Photoluminescent properties of Ba$_2$ZnS$_3$:Mn phosphors

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Abstract

Mn$^{2+}$ doped Ba$_2$ZnS$_3$ phosphor powders have been synthesized via the conventional solid-state reaction by the double-crucible method with ethanol as the reducing agent. XRD results indicate that the raw materials are completely sulfurized above 950 $^\circ$C and the crystallinity of the phosphors increases with the soaking time of the thermal treatment. The Ba$_2$ZnS$_3$:Mn$^{2+}$ powders possess an orthorhombic crystal structure with doping concentration from 0 to 0.9 mol%. The photoluminescence (PL) spectra show that the emission peaks are at 611 nm (under excitation at $\lambda_{ex}$ = 358 nm) independent of doping concentration. The high-luminance reddish orange emission results from the $^4$T$_1$ ($^4$G)-$^6$A$_1$ ($^6$S) transition in the Mn$^{2+}$ ion. These phosphors have broad emission spectra (550–700 nm) with FWHM (full width at half maximum broadband) about 55 nm. The Ba$_2$ZnS$_3$ doped with 0.5 mol% Mn$^{2+}$ appears to have the highest luminescent intensity after thermal treatment at 950 $^\circ$C for 16 h and the CIE coordinate is $x$ = 0.632, $y$ = 0.368.

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1. Introduction

Among many semiconductors, wide band gap II–IV compounds such as zinc chalcogenide ZnS [1–3] and ZnSe [4–6] and alkaline-earth chalcogenide MgS [7–9], CaS [10–12], SrS [13–15] and BaS [16–18] doped with activated emission centers are well known to be efficient luminescent materials for the realization of multicolor electroluminescent and cathodoluminescent devices. For emission centers, the transition metal ions and rare-earth ions are found to be suitable. The 3d transition metal ions utilized in commercial phosphors have three (in the case of Cr$^{3+}$ and Mn$^{4+}$) or five (Mn$^{2+}$ and Fe$^{3+}$) electrons occupying the outermost 3d orbitals of the ions. When the 3d ions are incorporated into liquids or solids, spectroscopic properties are considerably changed from those of gaseous free ions [19]. The wide band gap phosphor materials of Mn-doped ZnS is more interesting. The high efficiency of ZnS:Mn$^{2+}$ has drawn much research effort to shifting or broadening the yellow emission of Mn$^{2+}$ ($^4$T$_1$($^4$G) $\rightarrow$ $^6$A$_1$($^6$S)) to achieve a wider range of colors for phosphors of filtered white light displays. Several ternary II–VI compounds doped with rare earth or transition metal ions like Ca$_{1-x}$Sr$_x$S:Ce [20], Ca$_{1-x}$Sr$_x$S:Eu [21], Zn$_{1-x}$Sr$_x$S:Ce [22] and Zn$_{1-x}$Mg$_x$S:Mn [23–25] have also been investigated.

Barium zinc sulfide was first prepared by firing zinc oxide and barium oxide in an atmosphere of hydrogen sulfide (H$_2$S) [26]. The solubility of ZnS in BaS has been studied by Megson [27]; the barium zinc sulfide (Ba$_2$ZnS$_3$) was formed by firing BaS and ZnS (in the molar quantities 2BaS:1ZnS) in an oxygen-free nitrogen atmosphere. Its luminescent properties when activated by manganese (II) have been reported in the literature [28–30]. The results are different from ours due to different experimental procedures.

In this paper, the Mn$^{2+}$ doped barium zinc sulfide phosphors was produced by a double crucible method in a conventional solid-state reaction. The results of powder X-ray diffraction, the morphology and the effect of dopant concentration on the photoluminescence of Ba$_2$ZnS$_3$:Mn$^{2+}$ phosphors were studied.

2. Experimental details

2.1. Sample preparations

Two steps were taken to synthesize the Ba$_2$ZnS$_3$:Mn$^{2+}$ phosphors in this experimental procedure. Pure barium sulfide was produced first by using the...
starting ingredients consisting of BaCO₃ (NOAH), S (SHOW A) and ethanol (ACS reagent, ACROS). Two crucibles were put into a quartz tube furnace [31], one crucible contained the well mixed BaCO₃ and S and another crucible contained the proper amount of ethanol as the reducing agent, and both were fired at 1000 °C for 8 h.

In the second step, samples of Ba₂ZnS₃: xMn with 0.1 ≤ x ≤ 0.9 mol%, in increments of 0.2 mol%, were also prepared via the conventional solid-state reaction by a double-crucible method. The starting ingredients consisted of BaS, ZnS (CERAC), S (SHOW A), MnCl₂·4H₂O (ALFA) and ethanol. The required amount of MnCl₂·4H₂O was first dissolved in an aqueous ethanol. During continuous stirring, the stoichiometric amounts of BaS, ZnS and S were added to the ethanol solution and mixed at about 65 °C for 1 h until all ethanol was evaporated. Subsequently, the aforesaid two-crucible method was also used. These two crucibles were put into a quartz-tube furnace and fired at different temperatures and for times. Ethanol is a reducing agent to produce a reductive atmosphere.

2.2. Characterization

The structural effects of Mn doping and thermal treatment were carefully examined by X-ray powder diffraction using Cu Kα radiation (Rigaku Dmax-33 X-ray diffractometer) with a source power of 30 kV and 20 mA to identify the possible phases formed after sulfurization-treatment. The surface morphology was examined by high-resolution scanning electron microscopy (HR-SEM, S4200, Hitachi). All excitation spectra, luminescence spectra and decay time of these phosphors were recorded on a Hitachi F-4500 fluorescence spectrophotometer using a 150 W xenon arc lamp as the excitation source at room temperature. Optical absorption spectra were measured at room temperature using a Hitachi U-3010 UV–visible spectrophotometer.

3. Results and discussion

3.1. Structures

The powder X-ray diffraction patterns of samples with 0.5 mol% Mn²⁺ fired at 800–1050 °C for 30 min in a reductive atmosphere are shown in Fig. 1. When the fired temperature was below 850 °C, a small amount of residual BaS and ZnS mixed with the Ba₂ZnS₃ phosphors were observed. When the fired temperature was above 950 °C, it is clearly seen that all peaks of XRD patterns belong to the orthorhombic Ba₂ZnS₃ phase with space group Pnam (No. 62) and all residual BaS and ZnS disappear. When firing at 1050 °C, no other new phases were generated and only the stable Ba₂ZnS₃ compound existed.

The X-ray powder diffraction patterns of Ba₂ZnS₃ doped with 0.5 mol% Mn²⁺ calcined at 950 °C for 0.5, 4 and 16 h are shown in Fig. 2. As to prolonging the soaking time of thermal treatment, the structure of Ba₂ZnS₃ remains orthorhombic and no new phases or compounds appear. The FWHM (full width at half maximum) values from the peak of (131) plane (the highest peak in the XRD patterns) decrease from 0.215° for 0.5 h, 0.214° for 4 h to 0.209° for 16 h. It is indicated that the crystallinity is improved by prolonging the fire time. In addition, the crystal structures of Ba₂ZnS₃ doped with Mn²⁺ up to 0.9 mol% were also not changed.

The morphologies of Ba₂ZnS₃ powders were not much different for doping from 0.1 to 0.9 mol% Mn²⁺. The SEM images of Fig. 3 show the morphologies of the samples doped with 0.5 mol% Mn²⁺ ions at different firing times. It is clearly seen that as the firing time gets longer, the particle size becomes larger, about 2.5–4 μm for 0.5 h, about 4–7 μm for 4 h and about 6–11 μm for 16 h.
Fig. 3. SEM photographs of Ba$_2$ZnS$_3$:Mn$^{2+}$ (0.5 mol%) powders fired at 950°C for (a) 0.5 h, (b) 4 h and (c) 16 h.

3.2. Optical properties

Those photoluminescence (PL) excitation spectra of the different amounts of Mn doped Ba$_2$ZnS$_3$ phosphors measured at room temperature are similar. The PL excitation spectrum monitored from the emission peak at $\lambda_{\text{em}} = 611$ nm has a broad band ranging from 240 to 420 nm as shown in Fig. 4 for the 0.5 mol% Mn doped sample. The peak of the excitation band at around 358 nm ($\sim$3.5 eV) coincides with the band gap of the semiconductor Ba$_2$ZnS$_3$, suggesting that the total energy of the emitted light comes from the energy absorbed by the host.

The optical absorption spectrum of Mn$^{2+}$ doped in Ba$_2$ZnS$_3$ is shown in Fig. 5. The manifest broad band ranges from 200 to 400 nm with several peaks in the UV region belonged to the host (Ba$_2$ZnS$_3$) absorption. The peak at around 360 nm corresponds with the peak in the PL excitation spectrum. Compared with the host absorption spectrum, the region between 380 and 450 nm

Fig. 4. Photoluminescence excitation spectrum of Ba$_2$ZnS$_3$:Mn$^{2+}$ (0.5 mol%) prepared at 950°C for 16 h.

Fig. 5. Absorption spectra of Ba$_2$ZnS$_3$ (host) and Mn$^{2+}$ ions-doped-Ba$_2$ZnS$_3$ measured at room temperature.
Fig. 6. Photoluminescence spectra of Ba$_2$ZnS$_3$:Mn$^{2+}$ (0.5 mol%) fired at different temperature for 30 min excited at $\lambda_{ex}$ = 358 nm.

belongs to the energy absorbed by Mn$^{2+}$ ions. However, only the radiative transition can be measured in PL excitation, which is different from the absorption spectrum.

Fig. 6 shows the PL emission spectra under 358 nm UV ray excitation of Ba$_2$ZnS$_3$ doped with 0.5 mol% Mn$^{2+}$ fired at different temperatures for 30 min. When tuning the excitation wavelength from 200 to 500 nm, only one emission spectrum of Ba$_2$ZnS$_3$:Mn$^{2+}$ exists. Although the X-ray diffraction patterns of the samples fired at 750 and 850°C show that the BaS and ZnS phases exist, no peaks of BaS:Mn$^{2+}$ (540 nm) and ZnS:Mn$^{2+}$ (585 nm) and the shoulders appear in the PL emission spectrum. The reasons may be: (1) the amounts of the residual BaS and ZnS phases compared with Ba$_2$ZnS$_3$ are so small; (2) the Mn$^{2+}$ ions prefer to stay in the Ba$_2$ZnS$_3$ crystal because the crystal can offer an easy way for Mn$^{2+}$ ions to get into interstitial sites. In these PL emission spectra, the samples fired at 950°C have the highest PL intensity with the peak at 611 nm. Moreover, when a metal ion occupies a certain position in a crystal, the crystal field strength that affects the ion increases as the space containing the ion becomes smaller. For increases in the crystal field, the transition energy between the $^4T_1$ and $^6A_1$ levels is predicted to decrease (shift to longer wavelengths) [32], and the Mn-S distance in ZnS is shorter than that in BaS and longer than that in Ba$_2$ZnS$_3$. Therefore, the luminescence peak shifts to longer wavelengths in Mn$^{2+}$ (d–d transition) when the host lattice is varied from BaS to ZnS to Ba$_2$ZnS$_3$. This shift is reasonable from a theoretical point of view because the crystal field strength decreases in the above order.

The PL emission spectrum of Ba$_2$ZnS$_3$: $x$Mn with $0.1 \leq x \leq 0.9$ mol%, increment with 0.2 mol%, measured at room temperature are shown in Fig. 7. In these spectra, all samples show a reddish-orange color photoluminescence originating from the excited state $^4T_1$ ($^4G$) to the ground state $^6A_1$ ($^6S$) transition of the Mn$^{2+}$ ions. The red light emissions of Ba$_2$ZnS$_3$: $x$Mn$^{2+}$ have a broad emission spectrum in the range 550–700 nm with FWHM about 55 nm and the peak at 611 nm. Under 358 nm UV ray excitation, the photons absorbed by the Ba$_2$ZnS$_3$:Mn phosphors are quite similar to that of pure Ba$_2$ZnS$_3$ powders. This indicates that the excitation energy absorbed at the band edge of the Ba$_2$ZnS$_3$ host crystal can be efficiently transferred to the unexcited Mn$^{2+}$ ions.

As shown in Fig. 8, it is found that the luminescence intensities of those phosphors strongly depend on the activator concentration. In spite of the firing time, the PL intensity of Ba$_2$ZnS$_3$:Mn$^{2+}$ powders fired at 950°C increased gradually with doping concentration from 0.1 to 0.5 mol% reaching to a maximum PL intensity. As the doping concentration went over...
4. Conclusions

Mn$^{2+}$ doped Ba$_2$ZnS$_3$ phosphor powders were successfully synthesized by conventional solid-state reaction by a double-crucible method. Ba$_2$ZnS$_3$: xMn powders with $0.1 \leq x \leq 0.9$ mol% calcined at 950 $^\circ$C for 0.5, 4 and 16 h show a single orthorhombic structure. From SEM images, no obvious difference in morphology was observed as the doping concentration increased, but the particle size became larger with the firing time. The most efficient emission occurred at the excitation wavelength of $\lambda_{ex} = 358$ nm, and the reddish-orange emission light with peak wavelength of $\lambda_{em} = 611$ nm was obtained. The Ba$_2$ZnS$_3$ doped with 0.5 mol% Mn$^{2+}$ ions has the highest luminescent intensity and crystallinity as fired at 950 $^\circ$C for 16 h. The CIE color coordinate is $x = 0.632, y = 0.368$. The decay time for low Mn$^{2+}$ concentrations (<1 mol%) in Ba$_2$ZnS$_3$ was about 0.33 ms. The non-exponential decay curve in this case suggested that some of the Mn$^{2+}$ ions are in isolated sites, and the others formed pairs of Mn$^{2+}$ ions.

0.5 mol%, the luminescence intensity decreased by virtue of the concentration quench. It is also clear that for samples with the same doping concentration and the same firing temperature the PL intensity increased with the soaking time. The sample doped with 0.5 mol% Mn$^{2+}$ ions are in isolated sites, and the others formed pairs of Mn$^{2+}$ ions. The exponential decay curve in this case suggested that some of the Mn$^{2+}$ ions are in isolated sites, and the others formed pairs of Mn$^{2+}$ ions.

Fig. 9. Decay curve of Ba$_2$ZnS$_3$: 0.5 mol% Mn$^{2+}$ fired at 950 $^\circ$C for 16 h ($\lambda_{ex} = 358$ nm) of the $^4T_1$ ($^6G$) $\rightarrow ^6A_1$ ($^6S$) emission ($\lambda_{em} = 611$ nm) measured at room temperature.

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