Journal of Rare Earths 36 (2018) 125–129

Contents lists available at ScienceDirect

Journal of Rare Earths

journal homepage: http://www.journals.elsevier.com/journal-of-rare-earths

Synthesis and characterization of $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+},Ag^{+}$ phosphor☆

Rui Chen [a, *], Donghua Chen [b]

[a] College of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming 650500, China
[b] Hubei Key Laboratory for Catalysis and Material Science, College of Chemistry and Material Science, South Central University for Nationalities, Wuhan 430074, China

ARTICLE INFO

Article history:
Received 24 February 2017
Received in revised form
27 June 2017
Accepted 28 June 2017
Available online 18 August 2017

Keywords:
Phosphor
Transmission electron microscope
Luminescence
X-ray diffraction
Afterglow
Rare earths

ABSTRACT

$Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+},Ag^{+}$ phosphors were synthesized by solid-state reaction technique. The crystalline phase and luminescence performances of $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+},Ag^{+}$ were observed by X-ray powder diffractometer (XRD), transmission electron microscope (TEM), photoluminescence spectrometer and brightness meter, respectively. The addition of Ag^{+} can diminish in the crystal particle sizes of $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+}$. Because Ag^{+} can reduce the concentration of the undesirable defects in the phosphor, luminescence intensity of $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+},Ag^{+}$ is 2.3 times as high as that of $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+}$ at the same preparation condition. The effect of Ag^{+} on the persistent afterglow properties is to deepen the energy storage traps and enhance the energy transfer efficiency from $Ca_{0.9}Mg_{0.1}TiO_3$ to Pr^{3+}. The persistent afterglow properties of $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+},Ag^{+}$ are better than those of $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+}$ at the same preparation condition. In conclusion, $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+},Ag^{+}$ phosphor with molar ratio of Ag^{+} to Pr^{3+} 3:1 obtained at 900 °C for 4 h exhibits the optimal photoluminescence performances.

1. Introduction

$MTiO_3:Pr^{3+}$ (M = Ca, Sr, Ba), a potential oxide-based material is of special interest to researchers since $SrTiO_3:Pr^{3+}$[1] was reported to be a persistent phosphor.[2] The emission profile of $CaTiO_3:Pr^{3+}$ phosphor in a perovskite structure has shown a single narrow band peaking ($^1D_2$-$^3H_4$) at 613 nm. However, it is necessary to improve the phosphorescent performance of $CaTiO_3:Pr^{3+}$ for use in persistent afterglow devices due to its weak afterglow properties.

Since the composition, structure and preparation method of material can affect the luminescence intensity of $CaTiO_3:Pr^{3+}$,[3–23] some feasible measures have been taken to enhance the phosphorescence intensity of $CaTiO_3:Pr^{3+}$ by co-doped ions including Na^{+}, Tl^{+}, Ag^{+}, Ca^{2+}, Al^{3+}, Bi^{3+}, In^{3+} and La^{3+}.[15–22] These co-doped ions act as charge compensators, the role of which are to limit the concentration of the undesirable defects in $CaTiO_3:Pr^{3+}$ phosphor, leading to the reinforcement of the optical performances.[15] For example, $CaTiO_3:Pr^{3+}$ co-doped with Al^{3+} or Ca^{2+} prepared under sol–gel basic conditions was the most performant, with intensity gains estimated at around 200% and 260%, respectively. Diallo et al used Na^{+}, Tl^{+} or Ag^{+} as charge compensators to analyze the evolution of luminescence intensity in compensated and uncompensated samples.[16] The results reveal that the gain in the luminescence efficiency is around 30% in $CaTiO_3:Pr^{3+},Na^{+}$ or $CaTiO_3:Pr^{3+},Tl^{+}$ and 60% in $CaTiO_3:Pr^{3+},Ag^{+}$. Using Bi^{3+} as charge compensator, the UV excitation efficiency of $CaTiO_3:Pr^{3+},B^{3+}$ phosphor is improved in the wavelength range 250–430 nm.[20] It was reported that In^{3+} incorporation can enhance the intensity of the red emission and extend the afterglow decay time of the $CaTiO_3:Pr^{3+}$ phosphor considerably because In^{3+} can neutralize the additional positive charge generated by the Pr^{3+} ions when substituting in the Ca^{2+} ions site.[21] As a consequence, it is shown that charge compensator has an effect on the optical performances of $CaTiO_3:Pr^{3+}$.

In this paper, we selected Ag^{+} as charge compensator to study the effect of Ag^{+} on the phosphorescent performances of $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+},Ag^{+}$ phosphor. This was achieved when Ag^{+} was substituted in the site of Ti^{4+} to improve the luminescence intensity and persistent afterglow properties of $CaTiO_3:Pr^{3+}$, making it possible for this material to be used as a novel phosphor.

2. Experimental

2.1. Synthesis

$AgNO_3$ was dissolved in deionized water at a concentration of 0.01 mol/L. Pr_2O_3 was dissolved in HNO_3 to obtain Pr^{3+} solution. Stoichiometric amounts of $Ca(NO_3)_2\cdot 4H_2O$, $Mg(NO_3)_2\cdot 6H_2O$, TiO_2,

---

☆ **Foundation item:** Project supported by the Education Department of Yunnan, China (Grant No. 2015Y103).

* Corresponding author. Fax: +86 871 65941088.
E-mail address: rui_chen888@hotmail.com (R. Chen).

http://dx.doi.org/10.1016/j.jre.2017.06.005

H_3BO_3, Ag^+ and Pr^{3+} were mixed by ultrasonic at room temperature for 15 min and white mash was gained. In this experiment, the molar ratio of $Ca(NO_3)_2 \cdot 4H_2O$ to $Mg(NO_3)_2 \cdot 6H_2O$ was 9:1, the molar amount of TiO_2 was equal to the sum of the molar amounts of $Ca(NO_3)_2 \cdot 4H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$, and the molar ratios of H_3BO_3 and Pr^{3+} to mixture were 1:10 and 1:10,000, respectively. The mash was heated in an oven at 70 °C for 30 min to gain white powder. $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+},Ag^+$ phosphors were gained after the powder was sintered in air.

2.2. Characterization

The crystal structures were characterized by X-ray diffraction (XRD) using a DX-2700 X-ray powder diffractometer (Dandong Fangyuan Instrument Co., Ltd., China) with Cu Kα radiation. The morphology and dimension of the products were observed by transmission electron microscopy (TEM), which was taken on a JEM-2100 transmission electron microscope (JEOL Ltd, Japan). A sample for TEM examination was prepared by depositing an ultrasonically dispersed suspension of powder from a solution of alcohol on a carbon-coated copper grid. Photoluminescence spectra were tested using a Hitachi F-4500 luminescence spectrometer (Hitachi Co., Japan) with a xenon discharge lamp at room temperature. The decay curves were measured with the ST-86LA brightness meter (Beijing Normal University, China) after the samples were irradiated by UV light at 254 nm for 15 min at room temperature.

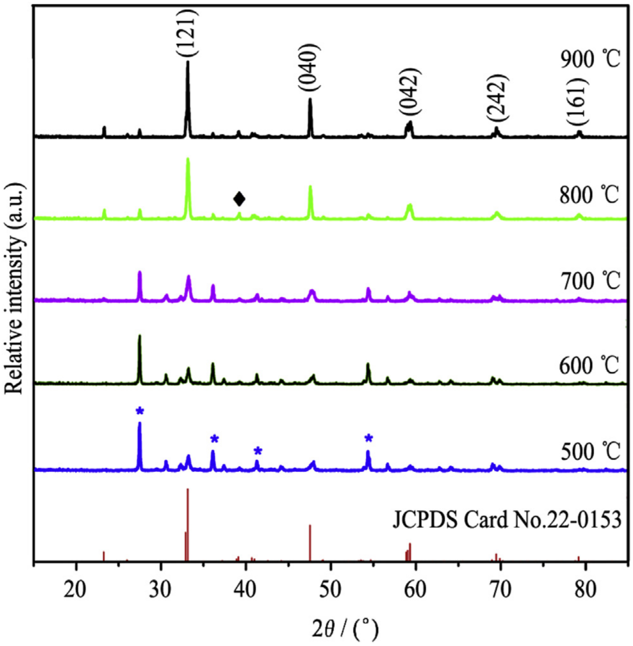

Fig. 1. XRD patterns of $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+},Ag^+$ sintered at different temperatures for 4 h.

3. Results and discussion

3.1. X-ray diffraction analysis

In Fig. 1, using H_3BO_3 as flux, the perovskite structure $CaTiO_3$ (labeled by •) (JCPDS Card No. 22-0153) is formed and a large quantity of TiO_2 (labeled by *) does not enter the crystal phases of $CaTiO_3$ and $MgTi_2O_5$ (labeled by ◆) at 500 °C. The content of residual TiO_2 remarkably reduces and $MgTi_2O_5$ phase is formed above 700 °C. With the increase of sintering temperature, the intensity of the diffraction peaks of $MgTi_2O_5$ increases, then reduces. The intensity of the diffraction peaks of $MgTi_2O_5$ is the strongest at 800 °C. The intensity of the main diffraction peaks (121, 040, 042, 242, and 161) of $CaTiO_3$ increases strongly with the sintering temperature, demonstrating a significant improvement of the powders' crystallinity. The crystal phases of sample are mainly composed of $CaTiO_3$ at 900 °C. That is, the effect of $MgTi_2O_5$ on the crystallinity of sample remarkably diminishes when the sample is prepared at 900 °C. It was observed that there is no effect on the crystal phases from Pr^{3+}, Ag^+ and H_3BO_3 due to their low content.

Scherrer equation, $L = K\lambda/\beta \cdot \cos\theta$, was used to calculate the crystallite size (L) by XRD radiation of wavelength λ (nm) from measuring half-width (β) of the reflections (042 and 242) and the lattice spacings of planes (042 and 242) in radian located at any 2θ in the patterns. The calculation result shows that the size range of $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+},Ag^+$ phosphor is 360–460 nm.

3.2. Transmission electron microscope analysis

Transmission electron microscope images of $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+},Ag^+$ and $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+}$ are shown in Fig. 2. All the particles show irregular and dense microstructure. The particle sizes of $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+},Ag^+$ are smaller than those of $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+}$ though some conglomeration phenomena appear in the TEM micrograph for the high temperature. It can be predicted approximately that the crystal particle sizes of $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+},Ag^+$ are near 500 nm, which agrees with the data from the XRD estimation. However, the particle size changes drastically as it is no longer possible to observe any fine granular structure. It reveals that the addition of Ag^+ could change the particle sizes of $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+},Ag^+$ red phosphors. However, with the sintering temperature the crystal phase of $CaTiO_3$ gains a

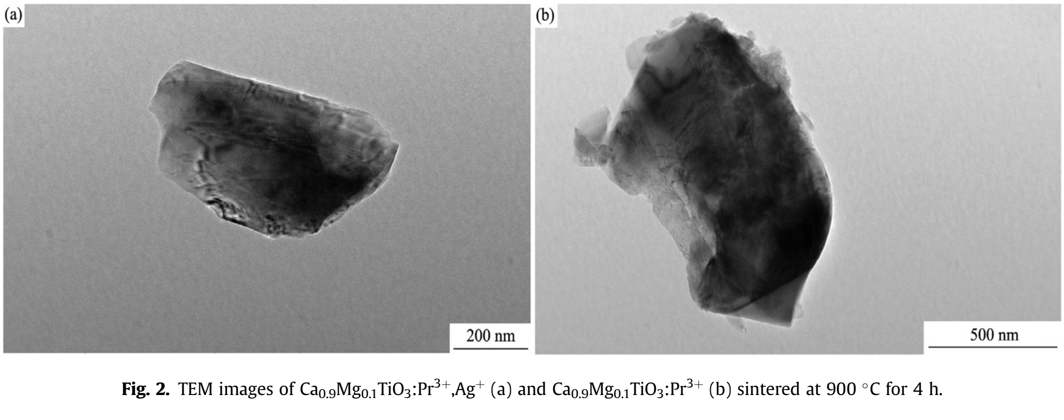

Fig. 2. TEM images of $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+},Ag^+$ (a) and $Ca_{0.9}Mg_{0.1}TiO_3:Pr^{3+}$ (b) sintered at 900 °C for 4 h.