UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF EUROPIUM DOPED WILLEMITE BASED GLASS-CERAMICS DERIVED FROM RICE HUSKS

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

August 2019

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Nowadays, researchers have been working on to produce glass phosphors using waste materials for optical application purpose but lack of study in producing europium (Eu^{3+}) doped zinc silicate (Zn_2SiO_4) glass ceramics derived from rice husk as raw material. Firstly, X-ray fluorescence spectroscopy (XRF) had confirmed white rice husk ash (WRHA) contains 90.926% of silica which suitable to produce zinc silicate glass (ZnO-SiO_2). Based on the X-ray diffractometer (XRD) analysis of different glass compositions, 60:40 ratio of zinc oxide (ZnO) against WRHA shows amorphous phase which made it optimum composition to produce Zn_2SiO_4 glass ceramics. Hence, a study on structural and optical properties with subject to sintering temperature (600-1000°C) and dopant concentration (1-5 wt.%) has been done. XRD revealed the intensity of α-Zn_2SiO_4 phases become sharper indicating good crystallization as temperature increased but drastically dropped due to structural distortion as dopant was added. Field emission scanning electron microscopy (FESEM) shows the particles have good connectivity due to crystallization when sintered while dopant addition had reduced the surface porosity. Meanwhile, Fourier transform infrared spectrometer (FTIR) analysed at 400-2000 cm^{-1} wavenumber had revealed that the broad bands of SiO_4 were getting narrower due to increase in the crystallinity while the presence of Eu^{3+} dopants had weakened the band by lattice defects. Ultra-violet visible spectroscopy (UV-Vis) analysis in the wavelength range of 220-800 nm shows the absorption at ~250-400 nm were uplifted towards higher wavelength due to crystal growth thus band gap values were decreasing from 4.01 eV to 2.98 eV as temperature increased. However, dopant addition increased band gap values from 3.39 eV to 3.67 eV as absorbance shifted to shorter wavelength due to lattice distortion. Photoluminescence spectroscopy (PL) analysis shows red emission exhibited at wavelength 612 nm due to Eu^{3+} transitions under 400 nm excitation. Therefore, this zinc silicate glass ceramics appeared to be a potential phosphor material for electronic devices.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SINTESIS DAN PENCIRIAN SERAMIK KACA WILLEMITE DOP EUROPIUM BERASASKAN DARIPADA SEKAM PADI

Oleh

RAHAYU EMILIA MOHAMED KHAIDIR

Ogos 2019

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Pada masa kini, para penyelidik telah berusaha untuk menghasilkan bahan fosfor menggunakan bahan terbuang untuk kegunaan aplikasi optikal namun kurang kajian dalam menghasilkan europium (Eu^{3+}) dop seramik kaca zink silica (Zn_2SiO_4) daripada sekam padi sebagai bahan asas. Pertamanya, pendarfluoran sinar-X (XRF) telah mengesahkan abu putih sekam padi (WRHA) mengandungi 90.926% silika dimana ia sesuai untuk menghasilkan kaca zink silika ($ZnO-SiO_2$). Berdasarkan analisa pembelauan sinar-X (XRD) tentang komposisi kaca yang berlainan, nisbah 60:40 dari zink (ZnO) dan WRHA menunjukkan fasa amorfus yang membuatkan ia komposisi optima untuk menhasilkan Zn_2SiO_4. Dengan itu, pembelajaran tentang sifat-sifat struktur and optikal bergantung pada suhu pembakaran (600-1000°C) dan kepekatan dopan (1-5 wt.%) telah dijalankan. XRD menunjukkan keamatan fasa α-Zn_2SiO_4 menjadi lebih tinggi menandakan penghabluran yang baik apabila suhu meningkat namun menurun secara drastic disebabkan distortasi struktur apabila dopan ditambah. Mikroskop pelepasan bidang imbasan elektron (FESEM) menunjukkan zarah-zarah mempunyai sambungan yang baik disebabkan oleh penghabluran semasa pembakaran sementara tambahan dopan telah mengurangkan liang permukaan. Sementara itu, spektroskopi inframerah (FTIR) dianalisa pada 400-2000 cm^{-1} telah menunjukkan jalur lebar SiO_4 menjadi kecil disebabkan oleh penghabluran yang meningkat sementara kehadiran dopant Eu^{3+} telah mengecilkan jalur lebar dengan kerosakan kekisi. Analisis spektroskopi ultraungu cahaya nampak merah (UV-Vis-NIR) dalam julat gelombang 220-800 nm menunjukkan penyerapan pada ~250-400 nm telah terbawa ke julat gelombang yang lebih tinggi disebabkan oleh pertumbuhan kristal justeru menurunkan jurang jalur dari 4.01 eV ke 2.98 eV apabila suhu meningkat. Namun begitu, tambahan dopan meingkatkan nilai jurang jalur dari 3.39 eV to 3.67 eV apabila penyerapan berubah ke jalur gelombang yang lebih rendah disebabkan oleh distortasi kekisi. Analisis spektroskopi kefotopendarcahayaan PL menunjukkan pancaran merah dihasilkan pada gelombang 612 nm berikutan peralihan Eu^{3+} di bawah pengujaan pada 400 nm. Oleh itu, kaca zinc silika silikat nampaknya menjadi bahan fosfor yang berpotensi untuk peranti elektronik.

ACKNOWLEDGEMENTS

Praises to Allah Almighty, for I am blessed with strength to finally accomplish this master project. First and foremost, it is a genuine pleasure to express my sincere gratitude to my project supervisor, Assoc. Prof. Dr. Yap Wing Fen for his dedication and keen interest above all his overwhelming support, invaluable lessons, sponsors and guidance throughout the process of completing this project. Thank you for all his precious time in motivating and guiding me to be a better researcher in the future. Not to forget, I would also like to give my special thanks to my co-supervisor Dr Mohd Hafiz bin Mohd Zaid for his generous help, meticulous guidance and scientific approach have helped me to a very great extent in accomplishing my research.

I would also like to express my highest appreciation to all staff members and science officers of Institute of Advanced Technology and Faculty of Science for all their unconditional time to assist me during analysis process and helps towards the success of my research and conferences. Apart from that, I also acknowledge the financial support for my study from Universiti Putra Malaysia (UPM) through Graduate Research Fellowship (GRF).

My deepest appreciation and thanks to all my seniors, friends, lab mates from Applied Optic Laboratory and Ceramic Ultrasonic Research Laboratory who have given me their valuable ideas, comments, support and helps during my master studies. My softball mates from Universiti Putra Malaysia, Snitchers team who always there to cheer me up and give moral support. A special word to my best friends, Fatin Amalina, Azmina, Ninna and Wana for their unconditional love and moral support throughout my master journey for I am always thankful to have them around in west Malaysia.

Last but not least, special thanks to my beloved family, especially to my parents, Mohamed Khaidir bin Mohamed Arebi and Puspasari binti Wahap, who have been very supportive in ensuring the completion of this project and thesis writing. I would not be where I am today without their care and prayers for I am always indebted and owe my success to them. To all my friends who have given direct or indirect helps, thank you for the helps during the hard times, thank you for everything.

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CRTs	Cathode ray tubes
EDX	Energy Dispersive X-Ray spectroscopy
FEAG	Filter Expansion Aerosol Generator
FED	Field-emission display
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectrometer
FWHM	Full width half maximum
JCPDS	Joint Committee on Powder Diffraction Data
NBOs	Non-bridging oxygens
PEG	Polymer-polyethylene glycol
PL	Photoluminescence spectroscopy
PVA	Polyvinyl alcohol
RE	Rare earth
SEM	Scanning electron microscopy
SLS	Soda lime silicate
UV-Vis-NIR	Ultra-violet visible spectroscopy
W-LED	White light emitting diode
WRHA	White rice husk ash
XRD	X-ray diffractometer
XRF	X-ray fluorescence spectroscopy

CHAPTER 1

INTRODUCTION

1.1 Zinc Silicate

Zinc silicate (Zn_2SiO_4), also known by its mineral name, willemite is discovered by Armand Lévy at Moresnet or now known as La Calamine, Belgium since the earliest year of 1829. The name of willemite was dedicated specially for the late King of Netherlands, Willem (I) of Orange-Nassau during the reign year of 1815 to 1840. Not long after that, willemite was getting more attention and found to be distributed to places such as Franklin, New Jersey and United States for its unique luminescence properties. In 1930s, willemite has been used as a phosphor material for fluorescent or neon lamp, colours television and several more displays while in present years, willemite has been used for more advanced technologies such as optoelectronic devices, lasers, sensor materials and many more electronic devices (Takesue et al., 2009a).

Zn_2SiO_4 has been found to be one of the inorganic optical based materials that acts as a very good host matrix for many rare earth ions and transition metal dopant ions that can exhibit luminescent properties (Rasdi et al., 2017a). This inorganic silicate phosphor has been used widely not only because it has great blue, green, and red luminescence properties but also chemically stable (El Mir et al., 2015). Zn_2SiO_4 exist either in alpha-α or beta-β phases where α-phase which is thermodynamically most stable compared to β-phase which is meta-stable when being treated to higher temperature (Rivera-Enríquez et al., 2016).

1.2 White Rice Husk Ash

Rice husk is a major by-product of agroindustry that can be obtained by extracting the hard coating on grain of rice. Rapid increase in world population has given a parallel impact in production demands. Most countries such as India, China and South East Asia are very high demands for rice productions as rice is their staple food (Pode, 2016). For example, Sri Lanka produces almost 3 million tons of paddy in 2002 making them at 18th highest country in producing paddy (De Silva & Surangi, 2017). Thus, results in an increase of waste products that leads to environmental pollutions due to inappropriate disposal. Therefore, researchers are trying to make use of the rice husks in industrial application to reduce the abundance of rice husk wastes. Utilizing the rice husks by recycling the biomass waste can either turning it into energy production to generate electricity by mill operation or material production such as cement and glass ceramics (Pode, 2016).

Generally, rice husk contains a huge amount of carbon and some silica content at pre-combustion process (Stochero et al., 2017). In this project, glass ceramics produced are derived from the white rice husk ash (WRHA). WRHA is a solid white coloured product formed after burning process of the rice husks at a certain temperature. It is high of porosity, light in weight and silica rich rice husk for about 90% and more silica content (De Silva & Surangi, 2017). Other than silica, it also consist of other components such as lignin, cellulose, hemicellulose, oxides, alkali earth metals, chloride and aluminium. The difference in origin of the rice husks differs the level of impurities of the rice husks. It affects the performance and efficiencies of rice husk ash in the industrial applications and provide excellent filler-matrix interaction when proper treatments are given to the rice husks (Hsieh et al., 2017).

1.3 Europium as Rare Earth Ions

In recent years, compound doped with rare-earth (RE) ions have attracted so much attention in developing the optical properties of glass ceramics. RE doped with glasses allow a various applications such as fluorescent display devices, white light emitting diode (W-LED), radiation detection sensor and optical fibres used for lasers. RE ions proved that they are most important functional materials due to the rich 4*f*-4*f* transitions in $4f^{th}$ ions specially for optical technologies and luminescence display (Qin et al., 2014). Thus, due to their 4*f* intra shell transitions, it gives RE ions to have better luminescent material because of their sharp and intense emission which is easier for human eyes to detect the monochromatic colours (Krishna et al., 2007). There are a few of RE elements that are usually being used in forming glass ceramics which are cerium (Ce^{3+}), neodymium (Nd^{3+}), samarium (Sm^{3+}), europium (Eu^{3+}), erbium (Er^{3+}), thulium (Tm^{3+}), ytterbium (Yb^{3+}) and others. Other than high in luminescence efficiencies in various host materials, they are also widely used due to the broad emission spectral range (Padlyak et al., 2014).

In this project, europium (III) oxide, Eu_2O_3 has been chosen to be the main dopant material to form europium doped zinc silicate glass ceramics samples that is derived from waste rice husks. Eu^{3+} is one of the RE elements that has been widely investigated structurally related to its great luminescence. Eu^{3+} has enormous potential in various applications among the lanthanides and it is frequently used in order to emit strong and sharp red or orange luminescence (Krishna et al., 2007). Considering this, Eu^{3+} ions are exceptionally useful since red emission phosphor is needed to develop W-LED that is considered as next-generation source of light due to its high brightness, good efficiencies, long lifetime and also environmental friendly as it could save up to 70% of energy (Jeon et al., 2015).

1.4 Glass-Ceramics

Glass ceramics can be formed when a pure amorphous glass sample with optimum composition is being treated with some sufficient amount of heat thus undergoes controlled crystallization to lower energy crystallize state or what we called as devitrification of glass. It has one or more crystalline phase that makes the glass ceramic is structurally polycrystalline. In 1953, glass ceramic was discovered by Stanley Donald Stookey when he accidentally overheated his lithium silicate glass sample in the furnace for about 900°C and surprised by the toughness of the sample after he observed a white material that is physically unchanged from the heat treatment (Zanotto, 1953). In recent years, development of glass ceramics have been given a lot of attention by the researchers due to the various different waste can be used to produce the glass ceramics. Not only because of it is environmental friendly by using waste materials, but also worthy as the glass ceramics produced have low thermal expansion coefficient, good transparency in the visible wavelength range for cooking ware, high in strength, chemically and physically high durability and low hardness for dental applications. Forming a glass ceramic is a heterogeneous transformation where it involves two stages, firstly a nucleation stage and next is a growth stage. During the nucleation process, stable volume and crystalline phases are formed in the parent glass. The rate of nucleation depends on the temperature (Janković et al., 2014). Once a stable nucleus is formed, crystal starts to grow in which the atoms or molecules in the sample move across the glass crystal. Other than that, there is also a single stage method where in this study, by using solid state method, where the powdered sample was compacted and sintered at high temperature to grow the crystallinity. This method ensures that the sample is fully sintered but not too rapidly that may cause unacceptable amount of porosity.

1.5 Problem Statements

In recent industrial development, silicate glasses are classified in a large group of inorganic optical based materials with other compounds such as aluminates, phosphates, borates, fluorides and other oxides that are widely used considering their potential in glass phosphor industries. Among those mentioned inorganic compounds, silicate glasses exhibit superior chemical resistance and are optically transparent at the excitation and lasing wavelengths (Zaid et al., 2012). However, the only mediocre of silicate glasses is its high melting temperature about 1700°C due to high purity silica content which requires high amount of energy resulting in high production cost (Omar et al., 2016d). Therefore, this can be overcome by replacing the conventional silica-rich sand used to synthesize silicate glass by other suitable silica source which can lower the melting temperature of high purity silicate glass. Recently, researchers have been using agricultural waste products such as rice husks ash, coconut shell ash and palm oil ash practically as a substituent of silica source for the glass phosphor (Madakson et al., 2012; Prasara-a & Gheewala, 2017; Lee et al., 2017a). Among all wastes, rice husk is believed to contain high percentage of silica content in the white rice husk ash (WRHA) compared to other wastes (Fernandes et al., 2016). Hence with that, it can lower the cost of production as rice husks are one of a major waste products that can be easily obtained in most countries around Asia (De Silva & Surangi, 2017). Furthermore, it may help to reduce waste abundance that can leads to environmental issues by fully utilize the waste products into a good benefit rather than abandoning the unwanted rice husks to be burned in open air by the farmers.

In course of previous investigation, silicate glasses are often fabricated and creatively modified by the researchers in order to study the ability of this type of glass to go beyond ordinary expectations (Kilcup et al., 2015). In facts, the inorganic compound can be added with zinc oxide (ZnO) to produce glass composite such as zinc aluminate glass, zinc borate glass and zinc phosphate glass which they turned out to be great promising glass phosphor for various applications (Hern et al., 2003; Davesnne et al., 2014; El Ghoul & El Mir, 2016). Perhaps, this is because zinc oxide (ZnO) is one of the essential and commercialized material which has been used widely in so many fields with different purposes such as cosmetics, medical additives, buildings, chemical catalyst, rubbers, electronic and etc (Bharat et al., 2019). The usage benefits of ZnO in modern solid state have intrigued the researchers to invent more on new technologies, while fabricating it as glass phosphor for optoelectronic applications is still under investigation (Zaid et al., 2016). Its wide band gap (3.37 eV) energy with low resistance at room temperature gives tremendous potential for it to have tendency in absorbing visible light within ultra violet (UV) range (Li et al., 2009). Other than that, ZnO is also varies in types and particle sizes which has been chosen differently according to their specific uses. The nanoparticles structured ZnO are rarely used due to its high chemical cost compared to the conventional ZnO powders. However, this highly cost but worth irresistible benefits of nanoparticle ZnO is said to be antibacterial hygienic agent, fast catalytic reactivity, thermally stable, chemically and optically better in performance owing to its large total surface area (Gunalan et al., 2013). The fine particles also help in better absorbing or scattering the UV radiation and useful for light emitting technologies, solar cells and piezoelectric devices (Kuo et al., 2010).

According to that fact, the silicate glass also would likely suitable to mix up with ZnO to create zinc silicate glass system (ZnO-SiO_2) for wide range of electronic appliances in our daily life. The fabrication of ZnO-SiO_2 glass has encountered much attention among researchers because of their excellent glass forming nature and its ability to become a great host matrix due to its high chemical stability and physically stable properties (Wang et al., 2015). Their specialties can be exposed more when being doped or added with ions from lanthanides group such as cerium (Ce^{3+}), europium (Eu^{3+}), erbium (Er^{3+}), neodymium (Nd^{3+}), thullium (Tm^{3+}), samarium (Sm^{3+}) and ytterbium (Yb^{3+}) where they can emit various luminescent colours which are useful for optical applications (Rasdi et al., 2017a). This is because of their location at 4*f* shells that well surrounded by $5s^2$ and $5p^6$ orbitals had dominated their sharp optical spectra (Chimalawong et al., 2012). The study of rare earth doped glasses is very much important as the change in consequent properties related to glass transition and softening temperature, physical, mechanical and refractive index were all influenced by the change in ionic radii in the structural system (Wang et al., 2011). Among all rare earths ions, Eu^{3+} is one of the effective activators which can be found to be in two oxidation states of Eu^{3+} and Eu^{2+} depending on preparation conditions (Davesnne et al., 2014). From practical viewpoint, europium is the most useful for numerous applications as a result of its ability to absorb blue light excitation and emit broad emission bands within 250 nm to 750 nm and beyond (Cherepy et al., 2016). Moreover, Eu^{3+} doped phosphor approach is also needed to produce white light emitting diodes (W-LEDs) and other devices due to luminescence efficiencies in red spectral wavelength region mainly from ${}^5D_0 \rightarrow {}^7F_{1,2}$ (Janković et al., 2014). However, there were lack of studies in adding Eu^{3+} into $ZnO-SiO_2$ glass phosphor derived from waste rice husks which surely has its own luminescent properties.

For instance, this $ZnO-SiO_2$ glass phosphor is believed to be a great host material for numerous applications related to optoelectronics, sensors, lasing and light emitting diodes due to its large band gap, high chemical stability and good transparency in UV region (Rashid et al., 2017). However, it must in line and considering the accurate composition, thermal sustainability, physical and structural endurance of the glass properties to produce a promising and good glass phosphor. Therefore, the $ZnO-SiO_2$ glass phosphors need to be conducted or annealed at certain temperature to transform glass into glass ceramics for better properties. Zinc silicate (Zn_2SiO_4) glass ceramics are generally used as the main host material to exhibit luminescent properties due to the wide and large energy band gap also excellent transparency in UV region (Zhang et al., 2001). The luminescence properties can be enhanced and encouraged by doping the glass ceramic phosphor with either rare earth ions or transition metal ions (Bharat et al., 2014). In this study, europium oxide (Eu_2O_3) was used as doping agent as it exhibits good emission within red spectral region (Syamimi et al., 2014). It is because of sharp luminescence they exhibit from 4*f*-5*d* orbital configurations (Omar et al., 2017)

Since all the materials needed to produce Zn_2SiO_4 sample are designed and figured out, the sample preparation method should be simple and able to produce in a large amount. These are to ensure that the method used is not complicated and time consuming also low in cost in the aspect of equipment. Thus in this research, solid state method has been selected to prepare the Zn_2SiO_4 samples of all other methods. Solid state method (Omar et al., 2017) is one of various methods used to fabricate the Zn_2SiO_4 phosphor other than several chemical methods such as the sol-gel method (Rasdi et al., 2017a), spray pyrolysis method (Sivakumar et al., 2012), hydrothermal method (Xu *et al*., 2010) and co-precipitation method (Rivera-Enríquez et al., 2016). Among these methods, solid state method is simpler that also save energy and time to produce large scale of Zn_2SiO_4 sample compared to chemical methods. This is because chemical methods have complicated steps where they need longer period of time to prepare the samples. Besides, chemical methods require more chemicals and expensive equipment to handle the sample preparation thus increase the research cost.

1.6 Objectives

1. To synthesis willemite phosphor (Zn_2SiO_4) doped with europium ions (Eu^{3+}) by using conventional melt-quenching and solid state method derived from waste rice husk ash.
2. To study the effect of different sintering temperatures towards structural and optical properties of zinc silicate doped with europium ions (Eu^{3+}).
3. To study the effect of doping towards structural and optical properties of zinc silicates doped with europium ions (Eu^{3+}).

1.7 Thesis Outlines

This thesis starts with the introduction of zinc silicate and the properties of important raw materials used in this research which are the WRHA and rare earth europium ions in Chapter 1. In Chapter 2, previous and current researches by other researchers will be reviewed to give more information related to this research. Next in Chapter 3, the methodology of this research including all calculations, materials and apparatus used to obtain zinc silicate doped with europium ions samples will be explained in this chapter. Then, in Chapter 4, each and every result obtained from the characterization will be analysed and elaborated comprehensively in this chapter. The results include the effects of different sintering temperatures towards the structural and optical properties of the samples. Finally, the last chapter will conclude this study and suggestions for any future works will be given in Chapter 5.

1.8 Scope of Studies

This project covers the scope of studies as below:

1. Fabrication of zinc silicate doped with europium ions prepared from waste white rice husk ashes, zinc oxide nanopowders, and europium oxide powders where the stoichiometric equation $(ZnO_{0.6}WRHA_{0.4})_{1-x}$ where x = 0.01, 0.02, 0.03, 0.04 and 0.05.
2. Different sintering temperatures from 600°C to 1000°C were applied to sinter the zinc silicate doped with europium ions glass ceramic.
3. Analysing the chemical composition of white rice husk ash by using X-ray fluorescence (XRF).
4. Analysing the structural properties which include phase formations, bond formations and surface morphologies of the zinc silicate doped with europium ions samples using X-ray diffractometer (XRD), Field emission scanning electron microscopy (FESEM) and Fourier transform infrared spectroscopy (FTIR).
5. Analysing the optical properties which include absorption, optical band gap and luminescence intensity of the samples by using ultraviolet visible spectroscopy (UV-Vis-NIR) and Photoluminescence spectroscopy (PL) characterization.

REFERENCES

Abo-Mosallam, H.A., Darwish, H., & Salman, S.M. (2010). Crystallization characteristic and properties of some zinc containing soda lime silicate glasses. *Journal of Materials Science: Materials in Electronics*. *21*, 889–896.

Ahmadi, F., Hussin, R., & Ghoshal, S.K. (2016). Judd-Ofelt intensity parameters of samarium-doped magnesium zinc sulfophosphate glass. *Journal of Non-Crystalline Solids*. *448*, 43–51.

Ahmadi, T.S., Haase, M., & Weller, H. (2000). Low-temperature synthesis of pure and Mn-doped willemite phosphor (Zn_2SiO_4:Mn) in aqueous medium. *Material Research Bulletin*. *35*, 1869–1879.

Alibe, I.M., Matori, K.A., Ab, H., Sidek, A., Yaakob, Y., Rashid, U., Zaid, M.H.M, Nasir, S., & Mohammed, M. (2018). Effects of polyvinylpyrrolidone on structural and optical properties of willemite semiconductor nanoparticles by polymer thermal treatment method. *Journal of Thermal Analysis and Calorimetry*. *7*, 2249–2268.

Almeida, M.P.S., Nunes, L.M., Gonçalves, R.R., Ribeiro, S.J.L., & Maia, L.J.Q. (2016). Structural properties and visible emission of Eu^{3+}-activated SiO_2–ZnO–TiO_2 powders prepared by a soft chemical process. *Optical Materials*. *62*, 438–446.

Al-Nidawi, A.J.A., Matori, K.A., Zakaria, A., & Zaid, M. H.M. (2017). Effect of MnO_2 doped on physical, structure and optical properties of zinc silicate glasses from waste rice husk ash. *Results in Physics*. *7*, 955–961.

Babu, B.C., & Buddhudu, S. (2013). Dielectric properties of willemite α-Zn_2SiO_4 nano powders by sol-gel method. *Physics Procedia*. *49*, 128–136.

Babu, B.C., & Buddhudu, S. (2014a). Analysis of structural and electrical properties of Ni^{2+}:Zn_2SiO_4 ceramic powders by sol–gel method. *Journal of Sol-Gel Science and Technology*. *70*, 405–415.

Babu, B.C., & Buddhudu, S. (2014b). Emission spectra of Tb^{3+}:Zn_2SiO_4 and Eu^{3+}:Zn_2SiO_4 sol-gel powder phosphors. *Journal of Spectroscopy and Dynamics*. *4*, 1-8.

Babu, K.S., Reddy, A.R., Reddy, K.V., & Mallika, A.N. (2014). High thermal annealing effect on structural and optical properties of ZnO-SiO nanocomposite. *Materials Science in Semiconductor Processing*. *27*, 643–648.

Belhouni, A., Gredin, P., Mortier, M., & Diaf, M. (2018). Structural , thermal and optical investigations of PbF_2:Eu^{3+} particles prepared by co-precipitation method. *Optical Materials*. *83*, 321–327.

Bharat, L.K., Jeon, Y. Il, & Yu, J.S. (2014). Synthesis and luminescent properties of trivalent rare-earth (Eu^{3+}, Tb^{3+}) ions doped nanocrystalline $AgLa(PO_3)_4$ polyphosphates. *Journal of Alloys and Compounds*. *614*, 443–447.

Bharat, T. C., Mondal, S., Gupta, H. S., Singh, P. K., & Das, A. K. (2019). Synthesis of doped zinc oxide nanoparticles : A review. *Materials Today: Proceedings*. *11*, 767–775.

Boda, R., Shareefuddin, M., Chary, M.N., & Sayanna, R. (2016). FTIR and optical properties of europium doped lithium zinc bismuth borate glasses. *Materials Today: Proceedings*. *3*, 1914–1922.

Braziulis, G., Stankeviciute, R., & Zalga, A. (2014). Sol-gel derived europium doped $CaMoO_4:Eu^{3+}$ with complex microstructural and optical properties. *Materials Science*. *20*, 90–96.

Cetinkaya Colak, S., Akyuz, I., & Atay, F. (2016). On the dual role of ZnO in zinc-borate glasses. *Journal of Non-Crystalline Solids*. *432*, 406–412.

Cho, D., Lee, S., Lim, J., Baek, S., & Park, I. (2017). Visible light-emission from Eu-doped ZnAl layered-double hydroxide. *Ceramics International*. *43*, 9686–9690.

Cherepy, N. J., Payne, S. A., Harvey, N. M., Åberg, D., Seeley, Z. M., Holliday, K. S., Lograsso, T. A. (2016). Red-emitting manganese-doped aluminum nitride phosphor. *Optical Materials*. *54*, 14–21.

Chimalawong, P., Kirdsiri, K., Kaewkhao, J., & Limsuwan, P. (2012). Investigation on the physical and optical properties of Dy^{3+} doped soda-lime-silicate glasses. *Procedia Engineering*. *32*, 690–698.

Chrapon, J. (2012). The microstructure of erbium–ytterbium co-doped oxyfluoride glass–ceramic optical fibers. *Optical Materials*. *34*, 944–950.

Cinkaya, H., Eryurek, G., Bilir, G., Erdem, M., & Di, B. (2017). Effect of pressure and temperature on the white light produced by ytterbium (III) doped and undoped yttrium silicate nanopowders excited by a laser diode. *Journal of Luminescence*. *181*, 321–326.

Davesnne, C., Ziani, A., Labbé, C., Marie, P., Frilay, C., & Portier, X. (2014). Energy transfer mechanism between terbium and europium ions in zinc oxide and zinc silicates thin fi lms. *Thin Solid Films*. *553*, 33–37.

De Silva, G.H.M.J.S., & Surangi, M.L.C. (2017). Effect of waste rice husk ash on structural, thermal and run-off properties of clay roof tiles. *Construction and Building Materials*. *154*, 251–257.

Deng, H., Hu, X., Andy, H., Luo, B., & Wang, W. (2016). Improved pore-structure characterization in shale formations with FESEM technique. *Journal of Natural Gas Science and Engineering*. *35*, 309–319.

Dias, J.D.M., Melo, G.H.A., Lodi, T.A., Carvalho, J.O., Filho, P.F.F., & Barboza, M.J. (2016). Thermal and structural properties of Nd_2O_3-doped calcium boroaluminate glasses. *Journal of Rare Earths*. *34*, 521–528.

Effendy, N., Abdul Wahab, Z., Mohamed Kamari, H., Matori, K.A., Hj. Ab Aziz, S., & Zaid, M.H.M. (2016). Structural and optical properties of Er^{3+}-doped willemite glass-ceramics from waste materials. *Optik*. *127*, 11698–11705.

Effendy, N., Hj, S., Aziz, A., Mohamed, H., Amin, K., Ha, M., & Zaid, M. (2019). Enhanced green photoluminescence of erbium doped Zn_2SiO_4 glass- ceramics as phosphor in optoelectronic devices. *Journal of Alloy and Compounds*. *783*, 441–447.

El Ghoul, J., Ghiloufi, I., & El Mir, L. (2016). Effect of annealing temperature on the luminescence properties of Zn_2SiO_4:V nanocomposite. *Journal of Luminescence*. *170*, 288–292.

El Mir, L., Omri, K., & El Ghoul, J. (2015). Effect of crystallographic phase on green and yellow emissions in Mn-doped zinc silicate nanoparticles incorporated in silica host matrix. *Superlattices and Microstructures*. *85*, 180–184.

Eltayeb, S., Liu, C., Zhao, Z., Li, K., & Zhao, X. (2018). Structure and optical properties of ZnO/Zn_2SiO_4 composite thin films containing Eu^{3+} ions. *Thin Solid Films*. *668*, 1–8.

Fernandes, I.J., Calheiro, D., Kieling, A.G., Moraes, C.A.M., Rocha, T.L.A.C., Brehm, F.A., & Modolo, R.C.E. (2016). Characterization of rice husk ash produced using different biomass combustion techniques for energy. *Fuel*. *165*, 351–359.

Gaft, M., Reisfeld, R., & Panczer, G. (2005). Modern luminescence spectroscopy of minerals and materials. Springer Science & Business Media.

Gunalan, S., Sivaraj, R., & Rajendran, V. (2013). Green synthesized ZnO nanoparticles against bacterial and fungal pathogens. *Progress in Natural Science: Materials International*. *22*, 693–700.

Halimah, M.K., Ami Hazlin, M.N., & Muhammad, F.D. (2018). Experimental and theoretical approach on the optical properties of zinc borotellurite glass doped with dysprosium oxide. *Spectrochimica Acta-Part A: Molecular and Biomolecular Spectroscopy*. *195*, 128–135.

Hee, C., Chan, Y., Youl, K., & Gill, J. (2005). Phosphor layer formed from the Zn_2SiO_4:Mn phosphor particles with spherical shape and fine size. *Materials Science and Engineering B*. *117*, 210–215.

Hegde, V., Viswanath, C.S.D., Upadhyaya, V., Mahato, K.K., & Kamath, S.D. (2017). Red light emission from europium doped zinc sodium bismuth borate glasses. *Physica B: Physics of Condensed Matter*. *527*, 35–43.

Hern, C.D., Garc, M., Mart, E., & Guzm, J. (2003). Characterization of europium doped zinc aluminate luminescent coatings synthesized by ultrasonic spray pyrolysis process. *Optical Materials*. *22*, 345–351.

Hsieh, Y., Tsai, Y., He, J., Yang, P., & Lin, H. (2017). Rice husk agricultural waste-derived low ionic content carbon–silica nanocomposite for green reinforced epoxy resin electronic packaging material. *Journal of the Taiwan Institute of Chemical Engineers*. *78*, 493–499.

Ivankov, A., Seekamp, J., & Bauhofer, W. (2006). Optical properties of Eu^{3+}-doped zinc borate glasses. *Journal of Luminescence*. *121*, 123–131.

Janković, B., Marinović-Cincović, M., & Dramićanin, M.D. (2014). Study of non-isothermal crystallization of Eu^{3+} doped Zn_2SiO_4 powders through the application of various macrokinetic models. *Journal of Alloys and Compounds*. *587*, 398–414.

Jeon, Y.Il, Bharat, L.K., & Yu, J.S. (2015). Eu^{3+} ions co-doped CLPO:Dy^{3+} single phase white-light emitting phosphors for near UV-based white LEDs. *Journal of Alloys* *and Compounds*. *649*, 531–536.

Kang, Y.C., & Park, S.B. (2000). Zn_2SiO_4:Mn phosphor particles prepared by spray pyrolysis using a filter expansion aerosol generator. *Materials Research Bulletin*. *35*, 1143–1151.

Kilcup, N., Werner-Zwanziger, U., Tonkopi, E., & Boyd, D. (2015). Unanticipated stabilization of zinc-silicate glasses by addition of lanthanum: Implications for therapeutic inorganic ion delivery systems. *Journal of Non-Crystalline Solids*. *429*, 83–92.

Klimesz, B., Lisiecki, R., & Ryba-Romanowski, W. (2017). Thermal and optical properties of oxyfluorotellurite glasses doped with europium ions. *Journal of Alloys and Compounds*. *704*, 180–186.

Kojima, Y., Numazawa, M., Kamei, S., & Nishimiya, N. (2012). Fluorescence properties and synthesis of green-emitting Tb^{3+}-activated amorphous calcium silicate phosphor by ultraviolet irradiation of 378 nm. *International Journal of Optics*. *2012*, 3–8.

Krishna, R., Haranath, D., Singh, S.P., Chander, H., Pandey, A.C., & Kanjilal, D. (2007). Synthesis and improved photoluminescence of Eu:ZnO phosphor. *Journal of Materials Science*. *42*, 10047–10051.

Krsmanovi, R.Ć., Anti, Ž.Ć., Marinovi, M.Ć.Ć., & Anin, M.D.D.Ć. (2009). Samarium and terbium doped Zn_2SiO_4 powders obtained by polymer induced sol-gel synthesis. *Journal of Optoelectronics and Advanced Materials-Symposia*. *1*, 37–41.

Kuo, C., Wang, C., Ko, H., Hwang, W., & Chang, K. (2010). Synthesis of zinc oxide nanocrystalline powders for cosmetic applications, *Ceramics International*. *36*, 693–698.

Lakshminarayana, G., Baki, S.O., Lira, A., Kityk, I.V., & Mahdi, M.A. (2017). Structural, thermal, and optical absorption studies of Er^{3+}, Tm^{3+}, and Pr^{3+}-doped borotellurite glasses. *Journal of Non-Crystalline Solids*. *459*, 150–159.

Lakshminarayana, G., & Qiu, J. (2009). Photoluminescence of Eu^{3+} , Tb^{3+} and Tm^{3+}-doped transparent SiO_2–Al_2O_3–LiF–GdF_3 glass ceramics. *Journal of Alloys and Compounds*. *476*, 720–727.

Lee, C.S., Matori, K.A., Ab Aziz, S.H., Kamari, H.M., Ismail, I., & Zaid, M.H.M. (2017a). Fabrication and characterization of glass and glass-ceramic from rice husk ash as a potent material for opto-electronic applications. *Journal of Materials Science: Materials in Electronics*. *28*, 17611–17621.

Lee, C.S., Matori, K.A., Ab Aziz, S.H., Mohamed Kamari, H., Ismail, I., & Zaid, M.H.M. (2017b). Influence of zinc oxide on the physical, structural and optical band gap of zinc silicate glass system from waste rice husk ash. *Optik*. *136*, 129–135.

Lee, T., Othman, R., & Yeoh, F.Y. (2013). Development of photoluminescent glass derived from rice husk. *Biomass and Bioenergy*. *59*, 380–392.

Li, J., Fan, H., Jia, X., Chen, J., Cao, Z., & Chen, X. (2009). Electrostatic spray deposited polycrystalline zinc oxide films for ultraviolet luminescence device applications. *Journal of Alloys and Compounds*. *481*, 735–739.

Loehman, R.E. (2010). Characterization of ceramics. New York. Momentum Press, LLC.

Madakson, P. B., Yawas, D. S., & Apasi, A. (2012). Characterization of coconut shell ash for potential utilization in metal matrix composites for automotive applications. *International Journal of Engineering Science and Technology*. *4*, 1190–1198

Mäntele, W., & Deniz, E. (2017). UV–VIS absorption spectroscopy: Lambert-Beer reloaded. *Spectrochimica Acta Part A : Molecular and Biomolecular Spectroscopy*. *173*, 965–968.

Marinovi, M., Jankovi, B., Mili, B., Anti, Ž., Krsmanovi, R., & Drami, M.D. (2013). The comparative kinetic analysis of the non-isothermal crystallization process of Eu^{3+} doped Zn_2SiO_4 powders prepared via polymer induced sol-gel method, *Powder Technology*. *249*, 497–512.

Mariselvam, K., Kumar, R.A., & Suresh, K. (2018). Optical properties of Nd^{3+} doped barium lithium fluoroborate glasses for near-infrared (NIR) emission. *Physica B: Physics of Condensed Matter*. *534*, 68–75.

Mbule, P.S., Mothudi, B.M., & Dhlamini, M.S. (2017). Mn^{2+}-Eu^{3+}-Dy^{3+} doped and co-doped Zn_2SiO_4 nanophosphors: Study of the structure, photoluminescence and surface properties. *Journal of Luminescence*. *192*, 853–859.

Mesfar, M., Horchani-naifer, K., Abdelhedi, M., Dammak, M., & Ferid, M. (2013). Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy Spectroscopic properties of Eu^{3+} doped $RbLaP_4O_{12}$ powders. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. *114*, 154–158.

Mindru, I., Gingasu, D., Patron, L., Marinescu, G., Calderon-Moreno, J.M., Diamandescu, L., Secu, M. & Oprea, O. (2017). Tb^{3+}-doped alkaline-earth aluminates: Synthesis, characterization and optical properties. *Materials Research Bulletin*. *85*, 240–248.

Mohan, S., Kaur, S., Singh, D.P., & Kaur, P. (2017). Structural and luminescence properties of samarium doped lead alumino borate glasses. *Optical Materials*. *73*, 223–233.

Murata, T., Moriyama, Y., & Morinaga, K. (2000). Relationship between the local structure and spontaneous emission probability of Er^{3+} in silicate, borate, and phosphate glasses. *Science and Technology of Advanced Materials*. *1*, 139–145.

Natarajan, V., Murthy, K.V.R., & Kumar, M.L.J. (2005). Photoluminescence investigations of Zn_2SiO_4 co-doped with Eu^{3+} and Tb^{3+} ions. *Solid State Communications*. *134*, 261–264.

Nazrin, S. N., Halimah, M.K., Muhammad, F.D., Yip, J.S., Hasnimulyati, L., Faznny, M.F., Hazlin, M.A., & Zaitizila, I. (2018). The effect of erbium oxide in physical and structural properties of zinc tellurite glass system. *Journal of Non-Crystalline Solids*. *490*, 35–43.

Omar, N.A.S., Fen, Y.W., & Matori, K.A. (2016a). Photoluminescence properties of Eu^{3+}-doped low cost zinc silicate based glass ceramics. *Optik*. *127*, 3727–3729.

Omar, N.A.S., Fen, Y.W., & Matori, K.A. (2017). Europium doped low cost Zn_2SiO_4 based glass ceramics: A study on fabrication, structural, energy band gap and luminescence properties. *Materials Science in Semiconductor Processing*. *61*, 27–34.

Omar, N.A.S., Fen, Y.W., Matori, K.A., Aziz, S.H.A., Alassan, Z.N., & Samsudin, N.F. (2016b). Development and characterization studies of Eu^{3+}-doped Zn_2SiO_4 phosphors with waste silicate sources. *Procedia Chemistry*. *19*, 21–29.

Omar, N.A.S., Fen, Y.W., Matori, K.A., Zaid, M.H.M., Norhafizah, M.R., Nurzilla, M., & Zamratul, M.I.M. (2016c). Synthesis and optical properties of europium doped zinc silicate prepared using low cost solid state reaction method. *Journal of Materials Science: Materials in Electronics*. *27*, 1092–1099.

Omar, N.A.S., Fen, Y.W., Matori, K.A., Zaid, M.H.M., & Samsudin, N. F. (2016d). Structural and optical properties of Eu^{3+} activated low cost zinc soda lime silica glasses. *Results in Physics*. *6*, 640–644.

Omri, K., Lemine, O.M., & El Mir, L. (2017). Mn doped zinc silicate nanophosphor with bifunctionality of green-yellow emission and magnetic properties. *Ceramics International*. *43*, 6585–6591.

Padlyak, B.V., Kindrat, I.I., Protsiuk, V.O., & Drzewiecki, A. (2014). Optical spectroscopy of $Li_2B_4O_7$, CaB_4O_7 and $LiCaBO_3$ borate glasses doped with europium. *Ukrainian Journal of Physical Optics*. *15*, 103–117.

Patra, A., Baker, G.A., & Baker, S.N. (2004). Synthesis and luminescence study of Eu^{3+} in Zn_2SiO_4 nanocrystals. *Optical Materials*. *27*, 15–20.

Petrovic, D.M., Nikolic, M., & Dramic, M.D. (2011). Judd–Ofelt analysis of luminescence emission from $Zn_2SiO_4{:}Eu^{3+}$ nanoparticles obtained by a polymer-assisted sol–gel method. *Physica B: Condensed Matter*. *406*, 2319–2322.

Pode, R. (2016). Potential applications of rice husk ash waste from rice husk biomass power plant. *Renewable and Sustainable Energy Reviews*. *53*, 1468–1485.

Prasara-a, J., & Gheewala, S. H. (2017). Sustainable utilization of rice husk ash from power plants : A review. *Journal of Cleaner Production*. *167*, 1020–1028.

Qin, L., Xu, C., Huang, Y., Kim, S.Il, & Seo, H.J. (2014). Spectroscopic and structural features of Eu^{3+}-doped zinc pyrophosphate ceramic. *Ceramics International*. *40*, 1605–1611.

Raju, C.N., Sailaja, S., Hemasundara Raju, S., Dhoble, S.J., Rambabu, U., Jho, Y.D., & Sudhakar Reddy, S. (2014). Emission analysis of CdO-Bi_2O_3-B_2O_3 glasses doped with Eu^{3+} and Tb^{3+}. *Ceramics International*. *40*, 7701–7709.

Rasdi, N.M., Fen, Y.W., Azis, R.S., & Omar, N.A.S. (2017a). Photoluminescence studies of cobalt (II) doped zinc silicate nanophosphors prepared via sol-gel method. *Optik*. *149*, 409–415.

Rasdi, N.M., Fen, Y.W., Omar, N.A.S., Azis, R.S., & Zaid, M.H.M. (2017b). Effects of cobalt doping on structural, morphological, and optical properties of Zn_2SiO_4 nanophosphors prepared by sol-gel method. *Results in Physics*. *7*, 3820–3825.

Rashid, S.S.A., Aziz, S.H.A., Matori, K.A., Zaid, M.H.M., & Mohamed, N. (2017). Comprehensive study on effect of sintering temperature on the physical, structural and optical properties of Er^{3+} doped ZnO-GSLS glasses. *Results in Physics*. *7*, 2224–2231.

Ravikumar, M., Ganesh, V., Shkir, M., Chandramohan, R., Arun, K.D., Valanarasu, S., Kathalingam, A., & Alfaify, S. (2018). Fabrication of Eu doped CdO (Al/Eu-nCdO/p-Si/Al) photodiodes by perfume atomizer based spray technique for opto-electronic applications. *Journal of Molecular Structure*. *1160*, 311–318.

Rifai, S.A.Al, & Kulnitskiy, B.A. (2013). Microstructural and optical properties of europium-doped zinc oxide nanowires. *Journal of Physical and Chemistry of Solids*. *74*, 1733–1738.

Rivera-Enríquez, C.E., Fernández-Osorio, A., & Chávez-Fernández, J. (2016). Luminescence properties of α- and β-Zn_2SiO_4:Mn nanoparticles prepared by a co-precipitation method. *Journal of Alloys and Compounds*. *688*, 775-782.

Sahu, I.P., Bisen, D.P., Brahme, N., & Tamrakar, R.K. (2015). Photoluminescence properties of europium doped di-strontium magnesium di-silicate phosphor by solid state reaction method. *Journal of Radiation Research and Applied Sciences*. *8*, 104–109.

Samsudin, N.F., Matori, K.A., Wahab, Z.A., Liew, J.Y.C., Fen, Y.W., Aziz, S.H.A., & Zaid, M.H.M. (2016). Low cost phosphors: Structural and photoluminescence properties of Mn^{2+}-doped willemite glass-ceramics. *Optik*. *127*(19), 8076–8081.

Sarrigani, G.V., Quah, H.J., Lim, W.F., Matori, K.A., Mohd Razali, N.S., Kharazmi, A., Hashim, M., & Bahari, H. R. (2015). Characterization of waste material derived willemite-based glass-ceramics doped with erbium. *Advances in Materials Science and Engineering*. *2015*, 1–8.

Shackley, M.S. (2011). An introduction to X-ray fluorescence (XRF) analysis in archaeology. *X-Ray fluorescence spectrometry (XRF) in geoarchaeology*. (pp. 1-231). Springer Science & Business Media.

Shajan, D., Murugasen, P., & Sagadevan, S. (2017). Studies on structural, optical and spectral properties of europium oxide doped phosphate glasses. *Optik-International Journal for Light and Electron Optics*. *136*, 165–171.

Shen, P., & Lin, C.C. (1994). Sol-gel synthesis of zinc orthosilicate. *Journal of Non-Crystalline Solids*. *171*, 281–289.

Sivakumar, V., Lakshmanan, A., Kalpana, S., Sangeetha Rani, R., Satheesh Kumar, R., & Jose, M.T. (2012). Low-temperature synthesis of Zn_2SiO_4:Mn green photoluminescence phosphor. *Journal of Luminescence*. *132*, 1917–1920.

Speghini, A., & Caldi, U. (2016). Blue and white light emission in Tm^{3+} and Tm^{3+}/Dy^{3+} doped zinc phosphate glasses upon UV light excitation. *Optical Materials*. *58*, 183–187.

Stochero, N.P., Marangon, E., Nunes, A.S., & Tier, M.D. (2017). Development of refractory ceramics from residual silica derived from rice husk ash and steel fibres. *Ceramics International*. *43*, 13875–13880.

Stopper, L., Bălşeanu, T. A., Cătălin, B., Rogoveanu, O. C., Mogoantă, L., & Scheller, A. (2018). Microglia morphology in the physiological and diseased brain – From fixed tissue to in vivo conditions. *Romanian Journal of Morphology and Embryology*. *59*(1), 7–12.

Su, J., Yang, X., Wang, L., Wang, C., & Ji, Y. (2011). Preparation, structure and optical properties of Pr:Gd_2O_3 phosphor. *Materials Letters*. *65*, 2852–2854.

Sun, J., Zhang, X., & Li, T. (2018). New Eu^{2+} -activated borophosphate phosphors $Ba_3(ZnB_5O_{10})PO_4$ for near-ultraviolet-pumped white light-emitting diodes. *Materials Letters*. *212*, 343–345.

Takesue, M., Hayashi, H., & Smith, R.L. (2009a). Thermal and chemical methods for producing zinc silicate (willemite): A review. *Progress in Crystal Growth and Characterization of Materials*. *55*, 98–124.

Takesue, M., Shimoyama, K., Shibuki, K., Suino, A., Hakuta, Y., Hayashi, H., Ohishi, Y., & Jr, S. (2009b). Formation of zinc silicate in supercritical water followed with in situ synchrotron radiation X-ray diffraction. *The Journal of Supercritical Fluids*. *49*, 351–355.

Tarafder, A., Rahaman, A., Mukhopadhyay, S., & Karmakar, B. (2014). Fabrication and enhanced photoluminescence properties of Sm^{3+}-doped ZnO-Al_2O_3-B_2O_3-SiO_2 glass derived willemite glass-ceramic nanocomposites. *Optical Materials*. *36*, 1463–1470.

Taxak, V.B., & Khatkar, S.P. (2013). Synthesis, structural and optical properties of Eu^{3+}-doped $Ca_2V_2O_7$ nanophosphors. *Current Applied Physics*. *13*, 594–598.

Verma, R.K., Rai, D.K., & Rai, S.B. (2011). Investigation of structural properties and its effect on optical properties: Yb^{3+}/Tb^{3+} co-doped in aluminum silicate glass. *Journal of Alloys and Compounds*. *509*, 5591–5595.

Vijaya, N., & Jayasankar, C.K. (2013). Structural and spectroscopic properties of Eu^{3+}-doped zinc fluorophosphate glasses. *Journal of Molecular Structure*. *1036*, 42–50.

Wagh, A., Manjunath, K., Hegde, V., & Kamath, S.D. (2018). Optik gamma irradiation on bismuth borate glasses doped by Eu^{3+} ions: Structural, optical and mechanical investigations. *Optik - International Journal for Light and Electron Optics*. *160*, 298–306.

Wang, Q., & Li, Y. (2011). Wet chemical synthesis and sintering of rare earth phosphate ceramics ($Y_{0.3}Ce_{0.7}PO_4$:Tb) and their green luminescence properties. *Journal of Non-Crystalline Solids*. *357*, 1008–1012.

Wang, Y., Zhu, G., Xin, S., Wang, Q., Li, Y., Wu, Q., Geng, W. (2015). Recent development in rare earth doped phosphors for white light emitting diodes. *Journal of Rare Earths*. *33*, 1–12.

Wu, Y., Sun, Z., Ruan, K., Xu, Y., & Zhang, H. (2014). Enhancing photoluminescence with Li-doped $CaTiO_3:Eu^{3+}$ red phosphors prepared by solid state synthesis. *Journal of Luminescence*. *155*, 269–274.

Xie, W., Wang, Y., Zou, C., Quan, J., & Shao, L. (2015). A red-emitting long-afterglow phosphor of Eu^{3+}, Ho^{3+} co-doped Y_2O_3. *Journal of Alloys and Compounds*. *619*, 244–247.

Xu, G.Q., Xu, H.T., Zheng, Z.X., & Wu, Y.C. (2010). Preparation and characterization of Zn_2SiO_4: Mn phosphors with hydrothermal methods. *Journal of Luminescence*. *130*, 1717–1720.

Yang, J., Li, X., Lang, J., Yang, L., Wei, M., Gao, M., Liu, Y., & Cao, J. (2011a). Synthesis and optical properties of Eu-doped ZnO nanosheets by hydrothermal method. *Materials Science in Semiconductor Processing*. *14*, 247–252.

Yang, J., Sun, Y., Chen, Z., & Zhao, X. (2011b). Hydrothermal synthesis and optical properties of zinc silicate hierarchical superstructures. *Materials Letters*. *65*, 3030–3033.

Yang, R., Liu, H., Wang, Y., Jiang, W., Hao, X., Zhan, J., & Liu, S. (2012). Structure and properties of ZnO-containing lithium-iron-phosphate glasses. *Journal of Alloys and Compounds*. *513*, 97–100.

You, M., Xu, J., Zhang, Z., & Zhou, Y. (2014). Eu^{3+}-doped $CdWO_4$ phosphor for red-light emission: Hydrothermal preparation and blue light excitation. *Ceramics International*. *40*, 16189–16194.

Zaid, M.H.M., Matori, K.A., Aziz, S.H.A, Zakaria, A., & Ghazali, M.S.M. (2012). Effect of ZnO on the physical properties and optical band gap of soda lime silicate glass. *International Journal of Molecular Sciences*. *13*, 7550–7558.

Zaid, M.H.M., Matori, K.A., Quah, H.J., Lim, W.F., Sidek, H.A.A., Halimah, M.K., & Wahab, Z.A. (2015). Investigation on structural and optical properties of SLS-ZnO glasses prepared using a conventional melt quenching technique. *Journal of Materials Science: Materials in Electronics*. *26*, 3722–3729.

Zaid, M.H.M., Matori, K.A., Aziz, S.H.A., Kamari, H.M., Wahab, Z.A., Effendy, N., & Alibe, I.M. (2016). Comprehensive study on compositional dependence of optical band gap in zinc soda lime silica glass system for optoelectronic applications. *Journal of Non-Crystalline Solids*. *449*, 107–112.

Zaid, M.H.M., Matori, K.A., & Aziz, S.H.A., (2017). Effect of sintering on crystallization and structural properties of soda lime silica glass. *Science of Sintering*. *49*, 409–417.

Zanotto, E. D. (1953). A bright future for glass-ceramics. *American Ceramic Society Bulletin*. *89*(8), 19–27.

Zhang, H.X., Buddhudu, S., Kam, C.H., Zhou, Y., Lam, Y.L., Wong, K.S., Ooi, B.S., Ng, S.L., & Que, W. X. (2001). Luminescence of Eu^{3+} and Tb^{3+} doped Zn_2SiO_4 nanometer powder phosphors. *Materials Chemistry and Physics*. *68*, 31–35.

Zhou, Y., Xu, J., Zhang, Z., & You, M. (2014). The spectroscopic properties of Dy^{3+} and Eu^{3+} co-doped $ZnWO_4$ phosphors. *Journal of Alloys and Compounds*. *615*, 624–628.

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LIST OF PUBLICATIONS

Papers

Rahayu Emilia Mohamed Khaidir, Yap Wing Fen, Mohd Hafiz Mohd Zaid, Khamirul Amin Matori, Nur Alia Sheh Omar, Muhammad Fahmi Anuar, Siti Aisyah Abdul Wahab, Aisyah Zakiah Khirel Azman. (2019). Optical band gap and photoluminescence studies of Eu^{3+}-doped zinc silicate derived from waste rice husks. *Optik*, 182: 486-495.

Rahayu Emilia Mohamed Khaidir, Yap Wing Fen, Mohd Hafiz Mohd Zaid, Khamirul Amin Matori, Nur Alia Sheh Omar, Muhammad Fahmi Anuar, Siti Aisyah Abdul Wahab, Aisyah Zakiah Khirel Azman. (2019). Exploring Eu^{3+}-doped ZnO-SiO_2 Glass Derived by Recycling Renewable Source of Waste Rice Husk for White-LEDs Application. *Results in Physics*, 102596.

Rahayu Emilia Mohamed Khaidir, Yap Wing Fen, Mohd Hafiz Mohd Zaid, Khamirul Amin Matori, Nur Alia Sheh Omar, Muhammad Fahmi Anuar, Siti Aisyah Abdul Wahab, Aisyah Zakiah Khirel Azman. (2019). Addition of ZnO nanoparticles on waste rice husk as potential host material for red-emitting phosphor. *Materials Science in Semiconductor Processing*, 104774.

Siti Aisyah Abdul Wahab, Khamirul Amin Matori, Sidek Hj Ab Aziz, Mohd Hafiz Mohd Zaid, Mohd Mustafa Awang Kechik, Aisyah Zakiah Khirel Azman, **Rahayu Emilia Mohamed Khaidir**, Mohammad Zulhasif Ahmad Khiri, Nuraidayani Effendy. (2019). Optik Synthesis of cobalt oxide Co_3O_4 doped zinc silicate based glass-ceramic derived for LED applications. *Optik*, 179: 919-926.

Muhammad Fahmi Anuar, Yap Wing Fen, Mohd Hafiz Mohd Zaid, Khamirul Amin Matori, **Rahayu Emilia Mohamed Khaidir**. (2018). Synthesis and structural properties of coconut husk as potential silica source. *Results in Physics*, 11: 1-4.

Aisyah Zakiah Khirel Azman, Khamirul Amin Matori, Sidek Hj Ab Aziz, Mohamad Hafiz Mohd Zaid, Siti Aisyah Abdul Wahab, **Rahayu Emilia Mohamed Khaidir**. (2018). Comprehensive study on structural and optical properties of Tm_2O_3 doped zinc silicate based glass–ceramics. *Journal of Materials Science: Materials in Electronics*, 29(23): 19861-19866.

Conferences

Oral presenter at 2^{nd} International Symposium on Advanced Materials and Nanotechnology (i-SAMN), Malaysia held from 15^{th} August – 16^{th} August 2018 at The Everly Putrajaya, Putrajaya.

Oral presenter at International Conference on X-Rays and Related Techniques in Research and Industry 2018 (ICXRI 2018), held from 18^{th} August – 19^{th} August 2018 at Grand Riverview Hotel, Kota Bharu, Kelantan.

Oral and poster presenter at Materials Technology Challenges 2019 (MTC 2019) on 27^{th} March 2019 at Dewat Sri Harmoni, 5^{th} College, UPM Serdang, Selangor.

Competition

Gold Medal Award at Materials Technology Challenges 2019 (MTC 2019) on 27^{th} March 2019 at Dewat Sri Harmoni, 5^{th} College, UPM Serdang, Selangor.

Best Poster Award at Materials Technology Challenges 2019 (MTC 2019) on 27^{th} March 2019 at Dewat Sri Harmoni, 5^{th} College, UPM Serdang, Selangor.

Best Presenter Award at International Conference on X-Rays and Related Techniques in Research and Industry 2018 (ICXRI 2018), held from 18^{th} August – 19^{th} August 2018 at Grand Riverview Hotel, Kota Bharu, Kelantan.

Participant in "Pertandingan Projek Penyelidikan Inovasi Nanoteknologi 2018 (PIN 18') held on 8^{th} October – 11^{th} October 2018 at Technology Park Malaysia, Bukit Jalil, Kuala Lumpur.

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