Preparation and Optical Properties of Cr\(^{3+}\) Doped CaAlBO\(_4\) Red Phosphor

Yan Wen, Zhisen Li, Dai Chen, and Shiqing Man*

School of Physics and Electronic Information, Yunnan Normal University, Kunming, Yunnan, 650500, China

*Corresponding author: sqman_ynnu@ynnu.edu.cn

Abstract. Calcium acuminate matrix (CaAlBO\(_4\)) was prepared at temperatures 1160°C by solid state reaction, a spectroscopy analysis of Cr\(^{3+}\) doped CaAlBO\(_4\) based on excitation spectrum and emission spectra was performed. Broad band excitation spectra are observed with 414 nm and 553 nm, respectively owing to the 4A\(_2\)→4T\(_1\) and 4A\(_2\)→4T\(_2\) transition of Cr\(^{3+}\) ion, and emission spectra with the strongest emission peak 694 nm owing to the 2E\(_2\)→4A\(_2\) transition of Cr\(^{3+}\) ion. Also, the influences of the concentration of Cr\(^{3+}\) ion on the luminescent properties in CaAlBO\(_4\) compounds were investigated, which the optimal concentration is 0.5mol%.

1. Introduction

In the field of luminescence, aluminate-based phosphors have the advantage of good chemical stability and thermal stability, high luminous efficiency and no pollution so on. in the field of luminescence has been the focus and attention of people.[1–3] Since their discovery, the uses of lanthanides in phosphors have found numerous applications in, for example, Scintillators, luminescence immunoassay and X-ray detector systems. One of the earliest applications was their use in phosphors for domestic lamps. The lanthanides possess unique properties which are responsible for their wide range of applications. [4, 5]

Related research findings, CaAlBO\(_4\): Cr\(^{3+}\) absorbs in both blue and yellow light ranges, and there is a single red-light emission at 690 nm, the monochromaticity is good, but the luminous intensity is weak. for the reason that, improving the luminous efficiency of Cr\(^{3+}\) activated CaAlBO\(_4\) phosphor has certain practical significance.[6, 7] Cr\(^{3+}\) doped materials are preferred because they possess wide absorptions, broadband emissions, high QE, and a good match with commercial blue or red LED chips.[8] In this work, we have prepared Cr\(^{3+}\) doped CaAlBO\(_4\) fluorescent materials by a large number of experiments, It indicates that CaAlBO\(_4\):Cr\(^{3+}\) phosphor has the potential value of developing LED optoelectronic devices. [9, 10]

This work has been undertaken to produce the Cr\(^{3+}\) ions doped CaAlBO\(_4\) phosphor with multiple concentrations. In order to gain pure phase samples, the sol-gel method is used in the synthesis procedure, which has advantages in control over purity and composition and easy introduction of doping elements. Besides the synthesis, the prepared samples are characterized by X-ray diffraction (XRD) and photoluminescence properties of samples with different doping concentrations were investigated. The results show that the Cr\(^{3+}\) doped CaAlBO\(_4\) phosphor has enough potential to be used as a deep-red luminescence material.
2. Experimental

Synthesis of CaAlBO₄:Cr³⁺ luminescent materials by high temperature solid-phase method, raw reagent is CaCO₃(AR), Al₂O₃(AR), H₃BO₃(AR), Cr (NO₃)₃(99.99%). Weigh the raw materials accurately according to the stoichiometric ratio and grind in an agate mortar for 30 minutes and mix well, after loading the corundum crucible, hold at 300℃ for two hours, make it fully react at low temperature, after cooling to room temperature, remove the powder and fully grind for 30 minutes, put it into the corundum crucible and keep it at 700℃ for 2 hours, sintered in air at 1160℃ for 3 hours. When the horse boiler is cooled to room temperature, a sample is obtained.

The samples were tested for crystal structure analysis using a max-RA X-ray diffractometer. XRD instrument’s radiation source is CR target, scan step size is 0.02℃, scanning range is 5 to 55℃. Test the luminescence performance of the sample at room temperature using a fluorescence spectrometer, its excitation light source is a pulsed xenon lamp, testing of samples is performed at room temperature. The photoluminescence (PL) and photo luminescence excitation (PLE) spectra were measured with Edinburgh Instruments FS5 (UK) which 150W Xenon lamp was used as an excitation source. The lifetime spectra were made by Edinburgh FS5 with pulsed Xenon lamp excitation (100 Hz). All the measurements above were carried out at room temperature.

3. Results and Discussion

The XRD patterns of the CaAlBO₄:0.5%Cr³⁺ is presented in Fig. 1. The patterns can well match the standard card of PDF selected from the international database for material structures. No impurity diffraction peaks were detected, which indicates that there was no obvious influence of the dopants on the crystalline structure of the host.

Figure 1. XRD patterns of CaAlBO₄:0.5%Cr³⁺ phosphors.

This agreement showed the formation of single-phase of CaAlBO₄ by the synthesis route in this work. In our previous studies, the calcination process was not applied in synthesis route, and it was found that
other phases were formed along with CaAlBO₄. To obtain pure CaAlBO₄ phase, the post-heat treatment was introduced into the process.

Generally, in octahedral symmetry, the trivalent chromium ions belong to d³ electronic configurations. The excitation spectra of CaAlBO₄:0.5%Cr³⁺ at room temperature is shown in Fig. 2. As seen, sample has two excitation bands of 530 nm to 580 nm and 390 nm to 450 nm. The excitation band of 500–600 nm is attributed to the ⁴A₂g(F)→⁴T₂g(F) transition of Cr³⁺, and the excitation of 380–450 nm is attributed to the ⁴A₂g(F)→⁴T₁g(F) transition of Cr³⁺

According to Tanabe–Sugano theory and the excitation spectra, in octahedral site, the local crystal field 10Dq could be approximately calculated as 17543.9 cm⁻¹ from the energy of the ⁴A₂g → ⁴T₂g transition. The approximate value of the Racah parameter B can be calculated by following equations:

$$\frac{B}{Dq} = \frac{\left(\frac{\Delta E}{Dq}\right)^2 - 10 \left(\frac{\Delta E}{Dq}\right)}{15 \left(\frac{\Delta E}{Dq} - 8\right)}$$

(1)

where ΔE is the peak energy difference between the ⁴T₂g and ⁴T₁g states. The approximate result is B = 641.7 cm⁻¹ and Dq/B ≈ 2.73 > 2.5 which indicate the Cr³⁺ ion dopent lies in a strong crystal field site.

**Figure 2.** Excitation intensity of CaAlBO₄:0.5%Cr³⁺ under 694 nm emission.
Fig. 3 shows the emission spectrum of the CaAlBO$_4$:0.5\%Cr$^{3+}$ sample under 414 nm excitation. It can be observed that the emission band has a sharp peak at 694 nm which could be attributed to the $^2$E$_2$→$^4$A$_2$ transition of Cr$^{3+}$ to generate the R line. The appearance of the R line also demonstrates that the doped ions are in a relatively strong crystal field.

The luminescent decay curves of the Cr$^{3+}$ doped system, recorded with 554 nm excitation and 694 nm emission, were shown in Fig. 4. The decay curve of 0.5 mol\% Cr$^{3+}$-doped CaAlBO$_4$ powder could be fitted into a single exponential component of ns by function as $I = A\exp(-t/\tau)$. It can be seen that the lifetime decreased with the increase of Cr$^{3+}$ concentration.

The single exponential component nature of the decay suggested that the Cr$^{3+}$ ion replace ‘Al’ from the lattice sites and not ‘Ca’, considering the ionic radius and charge compensation for Cr$^{3+}$. In this work, the dopant ions concentration was increased up to 5 mol\% and the resultant emission and decay time values were investigated. Fig. 4 shows the variation of the decay time value ($\lambda_{\text{ex}} = 554$ nm and $\lambda_{\text{em}} = 694$ nm) and the emission intensity (at 694 nm for $^2E_g \rightarrow ^4A_{2g}$ transition) as a function of dopant ion concentration. It is interesting that the lifetime and intensity values showed a different tendency with the increasing of mol\% of the dopant ion. The decay time showed a decreasing trend with the increasing of dopant concentration. However, the emission intensity indicated that concentration quenching was taking place in the system beyond 5 mol\% doping.
4. Conclusion
CaAlBO$_4$: Cr$^{3+}$ powder phosphor has been prepared as a single-phase material by sol-gel route. Phosphor prepared from the facile sol-gel route is simple, fast and easily available materials. The excitation spectrum consists of spin-allowed as well as spin-forbidden transitions. In this experiment, CaAlBO$_4$: Cr$^{3+}$ red phosphor was synthesized by high temperature solid phase method, and the optimal doping amount was about 0.5%. The excitation spectrum and emission spectrum of the sample show that CaAlBO$_4$: Cr$^{3+}$ phosphor can be excited by both blue light 414 nm and yellow light 556 nm, which belong to the transitions of 4A$_2$→4T$_1$ and 4A$_2$→4T$_2$ of Cr$^{3+}$ respectively: the emission spectrum appears at 694 nm The strongest peak belongs to the transition of Cr$^{3+}$ 2E$_2$→4A$_2$, and there is only red light emission at 694 nm.

It was observed that decay time showed a decreasing trend with the Cr$^{3+}$ concentration increasing, All the results suggested that the prepared sample of CaAlBO$_4$: Cr$^{3+}$ phosphor can be used as a red-emitting phosphor material with effectively color purity.

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References
[1] J. Zhou, Z. Liu, F. Li, Upconversion nanophosphors for small-animal imaging[J]. Chemical Society Reviews, 2012, 41(3): 1323-1349.
[2] Panlai Li,Zhijun Wang, Zhiping Yang,Qinglin Guo,Guangsheng Fu Materials Research bulletin 44 (2009)2068-2071.
[3] H. Mi, Y. Huang, Z. Lin, Cr$^{3+}$-doped CaMgSi$_2$O$_6$ crystal: a promising tunable laser and ultrashort laser crystal[J]. Cryst Eng Comm, 2014, 16(5): 763-765.
[4] Santos C N, Meneses D D, Echegut P, Newie D R, Hernandes A C and Ibanez A Appl. Phys. 94 (2009) 151901.

[5] K. Binnemans, Chem. Rev. 2009, 109, 4283-4374.

[6] R. Martinez-Martinez, E. Alvarez, A. Speghini, C. Falcony and U. Caldino, Thin Solid Films, 2010, 518, 5724-5730.

[7] Z. Pan, Y. Y. Lu, F. Liu, Sunlight-activated long-persistent luminescence in the near-infrared from Cr3+-doped zinc gallogermanates, Nat. Mater. 11 (2012) 58–63.

[8] M. G. Brik, J. Papan, D. J. Jovanović, et al. Luminescence of Cr3+ ions in ZnAl2O4 and MgAl2O4 spinels: correlation between experimental spectroscopic studies and crystal field calculations[J]. Journal of Luminescence, 2016, 177: 145-151.

[9] J. Xu, A. Gulzar, P. Yang, H. Bi, D. Yang, S. Gai, F. He, J. Lin, B. Xing, D. Jin, Recent advances in near-infrared emitting lanthanide-doped nanoconstructs: Mechanism, design and application for bioimaging. Coord. Chem. Rev. 381 (2019) 104-134. https://doi.org/10.1016/j.ccr.2018.11.014.

[10] Osmar M. de Sousa, Study of the structural, electronic, and optical properties of the host matrices of LiAl5O8 and LiGa5O8 via DFT. Comput. Theor. Chem. 1123 (2018) 96-101. https://doi.org/10.1016/j.comptc.2017.11.015