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Synthesis and luminescent characterization of zinc thiogallate

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Abstract

Eu doped zinc thiogallate, $ZnGa_2S_4:Eu^{2+}$, powders were prepared by solid state reaction process at H_2 atmosphere by introducing extra S vapor to compensate for the evaporation loss of S. A single phase $ZnGa_2S_4:Eu^{2+}$ could be obtained by firing above 850 °C for 3 h at 5% H_2 atmosphere. It exhibited a green emission band at 540 nm with an excitation wavelength of 465 nm that could be emitted from commercial blue LEDs. The maximum emission intensity could be achieved from 4 mol% Eu^{2+} doped $ZnGa_2S_4$ phosphors.

Keywords: Powders-solid state reaction; X-ray methods; Optical properties; Functional applications; Zinc thiogallate

1. Introduction

AB_2X_4 (A^{II} = Sr, Ca, Zn, Cd; B^{III} = Ga; X^{VI} = S, Se, Te) thiogallate compounds have been focused due to infrared (IR) transmission as well as their excellent photoconductive and nonlinear optical properties. Most of AB_2X_4 thiogallate have a defect chalcopyrite structure by replacing a half of A site cations with vacancies as shown in Fig. 1.[1,2]

Among thiogallate compounds, recently, $SrGa_2S_4:Eu^{2+}$ and $CaGa_2S_4:Eu^{2+}$ have been focused as green phosphors for white light emitting diodes (LEDs), because their photoluminescence (PL) spectra exhibited a very strong green emission around 520–540 nm with the excitation wavelength of 450–470 nm that could be emitted from commercial blue LEDs.[3,4] Besides $SrGa_2S_4$ and $CaGa_2S_4$, $ZnGa_2S_4$ is well known as a good IR-transmitting material in the range of 2.5–12 μm. It has the $I\bar{4}2m$ tetragonal structure.[2,4,5] The tetragonal unit cell has lattice parameter a_1 and c_1 of 0.5297 and 1.0363 nm, respectively.

Even though $ZnGa_2S_4$ has almost same crystal structure with that of $SrGa_2S_4$ and $CaGa_2S_4$, its luminescent properties as a phosphor have been rarely reported yet.

In this work, we synthesized Eu doped $ZnGa_2S_4$ thiogallate by solid-state reaction, and investigated the effects of firing conditions and Eu^{2+} doping on the synthesis and luminescent properties.

2. Experiment

Eu doped $Zn_{1-x}Eu_xGa_2S_4:Eu^{2+}$ phosphor was synthesized by solid state reaction with ZnS (Aldrich, 99.99%), Ga_2S_3 (Aldrich, 99.99%), and EuS (Kojundo, 99.9%). Instead of toxic H_2S gas, 5 and 1% H_2 gas was employed for the reduction atmosphere by the flow rate of 100 sccm, and extra S powders were put in the reaction crucibles together with reactants or separately in the furnace tube to compensate for the evaporation loss of S. Firing temperatures were ranged from 800 to 1150 °C, and Eu^{2+} doping concentrations varied from 1 to 5 mol%. The crystalline phases of $ZnGa_2S_4:Eu^{2+}$ phosphors were analyzed by X-ray diffractometer (XRD, SIEMENS D5005). Photoluminescence was measured by PL system (PSI Darsa-5000) with a Xe lamp and a monochrometer. Energy dispersive spectroscopy (EDS, JEOL JSM-6500F) and scanning electron microscope (SEM, JEOL JSM-6500F) were used to determine the atomic ratio and the particle shape.

3. Results and discussions

Fig. 2 shows XRD patterns of the mixture of ZnS and Ga_2S_3 (1:1) fired at 1100 °C under 5 and 1% H_2 atmosphere, respectively. A single phase $ZnGa_2S_4$ could be synthesized at 5% H_2, while $ZnGa_2O_4$ oxide phase was obtained at 1% H_2 due to the oxidation rather than the sulfuration. So our experiments were carried out at 5% H_2 atmosphere.

XRD patterns of 4 mol% Eu doped $ZnGa_2S_4$ phosphors heated at 800–1150 °C all exhibited strong characteristic peaks of $ZnGa_2S_4$. According to the phase map of ZnS–Ga_2S_3

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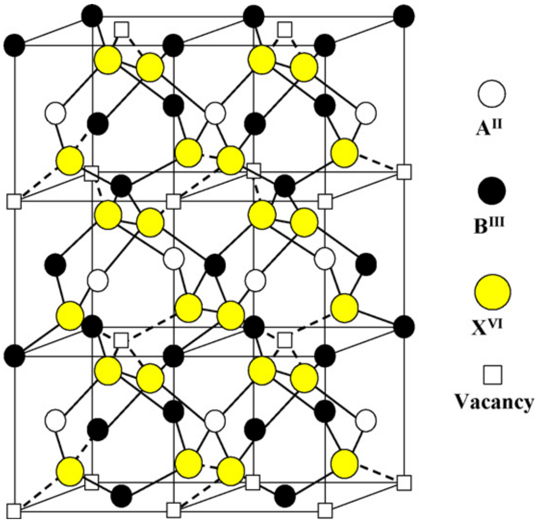

Fig. 1. A crystal structure of AB_2X_4 thiogallate compounds [1,2].

system,[5] there are three different solid-solution phases, namely, sphalerite (S), wurtzite (W), and the tetragonal thiogallate (T) and also three two-phases fields (S + W, S + T, W + T). $ZnGa_2S_4$ is the equilibrium compound at 50 mol% Ga_2S_3 above 650 °C. So a single phase of $ZnGa_2S_4$ had to be formed above 800 °C in our experiment, but weak peaks of Ga_2S_3 were observed at 800 °C. In our work, adding 4 mol% EuS instead of ZnS caused the small compositional deviation from the equilibrium composition of ZnS–Ga_2S_3 (1:1) system, leading to the decrease of the solubility of Ga_2S_3 in ZnS, and so the two-phases of $ZnGa_2S_4$ and Ga_2S_3 (T + W) appeared at 800 °C. Above 850 °C, a single phase of $ZnGa_2S_4:Eu^{2+}$ could be achieved.

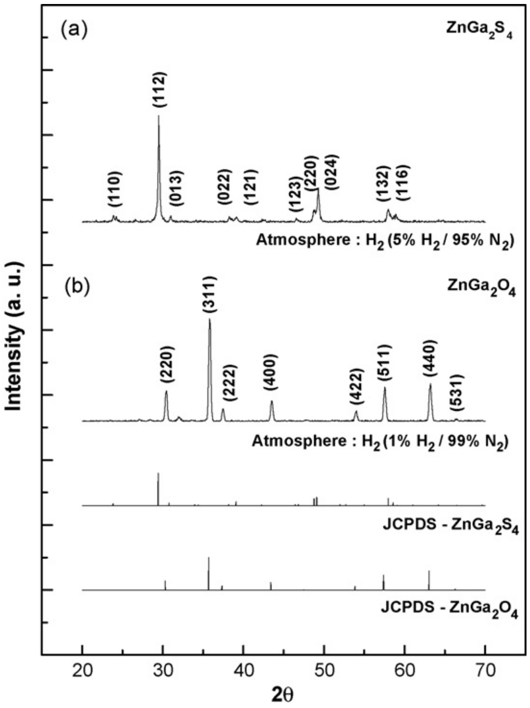

Fig. 2. XRD patterns of the mixture of ZnS and Ga_2S_3 (1:1) fired at 1100 °C under (a) 5% and (b) 1% H_2 atmosphere.

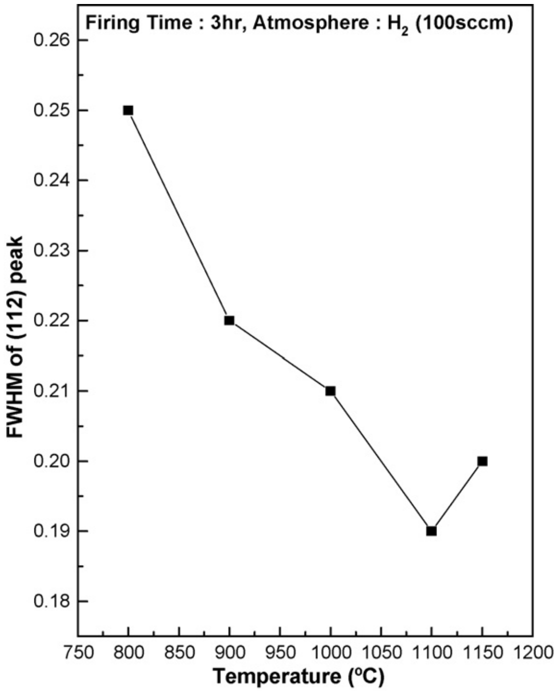

Fig. 3. FWHM of (1 1 2) peak of $ZnGa_2S_4:Eu^{2+}$ (4 mol%) powders as a function of firing temperature.

Full width of half maximum (FWHM) values of (1 1 2) main peak of $ZnGa_2S_4$ strongly depended on the firing temperatures as shown in Fig. 3. As firing temperature increased, FWHM gradually decreased up to 1100 °C, and then increased at 1150 °C. Since the powders initiated to dissolve partly at 1150 °C, the crystallinity was deteriorated, resulting in the increase of FWHM.

Excitation and emission spectra of $ZnGa_2S_4:Eu^{2+}$ (4 mol%) powders is shown in Fig. 4. Excitation spectrum for 540 nm emission exhibited a broad band peaking at 465 nm. At present, there are no reports concerning the emission band structure of $ZnGa_2S_4:Eu^{2+}$ and the transition mechanism of Eu^{2+} in it. But we can refer to other AB_2S_4 thiogallate compounds such as $SrGa_2S_4:Eu^{2+}$ and $CaGa_2S_4:Eu^{2+}$, because they have just same

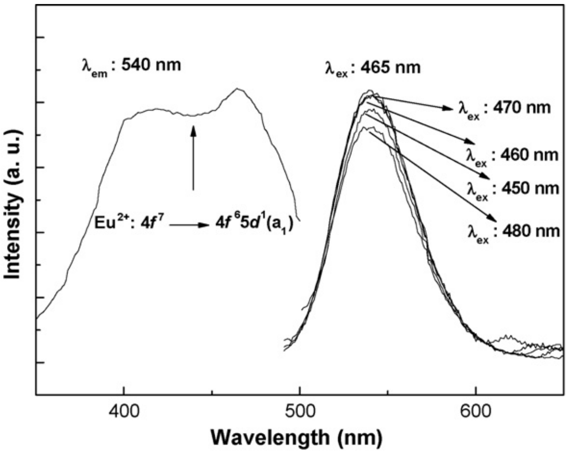

Fig. 4. Excitation and emission spectra of $ZnGa_2S_4:Eu^{2+}$ (4 mol%) powders for the emission of 540 nm.

crystal structure with one another. Even though their excitation spectra and emission positions strongly depend on the Eu^{2+} environment by choosing 'A', it is known that they all show the broad excitation due to the transition of $4f^6 5d^1$ (^7F) to $4f^7$ ($^8S_{7/2}$) ground state of Eu^{2+} ions.[6–8] Accordingly, the broad excitation spectrum peaking at 465 nm of $ZnGa_2S_4:Eu^{2+}$ could be thought to originate from $4f^6 5d^1$ to $4f^7$ transition. With regard to emission spectra of $ZnGa_2S_4:Eu^{2+}$ (4 mol%) at various excitation wavelengths, they all exhibited green emissions at the same positions of 540 nm. The highest PL emission intensity was observed at 465 nm excitation that corresponded to a peak of the excitation spectrum. For AGa_2S_4 thiogallate compounds such as $BaGa_2S_4:Eu^{2+}$ ($\lambda_{EM} = 497$ nm), $SrGa_2S_4:Eu^{2+}$ ($\lambda_{EM} = 535$ nm), and $CaGa_2S_4:Eu^{2+}$ ($\lambda_{EM} = 560$ nm), the red-shit and the emission wavelengths generally increase with decreasing the size of 'A' cation ($Ba^{2+} = 1.36$ Å, $Sr^{2+} = 1.26$ Å, $Ca^{2+} = 1.12$ Å).[9] However, in spite of smaller atomic size of Zn^{2+} (0.75 Å), this did not apply to $ZnGa_2S_4:Eu^{2+}$ ($\lambda_{EM} = 540$ nm). In this experiment, the emission wavelength of $ZnGa_2S_4:Eu^{2+}$ was almost same with $SrGa_2S_4:Eu^{2+}$. It could be explained by the crystal field splitting energy (ΔS), which was related to the atomic size of 'A' atoms and inversely to the distance between a metal and ligands. Even though Zn^{2+} size was smaller than Sr^{2+}, the lattice parameter of $ZnGa_2S_4$ was also small comparing with $SrGa_2S_4$, leading to the almost same ΔS, and so emission bands of these two phosphors were located at the similar wavelength.

To investigate the effects of Eu doping concentration on the crystal structure and PL properties, we measured FWHM of (1 1 2) peak of $ZnGa_2S_4:Eu^{2+}$ and PL intensity as shown in Figs. 5 and 6. With increasing the Eu doping concentration, FWHM values decreased up to 4 mol%, and increased again at 5 mol% in Fig. 5. This indicated that doping Eu improved the crystallinity of $ZnGa_2S_4$:Eu. The reason was not clear, but it could be speculated that doped Eu atoms were mainly substituted for Zn atoms and partly occupied the intrinsic Zn vacancy

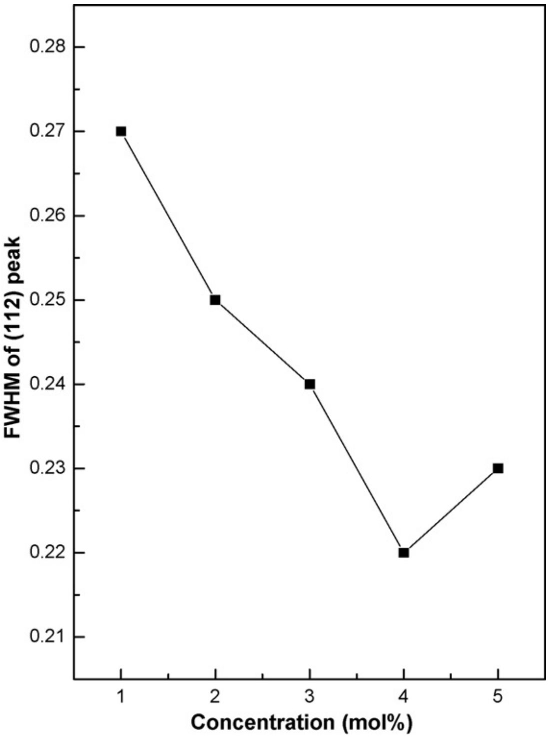

Fig. 5. FWHM of (1 1 2) peak of $ZnGa_2S_4:Eu^{2+}$ fired at 1100 °C with various Eu concentration.

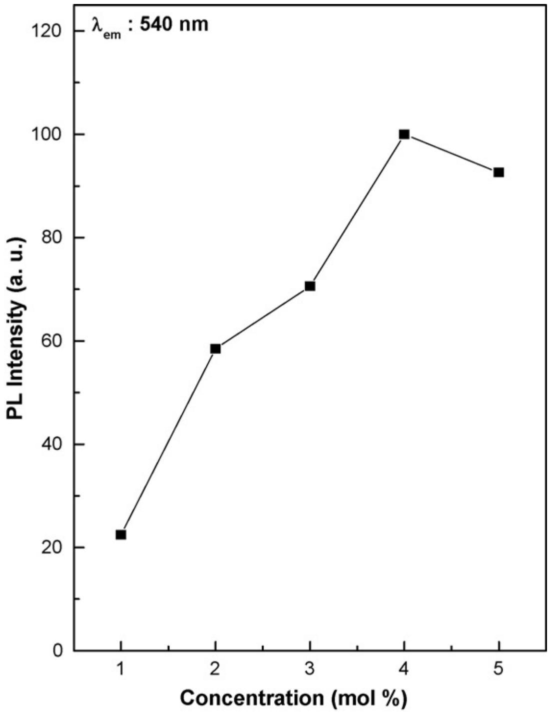

Fig. 6. PL intensity of $ZnGa_2S_4:Eu^{2+}$ fired at 1100 °C with various Eu concentration.

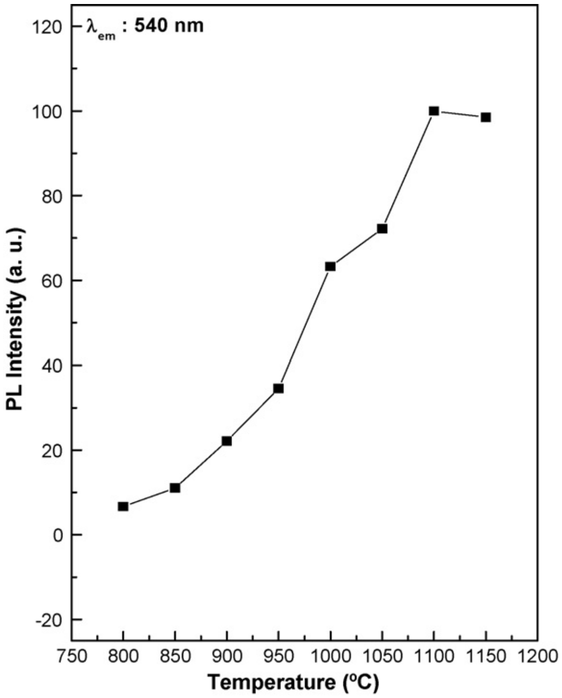

Fig. 7. PL intensity of $ZnGa_2S_4:Eu^{2+}$ as a function of firing temperature.

sites of a defect chalcopyrite structure in Fig. 1. The increase of FWHM at 5 mol% indicated that Eu concentration in $ZnGa_2S_4$ more than the optimum value (4 mol%) caused the lattice distortion and irregular distributions of Eu. As a result, the activator ions, Eu^{2+}, were paired and/or coagulated due to the high doping concentration, leading to concentration quenching in PL. As shown in Fig. 6, PL intensity peaked at 4 mol% Eu concentration and decreased at 5 mol%. This was inversely in accordance with the result of Fig. 5. The PL drop at 5 mol% was attributed to the concentration quenching effects as well as the deterioration of the crystallinity as show in Fig. 5. Finally, the Eu doping contributed to the increase of the luminescent activators and the crystallinity simultaneously resulting in PL enhancement. Fig. 7 shows PL intensity peaking at 1100 °C as a function of firing temperature, which was closely correlated with the results of Fig. 3. With increasing firing temperature up to 1100 °C, the crystallinity improved, leading to the higher PL intensity. At 1150 °C, the increase of FWHM led to the drop of PL intensity.

4. Conclusion

Eu doped zinc thiogallate, $ZnGa_2S_4:Eu^{2+}$ powders were prepared by solid state reaction process at 5% H_2 atmosphere by introducing extra S vapor. A single phase $ZnGa_2S_4:Eu^{2+}$ (4 mol%) could be obtained by firing above 850 °C for 3 h at 5% H_2 atmosphere. It exhibited a green emission band at 540 nm with an excitation wavelength of 465 nm. The firing temperature contributed to the formation of a single phase and to the increase of the crystallinity of $ZnGa_2S_4:Eu^{2+}$ leading to high PL intensity. The Eu doping caused the increase of the luminescent properties and the crystallinity simultaneously, resulting in PL enhancement.

Acknowledgement

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