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Effects of crystal structures on luminescent properties of Eu doped Ca–Al–O systems

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Abstract

To investigate the correlations between the structural transformations of calcium aluminates and luminescent properties, Eu doped Ca–Al–O system phosphors were synthesized by solid-state reaction process in H_2 atmosphere with $CaCO_3$, Al_2O_3, Eu_2O_3, and a flux, H_3BO_3 as starting materials. Various phases such as $CaAl_2O_4$, $CaAl_4O_7$, $Ca_3Al_2O_6$, and $Ca_{12}Al_{14}O_{33}$ were achieved depending on firing temperature, flux amounts, and the mixing ratio of CaO to Al_2O_3. Among various phases, only $CaAl_2O_4$ contributed to a strong blue emission at 440 nm with an excitation wavelength of 330 nm.

Keywords: A. Powders: solid state reaction; C. Optical properties; D. Al_2O_3; Aluminate

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1. Introduction

Many aluminates have been employed as host materials for phosphors by doping rare earth elements. Among them, Eu^{2+} doped $CaAl_2O_4$ and $SrAl_2O_4$ are well-known for blue and green phosphors, respectively [1–3].

Especially, $CaAl_2O_4:Eu^{2+}$ phosphors have been studied to replace $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM:Eu^{2+}) blue phosphor in PDP (Plasma display panel). BAM:Eu^{2+} phosphors have a disadvantage of the luminescence deterioration due to the oxidation of Eu^{2+} to Eu^{3+} after post-heating process [4,5]. It is reported that $CaAl_2O_4:Eu^{2+}$ phosphors can endure the oxidation process due to post-heating process, because $CaAl_2O_4:Eu^{2+}$ phosphors have more thermodynamically stable structure than BAM:Eu^{2+} (β-alumina structure) phosphors [5].

$CaAl_2O_4$ has a β-tridymite structure, where there are three Ca^{2+} sites. One of Ca^{2+} sites is nine coordinated by oxygen atoms, the others are six coordinated. Eu^{2+} ions prefer two six-coordinated sites, because larger spaces are required for the substitution of Eu^{2+} ions due to the atomic size difference (Ca: 1.12 Å, Eu: 1.30 Å) [6]. Each oxygen atom is shared by two calcium atoms, forming a continuous chain structure of Ca–(3)O–Ca [7]. To maintain the electroneutrality, Eu^{2+} ions are suitable to the substitution for Ca^{2+} sites, so the reduction atmosphere is favorable to protect the oxidation of Eu^{2+} to Eu^{3+} [8–10].

Besides $CaAl_2O_4$, calcium aluminate systems easily generate the multi-phases compounds such as $CaAl_4O_7$, $Ca_3Al_2O_6$, and $Ca_{12}Al_{14}O_{33}$ according to the firing conditions and the mole ratio of CaO to Al_2O_3. In spite of numerous works on $CaAl_2O_4:Eu^{2+}$ phosphors, the phase transformations of Eu doped calcium aluminate compounds and their effects on luminescent properties have been rarely reported until now.

In this study, Eu^{2+} doped calcium aluminates were synthesized by solid-state reaction. The effects of the firing conditions and the mole ratio of CaO to Al_2O_3 on the structural changes and luminescent properties of Eu doped Ca–Al–O systems were investigated.

2. Experimental procedure

Eu^{2+} doped calcium aluminates were prepared by solid-state reaction. $CaCO_3$ (High Purity Chemical, 99.99%), Eu_2O_3 (Aldrich, 99.99%), and Al_2O_3 (Aldrich, 99.99%) were used as raw materials. As a flux, H_3BO_3 (Aldrich, 99.99%) was added to decrease the firing temperature and control the particle shapes. The amount of H_3BO_3 ranged from 2 to 10 wt%. The mixture was ball-milled for 24 h and fired at 1100–1300 °C for

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3 h under 5% H_2 (50 cc/min) atmosphere with and without the calcinations. Also, structural transformations and luminescent properties were investigated with various mole ratio of raw material ($CaCO_3$:Al_2O_3).

The crystalline of prepared powders were analyzed by XRD (X-ray diffractometer, SIEMENS D5005) using CuKα radiation ($\lambda = 1.54056$ Å). The scanning angle and scanning speed were $2\theta = 20°–60°$ and 5°/min, respectively. PL (Photoluminescence) properties were measured by PL (PSI Darsa-5000) system that employed a xenon ramp as an excitation source.

3. Results and discussion

XRD patterns of $0.99CaCO_3–1Al_2O_3–0.01Eu_2O_3$ with various firing temperatures are shown in Fig. 1. At 1100 °C, $Ca_3Al_2O_6$ (C_3A) and $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$) phases were dominant, but $CaAl_2O_4$ (CA) and $CaAl_4O_7$ (CA_2) phase weakly appeared. With increasing the temperature up to 1300 °C, XRD peaks of CA and CA_2 increased, but C_3A and $C_{12}A_7$ phases perfectly disappeared at 1300 °C.

XRD peaks of CA and CA_2 phases increased as a function of the firing temperature, because the formation temperatures of CA and CA_2 phases were higher than C_3A and $C_{12}A_7$ as shown in Fig. 2, which showed a phase diagram of CaO–Al_2O_3 system compounds. The eutectic points of CA–$C_{12}A_7$ and CA–CA_2 are 1390 and 1600 °C, respectively. Multi-phases of calcium aluminates can be easily formed, even if the compositional ratio of CaO–Al_2O_3 is slightly deviated from the equilibrium. Furthermore, above eutectic temperatures, since solid and liquid states coexist, calcium aluminate multi-phases can be synthesized due to the coexistence of the meta-stable and stable phases during cooling process [11]. In this experiment, since 1 mol% Eu was added, the actual composition of CaO to Al_2O_3 was 0.99:1, leading to the deviation from the equilibrium composition for CA single phase. Moreover, adding a flux facilitated the reactions and lowered phase transformation temperature, resulting in the coexistence of solid and liquid phase.

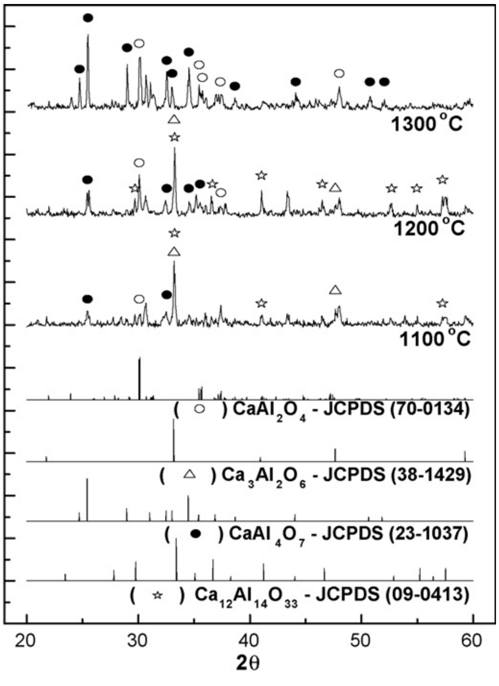

Fig. 1. XRD patterns of $0.99CaCO_3–1Al_2O_3–0.01Eu_2O_3$ as a function of various firing temperature with 5 wt% H_3BO_3.

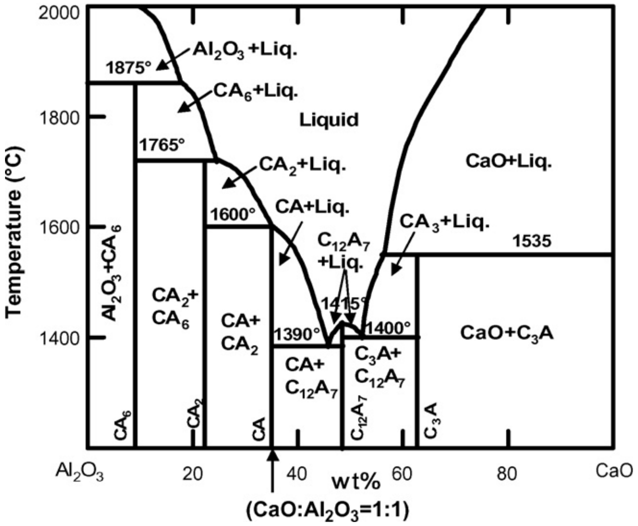

Fig. 2. Phase diagram of CaO–Al_2O_3 systems [17].

PL excitation spectrum of $0.99CaCO_3–1Al_2O_3–0.01Eu_2O_3$–5 wt% H_3BO_3 fired at 1300 °C for the blue emission of 440 nm is shown in Fig. 3. It exhibited a broad absorption band in the range of 320–370 nm, and the maximum absorption was observed around 330 nm.

Fig. 4 shows PL spectra of $0.99CaCO_3–1Al_2O_3–0.01Eu_2O_3$–5 wt% H_3BO_3 with various firing temperatures. A blue emission band around 440 nm was observed with an excitation wavelength of 330 nm. PL intensity increased with increasing firing temperature, and maximum PL intensity was achieved at 1300 °C. It was closely correlated with the phase transforma-

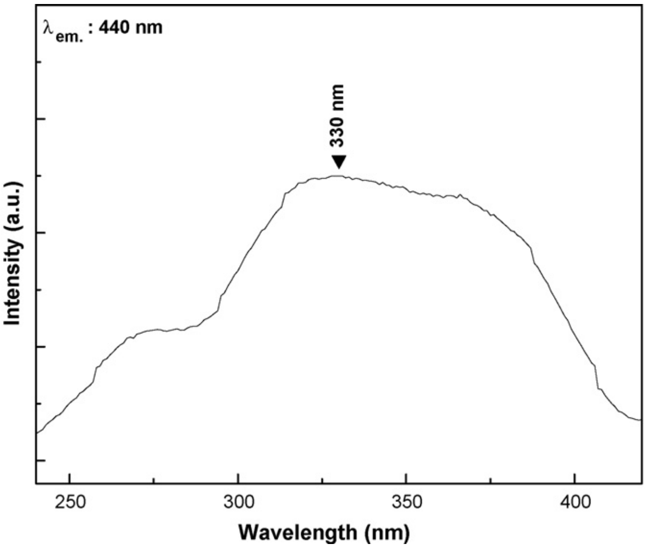

Fig. 3. PL excitation spectrum of $0.99CaCO_3–1Al_2O_3–0.01Eu_2O_3$ fired at 1300 °C with 5 wt% H_3BO_3 for the emission of 440 nm.

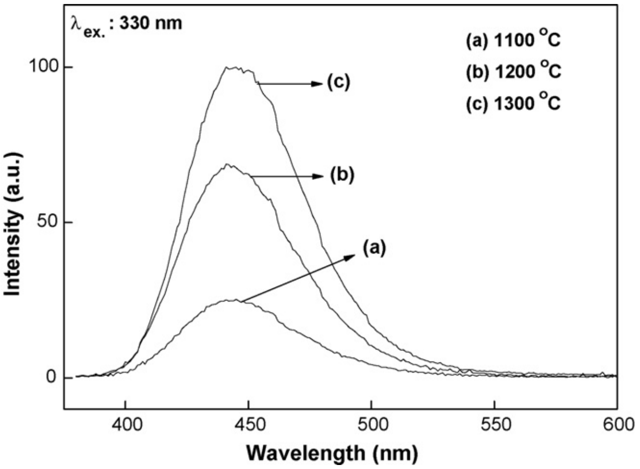

Fig. 4. PL spectra of $0.99CaCO_3–1Al_2O_3–0.01Eu_2O_3$ as a function of various firing temperature with 5 wt% H_3BO_3. (a) 1100 °C, (b) 1200 °C, and (c) 1300 °C.

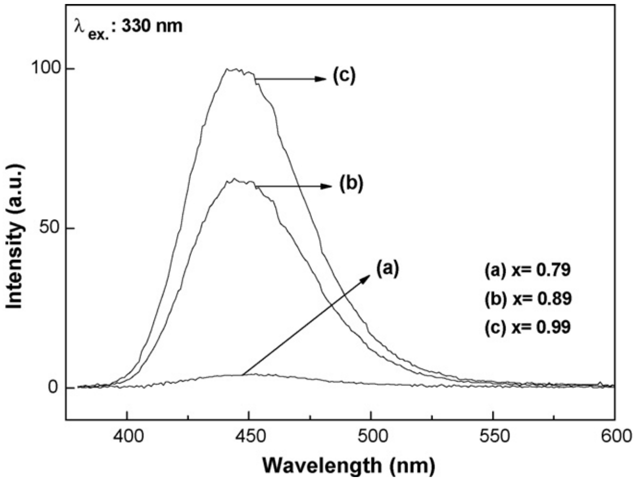

Fig. 6. PL spectra of $xCaCO_3–1Al_2O_3–0.01Eu_2O_3–5$ wt% H_3BO_3 ($x = 0.79$, 0.89, 0.99) fired at 1300 °C.

tions as shown in Fig. 1. At 1300 °C, CA and CA_2 phases were dominant and the PL intensity was high, while, at 1100 °C, XRD peaks of C_3A and $C_{12}A_7$ phases were strong exhibiting weak PL. This demonstrated that either CA or CA_2 might contribute to PL properties, but C_3A and $C_{12}A_7$ clearly did not. To verify it, phase transformations and the luminescent properties were investigated by changing the mole ratios of $CaCO_3$ to Al_2O_3.

XRD patterns and PL spectra as a function of various mole ratios of $CaCO_3$ to Al_2O_3 are shown in Figs. 5 and 6, respectively. As shown in Fig. 5, with decreasing amount of $CaCO_3$, CA phase decreased, while CA_2 phase increased. When the mole ratio of $CaCO_3$ to Al_2O_3 was 0.79:1, CA phase completely disappeared and only CA_2 phase was observed.

In Fig. 6, PL intensity increased with increasing the mole ratio of $CaCO_3$ to Al_2O_3. The highest PL intensity was observed with $0.99CaCO_3$, but PL was too weak with $0.79CaCO_3$ at which only CA_2 phase was observed. It revealed that CA_2 phase did not serve to the luminescence, but only CA phase. Fig. 6 shows the band that was peaking at 440 nm, symmetric, and non-winding, which meant the existence of only one luminescent center of $CaAl_2O_4:Eu^{2+}$ [1]. The emission spectra of $CaAl_2O_4:Eu^{2+}$ originated from the transition between the $^8S_{7/2}$ ($4f^7$) ground state and the excited $4f^65d^1$ configuration [2,9,12]. 5d electrons of Eu^{2+} are sensitive to the changes of the crystal field strength due to the shielding function of outer shell [8,9,12,13]. Conclusively, among Eu^{2+} doped various phases, CA, CA_2, C_3A, and $C_{12}A_7$, only CA contributed to PL emissions. This indicated the crystal fields surrounding the substituted Eu^{2+} ions are different in each phase, leading to the changes of luminescent properties.

Fig. 7 shows XRD patterns of $0.99CaCO_3–1Al_2O_3–0.01Eu_2O_3$ fired at 1300 °C for 3 h as a function of various flux amounts. A flux is known to contribute to facilitating the

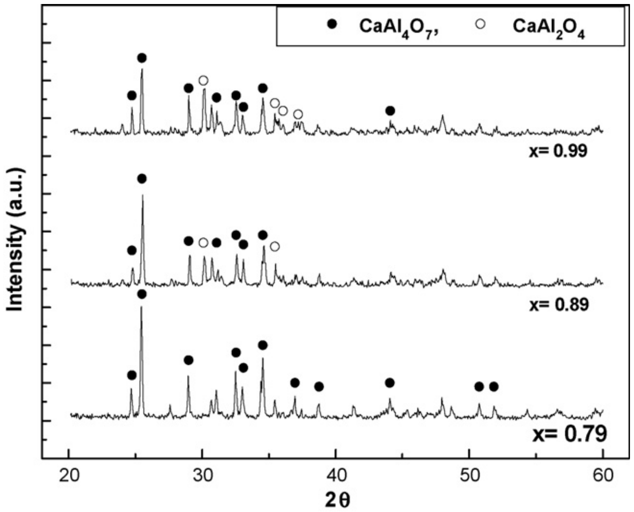

Fig. 5. XRD patterns of $xCaCO_3–1Al_2O_3–0.01Eu_2O_3–5$ wt% H_3BO_3 ($x = 0.79$, 0.89, 0.99) fired at 1300 °C.

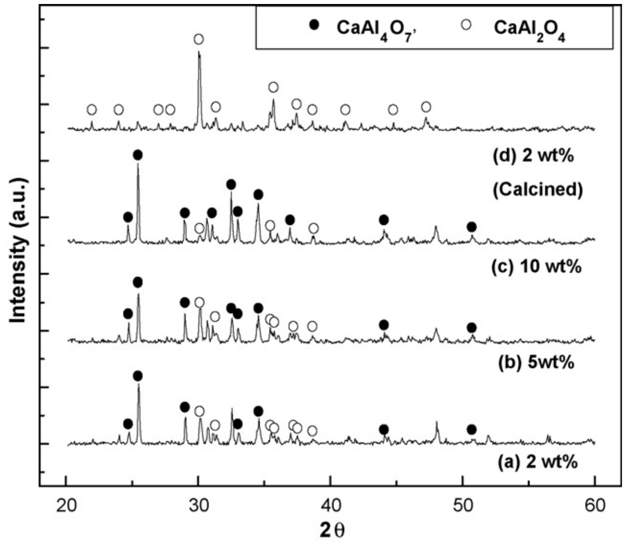

Fig. 7. XRD patterns of $0.99CaCO_3–1Al_2O_3–0.01Eu_2O_3$ as a function of various H_3BO_3 amounts fired at 1300 °C. (a) 2 wt%, (b) 5 wt%, (c) 10 wt%, and (d) 2 wt% (calcined).

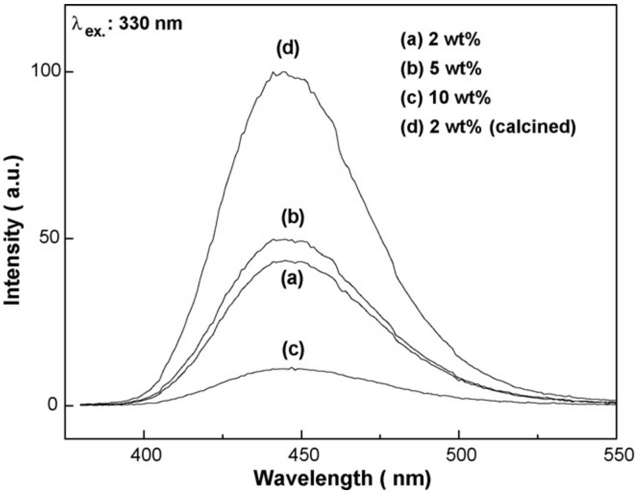

Fig. 8. PL spectra of $0.99CaCO_3$–$1Al_2O_3$–$0.01Eu_2O_3$ as a function of various H_3BO_3 amounts. (a) 2 wt%, (b) 5 wt%, (c) 10 wt%, and (d) 2 wt% (calcined).

reaction of powder type raw materials [10,14,15]. CA and CA_2 phases coexisted with 2 and 5 wt% H_3BO_3, but CA almost disappeared and CA_2 phase mainly existed with 10 wt%. Fig. 7(d) shows XRD pattern of $0.99CaCO_3$–$1Al_2O_3$–$0.01Eu_2O_3$–2 wt% H_3BO_3 fired at 1300 °C for 3 h after calcinations at 1100 °C for 4 h. CA_2 phase disappeared and only a single phase CA was observed.

The flux, H_3BO_3, acted an important role in synthesizing the phosphors. At a firing temperature, H_3BO_3 was decomposed into H_2O and B_2O_3, and B_2O_3 became a liquid phase that existed between CaO and Al_2O_3. B_2O_3 liquid phase promoted the rearrangement and reactions of solid particles. Pascoal et al. reported that second phases like CA_2 and $CaAl_2B_2O_7$ could be appeared due to the excess amount of B_2O_3 [13,16]. This was in accordance with our experimental result of Fig. 7(c) where CA_2 phase was dominant due to the large amount of H_3BO_3.

PL spectra as a function of flux amounts are shown in Fig. 8. PL was almost same at 2 and 5 wt% H_3BO_3, but abruptly decreased at 10 wt% H_3BO_3. These results corresponded to XRD of Fig. 7, which showed both CA and CA_2 phases at 2 and 5 wt% H_3BO_3, and only CA_2 phase at 10 wt% H_3BO_3. PL intensity closely depended on XRD peak intensity of CA phase. Finally, CA synthesized with calcined $CaCO_3$ exhibited the strongest PL emission.

4. Conclusions

Correlation between the structural transformation and luminescent properties of Eu^{2+} doped CaO–Al_2O_3 systems were investigated. Various phases of CA, CA_2, C_3A, and $C_{12}A_7$ were formed depending on the firing conditions and the mole ratio of CaO to Al_2O_3. Among them, only Eu^{2+} doped CA phase contributed to the blue emissions at 440 nm. With calcination process, a single phase CA could be perfectly achieved, and it exhibited strong blue emission band.

Acknowledgement

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