Effects of Sm^{3+} on Luminescent Properties of $LiEu_{(0.55-x)}Y_{0.45}$ $(WO_4)_2Sm_x$ Red Phosphor

N S Zailani[1,], M F Ghazli[1,2], R Hussin[3], S Z Abd Rahim[1,2] and M N Mat Saad[1,2]

[1]School of Manufacturing Engineering, Universiti Malaysia Perlis (UniMAP), Perlis Malaysia

[2]Center of Excellence Geopolymer & Green Technology (CEGeoGTech), Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia

[3]Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, Skudai, Johor, Malaysia

E-mail: fathullah@unimap.edu.my

Abstract. Phosphor materials have been widely applied in lighting and displays. Rare earth elements are amongst important elements in giving luminescent properties to the phosphor. The needs to reduce rare earth element in phosphor is of interest due to cost and environmental issue. The red phosphor $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2$ were synthesized by substituting Sm^{3+} in the lattice using solid-state reaction. The effect on the substitution of Sm^{3+} which acts as an activator will be analysed using X-ray powder diffraction (XRPD), scanning electron microscope (SEM) and photoluminescence spectra (PL). The structure of the compound was found to be as a monoclinic which referred to the reference patterns. The optimum amount was recorded for the activator to be obtained in the host lattice for replacing the Eu^{3+} place as well as enhancing the intensity of the emission. The findings reveal that $LiEu_{(0.55-x)}Y_{0.45}(MoO_4)_2Sm_x$ can be a more efficient red phosphor candidate used white light emitting diodes (WLEDs) applications.

1. Introduction

White light emitting diodes (WLEDs) have attracted significant attention due to their advantages such as high energy efficiency, energy-saving, environmental friendly, and long life time [1, 5]. The first commercialized LED has been produced in year 1996 by exhibit a yellow emission (usually Ce^{3+} - doped $Y_3Al_5O_{12}$) under blue excitation and combining with an InGaN blue LED chip [1, 3, 4, 6-8]. However, the existing WLEDs have some limitations such as less colour rendering index (CRI) (<75), limited indoor usage and less luminous efficiency [1, 6]. It also found that the lack of red spectral component in the host compound will reducing the emission and CRI of the phosphor near-UV region [7, 9]. Hence, this is motivated for find a good red phosphor candidate which can provided the higher CRI, higher luminous efficiency as well as high chromatic stability [2, 5]. There is an increasing number of research on searching the scheelite-type structure material such as as MR $(BO_4)_2$ (M = Li, Na, K, Ag; R = lanthanides (Ln), Y, Bi; B = W, Mo) as a luminescent materials due to their thermal and chemical stabilities, self-activated nature, wide emission spectra in visible region, can transfer their absorbed energy to the dopant ions and high density [2, 5, 10]. Eu^{3+} has a good potential to a red phosphor candidate which offer a high quantum efficiency and photostability in the red region [10-12]. There are some of the previous study on the searching the luminescence properties based on the tungstate and introducing the Eu^{3+} to the lattice; $LiY(MoO_4)_{2-x}(WO_4)_x:Dy^{3+}$, Eu^{3+}, $LiEu(WO_4)_{2-}$

$_x(MoO_4)_x$, $LiLn(MO_4)_2$:Eu^{3+} (Ln = La, Eu, Gd, Y; M = W, Mo) and $LiEu_{(1-x)}Y_x(WO_4)_2$ [1, 4, 13, 14]. The previous study by Fathullah et al. (2016) found the highest luminous efficacy of $LiEu_{(1-x)}Y_x(WO_4)_2$ found when the Eu^{3+} concentration at 55 mol% and Y^{3+} 45 mol% [14]. From this finding, it motivated to conduct this current work by introducing the Samarium (III) as a co-activator to the $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$ (x= 0 – 0.55) lattice. It expected that by introducing Sm^{3+} will help in reducing the usage of Eu^{3+} where the Eu^{3+} are more expensive. This work studied on the potential of the $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$ by analysing the effect on the crystal structure and the photoluminescence properties to be used as a red phosphor in WLEDs application.

2. Materials and methods
2.1. Sample preparation
The $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$ phosphors were prepared using solid-state reaction where changes the x concentration between 0 to 0.55. The starting materials were lithium carbonate 99.9%, yttrium, tungsten (VI) oxide 99+%, europium oxide (Eu_2O_3), and samarium oxide (Sm_2O_3). At first, the reactants were mixed with stoichiometric amount and then heated at 850 ℃ in open air for 3 hours. The compounds finally cooled at room temperature and gently ground for removing the sample powder from the crucible.

2.2. Characterization
The X-ray Powder Diffraction (XRPD) patterns were measured using a Bruker D2 Phaser with Cu Kα radiation ($\lambda = 1.54184\,\text{Å}$). The morphology of the samples were observed using Hitachi TM3000 scanning electron microscope (SEM). Photoluminescence properties were measured from Perkin Elmer, LS 55 spectrometer. All the emission intensity were collected at room temperature with the changes of concentration activator (Eu^{3+}) and co-activator (Sm^{3+}).

3. Results and discussions
3.1. XRPD analysis of $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$ samples
The overlaid XRPD patterns of $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$ (x = 0, 0.05, 0.20, 0.40 and 0.55 mol) is presented in Figure 1.
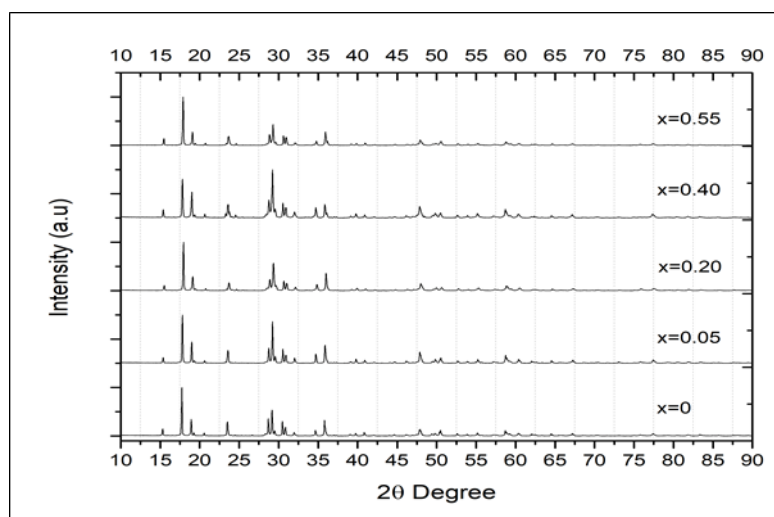

Figure 1. The XRPD stack patterns of $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$ (x=0, 0.05, 0.20, 0.40 and 0.55).

From this result, it clearly shows that there are no additional peaks or changes occurred as increases Sm^{3+} to the host lattice where indexed to the pure phases $LiEu(WO_4)_2$ (PDF 01-080-7695) and

$LiY(WO_4)_2$ (PDF cart 88-0854) by J. Postema et al., (2011) [15]. This confirms that the compound structure is a tetragonal scheelite structure with space group $I4_{1/a}$ and for sample $LiY_{0.45}(WO_4)_2Sm_{0.55}$ has found as a monoclinic with space group P2/n. This can be supported by referring to the refinement analysis to confirm their structures. Therefore, this findings also claimed that the present result clearly shown that there are two phases occurred since the concentration of Y^{3+} 0.45 mol which rejected the findings prepared by M. Fathullah et. al., (2016) [14] where found the compound $LiEu_{1-x}Y_x(WO_4)_2$ have two phases when the concentration of Y^{3+} at 55%. The sample $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$ were continued by refining the sample using the TOPAS software. From the refinement data, it seem like there have larger differences especially on the $LiY(WO_4)_2$ peaks. This confirms that the structure of $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$ samples have a tetragonal scheelite structure with space group $I4_{1/a}$ and the $LiY_{0.45}(WO_4)_2Sm_{0.55}$ was found as a monoclinic structure with space group P2/n with two phases. In Table 1 shows the results of the lattice parameters and cell volume of $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$. Based on this result, it shows the increasing of the lattice's volume about 0.33% from 300.336 $Å^3$ to 301.34 $Å^3$ as Sm^{3+} increases to the host lattice. This is due to the ionic radius of the Sm^{3+} is larger than Eu^{3+} and Y^{3+}. The highest R_{wp} calculated from the refinement of $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$ is 29.73. This result still can be accepted since the value of R_{wp} is better than other sample in this study and this phosphor has two phases that might have some problem to fitting with the reference models especially in the $LiY(WO_4)_2$ phase.

Table 1. Lattice parameters and cell volumes of $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$.

Eu^{3+}	Sm^{3+}	a(Å)	c(Å)	Vol($Å^3$)	R_{wp}
0.55	0	5.19465(55)	11.1300(18)	300.336(81)	29.73
0.50	0.05	5.19807(61)	11.1300(18)	300.732(86)	36.93
0.35	0.20	5.20168(83)	11.1300(26)	301.15(12)	34.25
0.15	0.40	5.20184(81)	11.1300(24)	301.17(11)	33.41
0	0.55	5.20333(81)	11.1300(27)	301.34(12)	33.11
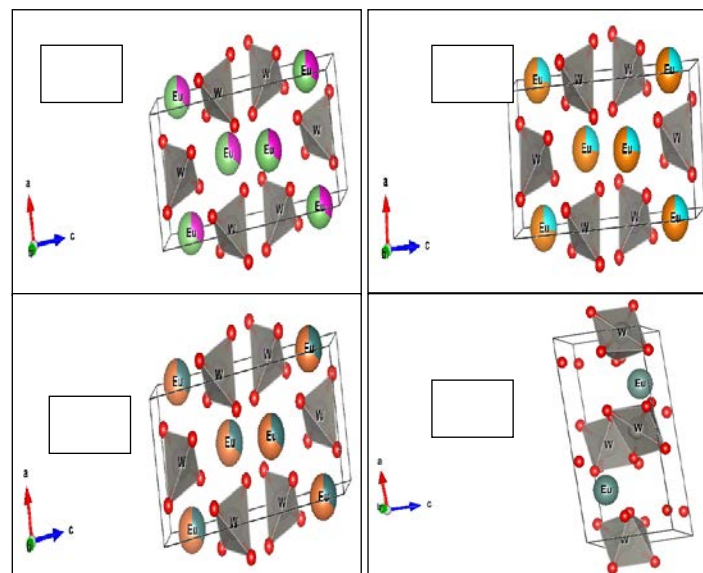
Figure 2. Modelled crystal structure of tetragonal (a) $LiEu_{0.55}Y_{0.45}(WO_4)_2$, (b) $LiEu_{0.40}Y_{0.45}(WO_4)_2Sm_{0.05}$, (c) $LiEu_{0.15}Y_{0.45}(WO_4)_2Sm_{0.40}$ and crystal structure of monoclinic (d) $LiY_{0.45}(WO_4)_2Sm_{0.55}$.

Figure 2 shows the modelled crystal structure of tetragonal (a) $LiEu_{0.55}Y_{0.45}(WO_4)_2$, (b) $LiEu_{0.40}Y_{0.45}(WO_4)_2Sm_{0.05}$, (c) $LiEu_{0.15}Y_{0.45}(WO_4)_2Sm_{0.40}$ and crystal structure of monoclinic (d) $LiY_{0.45}(WO_4)_2Sm_{0.55}$. From these figures, it clearly shows that the additional of Sm^{3+} are remain as the same patterns until Sm^{3+} had fully taking place of Eu^{3+} into the lattice. At 0.55 mol Sm^{3+}, the structure of the phosphor has changed as a monoclinic with space group P2/n. It can be seen that there are four oxygen coordination are surround each of the W^{6+} ions. Therefore, the ions in $LiY_{0.45}(WO_4)_2Sm_{0.55}$ are well-organized with octahedral coordination even though their lattice angles had slightly deformed.

3.2. Morphology of $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$ samples

Figure 3 shows the morphologies of $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$ with 1000% magnification of (a) 0 mol% (b) 0.05 mol% and (c) 0.55 mol% Sm^{3+} concentration. The structures show the angular particle shaped with irregular particle sizes between $1-8\mu m$.
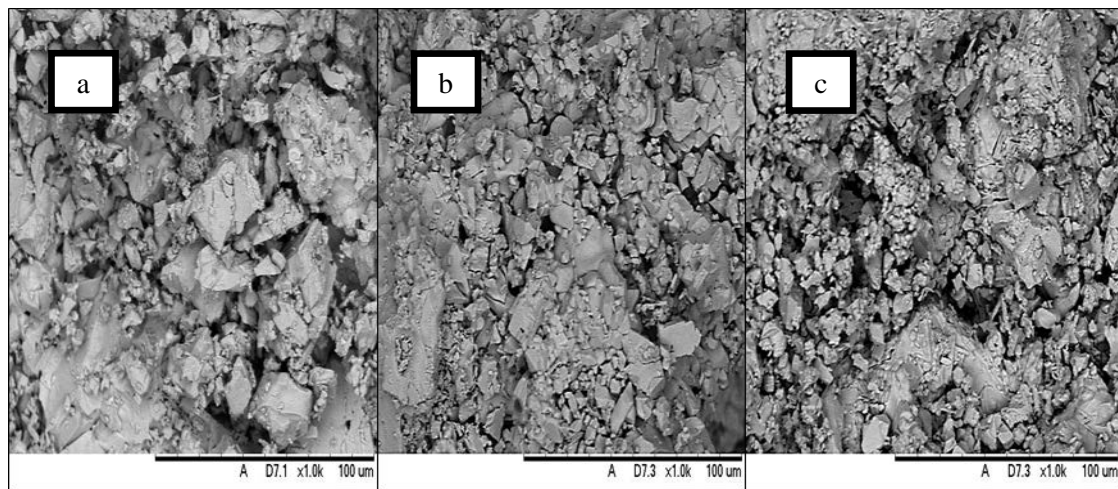

Figure 3. The morphologies of (a) $LiEu_{0.55}Y_{0.45}(WO_4)_2$, (b) $LiEu_{0.50}Y_{0.45}(WO_4)_2Sm_{0.05}$ and (c) $LiY_{0.45}(WO_4)_2Sm_{0.55}$ with 1000% magnification.

3.3. Photoluminescence properties

The emission spectra of $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$ in range 550 – 750 nm is shown in Figure 4.

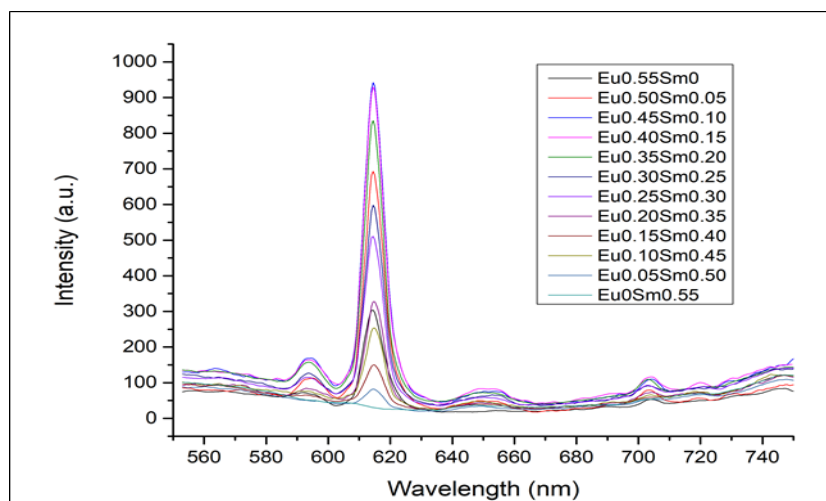**Figure 4.** Emission spectra of $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$ (x= 0 until 0.55) from 550 nm to 750 nm.

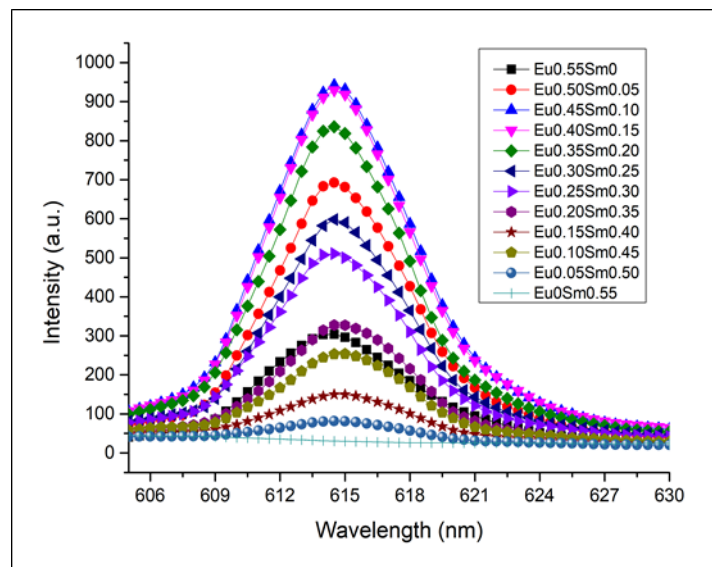**Figure 5.** Emission spectra of $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$ (x= 0 until 0.55) from 605 nm – 630 nm.

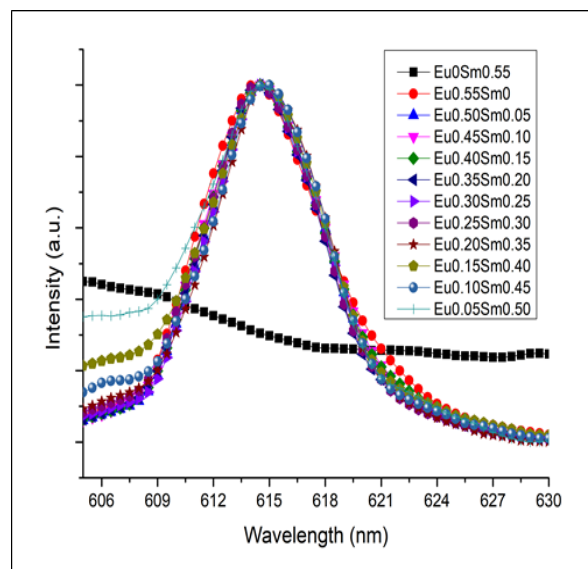**Figure 6.** Normalized graph of emission spectra of the $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$ (x= 0 until 0.55) from 605 nm – 630 nm.

The emission bands were observed at 588 – 600 nm ($^5D_0 \rightarrow {}^7F_1$), 610 – 630 nm ($^5D_0 \rightarrow {}^7F_2$), 640 – 662 nm ($^5D_0 \rightarrow {}^7F_3$) and 681 – 710 nm ($^5D_0 \rightarrow {}^7F_4$) transitions which indicating that the excited state of the Eu^{3+} in the host phosphor. At 615 nm, the highest emission intensity occurred and clearly show the increases of Sm^{3+} in the host lattice did not altered the emission centre. It already known that at 615 nm, the domain electric dipole ($^5D_0 \rightarrow {}^7F_2$ transition) has taken place which make the emission intensity influenced strongly by ligand ions in the crystal [3].

By introducing the Sm^{3+} ions to the $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2$, it can be seen that an increasea on the intensity occurs. Figure 5 presents the emission spectra of $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$ from 605 – 630

nm. Based on this figure, it shows that the additional of Sm^{3+} with 0.10 mol% provides the highest emission intensity. Therefore, Figure 6 shows the normalized graph which proving the results have no broadening effects. This proved that this compound did not undergo any changes in the crystal symmetry. Interestingly, it clearly shows a huge trend on the intensity increment when introducing Sm^{3+} to the host lattice. It was about 210.2% increment was recorded on the intensity from 303.71 a.u. ($LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2$) to 942.03 a.u. ($LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_{0.10}$). Hence, it can be suggested that the current finding has a good potential as a red phosphor to be applied in phosphor converted LEDs applications.

4. Conclusions
In summary, the $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2Sm_x$ have successfully synthesized using a solid-state reaction with concentration changes (x = 0, 0.05, 0,10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50 and 0.55). The structure of the compound are tetragonal scheelite structure with space group $I4_{1/a}$ and the sample $LiY_{0.45}(WO_4)_2Sm_{0.55}$ has a monoclinic P2/n structure with two phase's lattices conducted by XRPD analysis. The morphologies were found in the angular shaped with particle sizes between 1–8μm. Substituting of Sm^{3+} to the $LiEu_{(0.55-x)}Y_{0.45}(WO_4)_2$ causes an enhancement on the emission intensity at 615 nm when Sm^{3+} 0.10 mol% without affecting the lattice symmetry. The findings of the study suggest that the phosphors have a good potential as a red phosphor candidate with better efficiency.

5. References
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