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Effect of flux compounds on the luminescence properties of Eu^{3+} doped YBO$_3$ phosphors

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In this investigation, Eu^{3+} doped YBO$_3$ phosphors were synthesized by conventional solid state method at 1100 °C under atmosphere condition. Meanwhile, different amounts of LiCl, BaCl$_2$ and CaCl$_2$ were used as the flux compounds to modify the morphology of the phosphor particles and also final luminescent properties. It was concluded that even small amounts of fluxes play a vital role in the growth of particles. Then the emission and excitation photoluminescence spectra were measured respectively at λ_{exc} = 240 nm and λ_{em} = 610 nm and it was found that using 2 wt.% of flux compounds has a significant influence on the emission intensity of YBO$_3$ phosphors.

Keywords: *phosphors; solid state; flux compounds; luminescence*

1. Introduction

Red color luminescent materials based on phosphors are highly demanded in many fields of industry. Among them, RE (rare earth) doped orthoborate materials with a hexagonal crystal structure have attracted worldwide attention since they possess acceptable chemical stability and their ultraviolet (UV) transparency and vacuum ultraviolet (VUV) optical damage threshold are significant [1–4]. So, they have been used as lamp and plasma display panels (PDP) for a long time. In the group of orthoborates, YBO$_3$ has very notable luminescence properties when it is doped by Eu^{+3} [5]. Since the morphology and particle size affect the luminescence behavior of phosphors, [6, 7], so these materials have been synthesized via miscellaneous synthesizing methods, depending on desired final properties and applications. Many researchers have synthesized YBO$_3$ luminescent materials by the conventional solid-state reaction (SR), wet process (WP), sol-gel (SG), solvothermal, hydrothermal and spray pyrolysis techniques [1, 6, 8–11].

In case of synthesizing via solid state reaction, there are some drawbacks such as unacceptable crystallinity, heterogeneity and the need for high calcination temperatures. Hence, some reports of using flux compounds have been presented in order to solve the mentioned weak points [12–15]. Due to the fact that the melting point of a flux is lower than the solid-state reaction temperature, it may facilitate the reaction process of the compounds without participating in the reaction [16]. Alkaline earth metals with low melting temperatures have been used frequently in flux compounds and the most common fluxes are based on halides [17].

In this paper, Eu^{3+} doped YBO$_3$ phosphor was produced by solid state synthesis method. We evaluated also the effect of lithium, barium and calcium chlorides (LiCl, BaCl$_2$ and CaCl$_2$) on the microstructure and luminescence behaviors of these phosphors.

2. Experimental

2.1. Preparation

To produce YBO$_3$:1%Eu^{3+} phosphor via solid state synthesis, the starting materials including yttrium acetate (Y(CH$_3$COO)$_3$·H$_2$O), boric acid (H$_3$BO$_3$), europium oxide (Eu$_2$O$_3$), lithium chlorides (LiCl), barium chlorides (BaCl$_2$) and calcium chlorides (CaCl$_2$) were purchased at the highest possible grade from Aldrich. In a typical

synthesis of YBO_3:1%Eu^{3+} phosphor, specific amounts of yttrium acetate, boric acid and europium oxide were mixed in an alumina crucible, followed by heating in a tube furnace at 1100 °C for 2 hours.

2.2. Characterization

The crystal structures were analyzed by X-ray diffraction with CuKα radiation (λ = 1.54 Å). The morphology of the powders was observed by scanning electron microscope (JSM 6360) and field emission scanning electron microscope (JSM 6330F). Also, X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific, UK) and photoluminescence excitation and emission (PL, FTP Felix 32, Japan) were employed for characterization of synthesized phosphors.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD spectra of the synthesized solid state YBO_3:Eu^{3+} phosphors. The figure confirms that these materials are well crystallized with a hexagonal crystal structure (JCPDS# 16-277). Obviously, in the phosphors synthesized with only 2 % flux compounds, no remarkable differences can be observed compared to those synthesized without any additives. By contrast, when the amount of flux compounds reaches 5 % or 10 %, some extra peaks have emerged in the XRD spectra. For instance, when LiCl has been consumed, an extra peak at approximately 25° has arrived, while additional peaks have been generated at 25.5° and 36° for $BaCl_2$ and 30° for $CaCl_2$.

For the phosphors synthesized with small amounts of flux compounds, ICP analysis was employed to judge about the presence or absence of remaining flux compounds after solid state synthesis at 1100 °C. The results of ICP (not shown) confirmed the remaining of Li, Ba and Ca after solid state synthesis. Also, as the boiling points of LiCl, BaCl2 and $CaCl_2$ are 1382 °C, 1560 °C and 1935 °C, respectively, it is evident that the employed calcination temperature is not sufficient for evacuating the flux compounds.
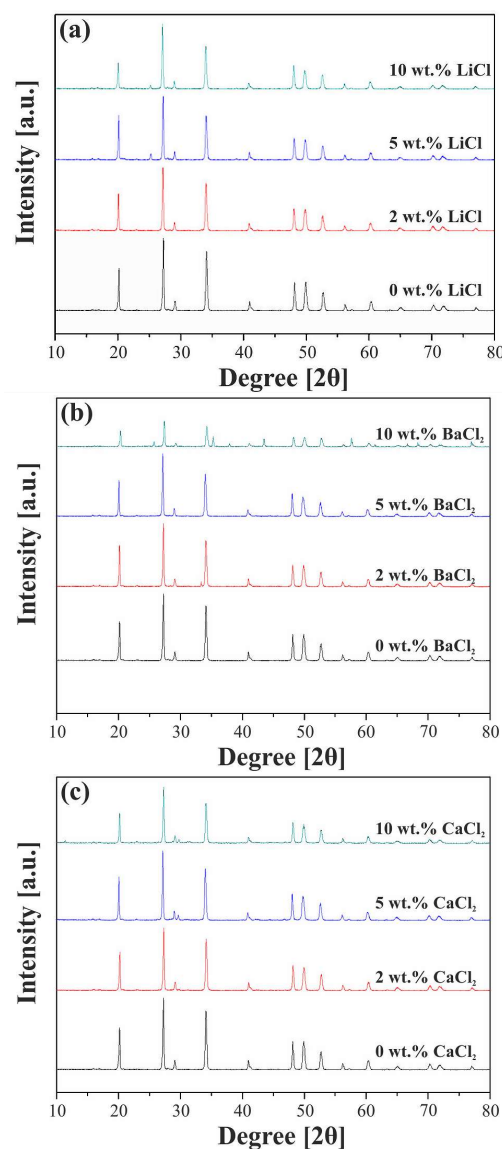

Fig. 1. X-ray diffraction patterns of solid state YBO_3:Eu^{3+} phosphors with different amounts of flux compounds (a) LiCl, (b) $BaCl_2$ and (c) $CaCl_2$.

3.2. Microstructure analysis

Fig. 2 shows the SEM microstructure of YBO_3:Eu^{3+} phosphors, without and with different concentrations of flux compounds. It is easily observed that in the presence of flux compounds, the particle size of phosphors increases significantly.

It can be found that the obtained average particle size is about 1.2 μm when no flux is used in the solid state procedure. Instead, in the presence
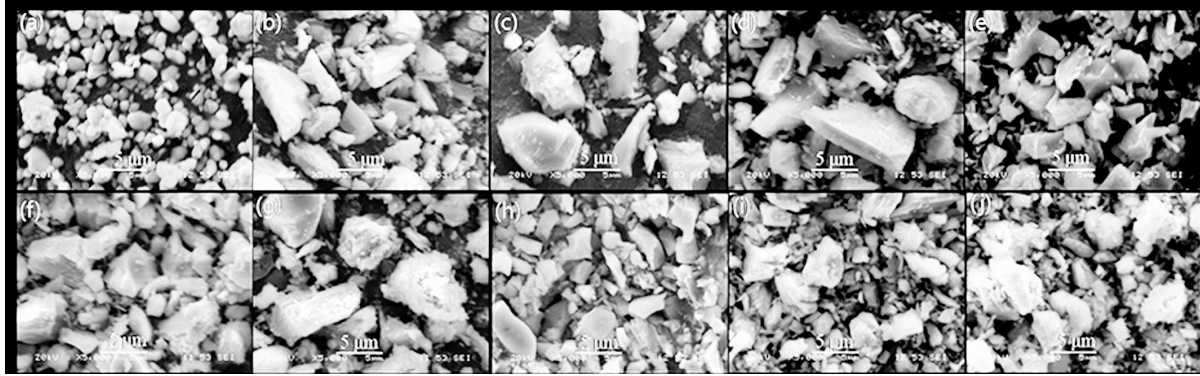
Fig. 2. SEM images of synthesized solid state YBO$_3$:Eu^{3+} phosphors with (a) no flux, (b) 2 wt.% LiCl, (c) 5 wt.% LiCl, (d) 10 wt.% LiCl, (e) 2 wt.% BaCl$_2$, (f) 5 wt.% BaCl$_2$, (g) 10 wt.% BaCl$_2$, (h) 2 wt.% CaCl$_2$, (i) 5 wt.% CaCl$_2$ and (j) 10 wt.% CaCl$_2$.

of flux compounds, the size of particles is in the range of 1.9 μm to 4.8 μm, depending on the type and quantity of employed flux compounds. Hence, it is concluded that regardless of flux type, the addition of flux compounds improves the sintering and the crystal growth. According to Fig. 3, it is seen that LiCl has the strongest effect on the growth of phosphor particles, increasing the particle size from 1.2 μm to 4.8 μm. Conversely, CaCl$_2$ has a relatively weak influence on the growth of particles. The growth rate of particles in the presence of flux compounds can be estimated from the following equation:

$$d\varphi/dt = A_{exp}\frac{-\Delta E}{KT} \qquad (1)$$

In this equation, dφ/dt, A, K, ΔE and T represent particle growth rate, flux related constant, Boltzmann constant, activation energy and synthesizing temperature, respectively [18]. Clearly, the particle growth in the presence of flux compounds depends mainly on the synthesis temperature and the activation energy. The above equation reveals that an increase of temperature and decrease of activation energy, accelerate the crystal growth. As the melting points of LiCl, BaCl$_2$ and CaCl$_2$ are about 610 °C, 962 °C and 775 °C, respectively, at the solid state synthesis temperature (T = 1100 °C), all the flux compounds are molten. So, it can be assumed that for the nuclei in the mixed
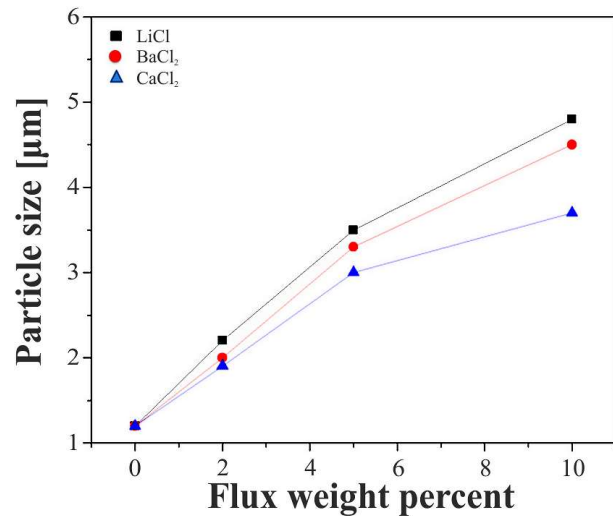

Fig. 3. Variation of phosphor particle size versus flux quantities.

oxide system, the activation energy can be written as [18]:

$$\Delta E = N(Gv + \sigma)\lambda \qquad (2)$$

$$\Delta E \sim N\sigma\lambda \qquad (3)$$

This implies that the change in free energy depends directly on the number of nuclei (N), surface energy (σ) and the volume of nuclei (λ).

It can be found that flux composition affects the surface energy and so activation energy, significantly. Also, referring to the presented comparison of growth rates, LiCl provides the lowest surface energy.
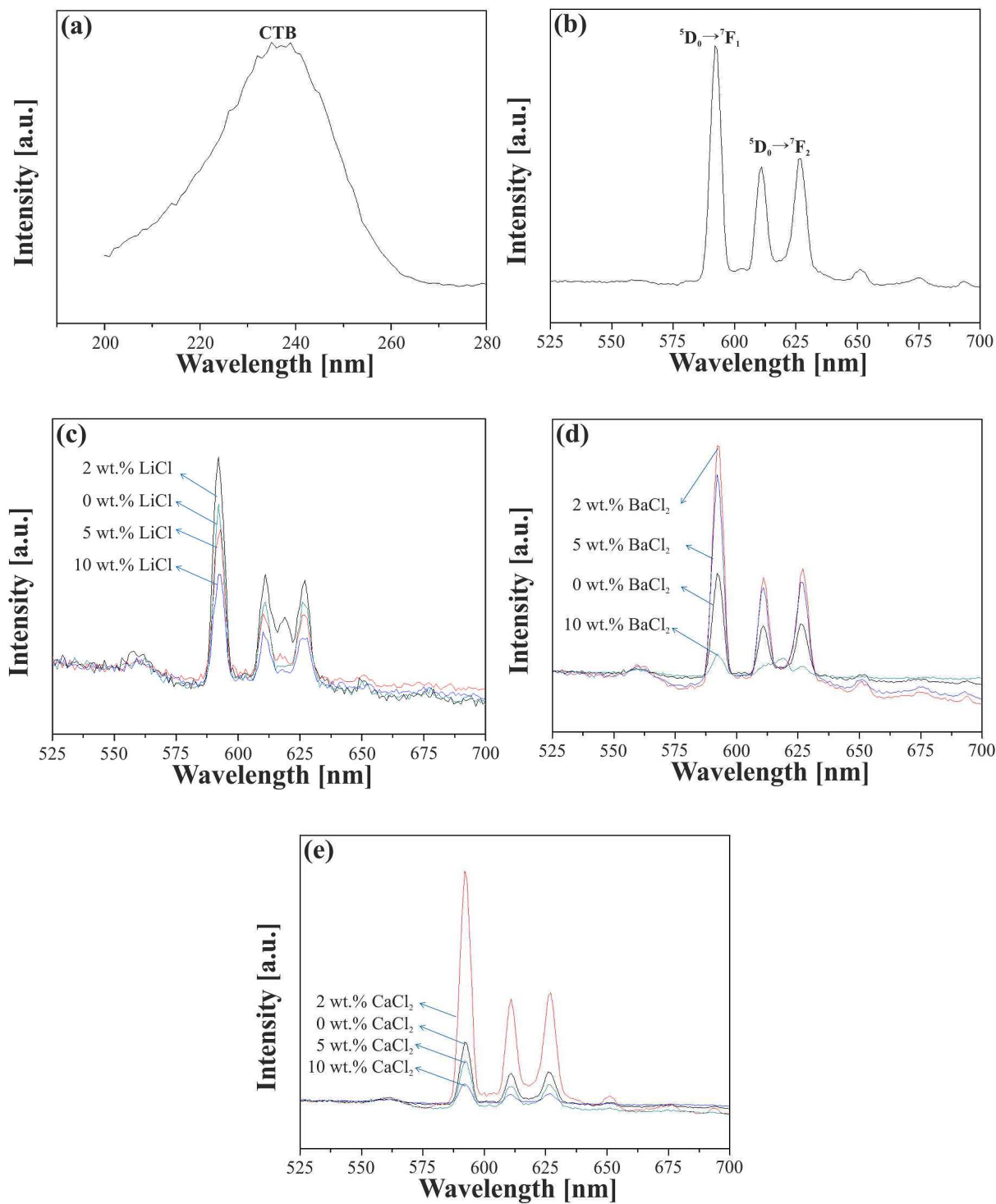
Fig. 4. Photoluminescence spectra (a) excitation ($\lambda_{em} = 592$ nm) and (b) emission ($\lambda_{exc} = 240$ nm) of solid state synthesized YBO_3:Eu^{3+} phosphors, and the influence of different weight percentages of (c) LiCl, (d) $BaCl_2$ and (e) $CaCl_2$ fluxes ($\lambda_{exc} = 240$ nm) in YBO_3:Eu^{3+} phosphors.

3.3. Photoluminescence properties

Fig. 4 shows the photoluminescence excitation (PLE) and emission spectra of synthesized solid state YBO_3:Eu^{3+} phosphors under $\lambda_{em} = 592$ nm and $\lambda_{exc} = 240$ nm, respectively. It has already been proved that the broad band in the range of 200 nm to 260 nm belongs to the charge transfer band (CTB) of Eu^{3+}–O^{2-}, since an electron transfers from the oxygen orbit ($2p^6$) to the empty states of Eu^{3+} ($4f$) [8]. Also, in the PL emission spectra, the observed emission peaks in the wavelengths larger than 575 nm are associated with the transitions from the excited $^5D_0$ level to ^7F_J (J = 1, 2, 3, 4) levels of Eu^{3+} activators [19]. The strong band observed at 592 nm is related to the $^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition of trivalent Eu ions. In 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 center implying a strong $^5D_0 \rightarrow {}^7F_1$ transition. Also, the bands at approximately 611 nm and 627 nm are attributed to the $^5D_0 \rightarrow {}^7F_2$ electric dipole transitions [20]. In the PL measurements of the phosphors synthesized with flux compounds, with an increase in the amount of fluxes, no main change in the shape or position of peaks could be observed, except the intensity of the peaks. Also, the addition of up to 2 wt.% of LiCl, $BaCl_2$ and $CaCl_2$ results in enhancement of the photoluminescence intensities. But the use of larger quantities of fluxes suppresses emission of YBO_3:Eu^{3+} phosphors. 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 size, explained elsewhere. On the other hand, as it was discussed for the XRD spectra, the use of relatively large amounts of flux compounds results in the formation of some impurities in the crystal structure of YBO_3 phosphors. This phenomenon plays a vital role in suppressing the photoluminescence intensities. Noteworthy, the intensity ratio of the $^5D_0 \rightarrow {}^7F_1$ transition to that of $^5D_0 \rightarrow {}^7F_2$ transition depends strongly on the local symmetry of Eu^{3+} ions. In short, when Eu^{3+} ions occupy the inversion center sites, this ratio will be larger and the produced phosphor looks more reddish.

4. Conclusions

Different amounts of LiCl, $BaCl_2$ and $CaCl_2$ were used as flux compounds in the solid state synthesis of YBO_3:Eu^{3+} phosphors. LiCl and $CaCl_2$ showed the strongest and weakest effect on the growth of particles, respectively. Also, it was argued that an addition of 2 wt.% of the mentioned fluxes increases the emission intensity of YBO_3:Eu^{3+} phosphors efficiently but further increase of these compounds suppresses it significantly.

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