Eu^{2+}-doped Thioaluminates: New Candidates for White LEDs

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Three Eu^{2+}-doped thioaluminate phosphors with different light-emitting colors, green, bluish-green, and blue were synthesized by the evacuated sealed quartz ampoule method. Under UV excitation, $CaAl_2S_4:Eu^{2+}$ (CAS), $SrAl_2S_4:Eu^{2+}$ (SAS), and $BaAl_2S_4:Eu^{2+}$ (BAS) exhibit strong emission bands peaked at 516, 496, and 470 nm, respectively. The fabricated LEDs of CAS, SAS, and BAS show intense green, bluish-green, and blue lighting. They are all believed to be good phosphor candidates for creating white light in phosphor-converted white LEDs.

Recently, the Eu^{2+}-doped thioaluminates have attracted more and more attention owing to their excellent electroluminescent (EL) performance. $BaAl_2S_4:Eu^{2+}$ was introduced as a bright and saturated blue-emitting phosphor for full-color EL devices.[1] Thereafter, the iFire Company adopted it as a new blue source and announced a full-color 34-in. thick dielectric electroluminescent (TDEL) screen using the Color-By-Blue (CBB) technique.[2] In 2003, $CaAl_2S_4:Eu^{2+}$ was also reported as a green-emitting thin film for EL applications with considerable high luminance 3041 cd/m^2 at a driving frequency of 1 kHz.[3] Since the absorptions of the 4f–5d transitions of the Eu^{2+}-doped thiogallates and thioaluminates extend to the visible region, they are also appropriate phosphors for excitation by near-UV or blue-emitting diodes for solid-state lighting (SSL) applications.[4] $CaGa_2S_4:Eu^{2+}$ and $Sr_2Ga_2S_5:Eu^{2+}$ greenish-yellow phosphors showed a higher luminescent efficiency (120 and 110%, respectively) than the commercial $YAG:Ce^{3+}$ phosphor, and they also can be fabricated with blue-chips to produce white light.[5,6]

This paper describes the photoluminescence properties and application of the thioaluminates $MAl_2S_4:Eu^{2+}$ (M = Ca, Sr, and Ba) in white LEDs. This family of materials was chosen for the following reasons:[7,8] (i) Eu^{2+}-doped thioaluminates show a broad absorption band extending from the near ultraviolet to the blue region which was a satisfaction to the requirements for LED fabrication, (ii) Eu^{2+}-doped thioaluminates have smaller Stokes shifts and narrower emission bands than Eu^{2+}-doped thiogallates, (iii) luminescence quenching temperatures are markedly higher for thioaluminates than for thiogallates. It is favorable for reducing the temperature effect brought by the LED's p–n junctions. All the characteristics indicate that Eu^{2+}-doped thioaluminates exhibit possibly a high luminous output. Nevertheless, Eu^{2+}-doped thioaluminates as high efficient phosphors have not been applied in the field of phosphor-converted white-light-emitting diodes (pc-WLED) up to now.

In this work, $MAl_2S_4:Eu^{2+}$ (M = Ca, Sr, and Ba) phosphors were synthesized and the optical properties of the phosphors were investigated. Finally, three intense light-emitting LEDs were fabricated through combining InGaN chips with these phosphors.

The starting sulfide materials CaS, SrS, BaS, and EuS were pre-prepared by a solid-state reaction method at high temperature in horizontal tube furnaces. Alkaline earth sulfides were prepared under flowing H_2S gas at 1000 °C for 2 h. EuS was prepared from Eu_2O_3 (99.99%) with CS_2 reducing atmosphere at 1200 °C for 3 h.

The stoichiometric amounts of the starting sulfide MS (M = Ca, Sr, and Ba), Al (AR), EuS, and 25 mass % excess S (AR) were thoroughly mixed and put in quartz ampoules and then evacuated to 1×10^{-6} Torr and sealed, finally fired at 1050 °C for 5 h.

Compared with reported preparation methods,[8,9] the cheap and stable aluminum powder was first used as the starting material instead of expensive and weakly hygroscopic Al_2S_3 to prepare $MAl_2S_4:Eu^{2+}$ under vacuum in sealed silica tubes.

The structure of the final products was examined by X-ray powder diffraction using a Rigaku D/max 2200 vpc X-ray diffractometer with Cu Kα radiation at 40 kV and 30 mA. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of phosphors were measured by a Fluorolog-3 spectrofluorometer (Jobin Yvon Inc/specx) equipped with a 450-W Xe lamp and double excitation monochromators. The emission spectra of the LEDs were recorded on an LED-1100 spectral/goniometric analyzer (Labsphere Inc.) under a direct current of 20 mA. The above measurements were carried out at room temperature.

The XRD patterns of $CaAl_2S_4:0.10Eu^{2+}$ (CAS), $SrAl_2S_4:0.10Eu^{2+}$ (SAS), $BaAl_2S_4:0.10Eu^{2+}$ (BAS) phosphors are shown in Figure 1. The XRD patterns of CAS, SAS, and BAS match well with 77–1186, 77–1188, and 76–1054 by JCPDS fingerprints. No second phases are observed indicating that all samples show a single phase. It is concluded that the cheap and stable aluminum powder can be used as a good substitute for aluminum sulfide (Al_2S_3) to prepare pure thioaluminates.

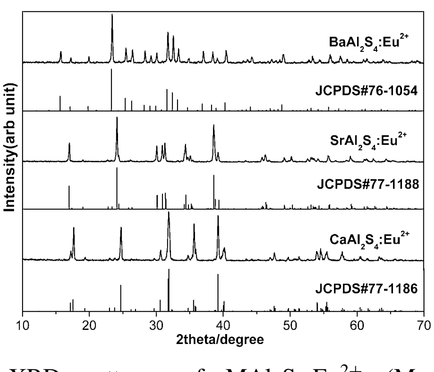

Figure 1. XRD patterns of $MAl_2S_4:Eu^{2+}$ (M = Ca, Sr, and Ba).

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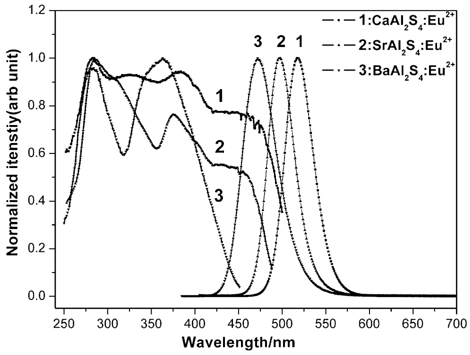

Figure 2. The normalized emission and excitation spectra of the thioaluminate phosphors CAS (**1**), SAS (**2**), and BAS (**3**) at room temperature ($\lambda_{ex} = 395$ nm, $\lambda_{em} = 516$, 496, and 470 nm, respectively).

The normalized emission and excitation spectra of the thioaluminate compounds CAS, SAS, and BAS doped with 10 mol % of Eu^{2+} are displayed in Figure 2. All the excitation spectra exhibit a broad band between 250 and 450 nm, which are well coupled with the emission of UV LEDs (350–410 nm). The excitation spectra of CAS and SAS even extend to the range 450–500 nm which overlaps the emission band of the blue LEDs (450–470 nm). It is, hence, suggested that all Eu^{2+}-doped thioaluminate phosphors could be good phosphor candidates for white LEDs. The first absorption bands of all the samples are caused by the transition between the valence and conduction bands of MAl_2S_4 host. The others are all attributed to the $4f^7 \rightarrow 4f^65d^1$ allowed transition of Eu^{2+} ions.

From the normalized emission spectra, it is obvious that the three phosphors emit visible light at different wavelengths. The peak wavelengths of the bands are 470 nm for BAS, 496 nm for SAS, and 516 nm for CAS. Full widths at half maximum are equal correspondingly to 47, 36, and 38 nm. Because of the covalence and nephelauxetic effect which effectively lowers the center of gravity of 5d orbitals of Eu^{2+} ions, the 5d $\rightarrow$ 4f emission bands of Eu^{2+} exhibit a red-shift behavior from BAS, SAS to CAS.[10]

In order to investigate the luminescent properties of the thioaluminate phosphors in UV LED, three light-emitting LEDs were fabricated through combining InGaN chips with these phosphors, the emission spectra of the LEDs are depicted in Figure 3. The applied voltage and direct current were approximately 3.6 V and 20 mA, respectively. Two distinct emission bands are clearly observed in the three curves. The emission bands ca. 400 nm in the three curves are attributed to the emission of the InGaN chip. The 516-, 496-, and 470-nm broad bands are ascribed to the transitions of Eu^{2+} ions in the CAS, SAS, and BAS host matrixes, respectively. These fabricated LEDs emit intense green, bluish-green, and blue light to the naked eye, respectively. In Figure 4, the CIE color coordinates of the fabricated LEDs are shown to be (0.158, 0.650) for CAS, (0.116, 0.374) for SAS, and (0.129, 0.122) for BAS, respectively. These thioaluminate phosphors show relatively poor chemical stability compared to oxides. But LED packaging process can enhance their resistance against damp.

In conclusion, we have synthesized three phosphors $MAl_2S_4:Eu^{2+}$ (M = Ca, Sr, and Ba) under vacuum in sealed silica tubes. The cheap and stable aluminum powder was first

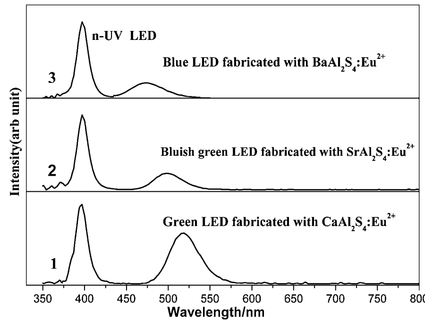

Figure 3. The electroluminescence spectra of the fabricated PC-LEDs combined with CAS (**1**), SAS (**2**), and BAS (**3**) phosphors under 20-mA forward-bias current.

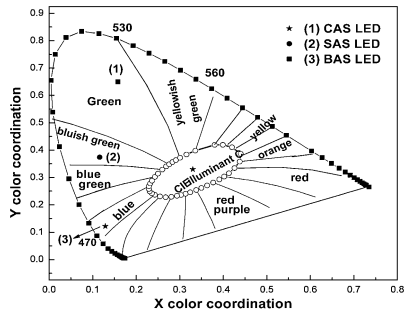

Figure 4. The CIE coordinates of PC-LEDs based on CAS (**1**), SAS (**2**), and BAS (**3**) under 20-mA forward-bias current in the CIE 1931 chromaticity diagram.

used as the starting material instead of expensive and weakly hygroscopic Al_2S_3. Under UV excitation, CAS, SAS, and BAS exhibit strong emission bands peaked at 516, 496, and 470 nm, respectively. The fabricated LEDs of CAS, SAS, and BAS show intense green, bluish-green, and blue lighting. They are believed to be good phosphor candidates for creating white light in phosphor-converted white LEDs.

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