Synthesis and Characterization of Eu^{2+} Doped $BaAl_2S_4$ Phosphor by Vacuum Heat Treatment

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Abstract

A Eu^{2+} doped $BaAl_2S_4$ phosphor was synthesized from BaS, EuS, Al and S powder by vacuum heat treatment. The synthesized powder at 850°C was composed of only $BaAl_2S_4$ phase. The photoluminescence of Eu^{2+} doped $BaAl_2S_4$ phosphor showed the blue emission centered at 470nm and CIE color coordinate at x=0.12, y=0.11.

1. Introduction

Inorganic electroluminescent (iEL) devices which are one of flat panel displays have many advantages such as wide view angle, high response time, simple solid state device, and resistance to shock and vibration.[1] However, iEL devices could not be applied in practical use because of a major draw-back as full color displays, which was lack of a blue-emitting material.

In 1999, Miura et al. applied $BaAl_2S_4$:Eu phosphor to iEL devices.[2] These devices were prepared by the two targets pulse-electron-beam evaporation which used BaS:Eu and Al_2S_3 pellet. The $BaAl_2S_4$:Eu iEL device showed a blue emission around 470nm and had an effective luminescent property as 65cd/m^2 under the 50Hz, which is the value to apply practical use.

The $BaAl_2S_4$:Eu powders ware synthesized by Le Thi et al..[3] BaS, Al_2S_3 and EuS powder were prepared and mixed. Synthesis reactions were performed in silica tube sealed under vacuum. The powder after synthesis also showed a blue photoluminescent emission at 467nm.

In most of previous works, BaS, Al_2S_3 and EuS powders were used for synthesis of $BaAl_2S_4$:Eu. Of these, Al_2S_3 is easy to react with water vapor and oxygen. So the powder after synthesis is easy to contain some impurities such as Al_2O_3 and other barium thioaluminate. In this work, Al_2S_3 is replaced by Al and S to decrease impurity contamination.

2. Results

A Eu^{2+} doped $BaAl_2S_4$ phosphor was synthesized form BaS (Kojundo 99.9%), EuS (Kojundo 99.9%), Al (Kojundo 99.99% up), and S (Aldrich 99.99%). The ratio of BaS, EuS, Al and S was 0.97: 0.03: 2: 3 for 3mole% Eu doping. To obtain pure $BaAl_2S_4$ phase, excess sulfur was added to the starting materials. The starting materials were mixed in a mortar under air condition. The mixture put into alumina crucible which put into quartz tube, and quartz tube sealed under less than 10^{-3}torr. Synthesis was performed from 600°C to 850°C.

The powder for property comparison was also synthesized form BaS, EuS and Al_2S_3 (Kojundo 98%). The ratio of BaS, EuS and Al_2S_3 was 0.97: 0.03: 1. In this case, mixing was performed under Ar condition because Al_2S_3 is easy to be oxidized in air or humid condition. After mixing, synthesis was performed in the same condition.

The phase was characterized by X-ray diffraction (XRD) operated at 40 kV and 45 mA using Cu Kα (λ=1.5405 Å) radiation. The scanning range 2θ was from 15° to 40°. The microstructure was measured using scanning electron microscopy (SEM). To investigate luminescent properties, the photoluminescence (PL) was measured. The excitation wavelength was 350nm.

Figure 1 shows the effect of sulfur ambient during vacuum heat treatment at 850°C. When the ratio of Al to S is 2: 3 which theoretically stoichiometric condition is, the synthesized powder contains sulfur-poor phase, $Ba_2Al_2S_5$. [4] Because that some sulfur gas remain inside quartz ampoule is more stable than that all sulfur react. When the sulfur ratio increases to 2: 6, sulfur-poor phase decreases relatively. When the ratio of Al to S is 2: 6, the synthesized powder is composed of only $BaAl_2S_4$ phase. When the sulfur ratio increases above 2: 6, BaS_3 appears.

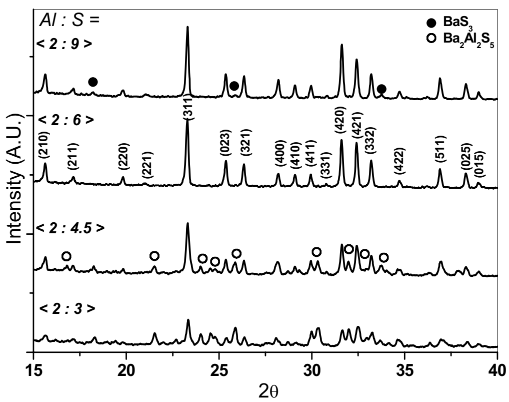
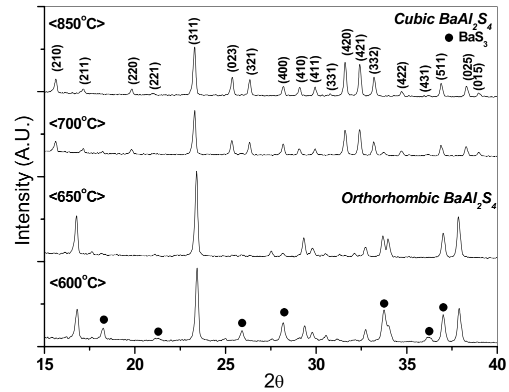
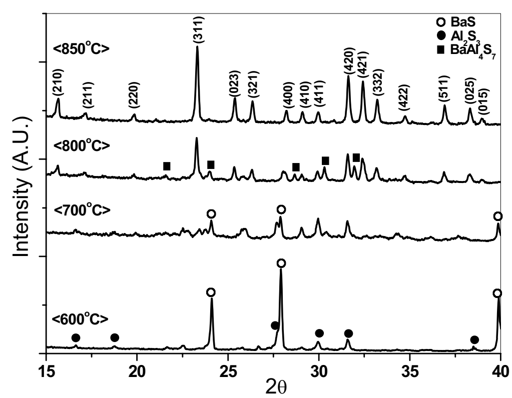


Figure 1. XRD patterns of synthesized powders with various ratios of Al and S after heat treatment at 850°C

Figure 2 (a) shows the effects of a sinter temperature when the ratio of Al to S is 2:6. When the sinter temperature is below 650°C, the orthorhombic $BaAl_2S_4$ phase appears. [5] And all starting materials are reacted and changed to $BaAl_2S_4$ phase or BaS_3 phase while the synthesis using Al_2S_3 remains much starting materials to 700°C in figure 2 (b). When the sinter temperature increases above 700°C, the synthesized $BaAl_2S_4$ powder has a cubic phase. The temperature of obtaining cubic $BaAl_2S_4$ using Al and S is lower than that using Al_2S_3 in this work and the report of *Smet et al*. [5]. The secondary phase, BaS_3 decreases as the sinter temperature increases and disappears at 850°C.



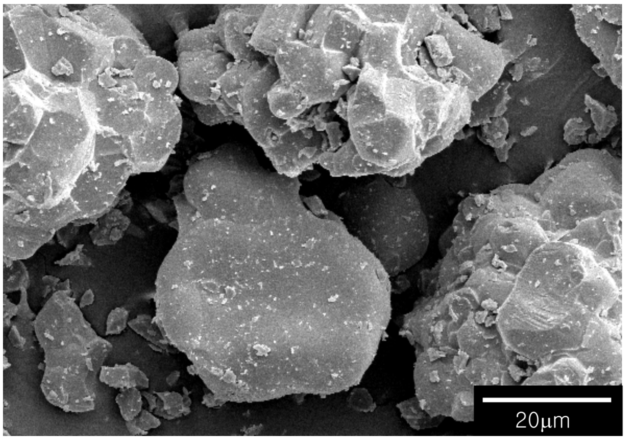
(a)



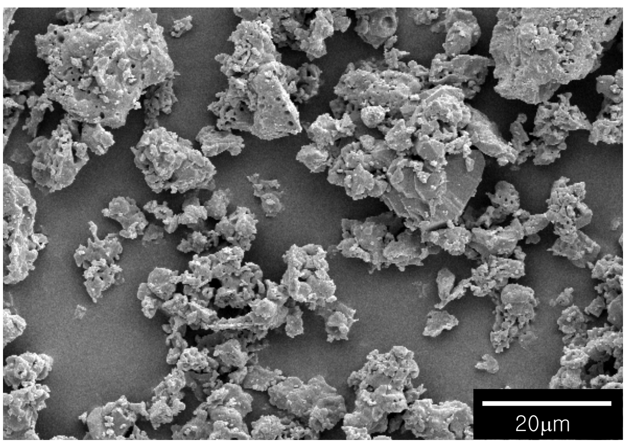
(b)

Figure 2. XRD patterns of synthesized powders with various temperatures using (a) Al and S (2: 6) and (b) Al_2S_3

Figure 3 shows microstructures of the synthesized powders at 850°C. The powder synthesized by Al and S [figure 3 (a)] has large grains between 5μm and 45μm in diameter while the grains of synthesized powder by Al_2S_3 [figure 3 (b)] are about several μm. It is cause by the liquid phase sintering between solid BaS and liquid Al.



(a)



(b)

Figure 3. SEM images of synthesized powders at 850^{o}C using (a) Al and S and (b) Al_2S_3

Figure 4 shows PL spectra of synthesized powders at 850^{o}C with various ratios of Al and S, 2: 3, 2: 4.5, 2: 6, and 2: 9. When the portion of sulfur increases to 2: 6, the peaks of synthesized powders shift from 483nm (FWHM: 51nm) to 470nm (FWHM: 43nm). It is caused by decrement and disappearance of Eu^{2+} doped $Ba_2Al_2S_5$ phase emitting at 487nm relatively to Eu^{2+} doped $BaAl_2S_4$ phase emitting at 467nm. When the ratio of Al and S is 2: 6, the powder has a blue emission centered at 470nm and CIE color coordinate at x=0.12 and y=0.11 due to luminescence from only cubic Eu^{2+} doped $BaAl_2S_4$ When the portion of sulfur more increases from 2: 6, the powder shows a small green shift to 473.5nm.

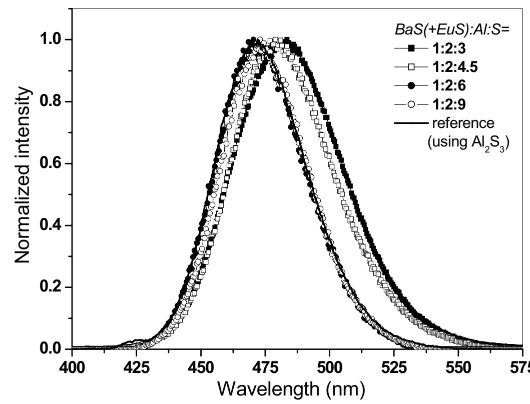


Figure 4. PL spectra of synthesized powders with various ratios of Al and S after heat treatment at 850^{o}C

Figure 5 shows PL spectra of synthesized powders with various sinter temperature when the ratio of Al and S is 2: 6. When the powder is composed of orthorhombic Eu^{2+} doped $BaAl_2S_4$ sintered below 650^{o}C, it has a peak at about 476nm. Synthesized at 700^{o}C, the powder contains a little BaS_3 in addition to cubic Eu^{2+} doped $BaAl_2S_4$ and has a peak at 473.5nm which is green shifted from the peak of only cubic Eu^{2+} doped $BaAl_2S_4$. When the powder is composed of only cubic Eu^{2+} doped $BaAl_2S_4$ sintered at 850^{o}C, it has a peak at 470nm.

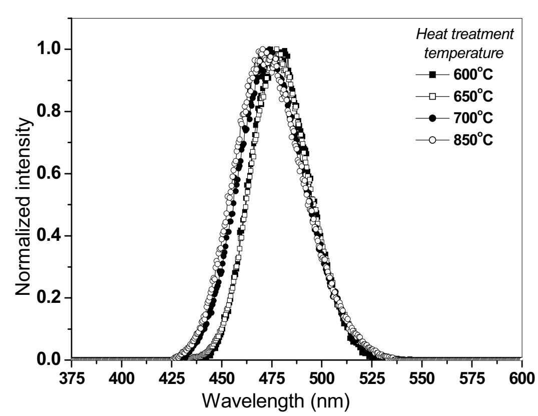


Figure 5. PL spectra of synthesized powders with various sinter temperature at Al: S= 2: 6

3. Conclusion

A Eu^{2+} doped $BaAl_2S_4$ phosphor was synthesized from BaS, EuS, Al and S powder by vacuum heat treatment. When the ratio of Al and S was 2: 6 at 850°C, only cubic $BaAl_2S_4$ phase appeared. When the sinter temperature was below 650°C, the powder consisted of the orthorhombic $BaAl_2S_4$ phase. The cubic $BaAl_2S_4$ phase appeared when the sinter temperature was above 700°C, which is lower temperature than reactions using Al_2S_3 in this work and the report of *Smet et al.* The photoluminescence of cubic $BaAl_2S_4$ showed the blue emission centered at 470nm and CIE color coordinate at x=0.12 and y=0.11.

4. References

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