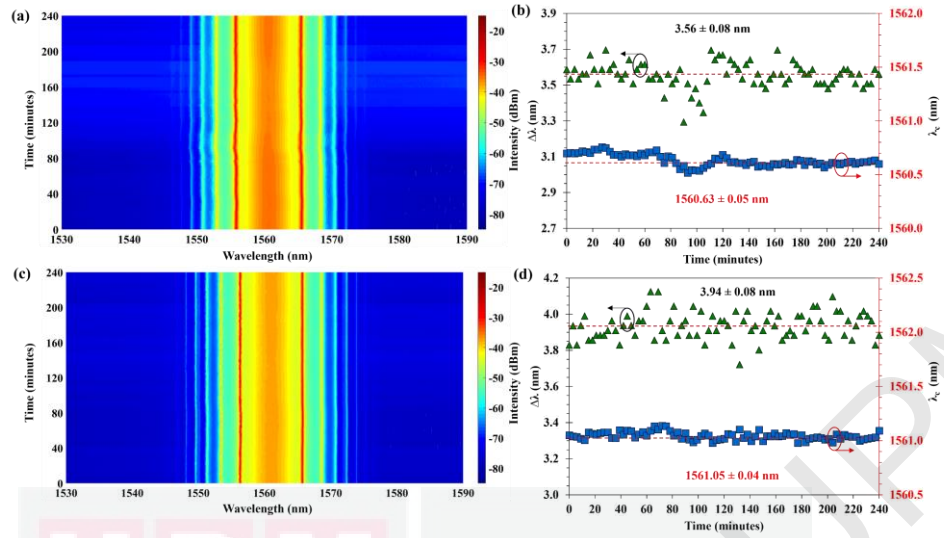


Figure A5: Stability evaluation of optical spectrum W10 (a) top view, (b) quantitative, W11 (c) top view and (d) quantitative.

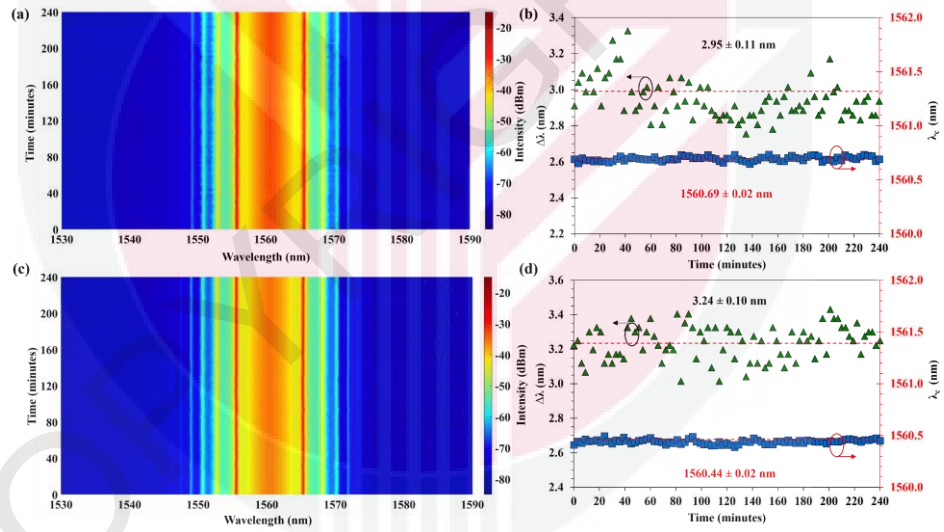


Figure A6: Stability evaluation of optical spectrum W12 (a) top view, (b) quantitative, W13 (c) top view and (d) quantitative.

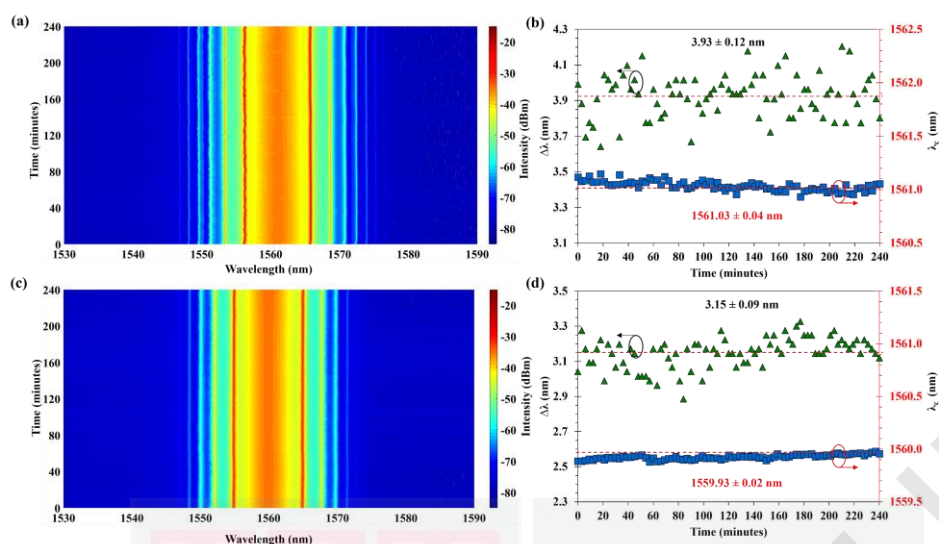


Figure A7: Stability evaluation of optical spectrum W14 (a) top view, (b) quantitative, W15 (c) top view and (d) quantitative.

Appendix B: Stability evaluation of autocorrelation trace of SA-WP in MLFL for different observation weeks

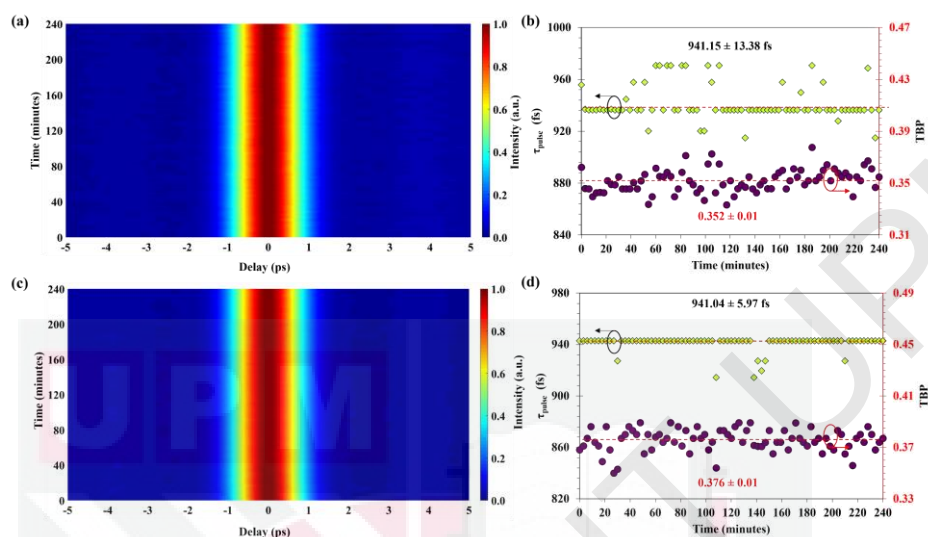


Figure B1: Stability evaluation of autocorrelation trace W2 (a) top view, (b) quantitative, W3 (c) top view and (d) quantitative.

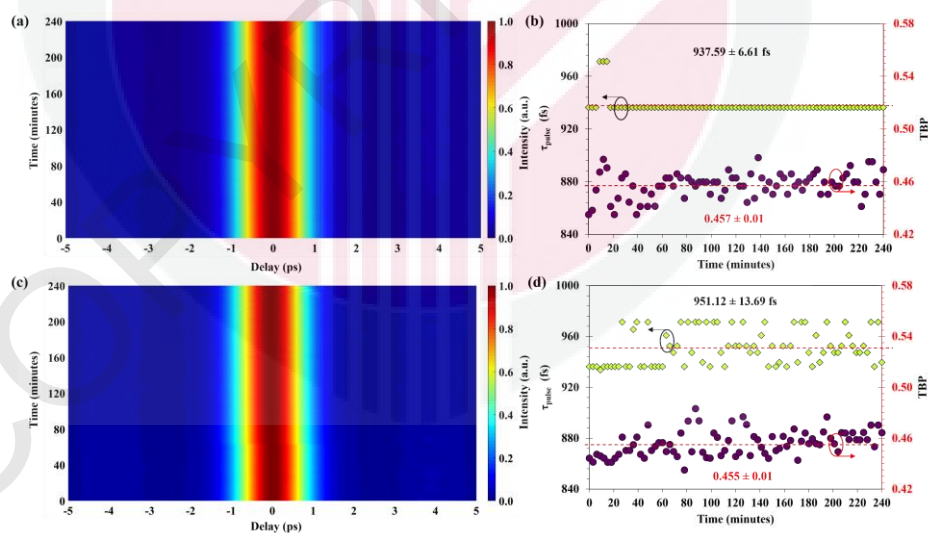


Figure B2: Stability evaluation of autocorrelation trace W4 (a) top view, (b) quantitative, W5 (c) top view and (d) quantitative.

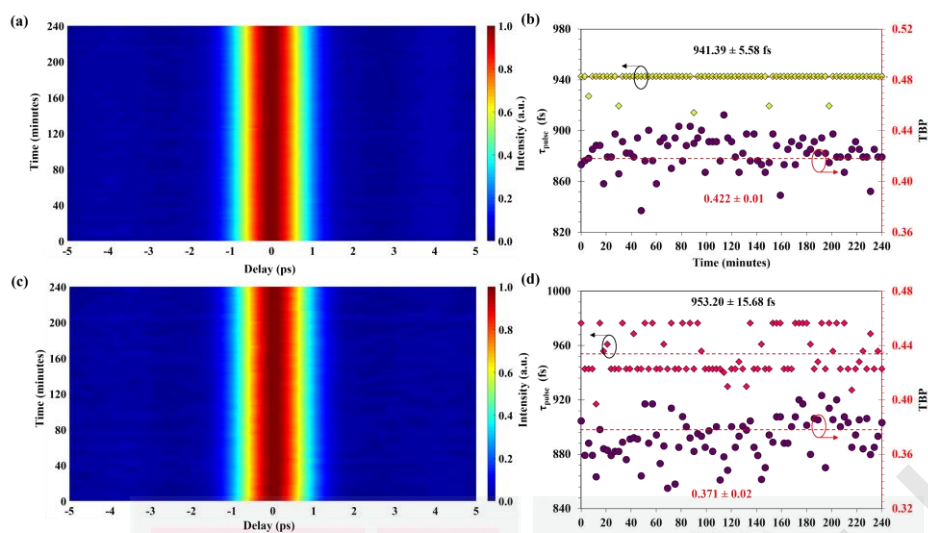


Figure B3: Stability evaluation of autocorrelation trace W6 (a) top view, (b) quantitative, W7 (c) top view and (d) quantitative.

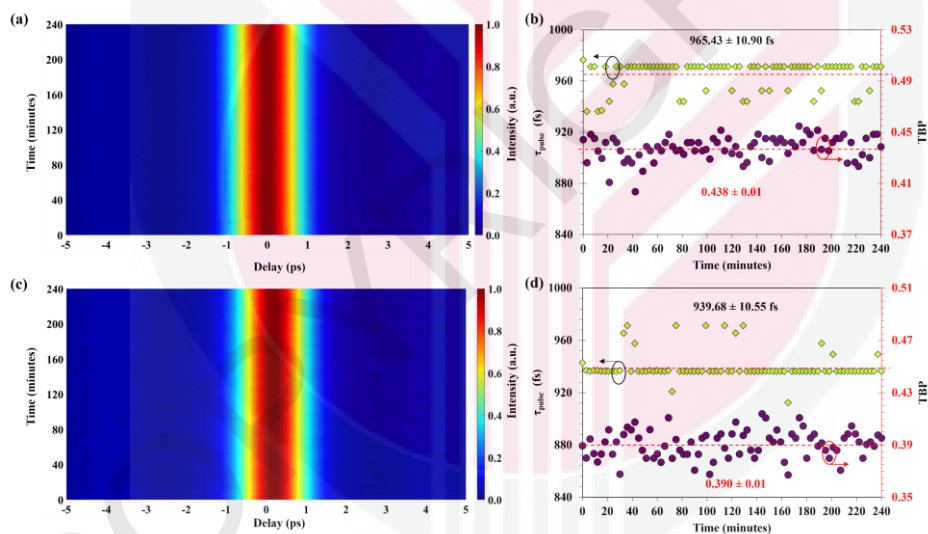


Figure B4: Stability evaluation of autocorrelation trace W8 (a) top view, (b) quantitative, W9 (c) top view and (d) quantitative.

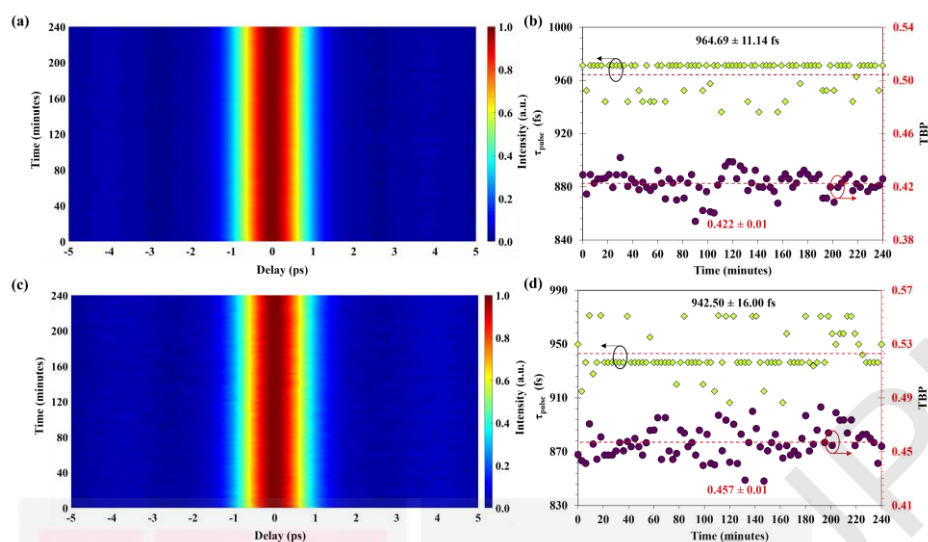


Figure B5: Stability evaluation of autocorrelation trace W10 (a) top view, (b) quantitative, W11 (c) top view and (d) quantitative.

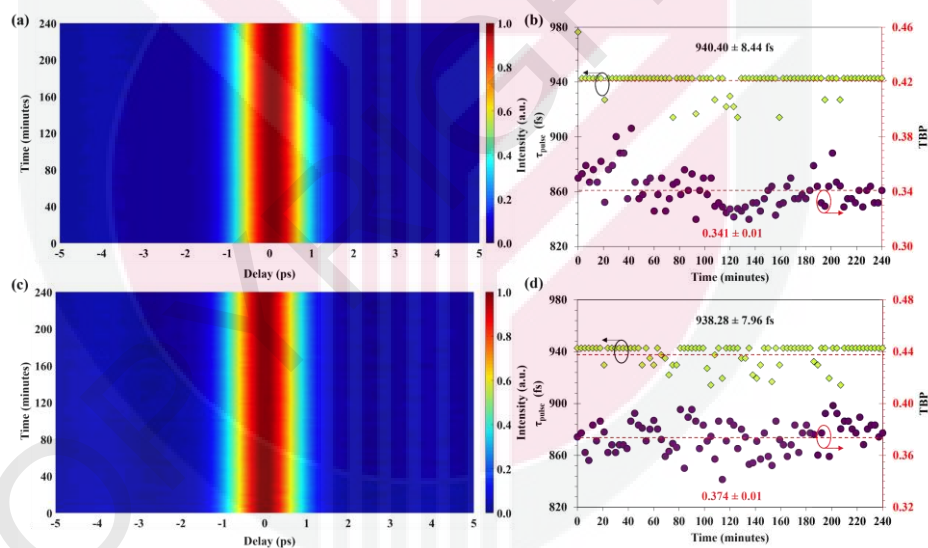


Figure B6: Stability evaluation of autocorrelation trace W12 (a) top view, (b) quantitative, W13 (c) top view and (d) quantitative.

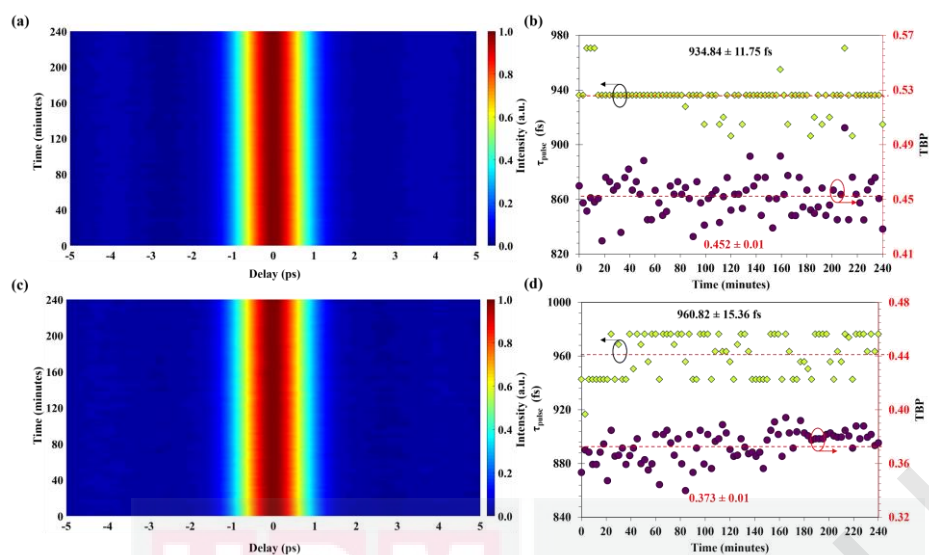


Figure B7: Stability evaluation of autocorrelation trace W14 (a) top view, (b) quantitative, W15 (c) top view and (d) quantitative.

Appendix C: Stability evaluation of optical spectrum of SA-WOP in MLFL for different observation weeks

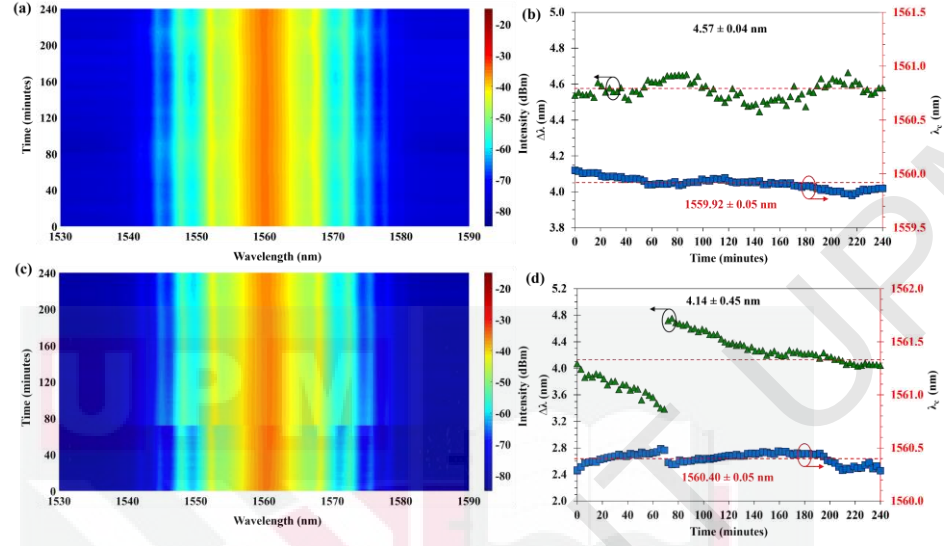


Figure C1: Stability evaluation of optical spectrum W2 (a) top view, (b) quantitative, W3 (c) top view and (d) quantitative.

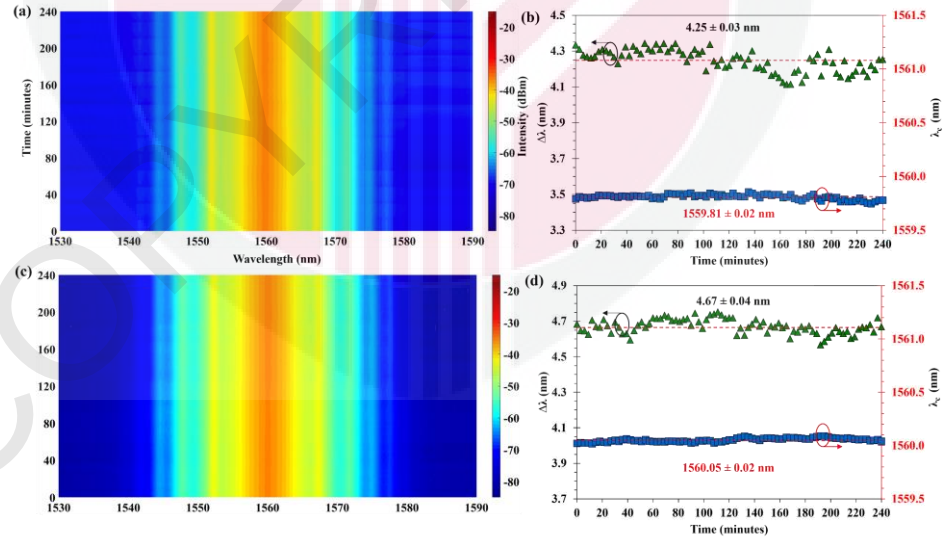


Figure C2: Stability evaluation of optical spectrum W4 (a) top view, (b) quantitative, W5 (c) top view and (d) quantitative.

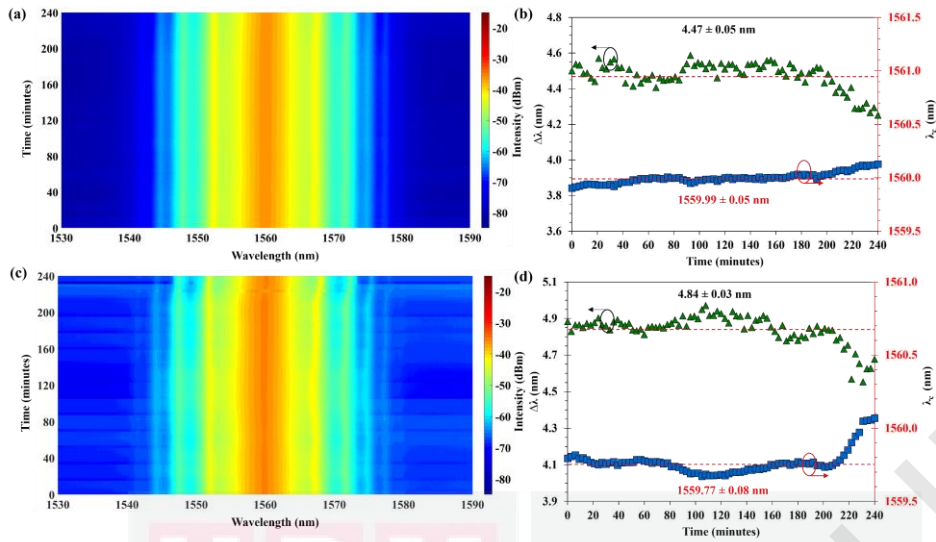


Figure C3: Stability evaluation of optical spectrum W6 (a) top view, (b) quantitative, W7 (c) top view and (d) quantitative.

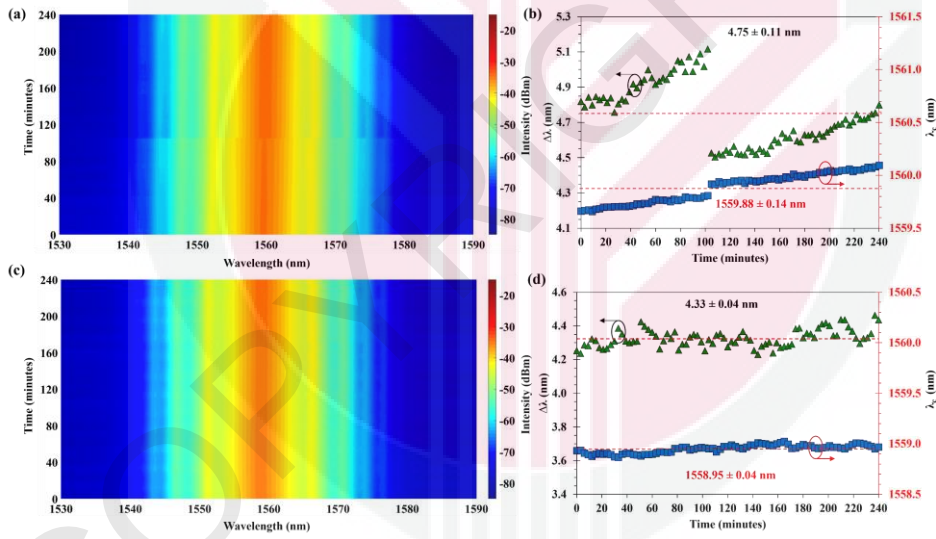


Figure C4: Stability evaluation of optical spectrum W8 (a) top view, (b) quantitative, W9 (c) top view and (d) quantitative.

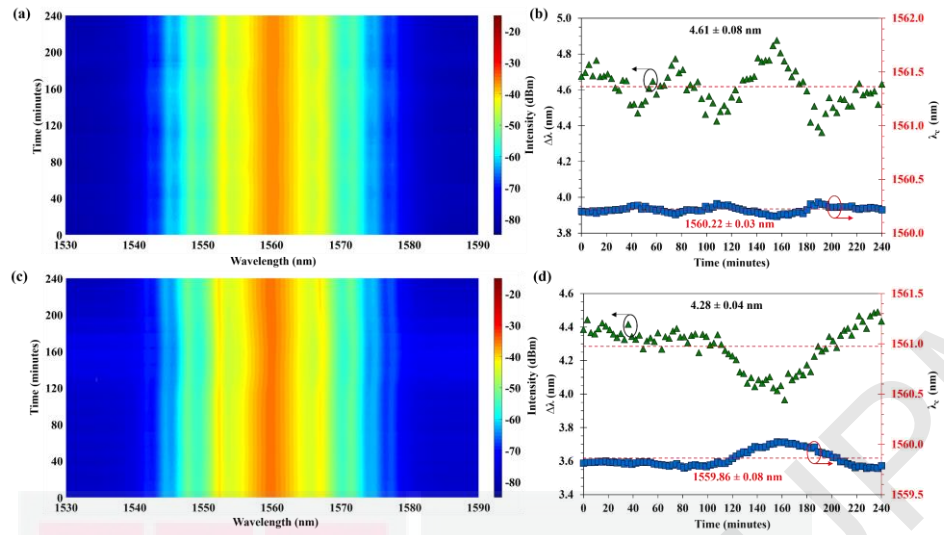


Figure C5: Stability evaluation of optical spectrum W10 (a) top view, (b) quantitative, W11 (c) top view and (d) quantitative.

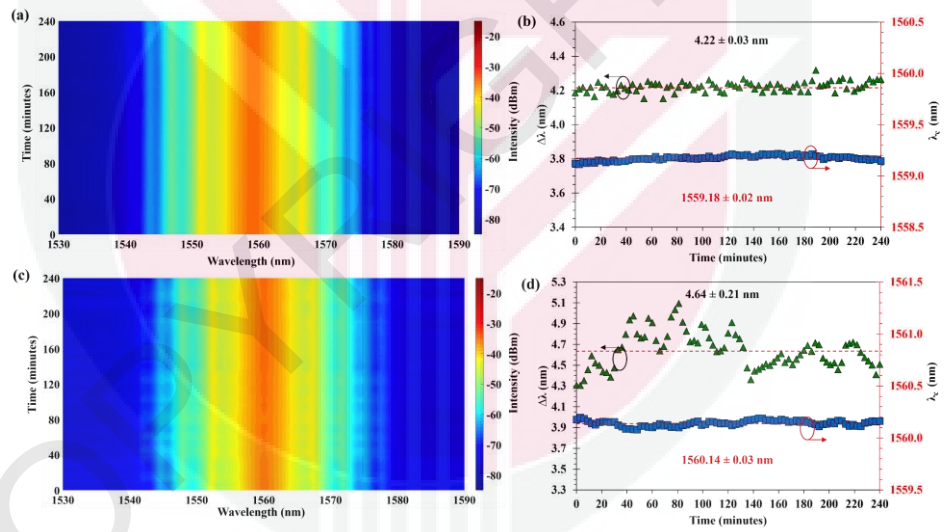


Figure C6: Stability evaluation of optical spectrum W12 (a) top view, (b) quantitative, W13 (c) top view and (d) quantitative.

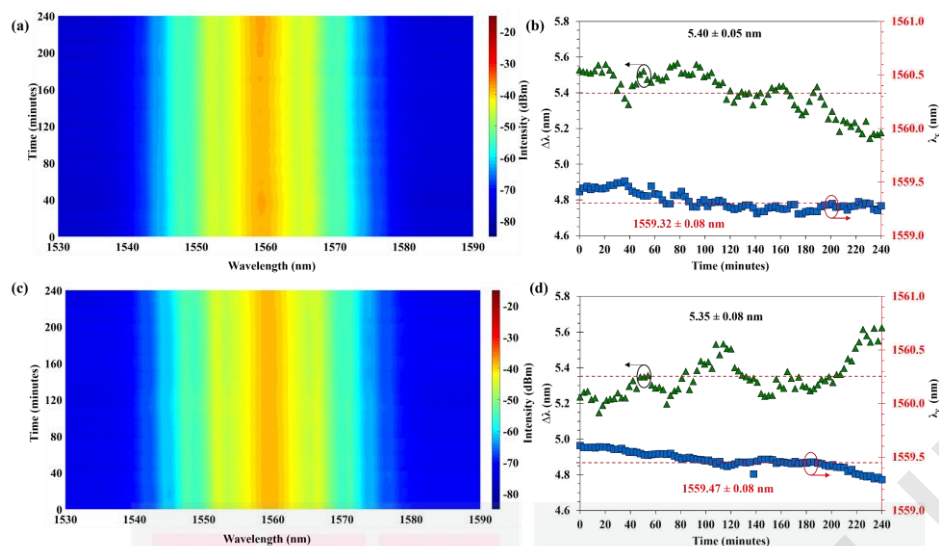


Figure C7: Stability evaluation of optical spectrum W14 (a) top view, (b) quantitative, W15 (c) top view and (d) quantitative.

Appendix D: Stability evaluation of autocorrelation trace of SA-WOP in MLFL for different observation weeks

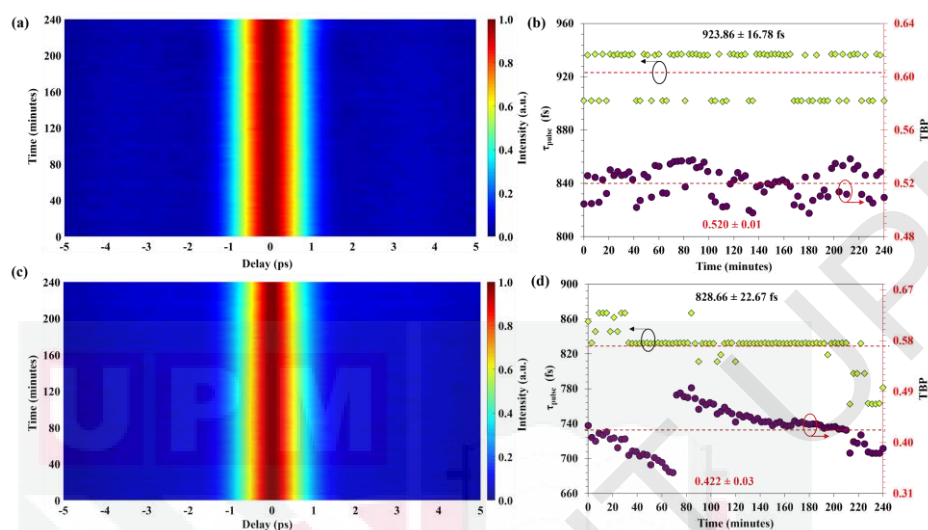


Figure D1: Stability evaluation of autocorrelation trace W2 (a) top view, (b) quantitative, W3 (c) top view and (d) quantitative.

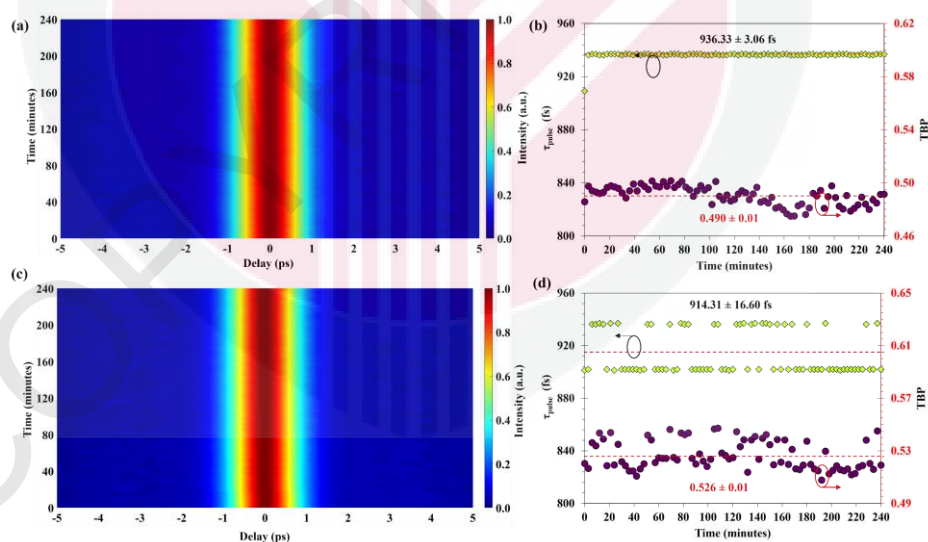


Figure D2: Stability evaluation of autocorrelation trace W4 (a) top view, (b) quantitative, W5 (c) top view and (d) quantitative.

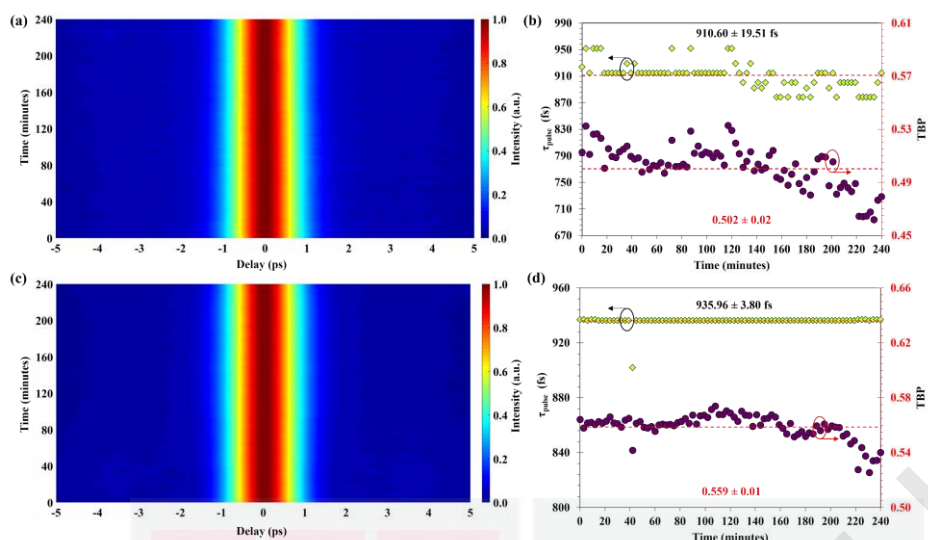


Figure D3: Stability evaluation of autocorrelation trace W6 (a) top view, (b) quantitative, W7 (c) top view and (d) quantitative.

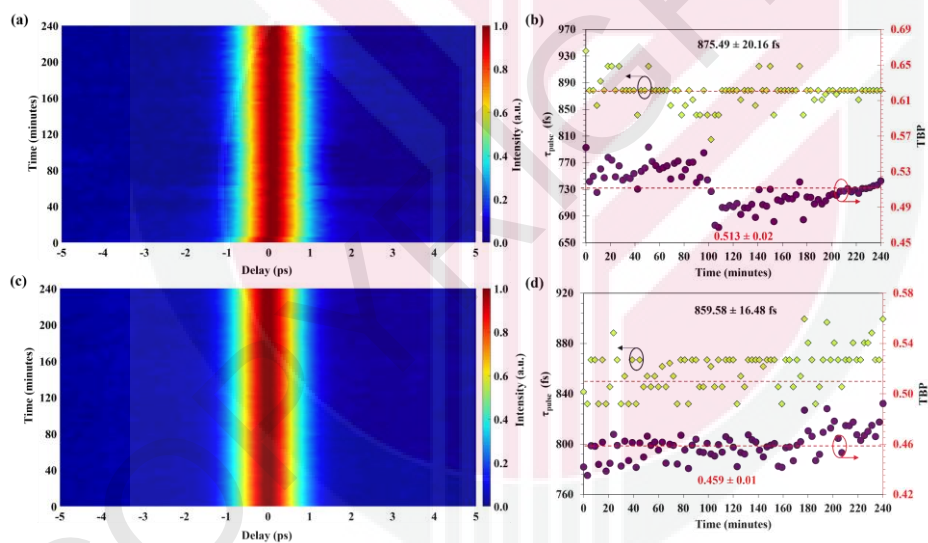


Figure D4: Stability evaluation of autocorrelation trace W8 (a) top view, (b) quantitative, W9 (c) top view and (d) quantitative.

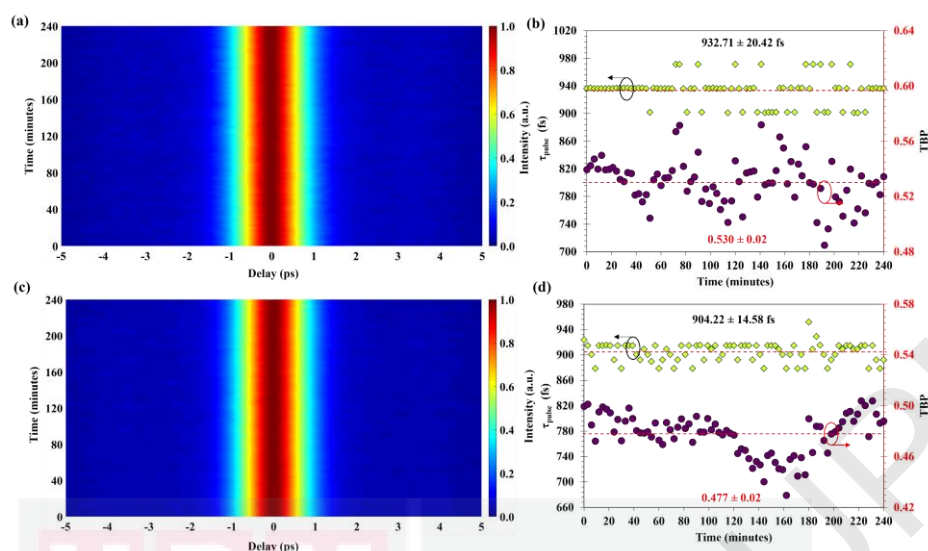


Figure D5: Stability evaluation of autocorrelation trace W10 (a) top view, (b) quantitative, W11 (c) top view and (d) quantitative.

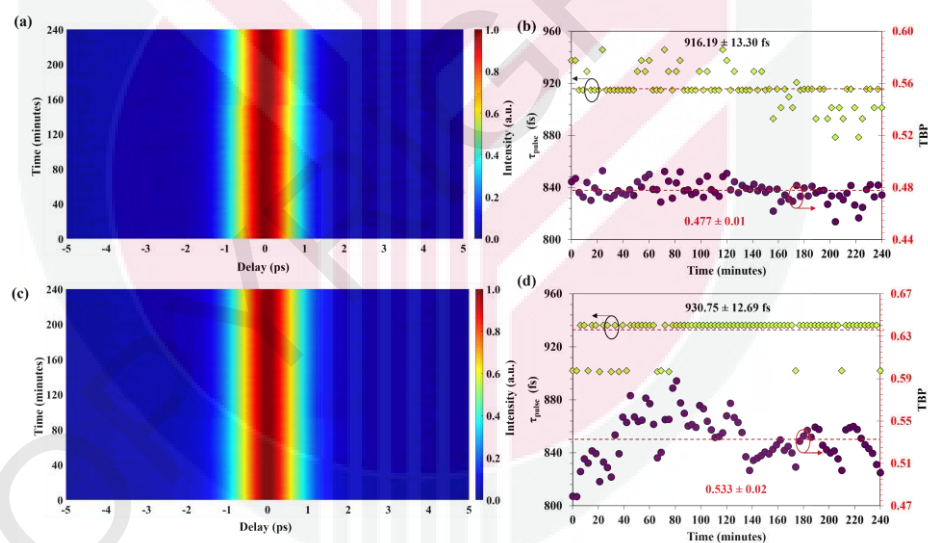


Figure D6: Stability evaluation of autocorrelation trace W12 (a) top view, (b) quantitative, W13 (c) top view and (d) quantitative.

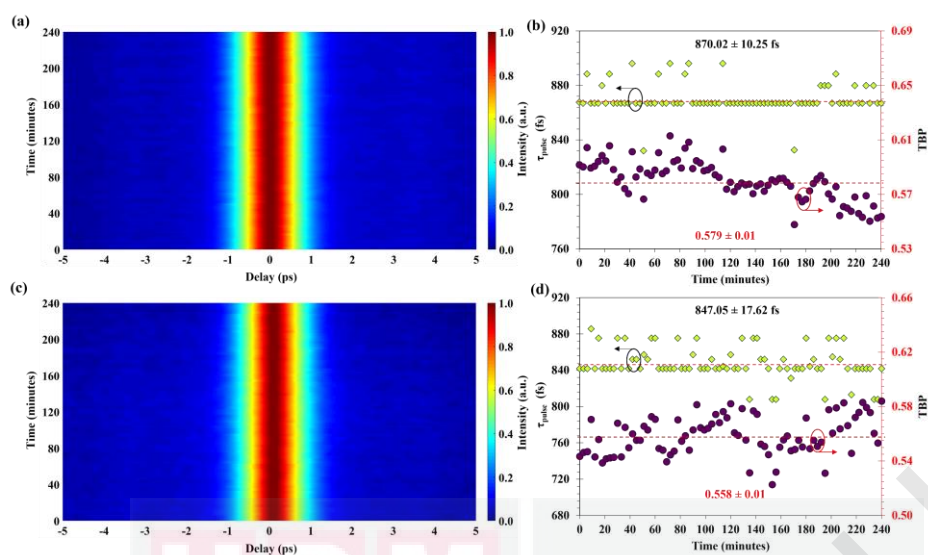


Figure D7: Stability evaluation of autocorrelation trace W14 (a) top view, (b) quantitative, W15 (c) top view and (d) quantitative.

LIST OF PUBLICATIONS

- [1] M. Mansor, N. H. Zainol Abidin, J. Y. Liew, M. T. Alresheedi, A. K. Garg, V. Janyani, and M. A. Mahdi, "Cerium oxide/polydimethylsiloxane composite tapered fiber saturable absorber for mode-locked pulsed erbium-doped fiber laser," *Infrared Physics & Technology*, vol. 125, p. 104220, 2022.
- [2] M. Mansor, N. H. Zainol Abidin, N. M. Yusoff, K. Y. Lau, J. Y. Liew, V. Janyani, A. K. Garg, M. T. Alresheedi, and M. A. Mahdi, "Tungsten trioxide nanocomposite for conventional soliton and noise-like pulse generation in anomalous dispersion laser cavity," *Nanotechnology Reviews*, vol. 12, no. 1, 2023.