Synthesis and characterization of a green CaAlxOy:Tb3+ phosphor using solution combustion method

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**Abstract.** CaAlxOy:Tb3+ green phosphors were obtained at low temperature (500 0C) by a solution- combustion method. The morphology and structural properties were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD), and the structural analysis revealed the presence of both CaAl4O7 and CaAl2O4 monoclinic. The characteristic luminescence properties were investigated using emission spectra. The optimal intensity was obtained when the concentration of Tb3+ was increased to 2 mol%.

1. Introduction

Long lasting phosphor can be used as a type of energy storing material, which can absorb the visible light, store the energy, and then release energy as visible light which lead to a long persistence afterglow in darkness [1, 2]. Afterglow phosphors have attracted considerable attention due to their potential application in various fields, including emergency signs, light sources, luminous paints, Optical data storage and dial plates of glow watches, etc. [3, 4]. Among various host matrix materials, aluminates are considered to possess high energy efficiency in a wide excitation wavelength range and a high quenching temperature range [5]. The CaAl2O4 host belongs to the stuffed tridymite structure and the framework consists of AlO4 tetrahedras, with Ca2+ ions in the cavities to balance the charge [6]. Terbium is one of the most widely use rare earth ion which emits strongly in the green region. The Tb3+ ions luminescence under UV excitation usually consists of four main emission bands around 490, 545, 580 and 620 nm [1]. Compared with other synthesizing methods, like Solid state reaction, Sol-gel technique, Microwave heating techniques, etc. the combustion method is very simple, safe, energy saving and takes only a few minutes [7,8] to prepare. In this study, we report on the synthesis and characterization of the phosphor calcium aluminate activated with different concentration of Tb3+ ions that was prepared with the solution combustion method.

1. Experimental procedure

Tb3+ doped CaAlxOy phosphor was prepared by the solution combustion method. The Ca(NO3)2.4H2O, Al(NO3)3.9H2O, Tb(NO3)3.6H2O, and CO(NH2)2 were taken as starting materials and were dissolved in 5ml of deionized water and stirred for 30 minutes. The doping concentrations of the Tb3+ ions were 0.25, 0.4, 0.5, 1, 1.5, 2 mol%, respectively. After stirring, the transparent solution was taken into a muffle furnace maintained at a temperature of 500 0C. The solution boiled and underwent dehydration, followed by decomposition with the escape of large amount of gasses (oxides of carbon, nitrogen and ammonia) and then a white foamy and voluminous ash was produced. The whole process was over within less than 5 min, after the product was cooled to room temperature. The foamy powder was crushed into a powder using a pestle mortar and the obtained white powder was used for characterization. The techniques used for characterization were X-ray diffraction (XRD), Scanning electron microscope (SEM), Energy dispersive spectroscopy (EDS) and Photoluminescence (PL).

1. Results and Discussion

*3.1 X-ray diffraction and morphology of the sample*

The XRD of the CaAlxOy host phosphor doped with different concentration of Tb3+ are shown in Fig. 1.The XRD peaks revealed both the CaAl2O4 monoclinic (JCPDS) card number 70-0134 and CaAl4O7 monoclinic (JCPDS) card number 74-1467 structure. The doping of the different concentration of Tb3+ ions on the host did not cause any significant change in the structure. Fig.2 shows the SEM images of CaAlxOy:Tb3+ with a 2 and 1.5 mol% concentration of Tb3+ ions. The surface aspect of the particles is found to be nonspherical and irregular. It was observed that the different concentration of the Tb ions have no effect on the morphology of the samples.



**Figure 1:**  X-ray diffraction patterns of CaAlxOy with different concentration of Tb3+ ions.

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(a)

(b)

**Figure 2:** SEM image of CaAlxOy:Tb3+ phosphor (a) 2 mol% and (b) 1.5 mol% at high magnification

Fig. 3 shows the EDS spectrum of the CaAlxOy:Tb3+ phosphor. The presence of CaAlxOy in the sample is confirmed with the Ca, Al, and O peaks. The C peak is coming from the carbon tape on which the sample was mounted. The Tb small peak is visible in the spectra due to the high concentration of Tb3+ in the 2 and 1.5 mol% samples. For 0.5 and 0.25mol% of Tb3+ in the sample the amount of Tb was too small to be detect by EDS.

*3.2 Photoluminescence spectra*

Fig. 4 illustrates the emission spectra of CaAlxOy:xTb3+ (where x= 0.25, 0.4, 0.5, 1.0, 1.5 and 2.0 mol%). The emission spectra show the peaks mainly at 493, 545, 588 and 622 nm respectively when



**Figure 3:** EDS spectra of CAlxOy:Tb3+ with different concentration of Tb3+ ions.

excited with a 239 nm excitation wavelength. The emission peaks are from transition of the 5D4 state to the 7FJ (J = 6, 5, 4, 3) state. It was found that with an increase in the concentration of Tb in the host lattice there was a significant increase in the intensity of all the intensities. The excitation spectra of the CaAlxOy:Tb3+ were recorded at an emission of 545 nm. It consists of 4f—5d transitions [2]. The broad band was centered at 239 nm. The intensity increased with an increase in the concentration of Tb3+. The PL intensity of CaAlxOy: *x*Tb3+ where x is the different mol percentages of Tb3+ (0.25 ≤ *x* ≤ 2.0) as a function of the Tb3+ concentrations is shown in Fig. 4(c). The emission peaks intensity increased when the amount of Tb increased, and a maximum value was found for *x* = 2 mol%.

 

(b)

(a)



**Figure 4:** (a) Photoluminescence excitation (b) emission spectra of CalxOy:Tb3+ and (c) PL intensity as a function of Tb3+ concentration.

(c)

Fig. 5 shows the decay curves of the CaAlxOy:Tb3+ phosphor with a Tb concentration of 0.25 and 2 mol%. The results indicate that the intensity of the phosphorescence decreased quickly at first and then at a slower rate. The curve of the sample doped with the higher concentration displays a higher intensity and long afterglow time than the curve for the lower Tb concentration(CaAlxOy:0.25%Tb3+).

The initial luminescence brightness was improved from 48 a.u to 147 a.u and the long afterglow time was prolonged from 10 ms to 20 ms.



**Figure 5**: Decay curves of CaAlxOy:Tb3+ phosphor for different Tb concentration as indicated.

**4. Conclusion**

CaAl2O4:Tb3+ phosphor was successfully synthesized by the combustion method. The XRD results implied that the phosphor has a monoclinic structure. The increase of the Tb3+ concentration in the sample showed a significant enhancement in the emission intensity of the phosphor. The brightness and the afterglow properties were enhanced with a higher doping concentration of Tb3+.

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**Reference**

[1] Huajie S, Donghua C, Wangjun T, Yuhua P, Displasys **29** (2008) 41-44.

[2] Zhengwei L, Yingliang L, Materials Chemistry and physics **93** (2005) 129-132.

[3] SHideo H, Takeru K, Hiroshi K, Masaaki Y,Yoshinori Y, Naruhito S, *J. Phys.: Condens.* *Matter* **10** (1998) 9541-9547.

[4] Xhuhui X, Yuhua W, Xue Y, Yanqin L, Yu G*, J. Am. Ceram.Soc*, 1-4 (2010)

[5] Zhang Y, Li L, Zhang X, Wang D, Zhang S, *Journal of Rare Earths,Vol*. **26** No 5, Oct. 2008, p.656.

[6] S Shin-Hei C, Nam-Hoon Y, Young-Hoon Y and Sung-Churl C, *Journal of Ceramic Processing* *Research.* Vol. **7**, No.1, (2006) pp. 62-65.

[7] Huajie S, Donghua C, *Luminescence* 2007; **22**: 554-558.

[8] Barrows B S, melo P S , Kiminami R H G A, Costa A C F M, de Sá G F, Alves Jr S, *J*  *Mater Sci* (2006) **41**:4744-4748.