



**METHYLAMMONIUM ORGANIC CATION-SUBSTITUTED CESIUM
BISMUTH BROMIDE-BASED PEROVSKITE PREPARED VIA
MICROWAVE-ASSISTED SOLVOTHERMAL METHOD FOR
PHOTOVOLTAIC APPLICATION**

By

LOW YIIN JIAN

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirements for the Degree of Doctor of Philosophy**

May 2024

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Chairman : Josephine Liew Ying Chyi, PhD

Institute : Nanoscience and nanotechnology

Improving Cs-Bi-Br-based perovskites for optoelectronic applications necessitates fast synthesis and thorough investigation of A-site elements. This thesis focuses on the optimization of a microwave-assisted solvothermal method which offers a rapid synthesis for single ($\text{Cs}_3\text{Bi}_2\text{Br}_9$) and double perovskite ($\text{Cs}_2\text{AgBiBr}_6$) materials. The microwave-assisted solvothermal method was optimized with solvent (isopropanol, hexane), ligand (oleic acid, oleylamine) and additive (hydrobromic acid) based on the Cs-Bi-Br-based perovskite materials. The structural and optical characteristics of the synthesized materials were investigated extensively for a better understanding on the material's properties. The research also explores the substitution effect of methylammonium organic cation (MA^+) on the material's properties of single perovskite ($\text{Cs}_{3-x}\text{MA}_x\text{Bi}_2\text{Br}_9$) and double perovskite ($\text{Cs}_{2-x}\text{MA}_x\text{AgBiBr}_6$). A phase segregation event happens in $\text{Cs}_{3-x}\text{MA}_x\text{Bi}_2\text{Br}_9$ when $x \geq 1.0$, causing the formation of $\text{Cs}_3\text{Bi}_2\text{Br}_9$ and $\text{MA}_3\text{Bi}_2\text{Br}_9$ structure with intermediate diffraction plane. Excess of MA^+ substitution in $\text{Cs}_{3-x}\text{MA}_x\text{Bi}_2\text{Br}_9$ reduces the ligands passivation effect and

induced a polydisperse morphology. No significant changes were found in absorption bandgap, Urbach energy and exciton binding energy as MA^+ substitution progress in $\text{Cs}_{3-x}\text{MA}_x\text{Bi}_2\text{Br}_9$. The passivation in non-radiative recombination induced by the intermediate phase formation enhanced the emission intensity and carrier lifetime. Specific thermal decomposition pathway in $\text{Cs}_{3-x}\text{MA}_x\text{Bi}_2\text{Br}_9$ was allocated when $x = 0.5$. While, insignificant amount of MA^+ substitution ($x = 0.2$) relieves the microstrain in $\text{Cs}_2\text{AgBiBr}_6$ structure, increases the volume and reduces the crystallite size without triggering the silver bromide impurities formation. MA^+ also induces defect in structure, causing an aggregation event happens in $\text{Cs}_2\text{AgBiBr}_6$. As the MA^+ substitution increased in $\text{Cs}_{2-x}\text{MA}_x\text{AgBiBr}_6$, the structural disorderment effect caused the absorption energy bandgap red-shifted, Urbach energy rose, and emission intensity reduced. Proper MA^+ substitution ($x = 0.6$) in $\text{Cs}_{2-x}\text{MA}_x\text{AgBiBr}_6$ enhanced the carrier lifetime, but came at the expense of generating a high density of non-radiative recombination. The thermal stability of the $\text{Cs}_{2-x}\text{MA}_x\text{AgBiBr}_6$ is minimally impacted by MA^+ substitution, as the allowed level of MA^+ substitution is limited. Photovoltaic performance of pure $\text{Cs}_2\text{AgBiBr}_6$ surpasses the other materials with a power conversion efficiency of 0.019 %. This research contributes fundamental insights into the investigation of pristine and MA^+ -substituted Cs-Bi-Br based perovskite materials for future photovoltaic applications.

Keywords: Cs-Bi-Br-based perovskites, $\text{Cs}_2\text{AgBiBr}_6$, $\text{Cs}_3\text{Bi}_2\text{Br}_9$, Methylammonium substitution, Microwave-assisted solvothermal synthesis.

SDG: GOAL 7: Affordable and clean energy

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

**PENGGANTIAN KATION ORGANIK METILAMMONIUM DALAM
PEROVSKIT BERASAS CESIUM BISMUTH BROMIDA MELALUI
KAEDAH SOLVOTHERMA BERBANTU MIKROGELOMBANG UNTUK
APLIKASI PHOTOVOLTAIC**

Oleh

LOW YIIN JIAN

Mei 2024

Pengerusi : Josephine Liew Ying Chyi, PhD

Institut : Nanosains dan Nanoteknologi

Penambahbaikan perovskit berasas Cs-Bi-Br untuk aplikasi optoelektronik memerlukan sintesis pantas dan kajian terhadap elemen tapak A. Tesis ini memberi tumpuan kepada pengoptimuman kaedah solvoterma berbantu mikrogelombang yang menawarkan sintesis pantas untuk bahan perovskit tunggal ($\text{Cs}_3\text{Bi}_2\text{Br}_9$) dan perovskit berganda ($\text{Cs}_2\text{AgBiBr}_6$). Kaedah solvoterma berbantu mikrogelombang telah dioptimumkan dengan pelarut (isopropanol, heksana), ligan (asid oleik, oleamine) dan bahan tambah (asid hidrobromik) berdasarkan bahan perovskite berasas Cs-Bi-Br. Ciri-ciri struktur dan optik bahan yang disintesis telah dikaji secara meluas untuk pemahaman yang lebih baik tentang sifat bahan. Penyelidikan ini juga meninjau kesan penggantian kation organik metilammonium (MA^+) pada sifat bahan perovskite tunggal ($\text{Cs}_{3-x}\text{MA}_x\text{Bi}_2\text{Br}_9$) dan perovskite berganda ($\text{Cs}_{2-x}\text{MA}_x\text{AgBiBr}_6$). Pengasingan fasa berlaku dalam $\text{Cs}_{3-x}\text{MA}_x\text{Bi}_2\text{Br}_9$ apabila $x \geq 1.0$, menyebabkan pembentukan struktur $\text{Cs}_3\text{Bi}_2\text{Br}_9$ dan $\text{MA}_3\text{Bi}_2\text{Br}_9$ dengan satah pembelauan perantaraan. Penggantian MA^+ berlebihan dalam $\text{Cs}_{3-x}\text{MA}_x\text{Bi}_2\text{Br}_9$ mengurangkan kesan pempasifan ligan dan

mendorong morfologi polidispersi. Tiada perubahan ketara didapati dalam jurang jalur serapan, tenaga Urbach dan tenaga ikatan eksiton semasa penambahan penggantian MA^+ dalam $\text{Cs}_{3-x}\text{MA}_x\text{Bi}_2\text{Br}_9$. Pempasifan dalam gabungan semula bukan sinaran yang disebabkan oleh pembentukan fasa perantaraan meningkatkan keamatan pancaran dan jangka hayat pembawa. Laluan penguraian terma khas dalam $\text{Cs}_{3-x}\text{MA}_x\text{Bi}_2\text{Br}_9$ diperuntukkan apabila $x = 0.5$. Manakala, jumlah penggantian MA^+ yang tidak ketara ($x = 0.2$) melegakan mikroterikan dalam struktur $\text{Cs}_2\text{AgBiBr}_6$, meningkatkan isipadu dan mengurangkan saiz kristalit tanpa mencetuskan pembentukan bendasing argentum bromida. MA^+ juga mendorong kecacatan dalam struktur, menyebabkan pengagregatan berlaku dalam $\text{Cs}_2\text{AgBiBr}_6$. Apabila penggantian MA^+ meningkat dalam $\text{Cs}_{2-x}\text{MA}_x\text{AgBiBr}_6$, kesan struktur tak tertib menyebabkan tenaga jurang jalur serapan beralih merah, tenaga Urbach meningkat dan keamatan pancaran berkurangan. Penggantian MA^+ yang sesuai ($x = 0.6$) dalam $\text{Cs}_{2-x}\text{MA}_x\text{AgBiBr}_6$ meningkatkan jangka hayat pembawa, tetapi mendatangkan penjanaan ketumpatan gabungan semula bukan sinaran yang tinggi. Kestabilan terma $\text{Cs}_{2-x}\text{MA}_x\text{AgBiBr}_6$ dipengaruhi secara minimum oleh penggantian MA^+ , disebabkan tahap penggantian MA^+ yang dibenarkan adalah terhad. Prestasi fotovolta $\text{Cs}_2\text{AgBiBr}_6$ tulen melepasi bahan lain dengan kecekapan penukaran kuasa sebanyak 0.019 %. Penyelidikan ini menyumbang wawasan asas dalam kajian bahan perovskit berasas Cs-Bi-Br yang murni dan digantikan oleh MA^+ untuk aplikasi fotovolta masa hadapan.

Kata Kunci: Perovskit berasas Cs-Bi-Br, $\text{Cs}_2\text{AgBiBr}_6$, $\text{Cs}_3\text{Bi}_2\text{Br}_9$, Penggantian metilammonium, Kaedah solvotherma berbantu mikrogelombang

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Josephine Liew Ying Chyi, PhD

Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Janet Lim Hong Ngee, PhD

Professor ChM.
Faculty of Science
Universiti Putra Malaysia
(Member)

Lim Kean Pah, PhD

Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Mohd Hafiz bin Mohd Zaid, PhD

Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

Choo Thye Foo, PhD

Research Officer
Materials Technology Group
Agensi Nuklear Malaysia
(Member)

ZALILAH MOHD SHARIFF, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 8 August 2024

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LIST OF ABBREVIATIONS

-	A span range of number
~	Approximately
1L	One-layered
2L	Two-layered
2D	Two dimensions
3D	Three dimensions
A-EtOH	Absolute ethanol
ACN	Acetonitrile
Ag(OAc)	Silver acetate
AgBr	Silver bromide
AgNO ₃	Silver nitrate
ANM	Malaysian Nuclear Agency
Bi(OAc) ₃	Bismuth acetate
Ba ₂ SO ₄	Barium sulfate
Bi ₂ O ₃	Bismuth oxide
BiBr ₃	Bismuth bromide
BiOBr	Bismuth oxide bromide
BzBr	Benzoyl bromide
CBM	Conduction band minima
CsBr	Cesium bromide
CS(OAc)	Cesium acetate
DFT	Density functional theory
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DOS	Density of state

DTG	Derivative thermogravimetry
EDX	Energy dispersive x-ray
ETL	Electron transport layer
EXAFS	Extended X-ray absorption fine structure
FESEM	Field-emission scanning electron microscopy
FTO	Fluorine-doped tin oxide
FWHM	Full-width half maximum
GBL	γ -butyrolactone
HBr	Hydrobromic acid
HIM	Hot-injection method
HTL	Hole transport layer
i-CRIM	Center for Research and Instrumentation Management
IPA	Isopropanol
IRF	Instrument respond factor
KBr	Potassium bromide
MABr	Methylammonium bromide
OA	Oleic acid
ODE	Octadecene
OLA	Oleylamine
PL	Photoluminescence spectroscopy
RM	Re-precipitation method
rpm	Rotation per minute
RR	Rietveld-refinement
TBABr	Tetrabutylammonium bromide
TDPL	Temperature-dependent photoluminescence spectroscopy
TGA	Thermogravimetric analysis
TiO ₂	Titanium dioxide

TMSBr	Trimethylsilyl bromide
TOPO	Trioctylphosphine
TRPL	Time-resolved photoluminescence spectroscopy
UPM	Universiti Putra Malaysia
UV-Vis	Ultraviolet-visible spectroscopy
VBM	Valence band maxima
WH	Williamson-Hall plot
XAFS	X-ray absorption fine structure spectroscopy
XANES	X-ray absorption near edge spectroscopy
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Overview of bismuth-based perovskite halides

Perovskite halides have emerged in recent years as a promising material for optoelectronic applications due to their low exciton binding energy, high carrier mobilities, versatility in material synthesis, and high diversification in materials structure (Dequillettes et al., 2019; Liu et al., 2020b; Ning et al., 2019; Zheng et al., 2015). Among these, lead-based perovskite has been extensively studied and performs well in solar cell and light-emitting diode applications, garnering significant attention from researchers (Miao et al., 2019; Turren-Cruz et al., 2018; Yang et al., 2016). However, the commercialization of lead-based perovskite is hampered by its toxicity and structural instability. Therefore, the discovery of lead-free materials exhibiting similar electronic properties to lead halide perovskites will be a critical step in the commercialization process.

Researchers are exploring the metal elements that are iso-valent to Pb^{2+} , such as germanium (Ge^{2+}) and tin (Sn^{2+}) to replace the lead-based perovskite materials. Germanium-based and tin-based perovskite materials exhibit a direct bandgap, excellent carrier mobility, and long diffusion length. In contrast, despite the favourable characteristics of Sn^{2+} and Ge^{2+} , they tend to undergo rapid degradation and oxidation into Sn^{4+} and Ge^{4+} under air conditions, respectively (Brandt et al., 2015). Furthermore, the search for alternatives to Pb^{2+} extends to hetero-valent metal cations

such as Tl^{3+} , Bi^{3+} , and Sb^{3+} . Nevertheless, it should be noted that Tl^{+} have higher toxicity compared to lead and is prone to rapid degradation into Tl^{3+} upon exposure to air (Li et al., 2021a). While, both Sb^{3+} and Bi^{3+} are abundant and non-toxic compared to Pb^{2+} , and their single oxidation state makes them promising for achieving environmental stability (Jin et al., 2020; Li et al., 2021a; Sani et al., 2018).

Among all the bismuth-based perovskite materials, all inorganic Cs-Bi-Br based perovskite materials are reported to feature a superior structural stability as they composed solely of inorganic Cs^{+} cation and Br^{-} anion that enhanced the thermodynamic of the materials structure, making them more robust and less prone to degradation while featuring a promising optical property (Luo et al., 2020; Xiao et al., 2016). Two different structures can be derived from the Cs-Bi-Br-based perovskite materials, that is the single perovskite ($\text{Cs}_3\text{Bi}_2\text{Br}_9$) and double perovskite ($\text{Cs}_2\text{AgBiBr}_6$) structure (Jin et al., 2020; Shi et al., 2020). Both of the perovskite structures feature exceptional and tunable optical properties that suit optoelectronic applications. Subsequently, the modification in the optical properties of Cs-Bi-Br-based perovskite materials is possible by employing compositional engineering and synthesis techniques.

The present study involved the optimization of a microwave-assisted solvothermal method to synthesize perovskite materials based on Cs-Bi-Br. The structural, morphological, optical, and thermal stability aspects of both pristine and MA^{+} -substituted materials were investigated extensively. Additionally, the photovoltaic performance of all Cs-Bi-Br-based perovskite materials, including both pristine and MA^{+} -substituted was evaluated. The findings of this study offer a novel pathway for

the synthesis of Cs-Bi-Br-based perovskite materials and provide a fundamental understanding of the effects of MA⁺-substitution on their properties for future photovoltaic applications.

1.2 Problem statement

The synthesis of perovskite materials based on Cs-Bi-Br is commonly achieved through the hot injection and re-precipitation method, which possesses both advantages and disadvantages. (Ahmad et al., 2021; Wu et al., 2021a; Zhou et al., 2018). The nucleation and crystal growth processes are separated in the hot injection method, enabling precise control over the material's particle size and morphology. Nevertheless, the hot injection method requires an inert atmosphere and a high-temperature reaction medium, complicating the experimental setup and limiting its applicability to organic-based studies (Ahmad et al., 2021; Wu et al., 2021a; Zhou et al., 2018). In contrast, the reprecipitation method benefits from its adaptable operating procedure and its room temperature process but is plagued by poor reproducibility. Therefore, it is essential to develop an alternative synthesis method with a simpler experimental setup, ensuring good reproducibility, and enabling organic-based studies of Cs-Bi-Br-based perovskite materials.

Generally, Cs-Bi-Br-based perovskite materials have been modified by engineering their composition through the A-site cation. The introduction of mixed A-site cation conditions in Cs-Bi-Br-based perovskite materials offers the potential to further adjust the energy bandgap and provide opportunities for carrier lifetime and strain engineering within the structure (Lee et al., 2022; Ünlü et al., 2020). However, current

research has predominantly focused on mixed inorganic A-site cations (Rb^+ , K^+ , Na^+ , Li^+) that are similar in size to Cs^+ in Cs-Bi-Br-based perovskite materials. Therefore, there is a pressing need to investigate mixed organic/inorganic A-site conditions for the future advancement of Cs-Bi-Br-based perovskite materials, as this strategy has the potential to improve optical properties while reserving material stability.

The following research questions have been addressed to justify the importance of the study:

1. What method is rapid, eco-friendly, features a simpler experimental setup, and enables organic-based studies of Cs-Bi-Br-based perovskite materials?
2. Why is the organic MA^+ cation chosen to improve the material characteristics in Cs-Bi-Br perovskite materials?
3. How does the substitution of MA^+ improve the photovoltaic performance of Bi-Br-based perovskite materials?

1.3 Hypotheses

The hypotheses based on the listed research questions are:

1. Microwave-assisted solvothermal method allows for rapid and environmentally friendly material synthesis (Gawande et al., 2014; Nayak et al., 2016). The method quickly converts electromagnetic waves into thermal energy, speeding up nucleation and particle growth without compromising quality. The experimental setup is simple, involving mixing reagents in a glass vial without needing an inert gas. Crucially, microwave-assisted solvothermal method is suitable for organic-based studies in Cs-Bi-Br-based perovskite

materials, as the reaction temperature conditions ($\leq 160^{\circ}\text{C}$) support mixed organic/inorganic perovskite formation. Therefore, microwave-assisted solvothermal method is ideal for synthesizing Cs-Bi-Br perovskite materials with mixed organic/inorganic A-site condition under optimized conditions.

2. The MA^{+} organic cation, similar in size to Cs^{+} , is favored over larger organic cations like ethylammonium and formamidinium for substituting the A-site cation in Cs-Bi-Br perovskite materials. Larger cations may cause phase segregation and increased lattice strain (Byranvand et al., 2022). The optimized substitution of MA^{+} cation in Cs-Bi-Br-based perovskite materials is expected to integrate well into the Cs-Bi-Br perovskite structure, enhancing its structural stability and extending carrier lifespan. While excessive MA^{+} cation substitution could lead to defects, the right amount is expected to reduce lattice strain, decrease the energy bandgap, prolong carrier lifetime, and enhance thermal stability.
3. The incorporation of MA^{+} cation could cause a red-shifted bandgap and prolong the carrier lifetime of Cs-Bi-Br-based perovskite materials. Hence, it is expected that optimizing the MA^{+} cation substitution could improve the photovoltaic performance of Cs-Bi-Br-based materials.

1.4 Objectives

Hence, based on the hypotheses mentioned above, the objectives of this study are:

1. to synthesize Cs-Bi-Br based single ($\text{Cs}_3\text{Bi}_2\text{Br}_9$) and double ($\text{Cs}_2\text{AgBiBr}_6$) perovskites via microwave-assisted solvothermal method.
2. to investigate the substitution effect of methylammonium (MA^+) organic cation on the structural, morphological, optical and thermal stability of Cs-Bi-Br-based perovskite.
3. to investigate the effect of MA^+ organic cation substitution on the photovoltaic application performance of Cs-Bi-Br-based perovskites.

1.5 Scope of study

This study optimized the synthesis process of Cs-Bi-Br-based perovskite materials, including single perovskite ($\text{Cs}_3\text{Bi}_2\text{Br}_9$) and double perovskite ($\text{Cs}_2\text{AgBiBr}_6$) via microwave-assisted solvothermal method. The synthesis parameters in the microwave-assisted solvothermal method such as solvents (isopropanol, hexane), ligands (oleylamine, oleic acid) and additive (hydrobromic acid) are optimized based on the materials. The material's structural, morphological, optical and thermal stability of pristine $\text{Cs}_3\text{Bi}_2\text{Br}_9$ and $\text{Cs}_2\text{AgBiBr}_6$ materials were investigated. Furthermore, the $\text{Cs}_3\text{Bi}_2\text{Br}_9$ and $\text{Cs}_2\text{AgBiBr}_6$ materials were subject to MA^+ substitution, aiming to investigate the impact of MA^+ substitution on the structural, morphological, optical, and thermal stability of perovskite materials. Finally, the synthesized perovskite materials were subjected to the photovoltaic application, regardless of pristine or MA^+ substituted $\text{Cs}_3\text{Bi}_2\text{Br}_9$ and $\text{Cs}_2\text{AgBiBr}_6$ materials.

1.6 Thesis outline

This thesis is composed of 5 chapters. A general introduction to Cs-Bi-Br perovskite materials and the objectives of the study were presented in chapter one. Recent progress in the bismuth-based perovskite materials, including properties and synthesis methods of Cs-Bi-Br-based perovskite were outlined in chapter two. All the experimental synthesis and materials characterizations of Cs-Bi-Br-based perovskite materials were described in chapter three. Following that, all the results acquired for Cs-Bi-Br-based perovskite materials to achieve the study objectives were presented and discussed in chapter four. Finally, all the research findings and future perspectives of the study were concluded in chapter five.

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