ACERP: Vol. 2, No. 2, (Spring 2016) 32-36

Advanced Ceramics Progress

Research Article

Journal Homepage: www.acerp.ir

Effect of LiCl on the Microstructure and Luminescence Properties of $YVO_4:Eu^{3+}$ and $YBO_3:Eu^{3+}$ Phosphors

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PAPER INFO

Paper history:
Received 29 April 2016
Accepted in revised form 25 July 2016

Keywords:
Phosphors
Solid State
flux compounds
Luminescence Properties

ABSTRACT

In this investigation, Eu^{3+} doped Yttrium Orthovanadate (YVO_4)/Yttrium Borate (YBO_3) phosphors were synthesized individually by conventional solid state method at 1100°C under atmospheric condition. Meanwhile, different amounts of lithium chlorides (LiCl) were used as the flux compound to modify the morphology of the phosphor particles and also final luminescence properties. It was concluded that even small amounts of fluxes play a vital role in the growth of particles. The photoluminescence emission spectra of the phosphors were measured at λ_{exc}= 240 and 310 nm, respectively. It was found that by using 2wt% of flux compounds, the emission intensities of $YVO_4:Eu^{3+}$ and $YBO_3:Eu^{3+}$ phosphors became respectively 6.8 and 1.3 times larger than those of phosphors without any flux addition.

1. INTRODUCTION

Due to the potential applications in the development of electro-luminescent displays (ELDs), plasma display panels (PDPs), field emission displays (FEDs) and cathode ray tubes (CRTs), extensive investigations has been focused on lanthanide doped phosphors [1-3]. A review of the literatures shows that among phosphors, YVO_4: Eu^{3+} and YBO_3: Eu^{3+} compounds have attracted great attentions of researchers during recent years [4-5]. These compounds have significant quantum efficiency. Clearly, Yttrium orthovanadate doped with Ln^{3+} is a famous and highly efficient optical material with a variety of emitting wavelengths, which has been remarkably used for lighting, displays and laser technology [6]. Among Ln^{3+} ions, based on the characteristics of the 4f–5d transitions parity forbidden, the Eu^{3+} ions usually show significant red light emissions [7]. Then in the group of orthoborates, YBO_3 has very notable luminescence properties when it is doped by Eu^{+3}[8].

As a matter of fact, to synthesize phosphors via solid state approach, high calcination temperatures are necessary. From the economic point of view, this is considered as a great drawback for solid state method. Fortunately, since the melting point of flux compounds is usually less than solid-state temperature, the use of flux compounds may solve the mentioned problem without entering to the reaction [9]. Noteworthy, through employing fluxes, the diffusion coefficients of components increase and then the solid state synthesis can be fulfilled at relatively lower temperatures [10].

In addition, the optical properties of phosphors can be affected by some parameters like defects, particle size, crystallinity, particle morphology, and homogeneity of composition. To improve the optical properties, the use of fluxes in raw materials has been suggested in many investigations [11-13].The literature survey reveals that alkaline earth metals and halides are of important compounds used as flux materials [14]. Among the explained flux compounds, LiCl has been intensively employed to decrease the temperature of solid state procedures, as well as improvement of optical properties [15-16].

Noteworthy, YVO_4 and YBO_3 materials are of great importance in light related technologies and the literature survey shows that these compounds have been reported by many investigators. In contrast, it should be considered that the literature is scarce on the use of flux materials, especially alkaline metal fluxes. Motivated by this background, in this paper, Eu^{3+} doped YVO_4 and YBO_3 phosphors were produced individually via solid state synthesizing method. Then in order to reduce the temperature of solid state synthesis and also modify the crystal structure and luminescence properties, different quantities of LiCl were used as the flux material.

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2. EXPERIMENTS

2.1. Preparation To produce YVO_4: 1 wt% Eu^{3+} and YBO_3: 1 wt% Eu^{3+} phosphors via solid state synthesis, analytical grades of yttrium oxide (Y_2O_3), vanadium oxide (V_2O_5), yttrium acetate ($Y(CH_3COO)_3.H_2O$), boric acid (H_3BO_3), europium oxide (Eu_2O_3), lithium chlorides (LiCl) were purchased from Aldrich Company with the highest purity. In a typical procedure for a stoichiometric YVO_4: 1 wt% Eu^{3+}, 5 g yttrium oxide, 4.068 g vanadium oxide and 0.0787 g europium oxide were ground in an alumina crucible. Also, to prepare the stoichiometric YBO_3: 1%Eu^{3+} phosphor, 5 g yttrium oxide, 0.083 g europium oxide and 2.75 g boric acid should be used similarly through grinding. Finally, the mixtures were calcined at 1100 °C for 2h in air.

2.2. Characterization The crystal structures were analyzed by X-ray diffraction with $Cu_{K\alpha}$ radiation (λ= 1.54 Å).

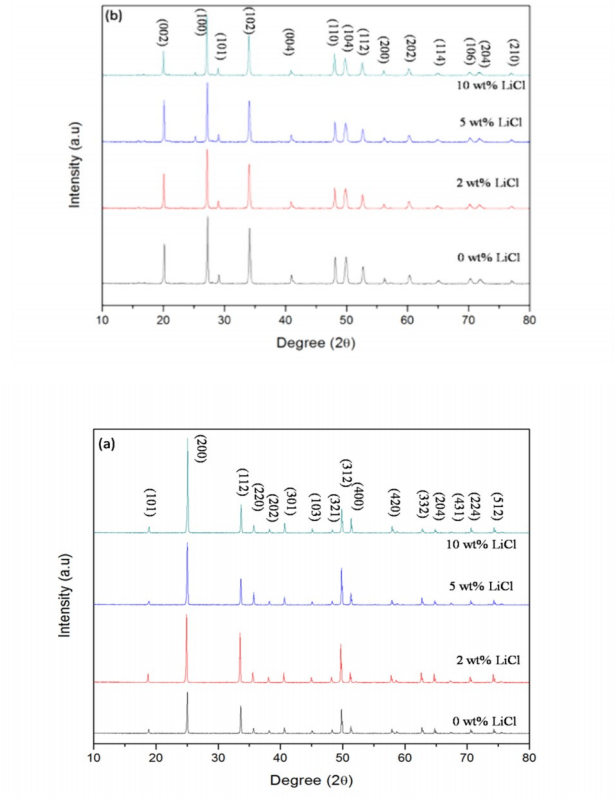

Figure 1. X-ray diffraction patterns of solid state synthesized (a) YVO_4: Eu^{3+} and (b) YBO_3:Eu^{3+} phosphors with different amounts of flux compounds.

3. RESULTS AND DISCUSSION

3.1. XRD analysis Figure 1. shows the XRD spectra of the solid state synthesized YVO4: Eu^{3+} and YBO_3:Eu^{3+} phosphors. These spectra show that the mentioned materials have been well crystallized with JCPDS 01-072-0861 and 16-277, respectively. As seen in Figure 1(a). even relatively high amounts of LiCl cannot be detected significantly in the obtained XRD spectrum. According to Figure 1(b). in the phosphors synthesized by 2% flux compounds, any evident peak contributed to the flux material cannot be seen. On the contrary, when the amounts of LiCl reach to 5 or 10%, an extra peak has been emerged approximately at 25°.

3.2. Microstructure Observations Figure 2. Shows the SEM microstructure of the YVO4: Eu^{3+} and YBO_3:Eu^{3+} phosphors, without and with different quantities of LiCl. It is simply observed that in the presence of flux compound, the particle size of phosphors increases significantly. It can be found that when no flux was used in the solid state procedure, the obtained average particle size for YVO_4: Eu^{3+} and YBO_3:Eu^{3+} phosphors are approximately 1.9 and 1.2µm, respectively.

In the synthesized YVO_4: Eu^{3+} and YBO_3:Eu^{3+} materials with different amounts of flux, the sizes of particles range from 2.3 to 5.6 µm and 1.9 to 4.8µm, respectively. In other words, it can be easily seen that with employing LiCl, growth of phosphor particles has occurred significantly. As the melting point of LiCl is about 610 °C, at the solid state synthesis temperature, this flux is in liquid form via solid state procedure. The investigations prove that while a flux material is melted, the surface tension of molten flux provides coagulation of particles [10]. So the presence of flux compounds plays the role of bridges to connect the phosphor particles. In addition, it has been shown that the presence of melted components during calcination results in easier movement of particles and consequently enhanced contacting and growth of particles [10, 17].

3.3. XPS analysis To study the surface composition of synthesized phosphors, XPS characterization has been known as a powerful method. As it was explained earlier, even relatively high amounts of the flux compounds cannot be detected significantly in the XRD spectra. So, XPS characterization was employed to study the effect of LiCl on the surface chemistry of synthesized phosphors. Figure 3. shows the photoelectron survey spectra of YVO_4:Eu^{3+} phosphors (synthesized with different weight percents of LiCl) in the binding energy from 0 to 1200 eV. It can be seen that the YVO_4:Eu^{3+} phosphor contains Y, V and O elements at 162.6, 519.9 and 527.4 eV, respectively [6].

Interestingly, it is evident that with the addition of LiCl flux material, the intensity of the shown elements increases remarkably. This observation is consistent with the related XRD pattern that was explained in details earlier. Also, it is seen that in the flux-free phosphor and the phosphor synthesized with 10 wt% LiCl, there is not any peak related to LiCl.

But when 20 wt% LiCl was introduced, a very weak peak of LiCl has been emerged.This issue is contributed to the fact that lithium is very light and cannot be efficiently detected by XPS method.

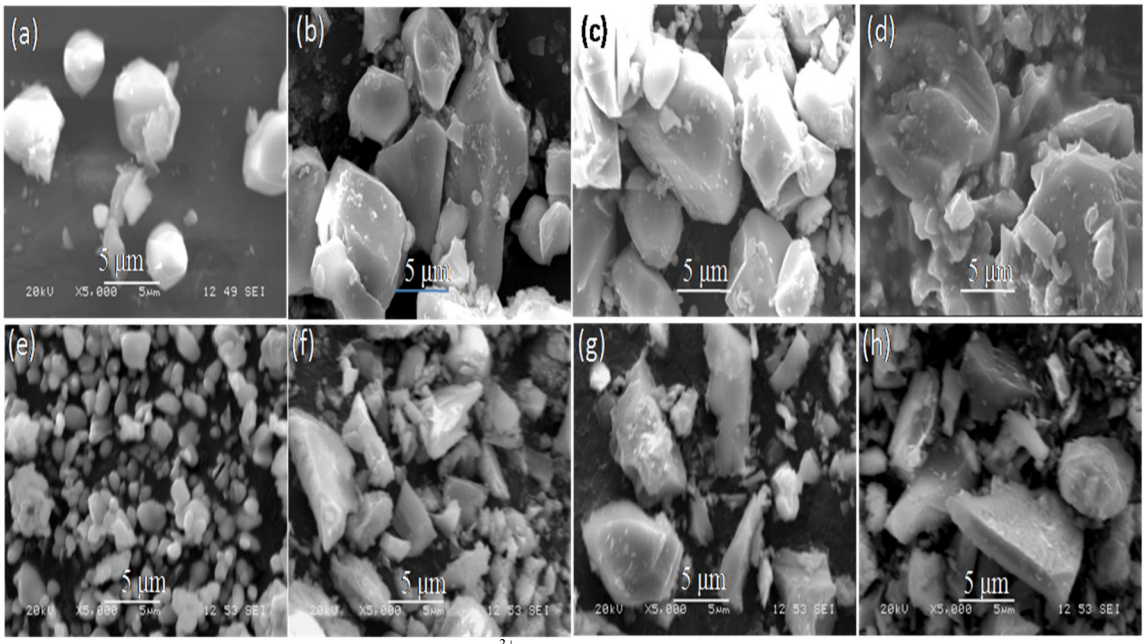

Figure 2. SEM images of solid state synthesized YVO_4: Eu^{3+} with (a) no flux, (b) 2 wt% LiCl, (c) 5 wt% LiCl, (d) 10 wt% LiCl; YBO_3:Eu^{3+} phosphors with (e) no flux, (f) 2 wt% LiCl, (g) 5 wt% LiCl, (h) 10 wt% LiCl.

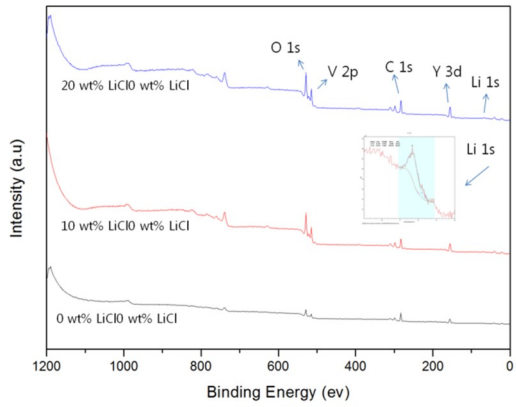

Figure 3. XPS spectra of the solid state synthesized YVO_4: Eu^{3+} with no flux, 10 wt% LiCl and 20 wt% LiCl.

3.4. Photoluminescence properties

In the YVO_4:Eu^{3+} phosphors, a strong and wide excitation band in the range of 235 to 350 nm with a maximum excitation at 310 nm is seen in Figure 4(a). The mentioned wide band with an effective energy transfer is attributed to the V^{5+}–O^{2-} charge transfer state of VO_4^{3-} [18]. According to Figure 4(b). the emission spectrum is dominated by the red $^5D_0$–$^7F_2$ hypersensitive transition of Eu^{3+} (λ_{exc}= 310 nm) [19]. The very evident crystal field splitting of Eu^{3+}, $^5D_0$ – $^7F_{1, 2, 4}$ transitions indicates that the sample is well crystallized.

Figures 4(c&d). show the photoluminescence excitation (PLE) and emission spectra of solid state synthesized YBO_3:Eu^{3+} phosphors under λ_{em}=592 nm and λ_{exc}=240 nm, respectively. It is already proved that the broad band in the range of 200-260 nm is belong to the charge transfer band (CTB) of Eu^{3+}–O^{2-}, since an electron transfers from the oxygen orbitals ($2p^6$) to the empty states of Eu^{3+} (4f) [20]. According to the PL emission spectra, the observed emission peaks in the wavelengths larger than 575 nm are associated with the transitions from the excited $^5D_0$ state to the ^7F_J (J= 1, 2, 3, 4) levels of Eu^{3+} activators [21]. The strong band observed at 592 nm is related to the $^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition of trivalent Eu ions. In the YBO_3 host lattice with a hexagonal crystal structure, since Eu^{3+} ions are substituted into Y^{3+} locations, similar to Y^{3+} ions, Eu^{3+} ions are also surrounded by BO_3 groups and possess a symmetry centre implying a strong $^5D_0 \rightarrow {}^7F_1$ transition. Also, the bands at approximately 611 and 627 nm are attributed to the $^5D_0 \rightarrow {}^7F_2$ electric dipole transitions [1].

In the PL measurements of the phosphors synthesized with flux compounds, with the increase of the amounts of fluxes, no main change in the shape or position of the peaks could be observed, except for the intensity of the peaks. Also, LiCl up to 2 wt% results in the improvement of photoluminescence intensities. But the use of more quantities of the mentioned flux material, suppresses the emission of YVO_4:Eu^{3+} and YBO_3:Eu^{3+} phosphors remarkably. The improvement of PL intensity in the presence of low amounts of flux compounds may be attributed to the improved crystallinity as well as the enlarged grain sizes, explained elsewhere. On the other side, as it was

discussed via XRD spectra, the use of relatively large amounts of flux compounds results in the formation of some impurities in the crystal structure of YVO_4/YBO_3 based phosphors. This phenomenon plays a vital role in decreasing the photoluminescence intensities.

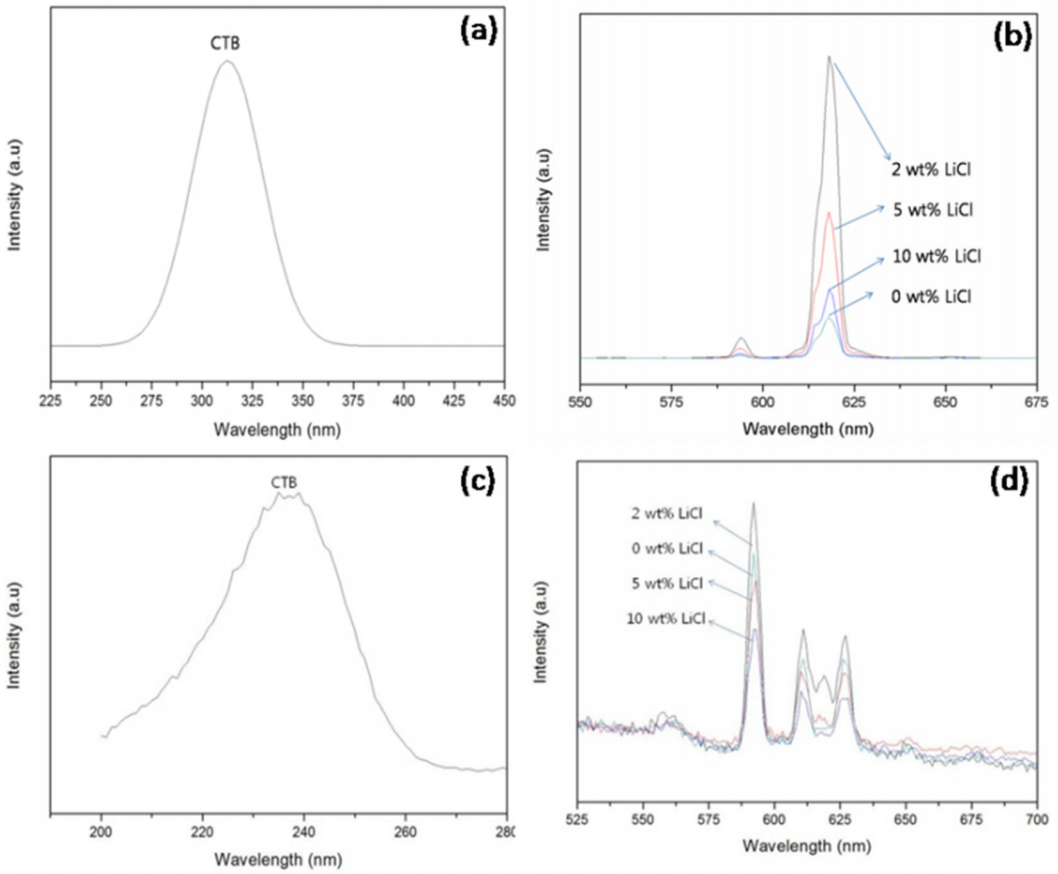

Figure 4. Photoluminescence (a) excitation (λ_{em}=618 nm) and (b) emission (λ_{exc}=310 nm) spectra of solid state synthesized YVO_4: Eu^{3+}, (c) excitation (λ_{em}=592 nm) and (d) emission (λ_{exc}=240 nm) spectra of solid state synthesized YBO_3:Eu^{3+} phosphors.

4. CONCLUSION

Different amounts of LiCl were used as flux compounds in the solid state synthesis of YVO4:Eu^{3+} / YBO_3:Eu^{3+} phosphors. It was observed that the use of LiCl results in the larger particle size of phosphors and the addition of 2 wt% LiCl flux increases the emission intensity of the phosphors efficiently. Also it was shown that further increase of the flux material suppresses the emission intensity significantly.

5. ACKNOWLEDGEMENT

The financial and practical support of Golpayegan University of Technology is appreciated.

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