Photoluminescence and thermal stability of yellow-emitting Pr^{3+} doped CaAl_2O_4 phosphors

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Pr^{3+} -doped CaAl_2O_4 phosphors with broad yellow emission were synthesized by conventional solid-state reaction in air and their structural and luminescent properties were investigated. A pure monoclinic structure can be obtained when the sintering temperature is 1400°C or above. With photoluminescence (PL) measurement, the excitation was observed at 450–500 nm, which covered the emission of the blue light-emitting diode (LED) chips. Emission of the phosphors showed a green band and a red band. So these phosphors showed great potential in application of warm white LEDs without reabsorption. Additionally, the optimal emission intensity was obtained when Pr doping level was at 0.2 mol%. Furthermore, the Pr-doped CaAl_2O_4 phosphors have the higher quenching temperature. With an increase in temperature, the emission bands of Pr-doped CaAl_2O_4 showed an abnormal blue-shift.

Keywords: Phosphors; CaAl_2O_4 ; yellow emission; blue excitation; thermal stability.

1. Introduction

White light-emitting diode (W-LED), as an indispensable solid-state light source for the next generation lighting industry and display system, has attracting tremendous attention in the recent years due to the merits of low electric consumption, high brightness, long lifetime and environment friendliness.¹ Among the technological strategy to manufacture W-LEDs, phosphor-converted white light-emitting diodes (pc-WLEDs) are believed the optimal choices.² To date, the W-LEDs market has been dominated by pc-WLEDs.³ Generally, there are two different approaches to manufacture pc-WLEDs.² One is using a blue-emitting diode that excites a yellow-emitting phosphor. Currently, the combination of a blue LED chip and a yellow-emitting phosphor of cerium-doped yttrium aluminum garnet (YAG: Ce^{3+}) is the conventional approach because of their simpler and lower cost, as well as their color stability over time.⁴ However, these pc-WLEDs suffer some weaknesses, e.g., poor color rendering index and low stability of color temperature.⁵ The other method is using an ultraviolet (UV) LED to stimulate red-green-blue (RGB) phosphors.² In this three-color-converter system, the white light shows high color rendering, high efficiency and high chromatic stability under different driving currents. Unfortunately, there are some disadvantages such as lack of efficient red phosphor, significant color altering and the luminous efficiency decreased by the reabsorption of

multiphase phosphors. Therefore, it is a challenge to develop new phosphors with more excellent properties and low cost.

Up to now, some conventional approaches have been done to solve the above problems. The major one is to develop the appropriate red emission phosphors with low cost, high efficiency and high chemical stability. Recently, the available red phosphors are either alkali earth sulfides/oxysulfides, such as $(\text{Ca}, \text{Sr})\text{S}:\text{Eu}^{2+}$, $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$, and $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$, $\text{CaZnOS}:\text{Eu}^{2+}$ (see Refs. 6–10) or nitrides/oxynitrides, such as $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}$ ($\text{M}=\text{Sr}, \text{Ca}, \text{Ba}$).¹¹ But these sulfide-based phosphors and nitride phosphors have their intrinsic drawbacks: sulfides/oxysulfides have rather low absorption efficiency and poor chemical stability. Nitrides/oxynitrides have good thermal stability but their synthesis need special conditions, such as high sintering temperature ($>1400^\circ\text{C}$) and N_2 protective atmosphere, which would lead to a higher cost. At the same time, the combination of the red phosphors with other color phosphors exist reabsorption. The reabsorption of the phosphors brings the crucial disadvantage: significant color altering and decreases the luminous efficiency.¹² Thus, the optimum phosphors excited by blue LED chip for white-LED applications have such properties: low cost, high absorption efficiency, chemical stability, single-phase but emission including the red and relative green light.

Calcium aluminate, CaAl_2O_4 (CAO), melt congruently at 1600°C (see Ref. 13) with high thermal and chemical

stability. These powders, as a kind of host material, have been used in the field of rare-earth-doped phosphors.^{14–16} In the rare earth elements, Pr is a useful activator. In different hosts, the emission spectra of Pr are obviously different which can be red, green, and even blue emission.^{17–19} Recently, red phosphors, such as Pr³⁺-doped (Bi_{0.5}Na_{0.5})TiO₃ (Ref. 20), Pr³⁺-doped CaBi₂Ta₂O₉ (Ref. 21), and Pr-doped BaMoO₄ (Ref. 22) have been synthesized. Also, it has been reported that SrAl₂O₄:Pr³⁺ had broad yellow orange emission, and weak green and relative strong red emission, with blue excitation.²³ As the best of our knowledge, there is no report about the less cost Pr-doped CAO. Therefore, it is necessary to research the luminescence of Pr³⁺-doped CaAl₂O₄.

In this paper, single-phase Pr³⁺-doped CaAl₂O₄ phosphors have been synthesized by using a simple conventional solid-state reaction in air. The green and red emission has been successfully observed for the first time. So the white LEDs based on a blue LED chip with a Pr-doped CAO phosphor will have a well color rendering index (CRI) because of the red part. At the same time, the white LEDs avoid the reabsorption problem by simply using red-emitting phosphors combined with the yellow-emitting phosphors. Here, we will report the investigation results on the synthesis, phase structure, photoluminescence of this phosphor, the corresponding CIE chromaticity coordinates and thermal stability.

2. Experimental Procedure

The Pr³⁺-doped CAO powders were signed according to the formula of Ca_{1-x}Pr_xAl₂O₄ (0 < x ≤ 0.02) and synthesized by a conventional solid-state reaction technique. The starting materials were CaCO₃ (99.99%, Sinopharm Chemical Reagent Co. Ltd.), Al₂O₃ (99.99% Sinopharm Chemical Reagent Co. Ltd.), Pr₆O₁₁ (99%, Alfa Aesar). In a typical process, the raw materials with a stoichiometric ratio were mixed thoroughly by grinding in an agate mortar in absolute ethanol media. After drying, the mixed powders were calcined in an alumina crucible at 800°C for 4 h in air. Then, the calcined powders were reground. Finally, the powders were sintered at different temperatures (1300°C, 1350°C, 1400°C, and 1450°C).

The conventional X-ray diffraction (XRD, Bruker D8 Advanced, Germany) technique was employed for phase identification. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra at room temperature were recorded by using a fluorescence spectrofluorometer (F-7000, Hitachi, Japan). The sample temperature was measured by a Pt-100 thermocouple located at a heating stage controlled by a TP 94 temperature controller (Linkam Scientific Instruments Ltd, Surrey, UK).

3. Results and Discussion

The XRD investigation was conducted to distinguish and clarify the phase structure of the powders. Figure 1 shows the

Fig. 1. The XRD patterns of the Ca_{1-x}Pr_xAl₂O₄:Pr³⁺ (x = 0.01) powders sintered at various temperatures.

typical XRD patterns of the powders for x = 0.01 sintered at different temperatures. When the temperature is lower than 1400°C, three phases can be observed. The main is cubic phase Ca₃Al₂O₆ (JCPDS: 38-1429), the second one is monoclinic phase CaAl₂O₄ (JCPDS: 53-0191) and the third one is the rhombohedra phase Al₂O₃ (JCPDS: 10-0173). When the temperature reached 1400°C, only the monoclinic structure CaAl₂O₄ (JCPDS: 53-0191) can be seen. So it indicates that the single phase CaAl₂O₄ of monoclinic structure was synthesized.

The excitation and emission spectra of Pr-doped CAO phosphor powders depicted in Fig. 2. The excitation spectra show three sharp excitation peaks at 446, 466, and 485 nm, which corresponded to the typical f-f transitions of ³H₄ → ³P₂, ³H₄ → ³P₁, ³H₄ → ³P₀ transitions, respectively.¹⁹ The intensity of peaks in excitation spectra was due to the influence of the host lattice on the optical absorption of a luminescent center. The excitation spectra cover the emission wavelength of all the blue light-emitting diode chips

Fig. 2. Room temperature PL and PLE spectra of Ca_{0.998}Al₂O₄: 0.2 mol% Pr³⁺.

(450–470 nm). This spectra show that the phosphors can be used in pc-WLEDs. For the emission spectra, a sharp green band at 520–570 nm and a red band at 570–660 nm were observed. The sharp green emission at 527 nm and 540 nm are attributed to the $^3P_1 \rightarrow ^3H_5$ and $^3P_0 \rightarrow ^3H_5$ transitions.²⁴ Two strong red emissions at 608 nm and 625 nm were induced by the lack of the inversion symmetry at the Pr^{3+} sites, which corresponded to the $^1D_2 \rightarrow ^3H_4$ and $^3P_0 \rightarrow ^3H_6$ transitions.²⁴ The weak red emission at 655 nm was due to the $^3P_1 \rightarrow ^3H_4$ transition.¹⁹ The PL results show that the Pr-doped CAO phosphor powders can emit sharp strong green and red light bands. The temperature dependence of the spectra was investigated. Compared with other thermal and chemical stable phosphors, Pr^{3+} -doped $(Bi_{0.5}Na_{0.5})TiO_3$, Pr^{3+} -doped $CaBi_2Ta_2O_9$, and Pr^{3+} -doped $BaMoO_4$, the Pr^{3+} -doped CAO has lower cost and more color band of green.^{20–22} Compared with the Pr^{3+} -doped $SrAl_2O_4$, the Pr^{3+} -doped $CaAl_2O_4$ has lower cost of starting materials and stronger green light. In comparison with the multiphase phosphors of RGB, the single-phase Pr-doped CAO comprising the green light and red light has its advantages without reabsorption. So these phosphors of Pr^{3+} -doped CAO is very suitable for the application of the White-LEDs.

Figure 3 shows the emission spectra of samples with different Pr^{3+} concentrations. The samples were prepared at 1400°C for 4 h. There are no shifts of the emission peaks by Pr doping in CAO phosphors. At the beginning, the PL intensity increased and reached the highest value at $x = 0.2$ mol%. Then, the PL intensity decreased with the increase of Pr^{3+} concentration. So the optimum Pr content for the intensity of the emission is at 0.2 mol%, which is similar for Pr-doped in other host.²⁵

Figure 4 gives a CIE chromaticity coordinates of the produced $Ca_{0.998}Pr_{0.002}Al_2O_4$ phosphor with the corresponding coordinates of a blue LED chip (460 nm). According to the CIE standards, the chromaticity coordinates based on the emission spectrum of $Ca_{0.998}Pr_{0.002}Al_2O_4$ (Fig. 3) were

Fig. 3. The luminescence spectra of $Ca_{1-x}Pr_xAl_2O_4$ ($x = 0.001, 0.002, 0.003, 0.004, 0.005, 0.01, 0.02$).

Fig. 4. CIE chromaticity coordinates of the produced $Ca_{0.998}Pr_{0.002}Al_2O_4$ phosphor with the corresponding coordinates of a blue LED chip (460 nm): (a) the green part of Pr-doped CAO; (b) the red part of the Pr-doped CAO; (c) the blue LED; (d) the final mixed Pr-doped CAO; (e) the calculated result with CAO: Pr and Blue LED.

calculated. From Fig. 4, the green part of Pr-doped CAO were calculated as $x = 0.2285$, $y = 0.7487$ (a); the red part of phosphors were calculated as $x = 0.6597$, $y = 0.34$ (b); the final mixed luminescence colors of the phosphors were yellow as $x = 0.5206$, $y = 0.4715$ (d). The white light comprised the blue light (c) and the yellow of Pr-doped CAO phosphors show its CIE chromaticity coordinate calculated at $x = 0.4156$, $y = 0.3489$ (e), in which its color temperature is approximately 3000 K. The calculated result of the CRI in the point (e) is 81. The above results show that the Pr-doped CAO is the excellent phosphors for the warm white LEDs.

Thermal stability is a critical characteristic of pc-LEDs because the temperature of high power lighting LEDs can increase to 200°C.²⁶ It can be seen, from Fig. 5, that the Pr-doped CAO phosphor has an excellent thermal stability on the temperature quenching effect. With the temperature increase from 300 K up to 500 K, the emission intensity of Pr-doped CAO remains unchanged. It was reported that with the increase in the temperature from 270 K up to 450 K the normalized emission intensity of commercially available YAG:Ce is decreased to 51.9% of the initial value (270 K).²⁷ Qin *et al.* reported that phosphors of $NaCaPO_4:Eu^{2+}$ have excellent thermal stability that, with the increase in the temperature up to 493 K, the normalized emission intensity of $NaCaPO_4:Eu^{2+}$ is decreased to only 90.0% of the initial value (293 K).²⁸ The results in this experiment could

Fig. 5. The emission spectra of $\text{Ca}_{1-x}\text{Pr}_x\text{Al}_2\text{O}_4$ ($x = 0.002$) measured at varying temperatures.

tentatively show that this quenching effect is better than the reported results as mentioned above. The red emission increased slightly with temperature (300–500 K) was proposed to be the result of two crossed excitation states in the configurational coordination diagram.²⁹

Figure 5 shows that the emission peaks of Pr-doped CAO was obviously blue-shifted from 612 nm to 602 nm with the temperature increased from 300 K to 600 K. The mechanism of temperature influence on the emission of Pr^{3+} is complicated. In general, the peak positions of the emission spectra are usually red-shifted with increasing temperature; for example the commercial phosphors of $\text{YAG}:\text{Ce}$.²⁶ The red-shift behavior has been explained by the Varshni equation for temperature dependence³⁰:

$$E(T) = E_0 - \frac{aT^2}{T + b}$$

Jung *et al.* found that a lower energy emission of $\text{CaAlSiN}_3:\text{Eu}^{2+}$, which was attributed to an Al-rich local environment, made the polyhedron around the Eu^{2+} activator smaller, while a Si-rich local environment resulted in a larger polyhedron and a higher energy emission.^{31,32} Consequently, the emission peaks of $\text{CaAlSiN}_3:\text{Eu}^{2+}$ were blue-shifted in a manner determined by the configuration coordinate, increasing the activation energy. So the blue-shift of Pr-doped CAO was also attributed to Al-rich local environment.

4. Conclusion

In summary, single-phase Pr^{3+} -doped CAO phosphors were successfully prepared by a simple solid-state method. The XRD patterns showed that a single phase of monoclinic CaAl_2O_4 was formed when the sintering temperature is higher than 1350°C. The photoluminescence of the samples

were investigated. The optimum of Pr content for the intensity of the emission is at 0.2 mol%. When the powder was excited by blue light, the emission spectra of the phosphors consist of three sharp green peaks at 520–570 nm and a red broad band at 570–660 nm. With the increase in temperature, the Pr-doped CAO phosphor showed good thermal luminescence stability. Meanwhile, the emission bands showed an anomalous blue-shift with increasing temperature. Furthermore, the CIE chromaticity coordination of the Pr-doped CAO and Blue LED also showed that the CAO: Pr could be potential materials for the use in warm white LEDs.

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