



Photoluminescence Studies of CaAl_2O_4 : Eu^{2+} Blue Phosphors Co-Doped with Nd^{3+} Ion Synthesized by Solid- State Reaction Method

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Abstract: In this work, the polycrystalline CaAl_2O_4 : Eu^{2+} , Nd^{3+} based blue phosphor was prepared by solid-state reaction method. The rare earth metal ions doped calcium aluminate phosphors have been studied in depth. The high quantum efficiency make them useful for anomalous long phosphorescence, good stability, luminous paints, radiation dosimetry, X-ray imaging, color display, and light emitting diodes. Phase, crystallinity and luminescent properties of the synthesized phosphors were examined by using powder X-ray diffraction (XRD). In the phosphor material, the photoluminescence (PL) spectrum has a broad emission peak of Eu^{2+} ion in blue region at ($\lambda_{\text{max}} = 440 \text{ nm}$) due to the energy transitions between the ground state $4f^7$ and the excited state $4f^65d^1$ of the Eu^{2+} ion. This has importance in making the visible phosphor devices from this material. In this study the single dopant phosphors were synthesized; therefore, it is important to improve the long afterglow of the phosphors by codoping. The phosphors of CaAl_2O_4 : Eu^{2+} , Nd^{3+} had long persistence luminescence. In these phosphors, Eu^{2+} ions play the role of activators. Whereas Nd^{3+} ions generate deep traps that lead to the long persistent phosphorescence and act as the co-activators in the phosphors simultaneously. The concentration of Nd^{3+} ion co-doped has strong influence on the luminescence of phosphor.

Keyword: Blue Phosphors, Calcium aluminate, solid-state reaction, rare earth ions.

Introduction

Calcium aluminates are the most widely used members of the alkaline earth aluminates MAl_2O_4 ($\text{M} = \text{Ca}, \text{Sr}$ and Ba). Aluminates of Ca, Sr and Ba doped with Eu^{2+} activator ion possess safer, chemically stable and intense photoluminescence (PL) in visible region [1,2]. Compared to the conventional sulphide based phosphors. These properties make them useful in many applications, such luminous paints in highway, airport, buildings and ceramics products, in textiles, dial

plate of glow watch, warning signs and the escape routes [3].

CaAl_2O_4 : Eu is one of the few materials exhibiting a long-lasting afterglow after excitation has ended, a phenomenon known as persistent luminescence. The afterglow duration can be improved by co-doping with other rare earths. The best co-dopant has been reported to be neodymium, which increases the afterglow intensity more than an order of magnitude compared to non-co-doped CaAl_2O_4 : Eu [4].



Rare earth and non-rare earth activated inorganic phosphors have great potential applications such as luminous paints, radiation dosimetry, X-ray imaging, color display, light emitting diodes, solar energy conservation, photonics, optoelectronics and biomedical engineering. Phosphor materials in visible region with long persistence are widely used in different displays in signing and devices [5, 6].

These interesting areas of application of phosphors have spurred researchers into finding new methods of synthesis and new ways of manipulating the phosphors through variables to arrive at unique characteristics for deeper applications. It is very important and convenient method of investigating the nature of traps and trapping level in crystals [7]. The solid-state reaction process has been used intensively for phosphor synthesis [8]. Alkaline earth aluminates materials, doped rare earth and transition metal ions can be synthesized by many methods such as sol-gel technique [9], micro-wave heating technique [10], hydroxide precipitation [11], an electric arc method [12] and combustion synthesis [13,14] have been applied to prepare rare earth ions activation alkaline earth aluminate and/or its phosphors. All these methods were conducted in liquid phases so that each component can be accurately controlled and uniformly mixed. The Eu^{2+} doped Calcium aluminates as CaAl_2O_4 : Eu^{2+} has been studied only infrequently, even if they also show persistent luminescence.

In the present work, the effect of Nd co-doping on crystal structure and PL characteristics of CaAl_2O_4 : Eu^{2+} based blue phosphor prepared by solid-state reaction method. X-ray powder

diffraction was performed to investigate the phase and crystallinity of the material. Photoluminescence (PL) and decay time measurements are under progress and will be reported soon.

Materials and Methods

Calcium aluminate phosphors were prepared by traditional ceramic (solid- state) synthesis method. The reaction involved is represented as:



Stoichiometric amounts of CaCO_3 and Al_2O_3 were weighed taking into account different concentrations of the dopants. High-purity (99.99%) raw materials; CaCO_3 , Al_2O_3 , Eu_2O_3 in appropriate quantities were used for preparation of the charge. 5-10 mol% of B_2O_3 was added as flux. To this mixture, the required weight of rare earth oxide was added and the resultant mixture was thoroughly mixed with ethanol in an agate mortar for about 2h. The mixture was dried at 80-100 °C in an air oven. The dry powder thus obtained was calcined at 900 °C for 6 h in air atmosphere. Finally, the powders were annealed at 1300 °C for 4h in a reducing atmosphere (5% H_2 and 95% N_2). The reducing atmosphere was used to ensure complete reduction of Eu^{3+} to Eu^{2+} . The prepared compositions were characterized for their phase and crystallinity by powder XRD using $\text{Cu K}\alpha$ radiation. The work related to other characterizations and PL measurements are under progress.



Phosphorescent mechanism of $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}$, Nd^{3+} :

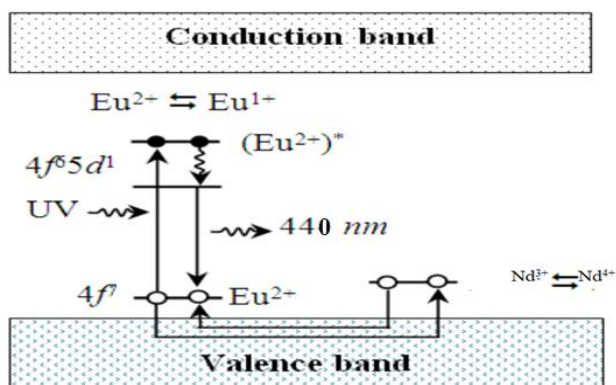


Fig. 2 Energy level diagram for $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}$, Nd^{3+} Phosphor

The de-trapping mechanism in $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$, Nd^{3+} is described in Fig 2. In this mechanism, Nd^{3+} acts as a hole trap and the holes move to the excited state of Eu^{2+} . After capturing, recombination occurs, followed by phosphorescence. Therefore, local distortions around co-dopant ions seem to affect the trap depth, and hence, optimization of the activator and co-activator composition is important to produce high phosphorescence intensity.

The role of Nd^{3+} doping in $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ can be explained by hole traps in the structure, Since Nd^{3+} has relatively low 4f–5d transition energies and high charge-transfer energies, they can act as hole traps. These holes migrate to the excited Eu^{2+} centres where they are captured, followed by recombination. Phosphorescence is caused by this trapping of photo-generated holes and/or electrons, which, following a delayed radiative return after recombination of the charge carriers causes luminescence. Therefore, phosphorescence is considered as thermo-luminescence with de-trapping at room temperature, and local distortions

around the co-dopant ions seem to affect the trap depth. The trapping level of the $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$, Nd^{3+} phosphor is known to be located a little shallower than that of the other phosphor, resulting in relatively shorter phosphorescence, which agrees with our observations. However, the trapping level of the $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$, Nd^{3+} phosphor is probably not so shallow to show a fast decay that does not last for long, but deep enough to show long phosphorescence at room temperature.

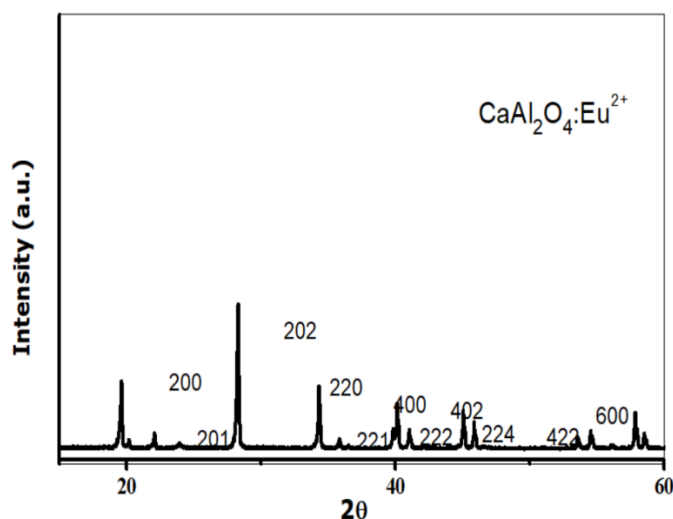


Fig. 3 Powder XRD patterns for $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$

Results and Discussion

The Calcium aluminate CaAl_2O_4 co-doped with Eu^{2+} was prepared and characterized for phase and crystallinity using powder X-ray diffraction (XRD). The XRD pattern for the parent material CaAl_2O_4 (without Eu doping) is plotted for comparison. Fig. 3 The XRD pattern of the prepared $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ is shown (Eu_2O_3 was kept constant at 1 mol%). The diffraction peaks correspond to the all planes which can be indexed to the pure monoclinic phase for CaAl_2O_4 . Calculated lattice parameters are as follows: $a = 8.703 \text{ \AA}$, $b = 8.097 \text{ \AA}$ and $c = 15.216 \text{ \AA}$. The XRD



pattern matched well with that reported for CaAl_2O_4 . The small amount of doped rare earth ions has almost no effect on CaAl_2O_4 phase composition. Appropriate phase was observed with good crystalline quality. The work related to other characterizations and PL measurements are under progress and will be reported elsewhere.

Conclusion

The polycrystalline CaAl_2O_4 : Eu^{2+} material were successfully prepared with a solid-state reaction. This material is very useful in the blue region of the spectrum. The phase and crystallinity of the prepared polycrystalline compositions were investigated by powder XRD. These materials have great potential for outdoor night-time display. In future, the preparation conditions and the dopant/co-dopant content need further studies to optimize the persistent luminescence performance of CaAl_2O_4 : Eu^{2+} which shows long after-glow phosphorescence with blue region phosphorescence.

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