

Luminescence properties of Mn⁴⁺-doped CaAl₂O₄ as a red emitting phosphor for white LEDs

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Received 6 January 2020; accepted 3 April 2020

Abstract:

A series of Mn⁴⁺-activated CaAl₂O₄ (CAO) compounds were synthesized by co-precipitation to seek a candidate for a red-emitting phosphor to be employed in a white LED. The crystal structure, morphology, and fluorescence properties of the as-obtained phosphors were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and photoluminescence (PL). The deep red luminescence of Mn⁴⁺ in CaAl₂O₄ is reported and discussed. The excitation spectrum exhibited broadband emission between 260 and 550 nm with three peaks dominating at 320 nm due to the transition of ⁴A₂→⁴T₁. The emission spectra between 600 to 720 nm displays an overwhelming emission peak at 654 nm owing to the ²E→⁴A₂ transition of Mn⁴⁺ ion. This research demonstrates the great promise of CaAl₂O₄:Mn⁴⁺ as a commercial red phosphor in warm white LEDs and opens up new avenues for the exploration of novel non-rare-earth red-emitting phosphors.

Keywords: CaAl₂O₄:Mn⁴⁺, co-precipitation, phosphors.

Classification number: 2.1

Introduction

Akin to the enormous number of discoveries made through luminescence materials, rare earth-doped aluminates are attractive materials for a new class of next generation displays and lighting devices that show merits like high chemical stability, brightness, and flexible industrial processing ability [1, 2]. Among the alkaline rare earth metal ion-doped aluminate MAI₂O₄ phosphors (M = Ca, Ba, Sr,...), CaAl₂O₄ is regarded as a potential host material for luminescence because of its chemical stability, high resistance to chemical attacks, low thermal expansion coefficient, and environmental friendliness [3]. Recently, most CaAl₂O₄ phosphors have been chiefly studied for their long-lasting luminescence [4] or luminescent properties when doped with expensive rare-earth ions such as Eu³⁺, Dy³⁺, or Ce³⁺ [5-8].

Mn⁴⁺ ions (d³) have exhibited a rather complicated optical spectra that is sensitive to crystalline fields [9] with a strong absorption in the UV and blue spectral ranges and emission of a deep red luminescence when the ions occupy the lattice sites of the host lattice. Thus,

Mn⁴⁺-doped red phosphors excited by blue LED chips can lessen the reabsorption effect when mixed with green or yellow phosphors. Besides, doping with Mn⁴⁺ ions is not likely to cause any significant structural changes due to the similar ionic radius between Al³⁺ and Mn⁴⁺ (Al³⁺:~0.535 Å and Mn⁴⁺:~0.54 Å). Over the years, other phosphors doped with Mn⁴⁺ have also been reported [10-14]. However, it is necessary to carefully study the luminescence properties of these phosphors to meet the requirements for their practical application in white LEDs.

Currently, there are several methods commonly used to prepare photoluminescence materials with small particle sizes such as by co-precipitation at room temperature, the sol-gel method, or through solid-state reactions. The advantage of co-precipitation over these other methods is that little effort is required to control the numerous factors (temperature, calcination time, pH, gelling substance/metal molar ratio, gelling temperature, etc.) that affect the formation of the single-crystalline phase. To our knowledge, CaAl₂O₄:Mn⁴⁺ red phosphors

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applied to white LEDs have been mostly prepared by solid-state reactions [6, 14-16], which is a much more complicated method compared to the previously mentioned methods. After careful consideration, we have chosen to prepare CaAl_2O_4 fluorescent powder-doped Mn^{4+} at low temperature where the combustion process is fast, simple, and safe. Consequently, the $\text{CaAl}_2\text{O}_4:\text{Mn}^{4+}$ phosphors in this work were prepared by co-precipitation and treated at various temperatures as well as under varied doping concentrations of Mn^{4+} to determine the optimum preparation conditions for this material.

Experimental

The Mn^{4+} -doped calcium aluminates were synthesized by co-precipitation. The stoichiometric raw materials $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2$, and NH_4OH were all analytical reagent grade. The chemical composition was prepared in the stoichiometric molar ratio of $\text{CaAl}_{2-y}\text{O}_4 \cdot y\text{Mn}^{4+}$ where y is the doping concentration of the Mn^{4+} ion that ranged from 0.2-5.0 mol.%. The stoichiometric amount of raw materials was weighed, dissolved by DI water, and then stirred to achieve an even mixture. Then, NH_4OH was slowly added to the mixture to precipitate in hydroxide form. The mixture was continuously stirred at room temperature for 2 h until reaction and then a homogeneous solution in the form of a suspension was obtained. This precipitated mixture was dried at 150°C for 5 h to evaporate excess water. The powder was sintered from 900 to 1300°C for 6 h in air. Ultimately, the $\text{CaAl}_2\text{O}_4:\text{Mn}^{4+}$ phosphor samples were obtained.

After annealing, the crystallinity of the prepared powders was analysed by XRD D8-ADVANCE equipment using a Cu tube with K_α radiation of 0.154046 nm wavelength working at 40 kV/30 mA with a scanning speed of 0.005°/s. A scintillation detector was used for the powder samples. The optical properties were measured on a Nanolog, Horiba Jobin Yvon that employed a 450-watt Xenon lamp as the excitation source. The surface morphology of the specimens was examined using a Jeol JSM-5500 SEM. The SEM in this work offers a relatively high spatial resolution ($<5 \mu\text{m}$ at 10 kV) and can operate over a wide range of acceleration voltages (10 kV). It is possible to operate the SEM in a high vacuum mode for the characterization of conductive materials in addition to low vacuum and environmental SEM (ESEM) modes. Measurements were performed at room temperature unless otherwise specified.

Results and discussion

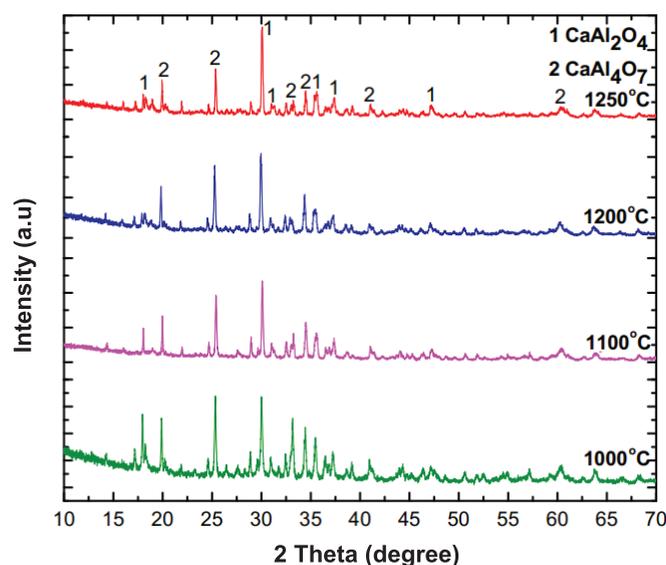


Fig. 1. X-ray patterns of Mn^{4+} -doped CaAl_2O_4 at various temperatures.

The XRD patterns of the $\text{CaAl}_2\text{O}_4:\text{Mn}^{4+}$ phosphors sintered at various temperatures from 1000 to 1250°C are shown in Fig. 1. Most of the diffraction peaks from these samples matched well with the standard Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 70-134 (CaAl_2O_4) and No. 23-1037 (CaAl_4O_7) with the following lattice parameters: $a=8.7 \text{ \AA}$, $b=8.092 \text{ \AA}$, $c=15.191 \text{ \AA}$, and $V=1069.45 \text{ \AA}^3$. The XRD patterns show two crystallization phases: the target product CaAl_2O_4 and a phase of CaAl_4O_7 . The appearance of the CaAl_4O_7 phase remained as the annealing temperature was raised from 1000°C to 1100°C , but the peak intensities decreased. Increasing the calcination temperature to 1250°C led to the most dominant diffraction peaks in terms of sharpness and intensity, which are attributed to the CaAl_2O_4 network. XRD peaks of the CaAl_2O_4 phase increased as a function of the firing temperature because the formation temperature of the CaAl_2O_4 phase is higher than CaAl_4O_7 as shown in Fig. 1.

Besides, doping Mn^{4+} ions into the host does not cause any significant structural changes due to the similar ion radius of Al^{3+} and Mn^{4+} ($\text{Al}^{3+} \sim 0.0535 \text{ nm}$ and $\text{Mn}^{4+} \sim 0.054 \text{ nm}$). Thus, the crystallization temperature of the co-precipitated Mn^{4+} -doped CAO powders is much lower than that of the solid-state reaction method for the same component (1350°C) [14].

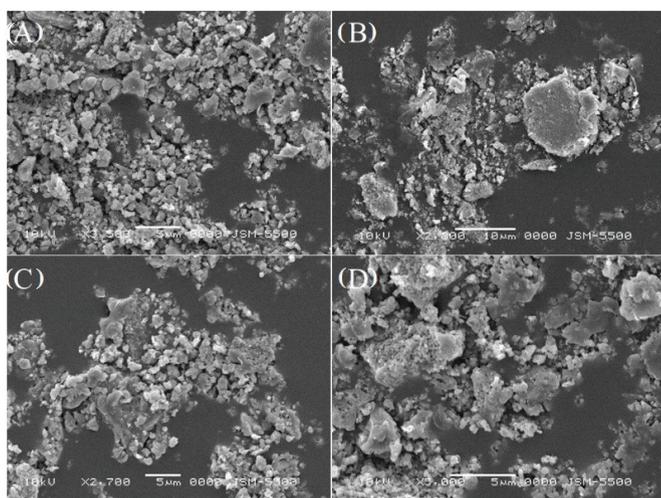


Fig. 2. SEM images of Mn⁴⁺ doped CaAl₂O₄ annealed at (A) 1000°C, (B) 1100°C, (C) 1200°C, and (D) 1250°C for 4 h.

To determine any morphological changes, SEM was utilized to investigate the effect of sintering temperature. The SEM image in Fig. 2 shows the co-precipitated CaAl₂O₄:Mn⁴⁺ annealed at 1000, 1100, 1200, and 1250°C for 4 h and after grinding with a pestle. The annealed samples' morphology was similar: they presented an irregular morphology with angularity over various grain sizes. The surface of the phosphor powder annealed at 1000°C consisted of uniform grains with a sphere-like shape and were 300-400 nm in diameter. It is important to note that when the annealing temperature was increased from 1100 to 1250°C, the powder began to exhibit irregularly-shaped particles due to melting and bonding of the sphere-like grains at high annealing temperatures.

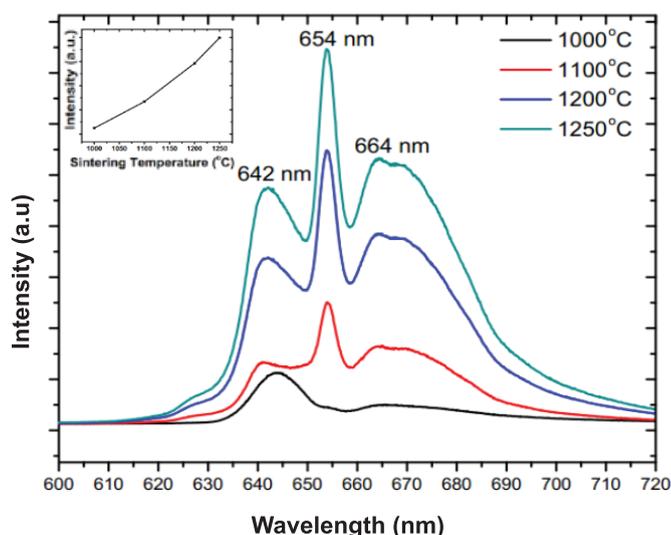


Fig. 3. PL spectra of CAO:1%Mn⁴⁺ phosphor at different annealing temperature.

To investigate the optical properties of the Mn⁴⁺-doped CaAl₂O₄ phosphors, PL spectra were measured and are shown in Figs. 3-5. The PL spectra of the Mn⁴⁺-doped CAO phosphors and the relationship between PL peaks' intensity and annealing temperature (1000 to 1250°C) are presented in Fig. 3. At 1000°C, the PL spectrum showed a very weak band around 644 nm while peaks located at 654 and 664 nm were not recognizable. This result can be explained by poor formation of the desired phase. With an increase of the calcining temperature to 1100°C, the emission intensities at 654 and 664 nm became more recognizable indicating the formation of the desired phase (CaAl₂O₄), however, it is still not very intense. The emission band around 654 nm exhibited the highest PL intensity when the calcining temperature grew to 1250°C. According to Fig. 3, the accepted annealing temperature is 1250°C, which is supposed to be the most achievable in this situation.

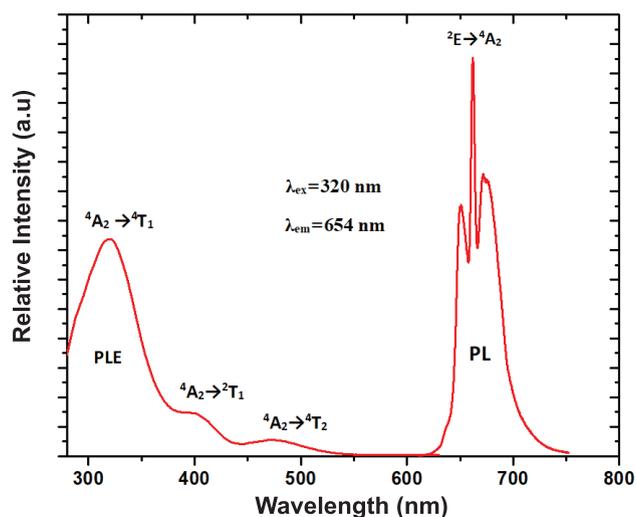


Fig. 4. PLE and PL spectra of CAO: Mn⁴⁺ phosphor annealed at 1250°C for 4 h in air at room temperature ($\lambda_{\text{ex}}=320$ nm, $\lambda_{\text{em}}=654$ nm).

To determine the absorption regions of the phosphor, the normalized room temperature photoluminescence excitation (PLE) spectra of the CaAl_{1.99}O₄:1 mol.% Mn⁴⁺ phosphor annealed at 1250°C was monitored at the main emission peak (654 nm), which is plotted in Fig. 4. The excitation spectrum exhibited broadband emission near the visible ultraviolet and blue spectral regions and displays the presence of three peaks that correspond to 320, 390, and 470 nm from the spin-allowed transitions of ⁴A₂→⁴T₁, ⁴A₂→²T₁, and ⁴A₂→⁴T₂ of the Mn⁴⁺ ions in octahedral coordination, respectively [14]. These PLE

spectra indicate that it is possible to produce white light-emitting diodes when combining these phosphors with UV (260-380 nm), near UV (380-420 nm), and blue (420-480 nm) chips.

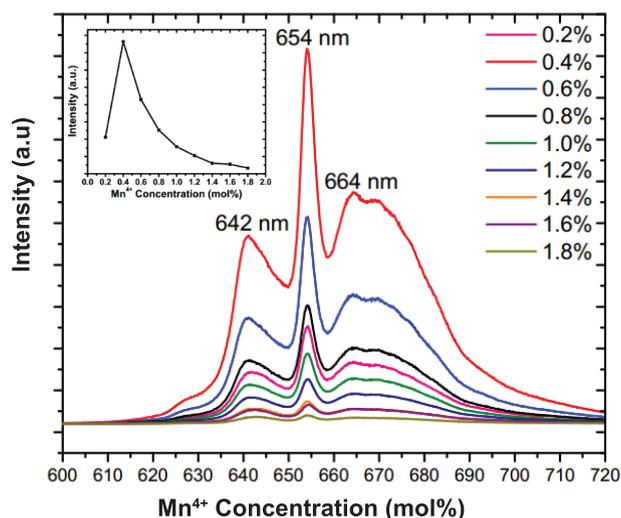


Fig. 5. PL spectra of $\text{CaAl}_2\text{O}_4:\text{yMn}^{4+}$ ($0.2 \leq \text{y} \leq 1.8$ mol%) phosphors annealed at 1250°C at room temperature ($\lambda_{\text{ex}} = 320$ nm).

To optimize the doping concentration of the phosphor, several $\text{CaAl}_{2-y}\text{O}_4:\text{yMn}^{4+}$ samples with different Mn^{4+} concentration were measured by PL (the concentration step size is 0.2 mol.%) calcinated at 1250°C . Fig. 5 reveals the high-resolution room temperature PL spectrum of phosphor calcined at 1250°C ($\lambda_{\text{ex}} = 320$ nm). The PL band covering 600 to 720 nm shows broadband emission with three primary peaks located at 642, 654, and 664 nm. The PL intensities were enhanced with increasing Mn^{4+} doping concentration in the range of 0.2 mol.% to 0.4 mol.% and decrease when the concentration exceeded 0.4 mol.% due to concentration quenching. This effect is explained by ion-ion interactions via transition metal ions that result in energy transfer and non-radiative relaxation from the emitting state. The cross energy transfer and non-radiative relaxation become dominant when the concentration of Mn^{4+} reaches a certain concentration [11].

Concentration quenching may be related to the mechanisms of the exchange interaction or the multipole-multipole interaction. In order to elucidate the mechanism responsible for the concentration quenching, an estimate of the critical distance (R_c) was performed according to the following relationship proposed by Blasse [9]:

$$R_c \approx 2 \left(\frac{3V}{4\pi X_c N} \right)^{1/3}$$

where V is the volume of the unit cell, X_c represents the critical concentration of the activator ion, and N stands for the number of sites in which the Mn^{4+} ion can be substituted in a unit cell. For $\text{CaAl}_2\text{O}_4:\text{Mn}^{4+}$, $N=4$, $X_c=0.4$, and $V=271.685\text{\AA}^3$, thereupon the R_c value is calculated to be 6.871\AA . When the critical distance R_c is smaller than 5\AA , the exchange interaction plays a primary role in the energy transfer among activator ions. Otherwise, the energy transfer mechanism belongs to the electric multipole interaction. Therefore, in our case, we infer that concentration quenching principally transpires via the electric multipolar interactions between the Mn^{4+} ions in the CaAl_2O_4 host [3, 10].

According to Ref. [14], the luminescence centre is from the Mn^{4+} ion. The strongest PL band peak located at 654 nm is due to the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition of Mn^{4+} ion and the two weak PL band peaks located at 642 and 664 nm are assigned to the anti-Stokes vibronic sidebands associated with the ${}^2\text{E}$ excited state of the Mn^{4+} ion and the vibronic transition of the Mn^{4+} ion with zero-phonon line, respectively [14].

Conclusions

In summary, a series of $\text{CaAl}_{2-y}\text{O}_4:\text{yMn}^{4+}$ (0.2 ≤ y ≤ 1.8 mol.%) phosphors were successfully synthesized by co-precipitation with the achievement of the desired phase of CaAl_2O_4 , which was investigated by XRD. The obtained red emission was demonstrated at the 642, 654 and 664 nm peaks of the PL spectrum due to the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition of the Mn^{4+} ion. The most efficient doping concentration and sintering temperature was determined to be 0.4 mol.% and 1250°C , respectively. The Mn^{4+} -doped CaAl_2O_4 phosphors with potential for integration as blend phosphors excited at either near UV and/or blue LED chips point out a desirable potential application as components in warm white light-emitting diodes.

ACKNOWLEDGEMENTS

The present research was supported by a Grant from the Can Tho University under Grant No. T2018-04.

COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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