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Photoluminescence of ZnS:Tb phosphors fritted with different fluxes

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Abstract

ZnS:Tb phosphor powders were prepared by solid-state synthesis. Without addition of flux, only emission from the host luminescence was observed. There is no the characteristic luminescence of Tb for ZnS:Tb without the additions of fluoride fluxes or chloride fluxes. For ZnS:Tb with LiF, NaF and KF additions, characteristic luminescence of Tb emerges, which corresponds to the transitions of $^5D_4 \rightarrow {}^7F_J$. The highest peak is located at 548 nm. For ZnS:Tb with additions of NaCl and KCl fluxes, both the characteristic luminescence of Tb and the luminescence of the host material were observed. However, only the host luminescence was shown in the spectrum for ZnS:Tb fritted with LiCl. It is difficult to observe the characteristic luminescence of Tb. The microstructure of ZnS:Tb fritted with chlorine fluxes show well crystallized uniform grains. However, with fluoride fluxes, huge crystalline grains with irregular morphology were obtained.

Keywords: ZnS; Tb; Flux; Phosphors; Luminescence properties

1. Introduction

ZnS is a common host material. Different activators, such as transition ions or rare earth ions, were used to modify the color of luminescence. Most reports regarding ZnS in the literature focused on the thin film form, particularly for use in thin film electroluminescent display devices [1–2]. Little research was found on ZnS phosphors in powder form [3]. In this study, ZnS:Tb phosphor powders were prepared using a solid-state method. There is no characteristic luminescence of Tb in the phosphor, for a simple ZnS:Tb fired mixture [4]. Addition of fluxes is necessary to create a liquid phase during firing, which promotes the contacts between the particles and thus reduces the activation energy. The charge compensation helps the energy transfer to the Tb ions, which leads to the radiation of the characteristic luminescence of Tb [5–8]. Halide fluxes including LiF, NaF, KF, LiCl, NaCl and KCl [9–13] were used in this study to investigate their effects on the physical characteristics, such as crystallite size and morphology, and the emission of the ZnS:Tb phosphors.

2. Experimental procedure

Terbium nitrate was first dissolved in deionized water, and then the flux and ZnS were added and mixed thoroughly by mechanical stirring. Since Halide fluxes were soluble in water, they were mixed with ZnS through a solution coating process to ensure a homogeneous distribution of the fluxes around the ZnS particles. The slurry was then dried in water bath, mixed with alcohol, and baked at 120 °C for 16 h in an oven. Subsequently, the mixtures were fired at 1125 °C for an hour under reducing atmosphere. The fired ZnS:Tb phosphors were then characterized. Most fluxes used in the process remained in the phosphors after firing. The morphologies and crystallite sizes of phosphor powders were observed by scanning electron microscopy (SEM). X-ray diffraction (XRD) was used to identify the structures of the products using a Rigaku D/Max B with Cu $K\alpha_1$ radiation at 40 kV. Emission spectra were measured by a spectrofluorophotometer (Shimadzu RF-5301PC), equipped with the standard lamp.

3. Results and discussion

Fig. 1 shows the XRD patterns of ZnS doped with various amount of Tb and fired at 1125 °C. The results indicate all to have a similar pattern, and contain a low temperature cubic

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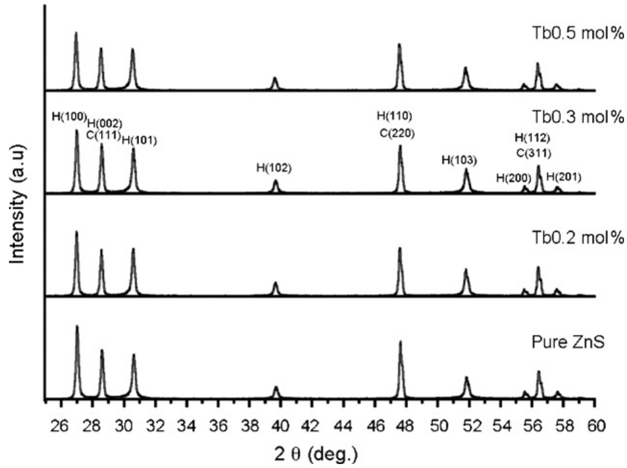

Fig. 1. X-ray diffraction patterns of ZnS doped with various amount of Tb and fired at 1125 °C.

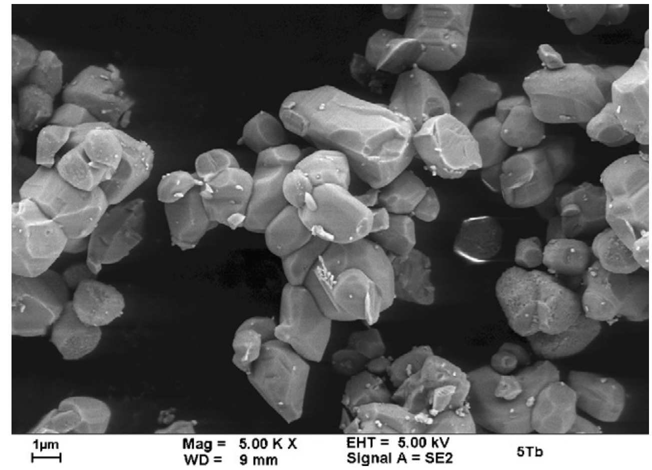

Fig. 3. SEM micrograph for ZnS:Tb (0.3 mol%) phosphor and fried at 1125 °C.

phase (zinc-blende phase) and a high temperature hexagonal phase (Wurtzite phase) of ZnS. No other peaks do exist in the XRD patterns, which indicates that most of the fluxes used in the process remained in the phosphors and formed a solid solution. For ZnS fired with different fluxes such as LiCl, NaCl, KCl, LiF and KF, the ratios of hexagonal to cubic phases vary. ZnS fritted with NaF flux will suppress hexagonal phase growth during firing, while others do not change the patterns significantly, as shown in Fig. 2. This is probably due to the relatively high melting point of NaF (996 °C) [14], and the absence of molten salt at a firing temperature of 1125 °C.

Fig. 3 shows SEM micrograph of ZnS doped with 0.3 mol% Tb, whereas Figs. 4 and 5 show the SEM micrographs of ZnS (0.3 mol% Tb) fritted with KF and KCl fluxes and fired at 1125 °C, respectively. As shown in Fig. 3, with 0.3 mol% Tb doped ZnS shows well crystalline grains with size ranging from 2 to 4 μm. For ZnS (0.3 mol% Tb) fritted with fluoride such as KF, an irregular morphology and a wide distribution of the grain were observed. Lots of small particles attached on the surfaces of the ZnS grains, as indicated in Fig. 4, were characterized as a Tb compound. For ZnS (0.3 mol% Tb) fritted with chloride (such as KCl), the morphology and the size of the crystalline grains are similar to those of ZnS (0.3 mol% Tb) without flux addition, as indicated in Fig. 5. Well crystalline grain and clean grain surfaces are obtained.

For ZnS doped with Tb, there is no characteristic luminescence of Tb in the spectrum. Only weak emission from the host luminescence was observed [4]. With the additions of fluoride flux, such as LiF, NaF and KF, the characteristic luminescence of Tb emerges, due to the electronic transitions $^5D_4 \rightarrow {}^7F_J$. They correspond to the $^5D_4 \rightarrow {}^7F_6$ (488 nm), $^5D_4 \rightarrow {}^7F_5$ (548 nm), $^5D_4 \rightarrow {}^7F_4$ (587 nm), $^5D_4 \rightarrow {}^7F_3$ (622 nm) and a weak $^5D_4 \rightarrow {}^7F_2$ (648 nm) transitions. This is due to the fact that the flux addition helps the recrystallization of ZnS, which enhances the solubility of Tb^{3+} in the host material. In addition, F ions are easy to form the characteristic luminescence center with Tb ions [15]. The intensity of the luminescence is dependent on the concentration of the Tb dopant. A typical example is shown in Fig. 6 for ZnS:Tb with KF addition. The emission intensity maximizes at 0.3% of Tb. As Tb concentration exceeds 0.3 mol%, the luminescence decreases due to concentration quenching [16]. Fig. 7 shows the photoluminescence of ZnS:Tb (0.3 mol%) with the additions of various fluoride fluxes

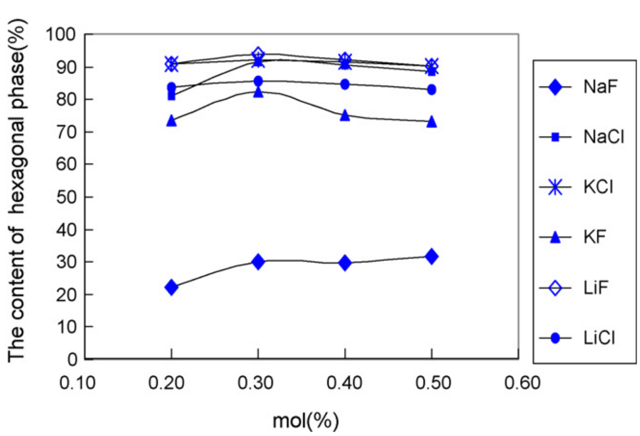

Fig. 2. Effects of the flux concentration on the content of the hexagonal phase in the phosphors.

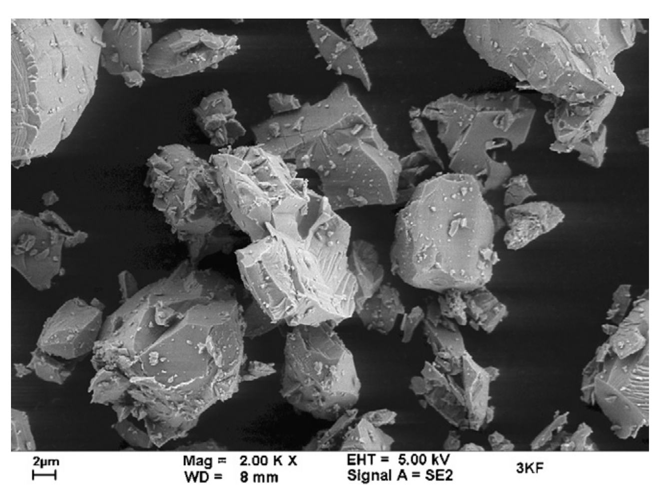

Fig. 4. SEM micrograph for ZnS:Tb (0.3 mol%) phosphor fritted with KF and fried at 1125 °C.

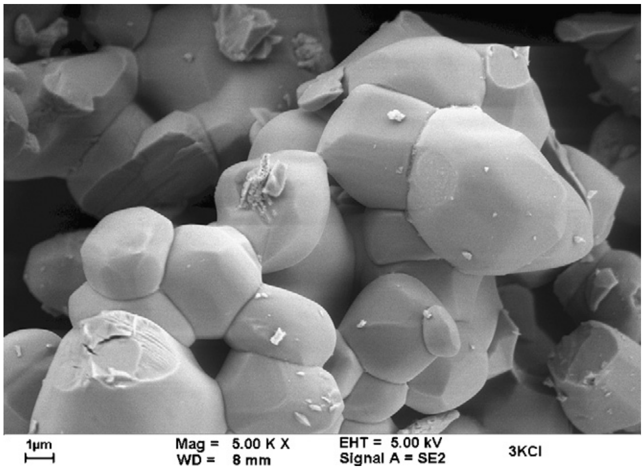

Fig. 5. SEM micrograph for ZnS:Tb (0.3 mol%) phosphor fritted with KCl and fried at 1125 °C.

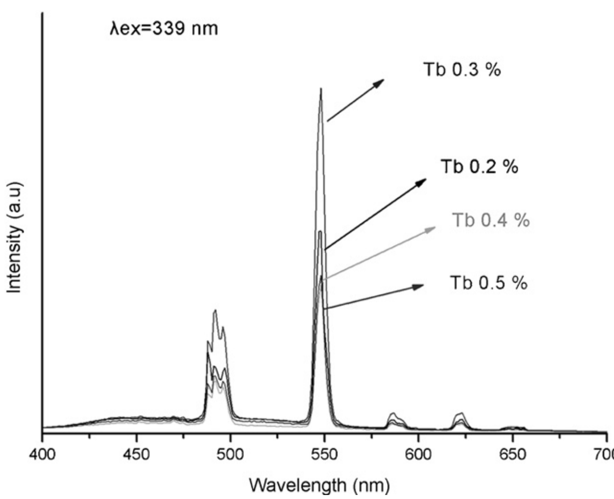

Fig. 6. Emission spectra of ZnS:Tb phosphors doped with various amount of Tb, fried at 1125 °C with KF flux.

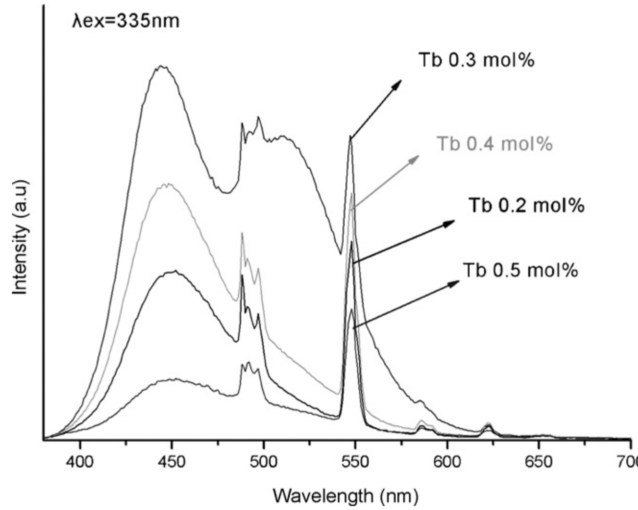

Fig. 8. Emission spectra of ZnS:Tb phosphors doped with various amount of Tb, fried at 1125 °C with KCl flux.

including LiF, NaF and KF. The relative intensity of luminescence for the fluxed ZnS:Tb (0.3 mol%) phosphors follows the sequence: KF > NaF > LiF. The K ions possess the largest ionic radius which induces a larger lattice distortion. It, in turn, results in a better defect luminescence mechanism [13].

The luminescence intensities of the ZnS:Tb fluxed with chlorides, including LiCl, NaCl and KCl, were also studied. ZnS:Tb with LiCl flux addition shows no characteristic luminescence of Tb. Only the host luminescence resulting from the self-activator was observed [4]. Both the host luminescence and the Tb characteristic luminescence were observed when ZnS:Tb was fritted with NaCl and KCl fluxes. This derives from the fluxes enhancing the solubility of the Tb ions in the host material and the Cl ions in ZnS lattices facilitating the formation of the host materials luminescence center [15]. A typical example is shown in Fig. 8 for the ZnS:Tb fluxed with KCl. The luminescence intensity varies with the Tb concentration, up to a maximum at 0.3 mol%. The relative luminescence intensity of the chloride fluxed ZnS:Tb phosphors follows the sequence:

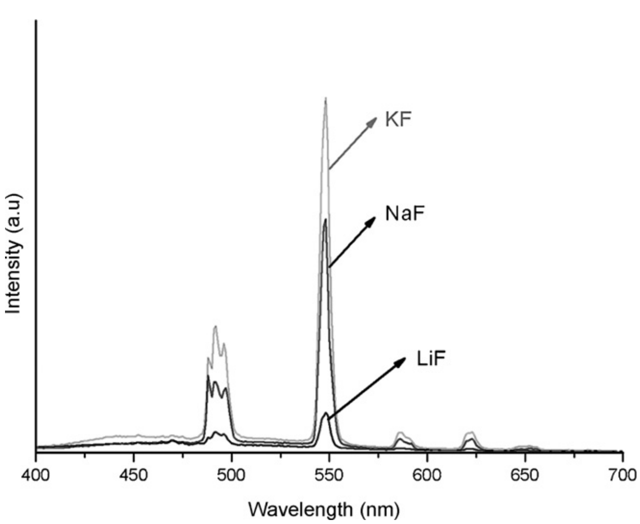

Fig. 7. Emission spectra of ZnS:Tb (0.3 mol%) phosphors fritted with various fluorides and fried at 1125 °C.

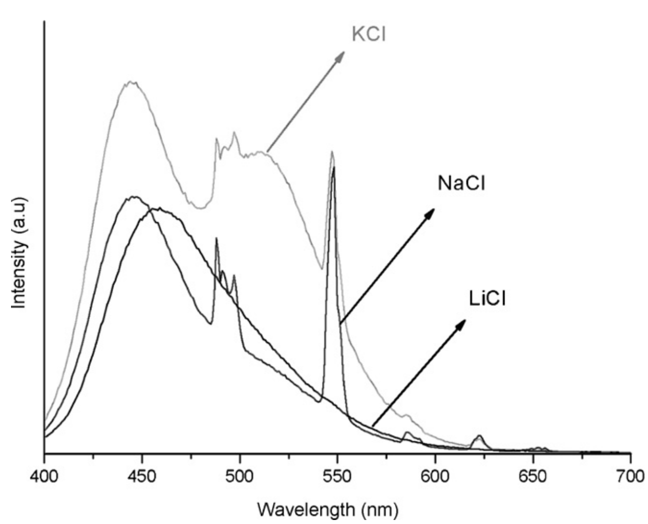

Fig. 9. Emission spectra of ZnS:Tb (0.3 mol%) phosphors fritted with various chlorides and fried at 1125 °C.

KCl > NaCl > LiCl, as indicated in Fig. 9. This is also due to the ionic size effect of the cations.

4. Summary

For the ZnS:Tb phosphor fired at 1125 °C under reducing atmosphere, no Tb characteristic luminescence takes place. Only faint emission from the host luminescence was observed. For the ZnS:Tb fritted with various halide fluxes, the following has been observed:

1. For ZnS:Tb phosphors with fluoride fluxes additions, characteristic luminescence of Tb emerges in the spectra. The ZnS:Tb fritted with chloride fluxes including NaCl and KCl, both the Tb characteristic luminescence and the ZnS host luminescence were observed. However, with the addition of LiCl flux, it is difficult to observe the characteristic luminescence of Tb, but the host luminescence was observed.
2. For ZnS:Tb phosphors fritted with halide fluxes, the best luminescence intensity is obtained at Tb concentration of 0.3 mol%.
3. For ZnS:Tb fluxed with chlorides, well crystallized grains were obtained. However, huge crystalline grains with irregular morphology were formed when ZnS:Tb was fritted with fluorides.
4. Among the fluxes, the larger the ionic radius of cation, the greater the luminescence intensity.

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