



**INVESTIGATION OF SAMARIUM (III) EFFECT
TO THE PROPERTIES OF RED PHOSPHOR AS A
POTENTIAL CO-ACTIVATOR**

by

**NUR SYAZWANIE BINTI ZAILANI
(1730512356)**

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LIST OF ABBREVIATIONS

CIE	Commission internationale de l'éclairage
CRI	Colour Rendering Index
CTB	Charge Transfer Band
FE-SEM	Field Emission Scanning Electron Microscope
LEDs	Light Emitting Diodes
Pc-LEDs	Phosphor Converted Light Emitting Diodes
PL	Photoluminescence
SEM	Scanning Electron Microscope
SSL	Solid State Lighting
UV	Ultra Violet
WLEDs	White Light Emitting Diodes
XRPD	X-ray Powder Diffraction

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LIST OF SYMBOLS

lm/W	Lumens per Watt
a.u.	Arbitrary Unit

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Penyelidikan Terhadap Kesan Samarium (III) ke Atas Sifat-Sifat Fosfor Merah Sebagai Potensi Penggerak Bersama

ABSTRAK

Fosfor merah merupakan satu daripada unsur-unsur nadir bumi (REEs) yang penting dalam aplikasi diod berwarna putih (WLEDs). Walau bagaimanapun, proses pelombongan REEs memudaratkan persekitaran dan menyebabkan harga REEs menjadi lebih mahal. Europium (III) (juga dikenali sebagai Eu^{3+}) adalah salah satu daripada REEs yang mempunyai potensi besar untuk digunakan sebagai fosfor merah kerana sifat pendaratan yang hebat. Walau bagaimanapun, harga Eu^{3+} sangat tinggi, oleh itu satu usaha untuk meminimumkan penggunaan Eu^{3+} adalah penting. Sebaliknya, Samarium (III) (Sm^{3+}) juga dikenali untuk meningkatkan sifat photoluminescence beberapa fosfor. Projek ini dijalankan untuk menyiasat kemungkinan meminimumkan penggunaan Eu^{3+} dengan menggantikan kation nadir bumi dengan pengaktifan Sm^{3+} dalam sebatian tungstate/ molybdate. Matlamat ini boleh dicapai melalui objektif berikut; untuk menilai sifat spektra dan menyelidik jumlah optimum Sm^{3+} yang boleh bekerja di dalam fosfor $\text{LiEu}_{(0.55-x)}\text{Y}_{0.45}(\text{MoO}_4)_2\text{Sm}_x$, $\text{LiEu}_{(0.45-x)}\text{Gd}_{0.55}(\text{MoO}_4)_2\text{Sm}_x$, $\text{LiEu}_{(0.55-x)}\text{Y}_{0.45}(\text{WO}_4)_2\text{Sm}_x$ dan $\text{LiEu}_{(0.50-x)}\text{Gd}_{0.50}(\text{WO}_4)_2\text{Sm}_x$. Selain itu, struktur kristal dalam sebatian tungstate/ molybdate sewaktu Sm^{3+} meningkat menggantikan Eu^{3+} juga telah dikaji. Fosfor ini disediakan dengan menggunakan teknik reaksi keadaan pepejal dengan perbezaan penumpuan antara Eu^{3+} dan Sm^{3+} dalam kekisi tuan rumah dengan kepekatan (x) dalam julat 0 hingga 0.55 mol. Eksperimen yang dijalankan ialah pembelahan serbuk sinar-X (XRPD), pengimbasan mikroskop elektron (SEM) dan kajian photoluminescence (PL). Ia didapati bahawa kerjasama Sm^{3+} di dalam kekisi tuan rumah menawarkan intensiti lebih baik apabila intensiti fosfor telah meningkat 288% berbanding campuran asal. Untuk keputusan PL, intensiti pelepasan diperhatikan pada 615 nm dan jumlah optimum Sm^{3+} dicatatkan di antara 0.10 hingga 0.20 mol yang mengakibatkan keamatan tertinggi setiap fosfor. Ia juga menemui bahawa campuran $\text{LiEu}_{(0.55-x)}\text{Y}_{0.45}(\text{MoO}_4)_2\text{Sm}_x$ dengan kepekatan (x) = 0.20 mol menawarkan intensity tertinggi berbanding campuran lain. Penemuan ini membuktikan bahawa penggunaan Eu^{3+} masih dapat dikurangkan di dalam fosfor merah yang mana membantu mengurangkan kos pembuatan WLEDs memandangkan harga Eu^{3+} sangat tinggi. Penemuan ini penting dalam memberi petunjuk bahawa ada ruang untuk fosfor tungstate/ molybdate merah yang dioptimumkan dan secara tidak langsung dapat mengurangkan penggunaan REEs.

Investigation of Samarium (III) Effect to the Properties of Red Phosphor as a Potential Co-Activator

ABSTRACT

Red phosphor is one of rare earth elements (REEs) that is important in white light emitting diodes (WLEDs) applications. However, the process of mining on the REEs is harmful to environment and it makes the prices of REEs to be expensive. Europium (III) (also known as Eu^{3+}) is one of the REEs which has a big potential to be used as a red phosphor due to their great luminescence properties. However, the price of Eu^{3+} is very high, therefore an effort to minimising the use of Eu^{3+} is essential. On the other hand, Samarium (III) (Sm^{3+}) is also known to enhance photoluminescence properties of several phosphors. This project is conducted to investigate the possibility of minimizing the use of Eu^{3+} by replacing the rare earth cations with co-activator Sm^{3+} in tungstate/ molybdate compound. This aim can be achieved by the following objectives; to evaluate the spectral properties and investigate the optimum amount of Sm^{3+} can be employed in $\text{LiEu}_{(0.55-x)}\text{Y}_{0.45}(\text{MoO}_4)_2\text{Sm}_x$, $\text{LiEu}_{(0.45-x)}\text{Gd}_{0.55}(\text{MoO}_4)_2\text{Sm}_x$, $\text{LiEu}_{(0.55-x)}\text{Y}_{0.45}(\text{WO}_4)_2\text{Sm}_x$ and $\text{LiEu}_{(0.50-x)}\text{Gd}_{0.50}(\text{WO}_4)_2\text{Sm}_x$ phosphors. Therefore, the crystal structure in tungstate/ molybdate compound as Sm^{3+} increases in replacing Eu^{3+} also had been evaluated. These phosphors were prepared by using solid-state reaction technique with different concentration between Eu^{3+} and Sm^{3+} in the host lattice with concentration (x) in range of 0 to 0.55 mol. The experiments conducted were X-ray powder diffraction (XRPD), scanning electron microscope (SEM) and photoluminescence study (PL). It was found that incorporation of Sm^{3+} into the host lattice offered the better intensity when the intensities of the phosphors increase until 288% compared to the parent compound. For the PL results, the emission intensity was observed at 615 nm, and the optimum amount of Sm^{3+} recorded in the range of 0.10 to 0.20 mol where resulted in the highest intensity of each phosphor. It also found that the compound $\text{LiEu}_{(0.55-x)}\text{Y}_{0.45}(\text{MoO}_4)_2\text{Sm}_x$ with concentration (x) = 0.20 mol offers the highest intensity compared the other compound. These findings proved that the use of Eu^{3+} can still be reduced in this red phosphor which helps to reduce the cost of manufacturing WLEDs since the price of Eu^{3+} is very high. This finding is significant in giving an indication that there are rooms for the red tungstate/ molybdate phosphors to be optimised and indirectly can minimise the use of REEs.

CHAPTER 1 : INTRODUCTION

1.1 Background of the Project

Rare earth elements (REEs) are one of important elements in contributing to the luminescence behaviour of phosphors. Normally, heavy rare earth elements such as yttrium, gadolinium, terbium, ytterbium etc., and light rare earth elements such as scandium, lanthanum, cerium, samarium, europium, and etc., are widely used in the luminescent properties studies.

REEs are usually used for many industries in their technologies and application due to its exceptional magnetic and conductive properties that can make them to be lighter, faster and stronger (Klinger et. al., 2018). Figure 1.1 shows the examples of applications that used the REEs. This work focuses on minimizing REEs in the phosphor for lighting application. This effort can be materialized by replacing or reducing the amount of heavy REEs used in phosphor with the light REEs within the host compound.

Therefore, global lighting industries especially have high demand on consuming the REEs due to the configuration electrons in their atomic structure which make the valuable emission in improving the lighting application efficiency (Chen, Chu, & Liu, 2012; Massari & Ruberti, 2013). However, due to the price of REEs and awareness to the environment, the industries are trying to find a solution for minimising the quantity of REEs usage (Humphries et al., 2012). Phosphor materials which rely heavily on REE's are not excluded in this case. In searching for high efficient and 'cost-saving' red phosphor

in lightings, the phosphor with optimum use of REEs without compromising the performance need to be researched.



Figure 1.1: Rare earth applications.
Source: Banerjee et. al., (2018)

1.2 Statement of the Problem

Many lighting industries depend on REEs for their applications such as red colour for displays, light emitting diodes (LEDs), phosphors and etc. (Humphries et al., 2012). However, the global crisis on the rare earth supplies affects many economic sectors, and the prices of the REEs become more expensive. The process of mining the REEs is also well known for its harmful to the environment and exposes safety risks to people (Massari & Ruberti, 2013). In addition, it was found that a recycling program is useful for maintaining the REEs supply. Unfortunately, this program has a big challenge to be implemented when the recycling program need to collect the electronic waste (Klinger et

al., 2018). Therefore, as an option, it is very important to search for phosphor compounds that require less amount of REE's.

As REE's are still required in producing a phosphor, the use of europium (III) as a red phosphor, is found to be essential in generating one of white light in LEDs applications due to the fact that they are great in the red spectral region (Haque, Lee, & Kim, 2009). Previous research reported that Eu^{3+} 0.55 with Y^{3+} 0.45, and Eu^{3+} 0.55 with Gd^{3+} 0.45 are the highest finding for the luminous efficacy of red phosphor compound (Fathullah et al., 2016), however many research works are still needed in finding the best formulae to increase the efficiency out of the compound. In addition, Zhou et al., (2014) found that there had an energy transfer from Sm^{3+} to Eu^{3+} at 614.5 nm in compound $\text{LiY}(\text{MoO}_4)_2$ and the red emission of the phosphor had largely enhanced. As long as the crystal structure does not change, the addition of co-activators such as samarium (III) Sm^{3+} can be a possible method to enhance the luminescence properties of this phosphor which will be explained further in Section 2.13 in Chapter 2.

1.3 Research Questions

Inspired by the previous research work, and after understanding the problem statements, this research is proposed to get solutions for the following questions;

- 1) What happens to the emission spectra of the phosphor when Sm^{3+} is introduced in the host lattices?

- 2) What is the optimum amount of Sm^{3+} ions can be employed in the $\text{LiEu}_{(0.55-x)}\text{Y}_{0.45}(\text{MoO}_4)_2\text{Sm}_x$, $\text{LiEu}_{(0.45-x)}\text{Gd}_{0.55}(\text{MoO}_4)_2\text{Sm}_x$, $\text{LiEu}_{(0.55-x)}\text{Y}_{0.45}(\text{WO}_4)_2\text{Sm}_x$ and $\text{LiEu}_{(0.50-x)}\text{Gd}_{0.50}(\text{WO}_4)_2\text{Sm}_x$ phosphors?
- 3) Are there any changes occurred with the crystal structures?

1.4 Objectives of the Study

This study examines the relationship between the photoluminescence properties of $\text{LiEu}_{(0.55-x)}\text{Y}_{0.45}(\text{MoO}_4)_2\text{Sm}_x$, $\text{LiEu}_{(0.45-x)}\text{Gd}_{0.55}(\text{MoO}_4)_2\text{Sm}_x$, $\text{LiEu}_{(0.55-x)}\text{Y}_{0.45}(\text{WO}_4)_2\text{Sm}_x$ and $\text{LiEu}_{(0.50-x)}\text{Gd}_{0.50}(\text{WO}_4)_2\text{Sm}_x$ phosphors with the change on its crystal structure in substituting with Sm^{3+} ions. This aim can be achieved by the following specific objectives;

- 1) To evaluate the spectral properties of $\text{LiEu}_{(0.55-x)}\text{Y}_{0.45}(\text{MoO}_4)_2\text{Sm}_x$, $\text{LiEu}_{(0.45-x)}\text{Gd}_{0.55}(\text{MoO}_4)_2\text{Sm}_x$, $\text{LiEu}_{(0.55-x)}\text{Y}_{0.45}(\text{WO}_4)_2\text{Sm}_x$ and $\text{LiEu}_{(0.50-x)}\text{Gd}_{0.50}(\text{WO}_4)_2\text{Sm}_x$ in the function of increasing Sm^{3+} ions.
- 2) To investigate the optimum amount of Sm^{3+} that can be employed in $\text{LiEu}_{(0.55-x)}\text{Y}_{0.45}(\text{MoO}_4)_2\text{Sm}_x$, $\text{LiEu}_{(0.45-x)}\text{Gd}_{0.55}(\text{MoO}_4)_2\text{Sm}_x$, $\text{LiEu}_{(0.55-x)}\text{Y}_{0.45}(\text{WO}_4)_2\text{Sm}_x$ and $\text{LiEu}_{(0.50-x)}\text{Gd}_{0.50}(\text{WO}_4)_2\text{Sm}_x$ phosphors.
- 3) To evaluate the effects of crystal structure in tungstate/ molybdate compound as Sm^{3+} increases in replacing Eu^{3+} .

1.5 Hypothesis

Excitation and emission spectra of the tungstate and molybdate phosphors are influenced by the selection rules that depend upon the symmetry of the host lattice sites as well as the properties of the Eu^{3+} as an activator and the Sm^{3+} as an activating agent. There have been a lot of researches on the efficiency of Eu^{3+} used in the red phosphor and recently a new finding has been found in 2016 stating that the $\text{LiEu}_{0.55}\text{Y}_{0.45}(\text{MoO}_4)_2$, $\text{LiEu}_{0.45}\text{Gd}_{0.55}(\text{MoO}_4)_2$, $\text{LiEu}_{0.55}\text{Y}_{0.45}(\text{WO}_4)_2$ and $\text{LiEu}_{0.50}\text{Gd}_{0.50}(\text{MoO}_4)_2$ have great luminous efficacy excited at 395 and 465 nm (M. Fathullah et. al., 2016).

Therefore as long as the crystal structure remains unchanged, the photoluminescence shall not change its spectral properties when Sm^{3+} ion is added into the $\text{LiEu}_{(0.55-x)}\text{Y}_{0.45}(\text{MoO}_4)_2\text{Sm}_x$, $\text{LiEu}_{(0.45-x)}\text{Gd}_{0.55}(\text{MoO}_4)_2\text{Sm}_x$, $\text{LiEu}_{(0.55-x)}\text{Y}_{0.45}(\text{WO}_4)_2\text{Sm}_x$ and $\text{LiEu}_{(0.50-x)}\text{Gd}_{0.50}(\text{WO}_4)_2\text{Sm}_x$ phosphors. It is expected that the intensities of the phosphor to be increased and the photoluminescence properties will be enhanced to its maximum efficiency when introducing the Sm^{3+} into the host phosphor due to the Sm^{3+} has good properties to be a co-activator in the red phosphor compound.

1.6 Scope of the Study

This study covers the $\text{LiEu}_{(0.55-x)}\text{Y}_{0.45}(\text{MoO}_4)_2\text{Sm}_x$, $\text{LiEu}_{(0.45-x)}\text{Gd}_{0.55}(\text{MoO}_4)_2\text{Sm}_x$, $\text{LiEu}_{(0.55-x)}\text{Y}_{0.45}(\text{WO}_4)_2\text{Sm}_x$ and $\text{LiEu}_{(0.50-x)}\text{Gd}_{0.50}(\text{WO}_4)_2\text{Sm}_x$ phosphor for phosphor-converted light emitting diodes (pc-LEDs) application with changing concentration of Sm^{3+} and Eu^{3+} where $x = 0, 0.0.5, 0.10, 0.15, 0.20, \dots 0.55$ by using solid-state reaction. The experiments conducted in this study are X-ray powder diffraction (XRPD), photoluminescence measurement and scanning electron microscope (SEM).

The XRPD method was conducted for the crystal structure analysis to characterise the structure, bond length, and crystallographic parameters such as crystal system and space group. For the crystal refinement analysis, the TOPAS version 3.0 software was used to fit a theoretical pattern with the actual pattern. Besides, the software was also used to quantify multi-phase mixtures, estimate crystallite sizes and the occupancy factors of various atoms. The comparison between the crystal and the effect on the intensity of the phosphor was also studied.

Furthermore, SEM was conducted for the morphology analysis, and the photoluminescence analysis was done by using photoluminescence spectrometer system for measuring the phosphor's spectra in the range of 250 nm to 750 nm wavelength. This photoluminescence analysis was measured the relative intensity of the phosphor at the emission spectra 615 nm while for the excitation spectra at 395 nm and 465 nm. The optimum amount of Sm^{3+} ions that can be employed in the compound were recorded as the highest intensity performed in the photoluminescence study.

1.7 Significant of Study

Due to the importance of REEs in many industrial sectors, it is important to control the use of REEs. By minimising the use of REEs, it helps to reduce the demands of REEs globally and therefore will help to reduce the cost for manufacturing phosphor based lighting devices in the current market. Apart from that, the environmental impact affected from the mining processes of REE's also can be minimised which directly sustains the green environment.

1.8 Thesis Outline

This chapter contains of the main aims, objectives, scopes, etc., why this project conducted based on the needed for finding the best ways to produce the red phosphor in LEDs application. The next chapter will discuss on the literature review on the previous study on the red phosphor. In Chapter 3, the methodology will be explained on the ways on conducting the project from the earlier until the end of this project. The results and discussions on the data collected will be discussed in the Chapter 4 and lastly the Chapter 5 will concluded the overall project and gave some suggestions for further research on the project.