

Characterization of luminescent properties of Sr–Ca–Al–O multi-phases oxide phosphors

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Abstract Multi-phases phosphors, which could exhibit red, green, and blue emission bands simultaneously, were synthesized by the solid-state reaction method with a flux. Starting materials of SrCO_3 , CaCO_3 , and Al_2O_3 were mixed and fired. H_3BO_3 and Eu_2O_3 were added as a flux and a dopant, respectively. Effects of the excitation energy and the mixing ratio of starting materials on the luminescent properties were investigated. Phase transformations and variations of luminescent properties were also observed as a function of H_3BO_3 flux amounts. Emission wavelength and intensity depended on the excitation energy as well as H_3BO_3 flux amounts. The mixture of $8\text{SrCO}_3\text{--}4\text{CaCO}_3\text{--}11\text{Al}_2\text{O}_3\text{--}0.8\text{H}_3\text{BO}_3\text{--}0.18\text{Eu}_2\text{O}_3$ showed red, green, and blue emission by exciting at near UV, while $8\text{SrCO}_3\text{--}4\text{CaCO}_3\text{--}11\text{Al}_2\text{O}_3\text{--}1.2$ and $1.6\text{H}_3\text{BO}_3\text{--}0.18\text{Eu}_2\text{O}_3$ exhibited strong red emissions.

Keywords White LED · Sr–Ca–Al–O · Phosphor · Multi-phases · Multi-emission

1 Introduction

White light emitting diodes (LEDs) for solid state lighting have been persistently focused due to many advantages

comparing with conventional lighting elements. One of several methods for white LEDs, ultra violet (UV) LEDs with RGB (red, green, and blue) phosphors are known as promising one [1–3]. The conventional fabrication method is packing UV LED with individual RGB phosphors in epoxy together.

Among the phosphors for near UV (nUV) excitation, $\text{SrO--Al}_2\text{O}_3\text{:Eu}$ (green or greenish blue), SrO:Eu (red), and $\text{CaAl}_2\text{O}_4\text{:Eu}$ (blue) are focused because of excellent luminescence. $\text{SrO--Al}_2\text{O}_3$ phosphors are synthesized by changing molar ratio of $\text{SrO/Al}_2\text{O}_3$. Various emission wavelengths can be obtained by doping Eu; $\text{SrAl}_2\text{O}_4\text{:Eu}$ (515 nm), $\text{Sr}_4\text{Al}_{14}\text{O}_{25}\text{:Eu}$ (495 nm), $\text{Sr}_3\text{Al}_2\text{O}_6\text{:Eu}$ (600 nm), $\text{Sr}_2\text{Al}_6\text{O}_{11}\text{:Eu}$ (460 nm), and $\text{SrAl}_{12}\text{O}_{19}\text{:Eu}$ (355 nm) [4]. In addition, SrO/Eu is known as a red phosphor which exhibited the emission at 615 nm [5, 6]. H_3BO_3 is well known as a flux that facilitates the synthesizing of $\text{SrO--Al}_2\text{O}_3$.

By substituting alkali earth metal ions such as Ca^{2+} for Sr^{2+} in $\text{SrO--Al}_2\text{O}_3$ phosphors, the emission wavelength could be changed [7]. The radius of Sr^{2+} ions is roughly equivalent to that of Eu^{2+} , while that of Ca^{2+} is smaller. So the crystallographic distortions in Eu-doped CaAl_2O_4 will affect the crystal field at the Ca^{2+} site, and consequently cause the change of luminescent properties.

The phosphors described above have similar composition systems of strontium aluminate, strontium oxide, and calcium aluminate. So it can be considered that multi-emission phosphors can be synthesized by mixing as raw materials in one batch and firing all together, if each phosphor can be formed independently.

In this experiment, for the first time, we made an attempt to multi-phases phosphors that exhibited two bands (greenish-blue or green, red) and three bands (blue, green, red) excited at near UV.

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2 Experiment

SrCO_3 (Aldrich, 99.9%+), Al_2O_3 (Aldrich, 99.9%), Eu_2O_3 (Aldrich, 99.99%), CaCO_3 (High Purity Chemical, 99.99%), and H_3BO_3 (High Purity Chemical, 99.99%) were used as raw materials. For two bands emission, SrCO_3 and Al_2O_3 were mixed at the mole ratio of 8:7, and an amount of Eu was fixed as 0.12 mol. Mixing ratio was based on the calculated formula for SrO and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$. As a flux, H_3BO_3 was added. The amount of H_3BO_3 ranged from 0.8 to 2.4 mol. For three bands emission, CaCO_3 was added for blue spectral region. SrCO_3 , CaCO_3 and Al_2O_3 were mixed at 8:4:11 for expected formation of SrO, CaAl_2O_4 , and $\text{SrAl}_{14}\text{O}_{25}$, and an amount of Eu was fixed at 0.18 mole. The mixture was ball-milled for 24 h and fired 5 h at 1300 °C in N_2 +vacuum atmosphere. N_2 gas was flowed at 5 cc/min while firing.

The crystalline of prepared powders were analyzed by XRD (X-ray diffractometer, SIEMENS D5005) using CuK_α radiation ($\lambda=1.5406 \text{ \AA}$), and luminescence was measured by PL (PSI Darsa-5000) system. Excitation source of PL was a Xe lamp. Various excitation wavelengths were refracted by a monochromator.

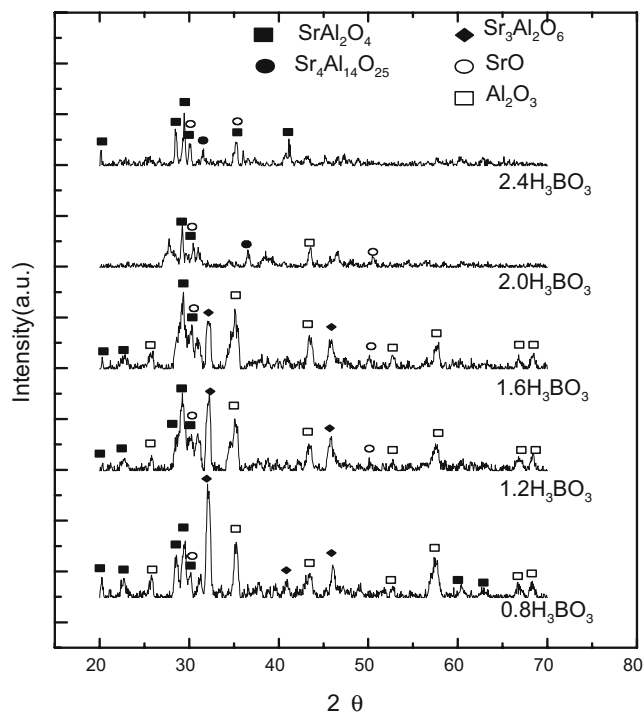


Fig. 1 XRD patterns of $8\text{SrCO}_3\text{-}7\text{Al}_2\text{O}_3\text{-}0.12\text{Eu}_2\text{O}_3$ with various H_3BO_3 amounts

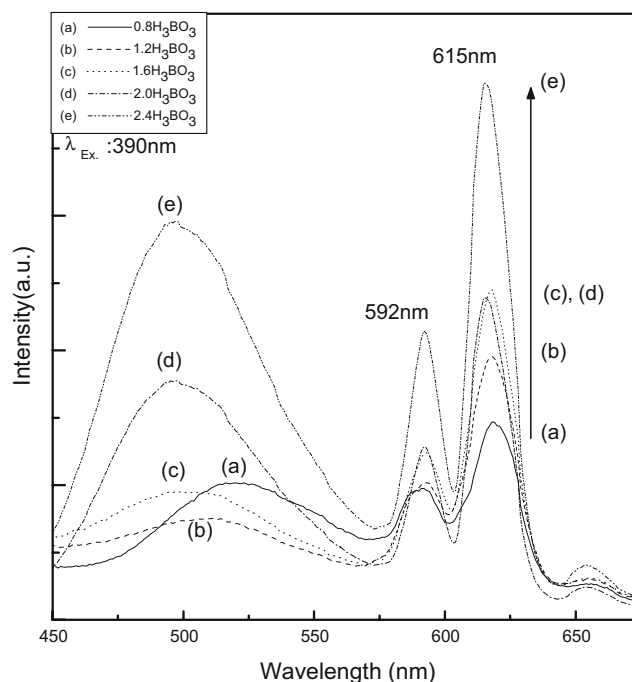


Fig. 2 PL spectra of $8\text{SrCO}_3\text{-}7\text{Al}_2\text{O}_3\text{-}0.12\text{Eu}_2\text{O}_3$ with various H_3BO_3 amounts

3 Result and discussion

To synthesize multi-phases phosphors for two bands (green or greenish-blue, red) emission, 8SrCO_3 , $7\text{Al}_2\text{O}_3$, $0.12\text{Eu}_2\text{O}_3$, and various amount of H_3BO_3 were mixed and fired together in one batch. Expected phases that would be formed after firing were $\text{SrAl}_2\text{O}_4/\text{Eu}$ and SrO/Eu for green and red emission, respectively.

Figure 1 shows XRD patterns of the mixture of $8\text{SrCO}_3\text{-}7\text{Al}_2\text{O}_3\text{-}0.12\text{Eu}_2\text{O}_3$ with various amount of H_3BO_3 after firing at 1300 °C for 5 h. Crystalline phases strongly depended on the amount of a flux, H_3BO_3 . At small amount of H_3BO_3 , SrAl_2O_4 , SrO, Al_2O_3 and $\text{Sr}_3\text{Al}_2\text{O}_6$ phases were shown in XRD. Unwanted $\text{Sr}_3\text{Al}_2\text{O}_6$ and residual Al_2O_3 phases were apparent. With increasing H_3BO_3 , $\text{Sr}_3\text{Al}_2\text{O}_6$ and Al_2O_3 peaks gradually weakened. At 2.0 H_3BO_3 , the peaks of $\text{Sr}_3\text{Al}_2\text{O}_6$ and Al_2O_3 disappeared perfectly, and those of SrAl_2O_4 began to appear dominantly. At 2.4 H_3BO_3 , strong and sharp peaks of SrAl_2O_4 and SrO were observed. This indicated that the flux, H_3BO_3 , acted an important role in synthesizing the phosphors. A flux is known to contribute to facilitating the reaction of powder type raw materials. At a firing temperature, H_3BO_3 is decomposed into H_2O and B_2O_3 , and B_2O_3 becomes a liquid phase that exists between SrO and Al_2O_3 . B_2O_3 liquid phase promoted the rearrangement and reactions of solid particles. So, as described above, at small flux amounts, unreacted Al_2O_3 remained, while, with increasing flux amounts, Al_2O_3 completely reacted with SrO, and was consumed perfectly to form SrAl_2O_4 .

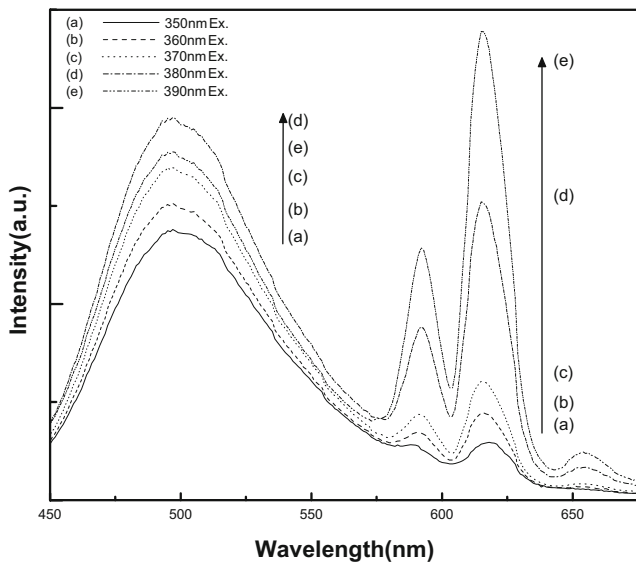


Fig. 3 PL spectra of $8\text{SrCO}_3-7\text{Al}_2\text{O}_3-0.12\text{Eu}_2\text{O}_3$ with $2.4\text{H}_3\text{BO}_3$ excited at various wavelengths

Figure 2 shows PL spectra excited at 390 nm, red emission peaks at 592 nm and 615 nm exhibited higher intensity with increasing H_3BO_3 . The emission peaks at the green region were very weak with small amount H_3BO_3 ,

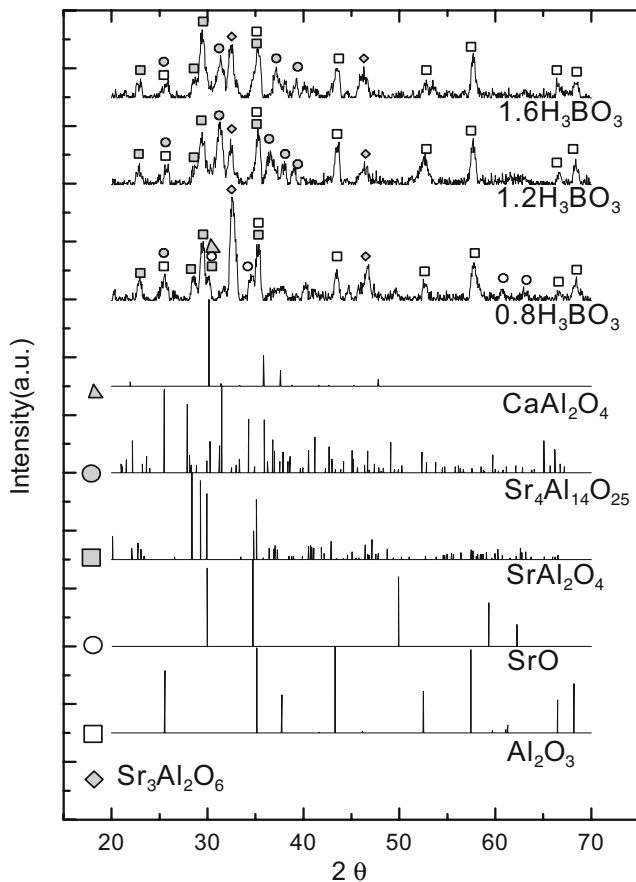


Fig. 4 XRD patterns of $8\text{SrCO}_3-4\text{CaCO}_3-11\text{Al}_2\text{O}_3-0.18\text{Eu}_2\text{O}_3$ with various H_3BO_3 amounts

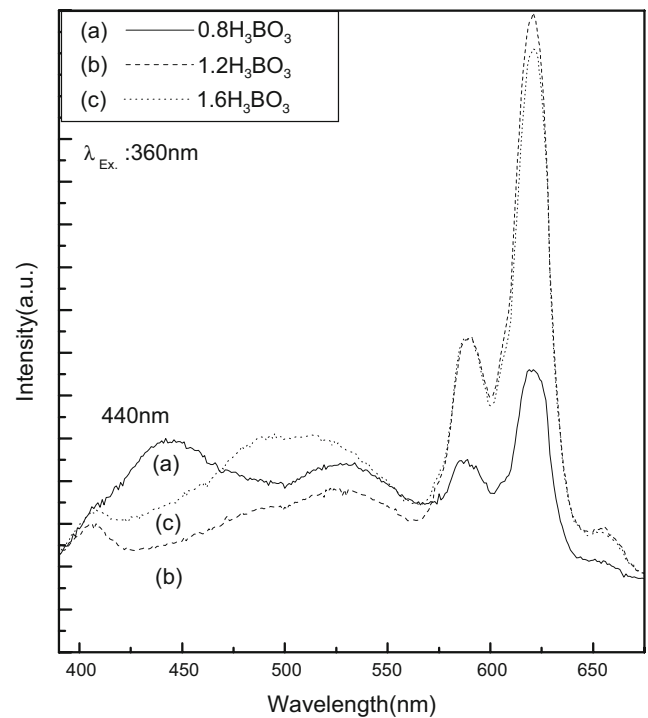


Fig. 5 PL spectra of $8\text{SrCO}_3-4\text{CaCO}_3-11\text{Al}_2\text{O}_3-0.18\text{Eu}_2\text{O}_3$ with various H_3BO_3 amounts

while they increased and showed strong green emission at around 500 nm with 2.0 and $2.4\text{H}_3\text{BO}_3$. Eventually, strong green and red emission peaks could be achieved with $2.4\text{H}_3\text{BO}_3$. This result was in good accordance with that of XRD spectra in Fig. 1. Conclusively, a multi-phases

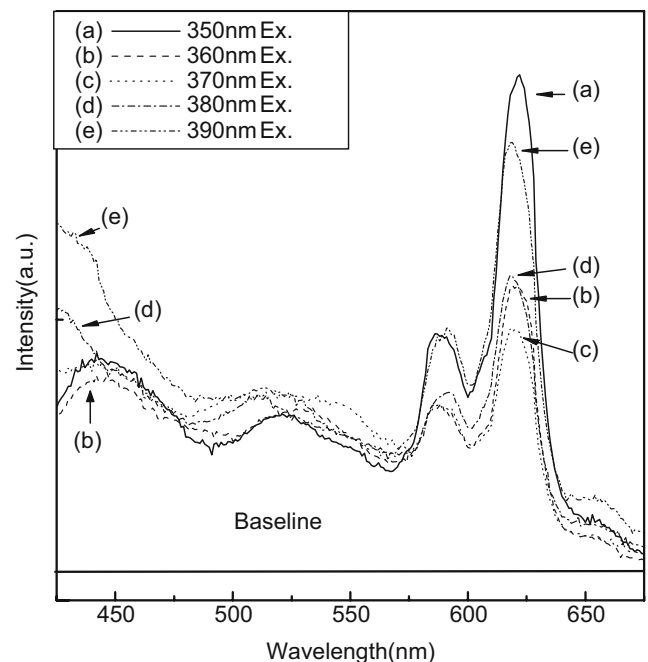


Fig. 6 PL spectra of $8\text{SrCO}_3-4\text{CaCO}_3-11\text{Al}_2\text{O}_3-0.18\text{Eu}_2\text{O}_3$ with $0.8\text{H}_3\text{BO}_3$ excited at various wavelengths

phosphor composed of SrAl_2O_4 and SrO could be obtained with adding $2.4\text{H}_3\text{BO}_3$ as respected, and accordingly its PL spectra exhibited strong multi-emission at red and green regions with the excitation wavelength of 390 nm.

Figure 3 shows PL spectra of the phosphor of $8\text{SrCO}_3-7\text{Al}_2\text{O}_3-2.4\text{H}_3\text{BO}_3$ excited at various wavelengths. The emission intensity at red spectral region increased with increasing excitation wavelength from 350 to 390 nm. On the other hand, the emission intensity at green region excited at 380 nm was higher than at 390 nm, but there was only a little difference between them. In conclusion, by changing the excitation wavelength, relative intensities of red and green spectral regions could be controlled and various luminescent characteristics could be obtained.

To synthesize multi-phases phosphors for three band emission (red, green, blue), CaCO_3 was added to $\text{SrO}-\text{Al}_2\text{O}_3$ system. Y. Lin et al. [7] reported that emission wavelength was changed by alkali earth metal ions substituting for Sr^{2+} . They reported that Eu-doped CaAl_2O_4 phosphors exhibited 440 nm blue emission. We prepared mixtures of 8SrCO_3 , 4CaCO_3 , and $11\text{Al}_2\text{O}_3$ doped with $0.18\text{Eu}_2\text{O}_3$ with adding various amounts of H_3BO_3 and fired together.

Figure 4 shows XRD patterns of multi-phases powders with various contents of H_3BO_3 after firing. As shown, XRD patterns were very complicated. At small amount of H_3BO_3 , SrAl_2O_4 was dominant, and unwanted peaks of $\text{Sr}_3\text{Al}_2\text{O}_6$ and residual Al_2O_3 were also strong. Even though peaks were weak, CaAl_2O_4 and SrO appeared overlapping with other major peaks. With increasing flux amount, peaks of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ became apparent, while those of SrAl_2O_4 weakened and CaAl_2O_4 disappeared. By adding H_3BO_3 , the phase change was noticeable, and PL spectra clearly exhibited the differences between samples as shown in Fig. 5. When the phosphors were excited at 360 nm, emission spectra of a sample with $0.8\text{H}_3\text{BO}_3$ exhibited the blue emission at 440 nm, green at 530 nm, and a couple of red bands at around 600 nm, but only green (500 nm) and red emissions was observed in the samples with 1.2 and $1.6\text{H}_3\text{BO}_3$, because CaAl_2O_4 that had a blue emission band was formed only when $0.8\text{H}_3\text{BO}_3$ was added to the mixture as shown in Fig. 4. Green emission at 530 nm of the multi-phases phosphors with $0.8\text{H}_3\text{BO}_3$ shifted to the shorter wavelength of about 500 nm with increasing H_3BO_3 , because a dominant phase was transformed from SrAl_2O_4 to $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$. SrAl_2O_4 and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ generally exhibited green emission at 510 nm and greenish-blue emission at 490 nm, respectively.

Figure 6 shows PL spectra of synthesized phosphors with $0.8\text{H}_3\text{BO}_3$ that clearly exhibited three emission bands with various excitation wavelengths. PL intensity of each band strongly depended on the excitation wavelengths. Consequently, changing the excitation wavelengths could easily control the intensity of each band. When excited at 350 nm, strong red, green, and blue emission could be achieved. The high emission below 450 nm of the samples excited at 380 nm and 390 nm did not originated from $\text{CaAl}_2\text{O}_4/\text{Eu}$, but from a source lamp.

At present, there are some problems in three bands emission phosphors in synthesis, because the phases are too complicated, and unwanted phases exist, too. However they can be solved in a future study.

This attempt was carried out for the first time, and the possibility for the multi-phases phosphors could be confirmed.

4 Conclusions

Multi-phases phosphors that could exhibit two bands emission (green and red), and three bands emission (red, green, and blue) could be synthesized by mixing all the starting materials together and firing them at the same time.

For two bands emission, mixture of 8SrCO_3 , $7\text{Al}_2\text{O}_3$, and $0.12\text{Eu}_2\text{O}_3$ doped with $2.4\text{Eu}_2\text{O}_3$ successfully showed green and red emission spectra. For three bands emission, mixture of 8SrCO_3 , 4CaCO_3 , and $11\text{Al}_2\text{O}_3$ doped with $0.18\text{Eu}_2\text{O}_3$ exhibited red, green, and blue emissions. The feasibility for the multi-emission phosphors could be confirmed through this work.

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