



# Long persistent and optically stimulated luminescence behaviors of calcium aluminates with different trap filling processes

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## ABSTRACT

Properties of long persistent luminescence (LPL) and optically stimulated luminescence (OSL) of  $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{R}^{3+}$  ( $\text{R}=\text{Nd}, \text{Dy}, \text{Tm}$ ) materials were investigated. The observed phenomenon indicates that  $\text{R}^{3+}$  ions ( $\text{R}=\text{Nd}, \text{Dy}, \text{Tm}$ ) have different effects on trap properties of  $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}$ . The greatly improved LPL performance was observed in  $\text{Nd}^{3+}$  co-doped samples, which indicates that the incorporation of  $\text{Nd}^{3+}$  creates suitable traps for LPL. While co-doping  $\text{Tm}^{3+}$  ions, the intensity of high temperature of thermoluminescence band in  $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}$  phosphors is enhanced for the formation of the most suitable traps which benefits the intense and stable OSL. These results suggest that the effective traps contributed to the LPL/OSL are complex, of which could be an aggregation formation with shallow and deep traps other than simple traps from co-doped  $\text{R}^{3+}$  ions. The mechanism presented in the end potentially provides explanations of why the OSL of  $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{R}^{3+}$  exhibits different read-in/read-out performance as well.

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## 1. Introduction

Electrons and holes can be trapped in electron trapping materials (ETM) in charging processes by exposing them to ultraviolet (UV) or visible light, and subsequently can be released by thermal radiation or optical stimulation through recombining electrons and holes to generate visible luminescence [1]. Long persistent luminescence (LPL) phenomenon is attributed to the recombination of charge carriers that are excited by thermal stimulation at room temperature, and has attracted considerable attention because of their various applications as security signs, emergency route signs, solar energy utilization and in vivo bio-imaging [2]. While the optically stimulated luminescence (OSL) phosphors, possessing traps deep enough to store energy permanently at room temperature, were also thoroughly investigated for their important applications, like medical imaging or dosimetry [3].

Mechanisms of the processes related to the photoluminescence have been well understood in the last century and now we can benefit from that knowledge, anticipating spectroscopic properties of various compositions, and consequently, we can quite deliberately design new phosphors. However, the mechanism of LPL and OSL processes have not been understood thoroughly [4]. Therefore, in order to improve the luminescence properties of ETM phosphors, it is important to know the mechanism of the phenomenon

profoundly. For both LPL and OSL rely upon the energy storage process, so the generation, capture, and release of carriers from the trap centers are of prime importance to shed light on the mechanism of these materials. To further understand the progresses of LPL and OSL, it is necessary to take the interactions among different types of traps as well as the tracks of the carriers in the both progresses into consideration.

One way to tailor the properties of an ETM phosphor is to introduce potential traps into the lattice matrix of the phosphor with creating nonstoichiometry. Such an effect is usually achieved by introducing cations or/and anions with a charge different from those of the original constituents of the lattice [5]. As we know, the alkaline earth aluminates doped with  $\text{Eu}^{2+}$  and rare earth ( $\text{R}^{3+}$ ) ions are the best candidate for commercial blue LPL materials such as  $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{R}^{3+}$ . It is evident that  $\text{Eu}^{2+}$  ion acts as a luminescent emitting center in  $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{R}^{3+}$ ; however, there is much less agreement on the role of the co-doped  $\text{R}^{3+}$  ions. The co-doped  $\text{R}^{3+}$  ion has been assumed to act as a trap or at least to modify the trap properties in this phosphor [6]. Therefore, it is necessary to make it clear that the influences of the co-doped  $\text{R}^{3+}$  ions on the generation, capture, and release processes of carriers from the trap center. Besides, to the best of our knowledge, the OSL properties of  $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{R}^{3+}$  has not been previously reported. Based on the previous observation of OSL by Setlur et al. on  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Tm}$  and  $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Tm}$ , it is potential that the co-doping of Tm ions optimized the OSL nature of the phosphors above. Thus, we lay more emphasis on the role of co-doped  $\text{Tm}^{3+}$  ion through the OSL process [7].

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In the present work, we focused on the nature of trapping levels in  $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}$  as well as the effects of the co-doping  $R^{3+}$  ions on the LPL and OSL properties of these materials in light of the results obtained, and proposed an alternative approach to control the trap depth by shifting the energy level location in the energy gap after co-doping with diverse  $R^{3+}$  ions. Based on the above, a new oxide ETM phosphor, exhibiting intense, stable OSL, and high sensitivity to near-infrared light, was explored.

## 2. Experimental

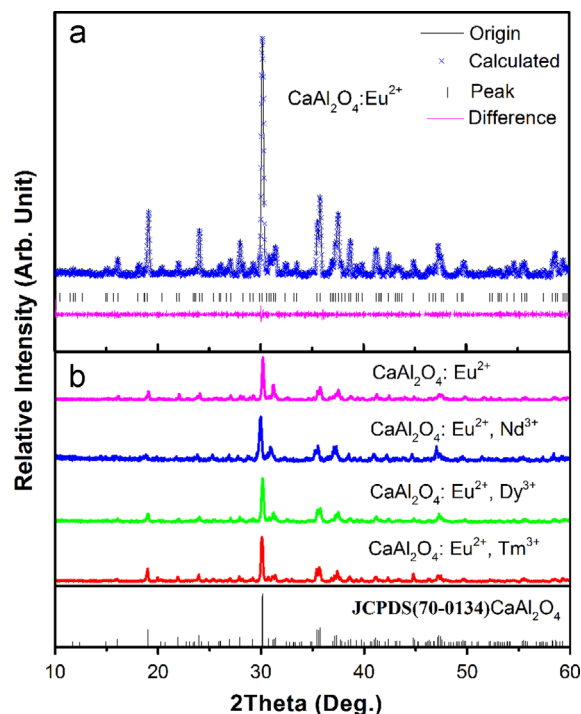
The polycrystalline  $\text{Eu}^{2+}$  doped and  $R^{3+}$  co-doped calcium aluminates,  $\text{Ca}_{0.995}\text{Al}_2\text{O}_4:0.0025\text{Eu}^{2+}, 0.0025 R^{3+}$  ( $R=\text{Nd, Dy, Tm}$ ), were synthesized by a conventional solid-state reaction method. The chemical reagents,  $\text{CaCO}_3$  (Aldrich, 99.99%),  $\text{Al}_2\text{O}_3$  (Aldrich, 99.99%),  $\text{Eu}_2\text{O}_3$  (Aldrich, 99.99%),  $\text{Nd}_2\text{O}_3$  (Aldrich, 99.99%),  $\text{Dy}_2\text{O}_3$  (Aldrich, 99.99%) and  $\text{Tm}_2\text{O}_3$  (Aldrich, 99.99%) with 0.4 wt%  $\text{H}_3\text{BO}_3$  (Aldrich, 99.99%) as a flux, were used as starting materials. The starting materials were ground in an alumina mortar to form homogeneous fine powder mixture. Then, the compacts were fired at 1380 °C for 4 h in a reducing atmosphere ( $\text{N}_2:\text{H}_2=95\%:5\%$ ) in a tube furnace. The relative heating rate of the annealing measurement is 8 °C/min on average starting from room temperature to 1380 °C. After annealing, the samples were cooled to room temperature in the furnace, and ground again into powder for subsequent use.

The phases of samples were identified by X-ray powder diffraction (XRD) with Ni-filtered  $\text{CuK}\alpha$  radiation at a scanning step of 0.02° in the  $2\theta$  range from 10° to 80°. The photoluminescence (PL) and OSL are recorded on a Hitachi F7000 spectrometer. The spectral resolution of PL measurements is 0.2 nm. Decay curves were recorded using a FLS-920T spectrometer at room temperature. Before measuring the OSL, the samples were pre-irradiated by 365 nm UV light for 20 min and then placed in dark for 24 h. A 980 nm laser diode is used as a stimulating source. The thermoluminescence (TL) curves were measured with a FJ-427A TL meter (Beijing Nuclear Instrument Factory). The samples weight was kept constant (0.002g). Prior to the TL measure, the samples were exposed to the radiation from UV light (254 nm) for about 15 min, then heated from room temperature to 650 K with a rate of 1 K/s.

## 3. Results and discussion

The phase and structural purities of  $\text{Ca}_{0.9975}\text{Al}_2\text{O}_4:0.0025\text{Eu}^{2+}$  compounds were confirmed using Rietveld Refinement as shown in Fig. 1(a). The refinement factors of the weighted profile R-factor (Rwp) and the expected R factor (Rp) were determined to be 9.21% and 6.12%, respectively, indicating that the refined results were reliable. Fig. 1(b) shows the XRD patterns of  $\text{Ca}_{0.995}\text{Al}_2\text{O}_4:0.0025\text{Eu}^{2+}, 0.0025R^{3+}$  ( $R=\text{Nd, Dy, Tm}$ ) samples. By comparing with JCPDS Card no. 70-0134, which was placed at the bottom of Fig. 1, no other phase or impurity peaks of samples were observed in the samples co-doped with  $R^{3+}$  ions ( $R=\text{Nd, Dy, Tm}$ ), which indicates that all the obtained samples were single phase and the doping ions of  $\text{Eu}^{2+}/R^{3+}$  incorporated into the host lattice successfully. In consideration of the match between each ionic radius of  $R^{3+}$  and unique  $\text{Ca}^{2+}$  sites ( $\text{CN}=9, \text{Ca}^{2+}=1.18 \text{ \AA}$ ;  $\text{CN}=6, \text{Ca}^{2+}=1.00 \text{ \AA}$ ) [8], the ionic radii of  $\text{Al}^{3+}$  ( $r_{\text{Al}^{3+}}=0.053 \text{ nm}$ ) are too small to be substituted by  $\text{Eu}^{2+}$  ( $r_{\text{Eu}^{2+}}=0.117 \text{ nm}$ )/ $R^{3+}$  ( $r_{\text{Nd}^{3+}}=0.0983 \text{ nm}$ ,  $r_{\text{Dy}^{3+}}=0.0912 \text{ nm}$ ,  $r_{\text{Tm}^{3+}}=0.0880 \text{ nm}$ ), therefore,  $\text{Eu}^{2+}/R^{3+}$  ions prefers to occupy  $\text{Ca}^{2+}$  sites.

The emission spectra of  $\text{Ca}_{0.9975}\text{Al}_2\text{O}_4:0.0025\text{Eu}^{2+}$  and  $\text{Ca}_{0.995}\text{Al}_2\text{O}_4:0.0025\text{Eu}^{2+}, 0.0025R^{3+}$  ( $R=\text{Nd, Dy, Tm}$ ) samples excited at



**Fig. 1.** (a) XRD pattern (solid line) of  $\text{Ca}_{0.9975}\text{Al}_2\text{O}_4:0.0025\text{Eu}^{2+}$  with the corresponding Rietveld refinement (blue cross) and residuals (bottom). (b) XRD patterns of  $\text{Ca}_{0.995}\text{Al}_2\text{O}_4:0.0025\text{Eu}^{2+}, 0.0025R^{3+}$  ( $R=\text{Nd, Dy, Tm}$ ) samples and JCPDS Card no. 70-0134. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

365 nm are shown in Fig. 2(a)–(d). Only the characteristic broad band emission of  $\text{Eu}^{2+}$  with the maximum at 440 nm was observed, which is corresponding to the allowed transition from the  $4f^65d$  to the  $4f^7$  levels of  $\text{Eu}^{2+}$  [9]. As shown in Fig. 2, both the samples co-doped with  $\text{Nd}^{3+}$  and  $\text{Tm}^{3+}$  exhibit a relatively lower emission intensity initially, while the emission intensity gradually increases with prolonged irradiated time, which peaked after 300 s irradiation. The phenomenon is in accordance with the observation that no blue emitting was observed in the initial time in these two samples, while increasingly brightness of the blue emission was appeared with prolonged irradiated time. On the contrary, the blue emission intensity of  $\text{Ca}_{0.9975}\text{Al}_2\text{O}_4:0.0025\text{Eu}^{2+}$  almost achieves the maximum in a short time, in other words, no significant change of the blue emission with the prolonged irradiated time was detected in  $\text{Ca}_{0.9975}\text{Al}_2\text{O}_4:0.0025\text{Eu}^{2+}$ . Similar tendency was observed in the co-doped  $\text{Dy}^{3+}$  sample. It could be speculated that there are some traps with deep depth in both the samples co-doped with  $\text{Nd}^{3+}$  and  $\text{Tm}^{3+}$ , which capture parts of the excited carriers. There is a competitive relationship between the existence of the traps with deep depth and the emission centers for carriers, which weakens the radiative emission of  $\text{Eu}^{2+}$ . In other words, it needs more time to achieve the intrinsic emission intensity of  $\text{Eu}^{2+}$  for the capturing processes of carriers as described above. In the other two samples, it could be making sense that there are lesser traps or traps with shallow depth, which has no obvious effect on the photoluminescence process. Furthermore, the relative low intrinsic emission intensity provides evidence that there is a large amount of defects acting as traps in the samples co-doped with  $\text{Nd}^{3+}/\text{Tm}^{3+}$ , which possess higher capacity in trapping carriers.

Decay curves of LPL at room temperature of  $\text{Ca}_{0.995}\text{Al}_2\text{O}_4:0.0025\text{Eu}^{2+}, 0.0025R^{3+}$  ( $R=\text{Nd, Dy, Tm}$ ) are displayed in Fig. 3. It is known that lattice defects acting as traps play an essential role for energy storage in LPL phosphor. All the doped samples show

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