Preparation and Optical Properties of CaAlBO4:Eu3+ Phosphor

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Abstract. A series of single-phase CaAlBO4: Eu3+ powder samples were synthesized by high-temperature solid-phase method, the main factors are temperature, time, concentration of rare-earth ion, etc. The results show that the maximum emission peak of the sample is located in the wide band spectrum of 467 nm, and belongs to the 4f65d to 4f7 transition of Eu3+. The maximum absorption peak is located at a narrow band of 678 nm. by a study of the relationship between the doping amount of Eu3+ and the luminescence property of the sample, The optimum doping content of Eu x 3+(x = 0.0025)

1. Introduction
In recent years, as a new solid light source, white LED has advantages such as environmental protection, high efficiency and energy saving, high lumen efficiency, long life, good color rendering, small size, light weight and other advantages compared with traditional fluorescent and incandescent lamps. These advantages in particular, the environmentally friendly advantages of high efficiency, energy saving, and environmental protection will make LEDs more in line with market demands under the current lack of various resources in the world, and will also create better economic and environmental benefits. Inorganic metal borates have long been a focus of research due to their variety of structure types, transparency to a wide range of wavelengths, high laser damage tolerance, and high optical quality. The BO3 and BO4 ligands are considered to be dominant in inorganic metal borates due to their physical and, especially, optical properties. [1, 2] Thus, alkaline-earth aluminum borates doped with rare earth ions have been investigated in detail by scientists.

Borate luminescent materials are often used in laser materials, nonlinear optical devices, high-efficiency fluorescent lamps, medical ultraviolet lamps and plasma display panels due to their advantages of stable chemical properties, simple synthesis process and high luminous efficiency. [3] The crust is rich in aluminum and boron reserves. Combining aluminum and boron can obtain compounds with low synthesis temperature, good thermal stability and low cost, and the study of the Al2O3-B2O3 binary system helps to design and find efficient light-emitting properties Luminescent materials. Currently studies shown, the spinel metal oxides are classified into the group of crystals to be used as host materials for NIR phosphor due to their complicated structure. [4, 5]

This work has been undertaken to produce the Eu3+ ions doped CaAlBO4 phosphor with multiple concentrations. [6] The emissions of Eu3+ ions depend on the strength of the crystal field and may occur either from the 5D0 to 7Fj (j=0 to 4) excited states, which could be weakly or strongly coupled to the lattice vibrational modes. In this paper, by adjusting the concentration change, and using high-
temperature solid-phase method, the synthesis of rare earth ion doped aluminum borate phosphors with different structures, to study the effect of synthesis conditions on the structure of fluorescent materials and the luminescent properties of rare earth ions. Besides the synthesis, the prepared samples are characterized by X-ray diffraction (XRD) and photoluminescence properties of samples with different doping concentrations were investigated. [7, 8]

2. Experiment methods
Synthesis of CaAlBO₄:Eu³⁺ luminescent materials by high temperature solid-phase method, the reaction raw materials required for the experiment are of analytical grade. raw reagent is CaCO₃ (AR), Al₂O₃ (AR), H₃BO₃ (AR), Eu₂O₃ (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°C 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°C for 3 hours, sintered in air at 1060°C for 3 hours. When the horse boiler is cooled to room temperature, a sample is obtained. Since boric acid is relatively volatile during heating, the excess of boric acid in the experiment is 10% (mole fraction).

The crystal structure of the test sample was analyzed using a Rigaku D/max-2550Pc X-ray powder diffractometer produced by Bruker, Germany. The radiation source was a Cu target, and the X-ray (Kα, λ = 1.5418 nm) was generated from the copper target. The tube voltage was 40 kV, tube current 200mA, scanning speed 6%/min, scanning range 2θ = 10°~80°, step width 0.02°. A Japanese Hitachi F-4600 fluorescence spectrometer was used to test the fluorescence performance of the samples. The excitation light source was a 150 W xenon lamp, the scanning range was 200 to 750 nm, the filter was 400 nm, the excitation and emission slits were both 1.2, and all tests were performed at room temperature.

3. Results and Discussion
X-ray diffraction analysis mainly uses X-rays to irradiate the test sample material, which acts on the crystal structure of the material, so that a phase corresponding to the material appears. During the research of materials science, the experimental sample prepared must first be determined What kinds of crystalline substances are contained in the sample material or in which crystalline state does the sample material exist.

The XRD patterns of the CaAlBO₄:0.25%Eu³⁺ 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.
The luminescence of a substance is mainly because the substance absorbs the applied energy and transmits it to the luminescence center, so that the luminescence center is excited to a high energy state, and the extra energy is released in the form of light when the luminescence center returns to the ground state energy level. Determine the luminous center of the sample and the relative luminous intensity of the material under the influence of different factors through the emission spectrum, and then clarify the best preparation process and the best doping concentration required when preparing the sample.
Fig. 2 shows the excitation spectrum for CaAlBO$_4$:0.25%Eu$^{3+}$ powder phosphors at room temperature respectively. The excitation spectrum consists of several peaks with peak positions at approximately 397nm and 465 nm, The PLE sharp lines between 340 and 570 nm were due to the 4f-4f transition of Eu$^{3+}$ ions. Among them, the strongest peak at 397nm.

The emission spectra in Fig.3 showed intense line peaked at 622 nm which is characteristic zero-phonon line of Eu$^{3+}$ ions caused by the spin-forbidden 5D$_0$ to 7F$_1$ transition. There have also been observed some of the weaker and broader side emission bands along with the 622 nm peak. These lines are attributed by transitions in chromium pairs connected by strong exchange interactions.

![Image of emission intensity](image)

**Figure 3.** Emission intensity of CaAlBO$_4$:0.25%Eu$^{3+}$ excited at 397 nm.

When a substance is excited by a laser, its molecule emits fluorescence through a transition, and then after removing the excitation light, the fluorescence intensity emitted by the molecule gradually decreases to 1/e of the maximum intensity of fluorescence I at the time of excitation. It should be explained here that when the substance is excited, the molecule will undergo two transitions. The first transition is the transition of the absorbed energy of the object molecule from the ground state to an excited state. The second transition is the return of the molecule to the ground state after the fluorescence is emitted by the radiation transition. When testing the fluorescence lifetime of the experimental sample in this experiment, the laboratory uses JASCO FP -6600 fluorescence spectrophotometer (made in Japan) was tested.

The luminescent decay curves of the Eu$^{3+}$ doped system, recorded with 622 nm excitation and 704 nm emission, were shown in Fig 4. The decay curve of 0.25% Eu$^{3+}$-doped CaAlBO$_4$ powder could be fitted into a single exponential component of MS by function as $I = Aexp(-t/\tau)$. It can be seen that the lifetime decreased with the increase of Eu$^{3+}$ concentration.
4. Results
Through phase analysis, diffractions which were corresponding to all the planes of pure cubic CaAlBO₄ phase. It was noticed that the introduction of Eu³⁺ ions did not create any additional or undesirable phases. The unit cell parameter value calculated from XRD pattern of CaAlBO₄:Euₓ³⁺ (x=0.0025) phosphor sample which was in good agreement with the literature value of PDF #19-0204.

5. Conclusion
CaAlBO₄: Eu³⁺ 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. The PLE sharp lines between 340 and 570 nm were due to the 4f-4f transition of Eu³⁺ ions. The PL spectrum exhibited typical line emission assigned to the emission of 5Dₐ to 7Fₖ. the highly intense line at 465 nm is due to the magnetic dipole 5D₂ to 7F₁ transition and the stronger line at 622 nm is associated with the electric dipole transition. Hence, the dominant emission peak of CaAlBO₄: Eu³⁺ located at 622 nm indicated that Eu³⁺ ions occupied the site of noninversion symmetry. The emission peak at 465 nm originating from the 5D₂ to 7F₀ is a forbidden transition. In general, the 5D₂ to 7F₀ emission can be observed when Eu³⁺ occupies a lattice site.

In conclusion, The XRD of the obtained CaAlBO₄ phosphor sample is consistent with the standard card, indicating that the rare earth ions have been successfully incorporated into the CaAlBO₄ matrix but still contain a small amount of miscellaneous phase. With the gradual increase of the fluorescence lifetime of CaAlBO₄:0.25%Eu³⁺ (x = 0.0005-0.0025) ions, the fluorescence lifetime of CaAlBO₄ phosphors is gradually shortening.

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