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Luminescent properties of $CaAl_4O_7$ powders doped with Mn^{4+} ions

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Abstract

In this work, the effects of firing conditions, the Mn concentration, and a flux on the structural and luminescent properties of Mn^{4+} ion doped $CaAl_4O_7$ (CA_2) powders were investigated. The photoluminescence excitation spectra of $CA_2:Mn^{4+}$ powders exhibited a broad band, covering from around 320 to 400 nm. Four red emission bands were observed at around 644, 656, 666, and 671 nm, while the 656 nm emission was observed as the strongest one. $CA_2:Mn^{4+}$ was believed to be a good candidate as a red phosphor for white light emitting diodes (LEDs) using near ultraviolet chips.

Keywords: A. Powders: solid state reaction; C. Optical properties; D. Alkaline earth oxides; Calcium aluminates

1. Introduction

Aluminate compounds have been recognized as excellent host materials for phosphors because of their high luminescent efficiency, chemical stability, and durability. Accordingly, rare-earth ions doped calcium and strontium aluminates have been widely investigated [1–4]. Park et al. suggested that various phases such as $CaAl_2O_4$ (CA), $CaAl_4O_7$ (CA_2), $Ca_3Al_2O_6$, and $Ca_{12}Al_{14}O_{33}$ could be achieved, depending on the ratios of CaO to Al_2O_3, while the $CA:Eu^{2+}$ phase dominantly contributed to a strong blue emission at 440 nm with an excitation wavelength of 330 nm [3].

Mn^{4+} doped $CaAl_{12}O_{19}$ (CA_6) is well known as a red phosphor that can be excited by near ultraviolet light [5–9]. Meanwhile, CA_2 can be a good host crystal for phosphors, because it also has some merits as the other aluminates do. CA_2 has a monoclinic structure ($a=1.289$ nm, $b=0.889$ nm, $c=0.544$ nm, and $\beta=106.93°$) [10,11]. It was suggested that Tb^{3+}/Ce^{3+} and Eu^{3+} ions doped CA_2 exhibited green and red emissions, respectively [12,13]. However, CA_2 doped with Mn^{4+} ions has not been reported yet.

Therefore, in this work Mn^{4+} doped CA_2 powders were prepared by a solid-state reaction method and their optical properties were systematically investigated.

2. Experiment

$CA_2:Mn^{4+}$ powders were prepared by a solid-state reaction method using $CaCO_3$ (High Purity Chemicals, 99.99%), Al_2O_3 (High Purity Chemicals, 99.99%), and $MnCO_3$ (Aldrich, 99.99%). H_3BO_3 (Aldrich, 99.99%) was used as a flux to promote the reaction between elements. The stoichiometric mixtures were ball-milled for 24 h and fired at 1200–1500 °C for 3 h under N_2 (30 sccm) atmosphere. A flux was added into the mixtures at 0–15 wt%.

The crystal structure was determined by an X-ray diffractometer (XRD, Rigaku, Miniflex II) using Cu K_α radiation ($\lambda=1.5406$ Å). The scanning angle (2θ) and speed were 20°–70° and 5°/min, respectively. The particle size and morphology were observed by a field-emission scanning electron microscope (FE-SEM, JEOL, JSM-6700F). The photoluminescence (PL) spectra were measured by a PL system (PSI, Darsa-5000) with a 500 W xenon lamp as an excitation light source.

3. Results and discussion

$CA_2:0.01Mn^{4+}$ powders were prepared at various temperatures with 5 wt% H_3BO_3, and their XRD patterns are shown in Fig. 1. CA_2 was attained as a dominant phase at 1200 °C, while un-reacted Al_2O_3 weakly appeared. On the other hand, very weak CA_6 peaks as well as CA_2 peaks were apparently observed at 1300 °C and more. According

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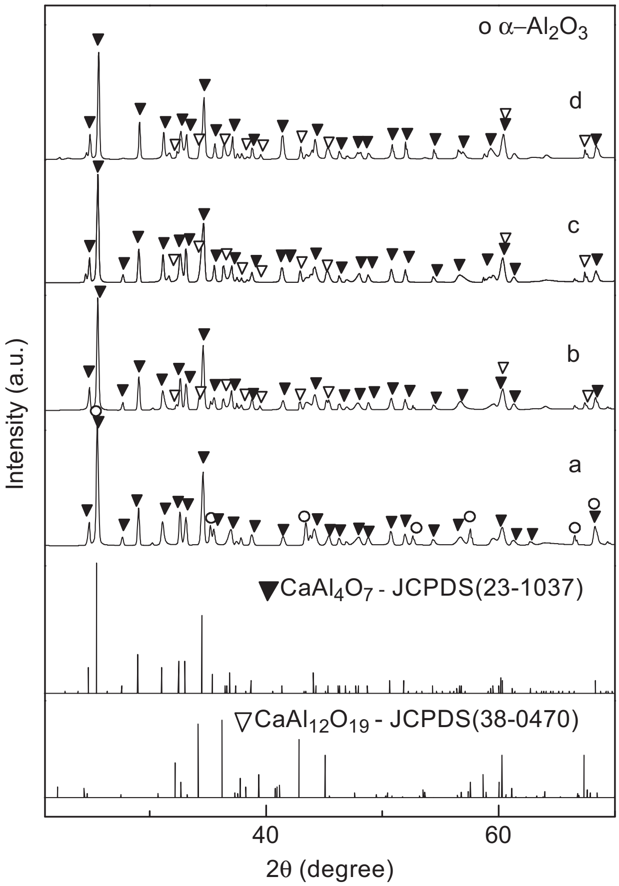

Fig. 1. XRD patterns of CA_2:Mn^{4+} prepared at various firing temperatures: (a) 1200 °C, (b) 1300 °C, (c) 1400 °C, and (d) 1500 °C.

to the phase diagram of the CaO–Al_2O_3 system [14], CA_2+CA_6 or CA_2+CA can be produced, if the composition deviates from the stoichiometric CA_2 composition at above 1200 °C.

The PL excitation (PLE) and PL spectra of CA_2:Mn^{4+} prepared at various firing temperatures are shown in Fig. 2. The PLE spectra at 1300 and 1400 °C are composed of two strong and a weak peaks at around 335, 380, and 467 nm, respectively, which are assigned to $^4A_2 \rightarrow {}^4T_1$, $^4T_2$ transitions of Mn^{4+} ions [6–11]. On the other hand, they are insignificant at 1200 and 1500 °C. The corresponding PL spectra show emission peaks at around 643, 656, 666, and 670 nm due to the ^2E, $^2T_1 \rightarrow {}^4A_2$ transitions of Mn^{4+} ions, while the 656 nm emission appears as the strongest one. These PLE and PL spectra profiles coincided with those of the previous works on CA_6:Mn^{4+} [6–11], indicating that manganese ions were incorporated into CA_2 lattices as Mn^{4+} ions. It was suggested that Mn^{4+} ions in CA_6 were substituted for Al^{3+} ions coordinated by six oxygen atoms, leading to red emission peaks at around 600–700 nm. Mn^{4+} ($r=0.054$ nm) ions can readily replace Al^{3+} ($r=0.053$ nm) ions because of the similarity in size, whereas they are unlikely to be substituted for larger Ca^{2+} ($r=0.134$ nm, CN$=12$) ions [8]. Meanwhile, since all transitions from the ground state to every excited energy level of Mn^{2+} (d^5) are spin-forbidden, Mn^{2+} doped phosphor body colour is white due to the weak optical absorption intensity [15].

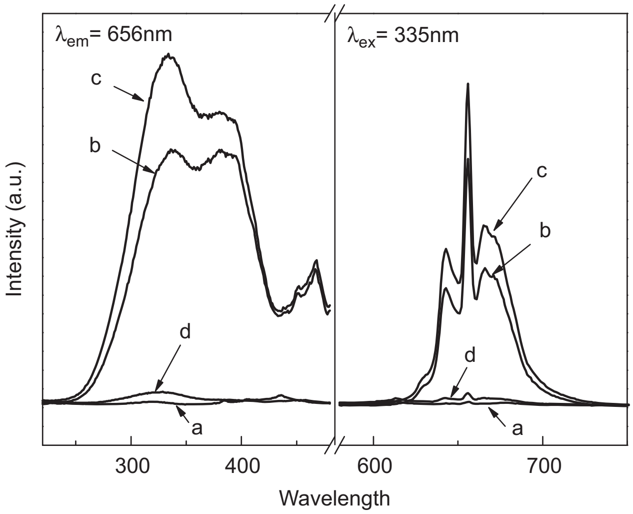

Fig. 2. PLE (left) and PL (right) spectra of CA_2:Mn^{4+} with various firing temperatures. (a) 1200 °C, (b) 1300 °C, (c) 1400 °C, and (d) 1500 °C.

On the other hand, the colour of the obtained powders in this work were pink, because strong absorption bands, which were assigned to the $^4A_2 \rightarrow {}^4T_1$, $^4T_2$ spin-allowed transitions of Mn^{4+} ions, were attained in the visible to near UV region. Additionally, if Mn^{2+} ions exist, a narrow absorption band at around 425 nm due to $^6A_1 \rightarrow {}^4A_1$, ^4E should be observed, but not appear. Accordingly, the comparison with previous works leads to the speculation that Mn^{4+} ions were possibly substituted for Al^{3+} ions of CA_2. On the other hand, Ce^{3+}, Tb^{3+}, and Eu^{3+} ions were presumed to replace Ca^{2+} ions in CA_2, because the difference in size was small. The CA_6:Mn^{4+} phase could also generate the red emission, but its contribution on the emission was thought to be negligible because of its very small amount in samples. CA_2:Mn^{4+} at 1200 °C was not luminescent, because this low temperature was not enough to activate Mn^{4+} ions. The higher temperatures of 1300 and 1400 °C enhanced the incorporation and activation (oxidation) of Mn^{4+} ions in the host, leading to the drastic increase in the PL intensity. However, CA_2:Mn^{4+} at 1500 °C exhibited very low emission intensity, even though its crystallinity was almost the same with those at 1300–1400 °C. However, the reasons for this behaviour are unclear at this stage.

The variation of the PL intensity of CA_2:$x$$Mn^{4+}$ as a function of the Mn concentration is depicted in Fig. 3. With increasing Mn content (x) from 0.1 to 0.3 mol%, the PL intensity increased, and then it continuously decreased at 0.5 mol% and more. This decrease in the PL intensity was attributed to the structural defects and a concentration quenching effect. By substituting Mn^{4+} ions for Al^{3+} ions, positive $Mn_{Al}^{\bullet}$ defects might be produced, resulting in the creation of negative defects such as V_{Ca}'' for charge compensation. These charged defects,

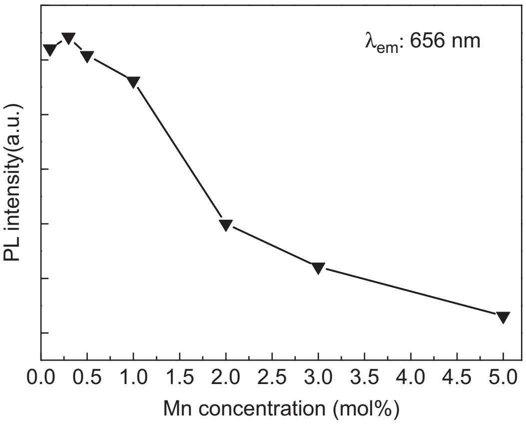

Fig. 3. The variation of the PL intensity of CA_2:Mn^{4+} as a function of the Mn concentration. (Prepared at 1400 °C).

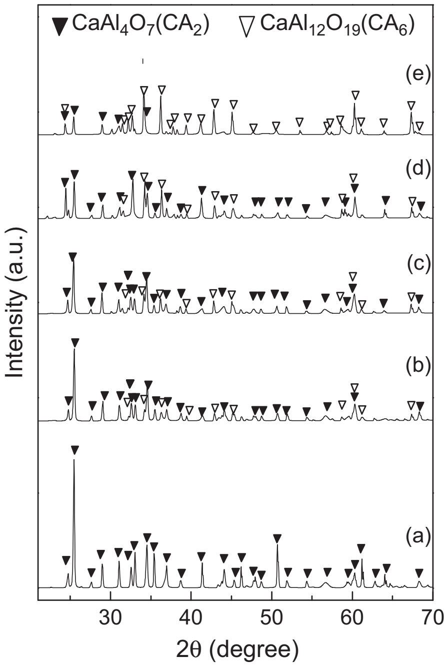

Fig. 4. XRD patterns of samples prepared with various H_3BO_3 amounts. (a) 0 wt%, (b) 5 wt%, (c) 7 wt%, (d) 10 wt%, and (e) 15 wt% ($0.003Mn^{4+}$).

which act as luminescent killers, increase with the increase in x values, reducing the emission intensity. Kang et al. suggested that the strongest emission intensity was achieved for 2 mol% Mn^{4+} ions doped CA_6 powders due to the lowest chemical complexity and structural heterogeneity [9].

The effects of the amount of H_3BO_3 on the phase transition are shown in Fig. 4. When the samples were prepared at 1400 °C without a flux, the pure CA_2 phase was obtained. On the other hand, with increasing the amount of H_3BO_3, the CA_2 phase gradually decreased, whereas the CA_6 phase increased and finally became a dominant phase at 15 wt%. The addition of H_3BO_3 was thought to be favorable to the formation of the CA_6 phase rather than the CA_2 phase. It was reported that fluorides such as MgF_2 and CaF_2 were very effective for the synthesis of the CA_6 phase [5,6]. The addition of AlF_3 was performed in this work, but it was not effective compared with above fluorides.

Fig. 5 exhibits the variation of the PL intensity of samples prepared with various H_3BO_3 amounts. The emission intensity continuously increased with the increase in the amount of H_3BO_3 up to 10 wt%, and then rather decreased at 15 wt%. As described in Fig. 4, the phase transition from CA_2 to CA_6 is observed with the amount of H_3BO_3, while both CA_2:Mn^{4+} and CA_6:Mn^{4+} can generate the same red emission due to Mn^{4+} ions. Therefore, it may be presumed that the red emission is mainly ascribed to the CA_6:Mn^{4+} phase. However, this speculation is not sure, because the PL intensity decreases at 15 wt% despite the increase in the amount of the CA_6:Mn^{4+} phase. Conclusively, both the CA_2:Mn^{4+} and CA_6:Mn^{4+} phases were responsible for red emissions, but it was uncertain which one was predominant at various amounts of H_3BO_3. Another possible effect is the increase in the grain size. As shown in Fig. 6, the grain size largely developed at 15 wt% compared with 5 wt%. Murata et al. also suggested that the enlarged particle size of CA_6:Mn^{4+} was observed by the addition of a flux, CaF_2, resulting in the increase in the PL intensity [5].

4. Conclusion

The structural and luminescent properties of CA_2:Mn^{4+} powders were closely correlated with firing temperatures, Mn concentrations, and a flux. CA_2:Mn^{4+} was obtained as a dominant phase at 1300–1500 °C, while the CA_6:Mn^{4+} phase weakly appeared as a minor phase. The PLE spectra of CA_2:Mn^{4+} powders exhibited broad bands, ranging from around 320 to 400 nm. Four emission peaks were observed in the red region, and the strongest one appeared at 656 nm. The emission intensity was continuously enhanced with increasing firing temperatures up to 1400 °C, but it was insignificant at the high temperature of 1500 C. The addition of H_3BO_3 caused the phase transition from CA_2 to CA_6, and

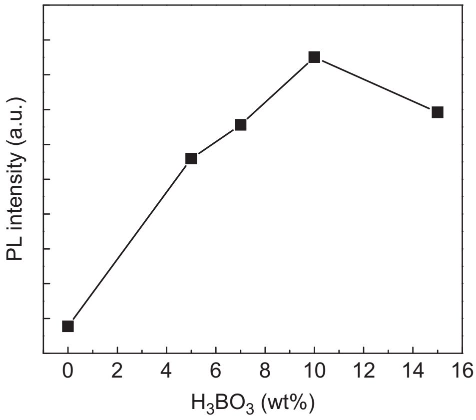

Fig. 5. The variation of the PL intensity of samples prepared with various H_3BO_3 amounts.

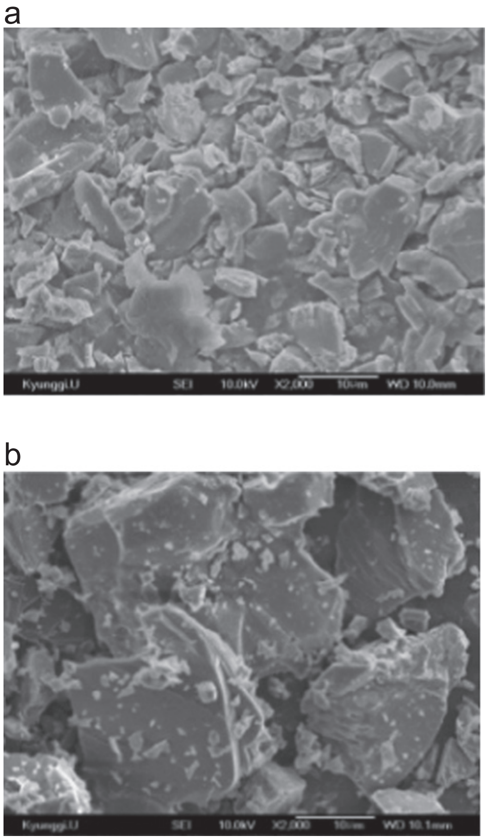

Fig. 6. SEM micrographs of samples prepared with (a) 5 wt% and (b) 10 wt% H_3BO_3.

CA_6 was predominant at 15 wt% H_3BO_3. CA_2:Mn^{4+} was believed to be a suitable red phosphor for white light emitting diodes using near ultraviolet chips.

Acknowledgements

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