Effects of Sm$^{3+}$ on Luminescent Properties of LiEu$_{(0.55-x)}$Y$_{0.45}$(WO$_4$)$_2$Sm$_x$ Red Phosphor

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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$_4$)$_2$Sm$_x$ 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$_5$Al$_3$O$_{12}$) 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$$_{(2-x)}$(WO$_4$)$_2$:Dy$^{3+}$, Eu$^{3+}$, LiEu(WO$_4$)$_2$,
x(MoO₄)ₓ, LiLn(MO₄)₂:Eu³⁺ (Ln = La, Eu, Gd, Y; M = W, Mo) and LiEu₁₋ₓYₓ(WO₄)₂ [1, 4, 13, 14]. The previous study by Fathullah et al. (2016) found the highest luminous efficacy of LiEu₁₋ₓYₓ(WO₄)₂ found when the Eu³⁺ concentration at 55 mol% and Y³⁺ 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)Y₀.₄₅(WO₄)₂Smₓ (x= 0 – 0.55) lattice. It expected that by introducing Sm³⁺ will help in reducing the usage of Eu³⁺ where the Eu³⁺ are more expensive. This work studied on the potential of the LiEu(0.55-x)Y₀.₄₅(WO₄)₂Smₓ 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)Y₀.₄₅(WO₄)₂Smₓ 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 (Eu₂O₃), and samarium oxide (Sm₂O₃). 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 (λ = 1.54184 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 (Eu³⁺) and co-activator (Sm³⁺).

3. Results and discussions

3.1. XRPD analysis of LiEu(0.55-x)Y₀.₄₅(WO₄)₂Smₓ samples

The overlaid XRPD patterns of LiEu(0.55-x)Y₀.₄₅(WO₄)₂Smₓ (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)Y₀.₄₅(WO₄)₂Smₓ (x=0, 0.05, 0.20, 0.40 and 0.55).](image)

From this result, it clearly shows that there are no additional peaks or changes occurred as increases Sm³⁺ to the host lattice where indexed to the pure phases LiEu(WO₄)₂ (PDF 01-080-7695) and...
LiY(WO₄)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/a, and for sample LiY₀.₄₅(WO₄)₂Sm₀.₅₅ 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 Y³⁺ 0.45 mol which rejected the findings prepared by M. Fathullah et. al., (2016) [14] where found the compound LiEu₁₋ₓYₓ(WO₄)₂ have two phases when the concentration of Y³⁺ at 55%. The sample LiEu₀.₅₅₋ₓYₓ(WO₄)₂Smₓ 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(WO₄)₂ peaks. This confirms that the structure of LiEu₀.₅₅₋ₓYₓ(WO₄)₂Smₓ samples have a tetragonal scheelite structure with space group I₄/a and the LiY₀.₄₅(WO₄)₂Sm₀.₅₅ 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 LiEu₀.₅₅₋ₓYₓ(WO₄)₂Smₓ. Based on this result, it shows the increasing of the lattice’s volume about 0.33% from 300.336 Å³ to 301.34 Å³ as Sm³⁺ increases to the host lattice. This is due to the ionic radius of the Sm³⁺ is larger than Eu³⁺ and Y³⁺. The highest R_wp calculated from the refinement of LiEu₀.₅₅₋ₓYₓ(WO₄)₂Smₓ 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(WO₄)₂ phase.

Table 1. Lattice parameters and cell volumes of LiEu₀.₅₅₋ₓYₓ(WO₄)₂Smₓ.

| Eu³⁺ | Sm³⁺ | a(Å)         | c(Å)         | Vol(Å³)   | 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) LiEu₀.₅₅₋ₓYₓ(WO₄)₂, (b) LiEu₀.₄₀₋ₓYₓ(WO₄)₂Smₓ₀.₀₅ , (c) LiEu₀.₁₃₋ₓYₓ(WO₄)₂Smₓ₀.₄₀ and crystal structure of monoclinic (d) LiY₀.₄₅(WO₄)₂Sm₀.₅₅.
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$_4$)$_2$Sm$_{0.05}$, (c) LiEu$_{0.15}$Y$_{0.45}$(WO$_4$)$_2$Sm$_{0.40}$ and crystal structure of monoclinic (d) LiY$_{0.45}$(WO$_4$)$_2$Sm$_{0.55}$. 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$_4$)$_2$Sm$_{0.55}$ 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$_4$)$_2$Sm$_x$ samples

Figure 3 shows the morphologies of LiEu$_{(0.55-x)}$Y$_{0.45}$(WO$_4$)$_2$Sm$_x$ 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 1–8µm.

3.3. Photoluminescence properties

The emission spectra of LiEu$_{(0.55-x)}$Y$_{0.45}$(WO$_4$)$_2$Sm$_x$ in range 550 – 750 nm is shown in Figure 4.
Figure 5. Emission spectra of LiEu(0.55-x)Y0.45(WO4)2Smx (x= 0 until 0.55) from 605 nm – 630 nm.

Figure 6. Normalized graph of emission spectra of the LiEu(0.55-x)Y0.45(WO4)2Smx (x= 0 until 0.55) from 605 nm – 630 nm.

The emission bands were observed at 588 – 600 nm (5D0 → 7F1), 610 – 630 nm (5D0 → 7F2), 640 – 662 nm (5D0 → 7F3), and 681 – 710 nm (5D0 → 7F4) transitions which indicating that the excited state of the Eu³⁺ in the host phosphor. At 615 nm, the highest emission intensity occurred and clearly show the increases of Sm³⁺ in the host lattice did not altered the emission centre. It already known that at 615 nm, the domain electric dipole (5D0 → 7F2 transition) has taken place which make the emission intensity influenced strongly by ligand ions in the crystal [3].

By introducing the Sm³⁺ ions to the LiEu(0.55-x)Y0.45(WO4)2, it can be seen that an increasea on the intensity occurs. Figure 5 presents the emission spectra of LiEu(0.55-x)Y0.45(WO4)2Smx from 605 – 630



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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)Y0.45(WO4)2) to 942.03 a.u. (LiEu (0.55-x)Y0.45(WO4)2Sm0.10). 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)Y0.45(WO4)2Sm 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 LiY0.45(WO4)2Sm0.55 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)Y0.45(WO4)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
[1] Liang Y et al. 2017 J. Alloys Compd. 716 56–64
[2] Zhou L et al. 2016 Mater. Res. Bull. 84 429–436
[3] Shang M, Li G, Kang X, Yang D and Lin J 2011 J. Electrochem. Soc. 158(5) H565
[4] Chiu C H, Wang M F, Lee C S and Chen T M 2007 J. Solid State Chem. 180(2) 619–627
[5] Ramakrishna P V, Rao T L, Singh A, Benarji B and Dash S 2017 J. Mol. Struct. 1149 426–431
[6] Zhao D, Shi J-C, Nie C-K and Zhang R-J 2017 Opt. - Int. J. Light Electron Opt. 138 476–486
[7] Li L et al. 2016 Mater. Res. Bull. 78 26–30
[8] Cao F 2012 J. Lumin. 132(3) 641–644
[9] Wang Q F et al. 2015 J. Alloys Compd. 625 355–361
[10] Kumari L S and Gopchandran K G 2015 Mater. Today Proc. 2(3) 1007–1011
[11] Hwang K-S, Kang B-A, Hwangbo S, Kim Y-S and Kim J-T 2010 Electron. Mater. Lett. 6(1) 27–30
[12] Ru J, Ying S, Zheng W and Chen J 2016 Mater. Res. Bull. 84 468–473
[13] Liu Y et al. 2014 RSC Adv. 4(9) 4754
[14] Postema J M, Fu W T and Ijdo D J W 2011 J. Solid State Chem. 184(8) 2004–2008

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