Photoluminescent Properties of Europium-Activated Zn_2SnO_4 Phosphors

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Zn_2SnO_4 , which has an inverse spinel structure, was adopted as the host material of a new green emitting phosphor. The photoluminescent (PL) properties of a series of europium-activated zinc stannate synthesized by vibrating milled solid state reaction have been investigated. One broad emission band from the $\text{Zn}_2\text{SnO}_4:\text{Eu}^{2+}$ phosphor calcined at 1000°C to 1200°C for 3 h in air atmosphere is clearly observed at 525 nm under 374 nm UV ray excitation. The emission band from $\text{Zn}_2\text{SnO}_4:\text{Eu}^{3+}$ can also be observed under 464 nm-ray excitation. The reduction of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ was firstly discovered in stannate phosphor of $\text{Zn}_2\text{SnO}_4:\text{Eu}$ synthesized in air condition.

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1. Introduction

In recent years, the developments of the flat panel display devices, such as field emission displays (FED), plasma display panels (PDP) and thin film electro-luminescent devices (TFEL), require efficient luminescent materials under vacuum ultraviolet (VUV) radiation and low-voltage electron bombardment. The efficiency of phosphors has been advanced by both a new host material and improved synthetic technique.^{1,2)}

Generally, the luminescent properties of phosphors are strongly dependent on the crystal structure of the host materials. SnO_4^{4-} anions are reported to be optically-inert, and could be a candidate for host materials.³⁾ There were only a few researches of SnO_4^{4-} anions based oxides of luminescent properties in the literature.¹⁾ Simple oxide spinels are represented by AB_2O_4 , where A and B are cations satisfying the charge neutrality. A “normal spinel” has the A cations completely distributed in the available tetrahedral sites, while the B cations are distributed in the octahedral sites. It is known as “inverse spinel” for one half of A cations occupy tetrahedral sites and the other half of A cations are in the octahedral sites with all B cations.

Zinc stannate, Zn_2SnO_4 , forms in the inverse spinel crystal structure and is the focus of this investigation. N-type semiconducting Zn_2SnO_4 with a reported wide band gap (E_g) of 3.6 eV was found to crystallize in a cubic inverse spinel with the space group $\text{Fd}\bar{3}\text{m}$ and the lattice parameter is $a = 0.866 \text{ nm}$.⁴⁻⁶⁾ Because of its highly thermodynamic stability, optical transparency and semiconductivity, Zn_2SnO_4 as an gas-sensing and transparent conducting oxide material has attracted wide interest.^{5,7-9)} It has been reported that Zn_2SnO_4 powders could be prepared by solid-state reaction, usually performed at a higher temperature over 1000°C .¹⁰⁾

Furthermore, rare earth ions have been widely used as activators for different host materials. Divalent europium ions are known to exhibit as activators in blue-to-yellow emitting phosphors.¹¹⁻¹³⁾ Therefore, many researchers worldwide have studied the luminescent properties of Eu^{2+} ions in

various matrix compounds. Eu^{3+} could be reduced to Eu^{2+} in most of matrix compounds if preparations were carried out in reducing atmospheres. It has also been found that in some special compounds the reduction of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ could occur when samples were prepared in air condition at high temperature.^{11,14)} This paper presents the study on the luminescent properties of Eu^{2+} -activated Zn_2SnO_4 phosphors prepared by solid state reaction.

2. Experimental

The $\text{Zn}_2\text{SnO}_4:x\text{Eu}$ ($x = 1-5 \text{ mol}\%$) compound was prepared by using oxides of the high purity (99.99%). An initial mixture of $2\text{ZnO}:\text{SnO}_2$ with different contents of Eu_2O_3 was mechanically activated by grinding in a vibro-mill for 1 h. The mixture was calcined at 1000°C up to 1200°C for 3 h in ambient air; however, no flux was used in the synthesis.

The phase purity and homogeneity of the as-prepared $\text{Zn}_2\text{SnO}_4:x\text{Eu}$ samples were investigated by X-ray diffraction (XRD). The XRD profiles were measured with a Rigaku D/max X-ray diffractometer, using $\text{CuK}\alpha$ ($\lambda = 0.15406 \text{ nm}$). The ambient temperature photoluminescence (PL) spectra were obtained at room temperature by scanning wavelength region from 300 to 700 nm under an excitation light source by Xe lamp.

3. Results and Discussion

The crystal structure of Zn_2SnO_4 was originally described by Hill *et al.*¹⁵⁾ The XRD profiles for $\text{Zn}_2\text{SnO}_4:x\text{Eu}$ phases with $x = 0, 1\%, 3\%$ and 5% calcined at 1200°C are shown in Fig. 1. As a result, a typical Zn_2SnO_4 pattern was observed in the XRD profiles for all samples investigated. However, the presence of a second phase in the proportion of any Eu^{2+} concentration can be pointed out as europium tin oxide ($\text{Eu}_2\text{Sn}_2\text{O}_7$) and can not be ruled out for the samples. Europium ions could not substitute the Zn^{2+} sites completely due to the difference between the Eu^{2+} ionic radius and the Zn^{2+} ionic radius (*e.g.* $r_{\text{Eu}^{2+}} = 0.117 \text{ nm}$, $r_{\text{Zn}^{2+}} = 0.083 \text{ nm}$). The crystallinity of the zinc stannate with different levels of Eu_2O_3 dopants was the same, but the contents of the $\text{Eu}_2\text{Sn}_2\text{O}_7$ phase increased with increasing x . Figure 2 shows the XRD patterns of $\text{Zn}_2\text{SnO}_4:3\%\text{Eu}$ calcined at 1000°C , 1100°C and 1200°C in air. The samples calcined at different

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Fig. 1 The X-ray diffraction patterns of the Zn_2SnO_4 : $x\text{Eu}$ calcined at 1200°C for 3 h: (a) $x = 0$; (b) $x = 1\%$; (c) $x = 3\%$; and (d) $x = 5\%$.

Fig. 2 The X-ray diffraction patterns of the Zn_2SnO_4 : $3\%\text{Eu}$ calcined at different temperature: (a) 1000°C ; (b) 1100°C ; and (c) 1200°C for 3 h.

temperature without changes of the contents and FWHM of the Zn_2SnO_4 and the $\text{Eu}_2\text{Sn}_2\text{O}_7$ phases.

The photoluminescence spectra were measured under an

Fig. 3 The photoluminescence properties of Zn_2SnO_4 : $x\text{Eu}$ under 374 nm UV ray excitation: (a) the PL spectrum of 3% Eu; (b) the PL intensity versus Eu concentration.

excitation light source from 300 to 700 nm. Three notable excitation bands could be observed at 347 nm, 374 nm and 464 nm. The emission spectrum of Zn_2SnO_4 : $3\%\text{Eu}$ phosphors under 374 nm UV ray excitation and the dependence of emission intensity with Eu concentration are expressed in Fig. 3. The doping of different levels of Eu^{2+} ion in Zn_2SnO_4 host material results in green emission. The emission process from this material is attributed to $4f^65d^1 \rightarrow 4f^7$ transition for the Eu^{2+} ions acting as an activating center. Generally, the divalent europium doped phosphor brings blue emission. In contrast, the emission spectrum of Zn_2SnO_4 : Eu phosphor due to the different crystal field is centered around 525 nm, it is presumed that energy from the 374-nm excitation band may be trapped at the Eu^{2+} ion, and appears greenish-white to the naked eyes.

As can be seen in Fig. 3(b), the emission intensity of Zn_2SnO_4 : $x\text{Eu}$ increases with the concentration of Eu at the lower Eu region. The probability of an energy transfer among Eu^{2+} ions increases when the Eu^{2+} concentration increases.¹⁶⁾ It reaches a maximum at Eu concentration at 3 mol% and diminishes with increasing Eu contents, indicating concentration quenching. A non-radiative energy transfer from one Eu^{2+} ion to another Eu^{2+} ion usually occurs as a result of an exchange interaction, radiation reabsorption or a

Fig. 4 The PL spectra of Zn_2SnO_4 : 3%Eu under 374 nm UV ray excitation calcined at different temperatures: (a) 1200°C (b) 1100°C (c) 1000°C.

multipole-multipole interaction. Since the $4f$ - $5d$ transition of Eu^{2+} is allowed, the energy transfer will occur only as a result of an electric multipolar interaction.¹⁶⁾

As mention above, the emission intensity of Zn_2SnO_4 : xEu reaches a maximum of Eu concentration at 3 mol%. Figure 4 shows the PL spectra of Zn_2SnO_4 :3%Eu under 374 nm UV ray excitation with different calcined temperatures at 1000°C, 1100°C and 1200°C. The broadness of the emission band indicates an interaction between the host and the activator, which can be attributed to the presence of an excited electron in an outer shell of the Eu^{2+} ion.¹⁷⁾ The emission band at about 525 nm shifts slightly to a longer wavelength with an increase in calcined temperature. It could be attributed to some changes in the crystal field around Eu^{2+} ions that increased the calcined temperature, although there was no change in XRD profiles. The emission intensity under 374 nm-ray excitation of the samples calcined at 1200°C is much stronger than the samples calcined at 1000°C. Under shown in 464 nm-ray excitation, the emission spectra are shown in Fig. 5. The emission spectra can be indicated to that there were still little amount trivalent europium ions act as activators in Zn_2SnO_4 matrix. In Fig. 5, the emission intensity of Eu^{3+} ions opposite to Eu^{2+} ions (Fig. 4) decreased with increasing calcined temperature. Combination of Fig. 4 and Fig. 5, the reduction of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ plays an important role of the luminescent properties in zinc stannate. The reduction of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ occurs in the compound due to two reasons.¹¹⁾ One of them is no oxidizing ions present in the host compounds. The other one is the dopant trivalent europium ion replaces the divalent cation in the host. Eu^{3+} ions could be more easily reduced to its divalent states at higher temperature in air atmosphere, and increase luminescent efficiency of Zn_2SnO_4 : Eu^{2+} phosphors.

4. Conclusions

We have successfully synthesized a Eu^{2+} -activated Zn_2SnO_4 green phosphor by solid state reaction. The spinel phase of Zn_2SnO_4 is formed by firing above 1000°C in

Fig. 5 The PL spectra of Zn_2SnO_4 : 3%Eu under 464 nm-ray excitation calcined at different temperatures: (a) 1200°C (b) 1100°C (c) 1000°C.

ambient air. The second phase, $\text{Eu}_2\text{Sn}_2\text{O}_7$, appears with Eu_2O_3 doped at all conditions. The emission spectrum of Zn_2SnO_4 :Eu phosphor is centered around 525 nm, and shows greenish-white light. The optimum concentration of Eu^{2+} showing the maximum PL intensity was 3 mol%.

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