

A Comprehensive Review on Eu Doped Zinc Aluminate Phosphor for Solid-State Lighting

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ABSTRACT

Zinc based aluminate materials are the member of spinel oxide. Zinc Aluminate is a wide bandgap semiconductor. In this report, rare earth Eu doped zinc aluminate phosphor is discussed in detail. Eu³⁺ doped ZnAl₂O₄ phosphor with efficient orange-red light emission is useful for solid-state lighting and optoelectronic devices. Therefore, it is important to discuss the properties and utility of the material for phosphor applications. Different synthesis routes have been used for the preparation of Eu doped ZnAl₂O₄. The effect of doping concentration, calcination time, duration, and various other parameters affect the crystal structure and luminescence properties of Eu doped ZnAl₂O₄ spinel. The effect of doping concentration, calcination temperature, and synthetic route on luminescence properties are discussed in brief. The review explains the luminescence mechanism, their emission spectrum and potential application for Eu activated ZnAl₂O₄ phosphor.

Keywords - Zinc Aluminate, Luminescence, Rare Earth Ions, Eu Doped, Synthesis Method

I. INTRODUCTION

Luminescence is the most favorable phenomenon of light. It is characterized as the radiation emitted by a molecule or an atom after it had retained energy to go to the excited state. Luminescence comprises of two main types: fluorescence and phosphorescence. Phosphor emits a photon when excited by an external energy source. The optical center in the material is irradiated by an external energy source and makes a transition to an excited energy state from the ground state. The excited state ultimately returns to the ground state via the radiative or non-radiative process. Radiative transition is called luminescence. Aluminates are compounds consists of an oxyanion of aluminum such as zinc aluminate. Zinc based

aluminate materials are the member of spinel oxide having general formula AB₂O₄ where A and B represent divalent and trivalent metal ion respectively[1]. It is a wide bandgap semiconductor with a gap of 3.8 eV [2]. It is widely used as ceramic and catalytic material due to its extremely diversified properties such as high mechanical and thermal resistance, hydrophobic nature, high quantum efficiency, high chemical, and thermal stability. Zinc aluminate is a promising host material with high luminescence efficiency and stability. Therefore, in solid-state lighting, it is being used as a host material with rare earth and transition metal dopant ions as phosphor. Rare-earth doped Zinc aluminate phosphor has been studied mostly due to stability and high

quantum yields in the visible region [3]. Rare earth (RE) doped phosphors are widely used in lighting applications, such as in fluorescent lamps, cathode-ray tubes, light-emitting diodes (LEDs) for the lighting industry, field-emission displays [4]. Among all the RE ions, the europium (Eu) activator is capable of red and green emission in trivalent Eu^{3+} and divalent Eu^{2+} states respectively. In Eu^{3+} ions, the line emission occurs from 5D0 excited state to 7FJ ground state transition [5].

II. METHODS AND MATERIAL

Structural Information-

Among spinel oxides, ZnAl_2O_4 offers high interest for solid-state lighting. It is metal aluminates having spinel face-centered cubic crystal structure with space group $\text{Fd}\bar{3}\text{m}$ where Zn^{2+} ions occupy tetrahedral sites and Al^{3+} ions occupy octahedral sites [6]. It is represented as AB_2O_4 since occupied divalent cations on tetrahedral site, occupied trivalent B^{3+} cations on octahedral voids, and oxide ions make the ratio of $\text{A}^{2+}:\text{B}^{3+}:\text{O}^{2-}$ is 1:2:4. In the ZnAl_2O_4 spinel structure, octahedral sites possess high coordination number six. Depending on preparation methods, ZnAl_2O_4 ions can crystallize in normal or inverse spinel structure [1]. In the inverse spinel structure, there is mixed occupation of divalent and trivalent cations on octahedral sites while tetrahedral sites are occupied only by trivalent B^{3+} cations. Furthermore, it is polycrystalline and exhibits high reflectivity in the UV region. The theoretical results on the electronic band structure of ZnAl_2O_4 reveal that 3d electron of the spinel oxides facilitates the electronic properties.

III. RESULTS AND DISCUSSION

Synthesis and Characterization of Eu doped ZnAl_2O_4 Phosphor

The binary compound ZnAl_2O_4 has been prepared by many synthetic routes such as solid-state reaction

method [7], combustion method [8, 9], Sol-gel method, chemical [10] Co-precipitation method [5], etc. However, each method has some advantages and limitations. Among the above-mentioned chemical methods, combustion reaction synthesis is the most reliable process to obtain small grain size oxide phosphors. It is relatively fast, less energy consumption, and simple route, with no obligation of midway calcination stages [7,8]. Moreover, fine particle size and high purity are the two major advantages of this method. Barros et al. used combustion reaction synthesis for the preparation of Eu^{3+} doped zinc aluminate phosphor [9]. Stoichiometric compositions of metal nitrates and rare oxide as urea were taken. Single phase ZnAl_2O_4 spinel structure was found. However secondary ZnO phase was observed in Eu doped ZnAl_2O_4 nanoparticles. It was attributed to the formation of vacancies resulting from the incorporation of rare-earth ions into the host lattice [9]. Due to mismatching of valence states of substitute trivalent Al^{3+} ions and divalent Zn^{2+} ions and large ionic radius of Eu^{3+} (0.95 \AA) ions and Al^{3+} (0.53 \AA), trivalent Al^{3+} ions occupied octahedral sites in ZnAl_2O_4 spinel structure [10]. Moreover, the crystallinity and particle size of the ZnAl_2O_4 were also decreased with Eu^{3+} doping due to the difference between the ionic radius. Another widely used and most preferable method is Sol-gel chemical synthesis. It is a series of chemical processes that include hydrolysis, gelation, drying, and thermal treatment [10]. Lei et al. have reported a series of Eu^{3+} doped ZnAl_2O_4 phosphor prepared via the sol-gel method [11]. They studied the effect of calcination temperature on crystallization, grain size and luminescence properties. XRD patterns have revealed pure spinel phase of high crystallinity can be achieved with doping percentage of Eu^{3+} up to 5% and secondary calcination temperature in the range of 600-900°C. At 500°C calcination temperature, some characteristic peaks of zinc aluminate were observed

but the intensity was weak. When the temperature was raised from 600-900° C, no shift in the diffraction was found, it shows little effect of calcination temperature on the crystal structure. However, with increasing temperature, a secondary phase of ZnO and EuAlO₃ was found. Moreover, the grain size of the Eu doped ZnAl₂O₄ nanoparticles increased with raising the temperature, which indicates that high temperature affects the process of crystal growth and crystallinity. The best results were observed for 5% Eu doping and 800°C secondary calcination temperature. Over the past few years, different synthesis processes have been applied for Eu doped zinc aluminate spinel [7-10]. Most studies investigated the effect of concentration of dopant ions and annealing temperature on structure, morphology, and luminescence behavior. Streck et al. prepared Eu doped zinc aluminate spinels by hydrothermal synthesis route [4]. The calcination temperature raised up to 1273K for 1 wt.% of Eu. In agreement with the previously discussed results, they observed the complex nature of Eu³⁺ doping on ZnAl₂O₄[4]. They reported that Eu³⁺ creates additional sites in nanocrystals due to the high surface effect. Wiglusz et al. studied the effect of calcination temperature on Eu doped zinc aluminate nanoparticles in temperature range of 700-1400° C [10]. The reported average particle size is in the range of 10-30 nm depends on the annealing temperature. smallest crystallite size in the temperature range of 700-1200°C was found for 5% Eu doping. Similarly, Osorio et.al. have prepared Eu doped ZnAl_{2-x}Eu_xO₄ (x=0,0.01,0.03,0.06,0.09,0.12) via co-precipitation method [12]. It was seen that at low temperatures below 300°C, samples showed amorphous nature, while with increasing the temperature the crystallinity improved, and after heating treatment at 900°C for two hours spinel, ZnAl₂O₄ phase was found[12]. The Rietveld refinements analysis confirmed the presence of Eu³⁺ ions in the octahedral sites only. Doping concentration has a high impact on

the crystallite size. No difference in the crystallinity was noticed with different Eu doping concentration. In 2006, Cheng et al. reported Eu³⁺ doped ZnAl₂O₄ spinel nanorods by co-precipitation method. They obtained high surface area, and narrow size distribution of porous nanorods through a transition of layered composite precursors at high temperature(900°C)[13]. In the post-annealing treatment at 900°C, the sample was shown FCC cubic structure with single-phase formation. ZnAl₂O₄ nanostructure and bulk have been prepared via a solid-state reaction of zinc and aluminum oxides above 800 °C [7].

Luminescence Study of Eu doped ZnAl₂O₄ Phosphor

The photoluminescence emission spectra of Eu³⁺ doped zinc aluminate nanoparticles consist of a band in the orange-red visible region. Lei et al. observed five emission peaks at 580,593,618,653,700 nm for doped ZnAl₂O₄ with 5% Eu³⁺. These emissions correspond to allowed transitions from the lower excited state 5D₀ to multiplets 7F₀₋₄ of 4F ground states of Eu³⁺. PL was excited by 395 nm [11]. The electric dipole transition 5D₀→7F₂ is highly sensitive to site symmetry. Therefore, the luminescence properties of this transition influenced by the local environment and surrounding ligands. The highly intense emission peak at 618nm belongs to the 5D₀-7F₂ transition. However, orange-red emission corresponds to 5D₀-7F₁ magnetic dipole transition did not show any change in intensity. As suggested, it was due to inversion symmetry [10]. Also, they observed the concentration effect on luminescence characteristic of phosphor. Results indicated that with the increase of doping concentration up to 5 at. %, the PL intensity increased. The maximum intensity of luminescence peaks was observed for 5at% of Eu³⁺ doping. Thereafter, with increment in concentration, luminescence peaks were quenched. In the case of rare-earth ions doped phosphor, concentration quenching can occur due to different mechanisms. To study, Blass proposed a method by calculating crystal

critical distance R_c [14]. Lei et al. was suggested that the cause of concentration quenching was radiation reabsorption since calculated $R_c > 0.5$ nm[11]. Because of the larger number of Eu states multipolar interaction occur consequently, more energy transfer takes place. Hence beyond 5% Eu^{3+} doping, the distance between activator ions decreased and lower intensity was obtained. The CIE color coordinates of 5% doped sample confirmed the red color emission of phosphor. Thus, $\text{Zn}_{0.95}\text{Eu}_{0.05}\text{Al}_2\text{O}_4$ can be used as a near UV-LED based red phosphor for solid-state lighting and display. Later, PL investigations [10,11] found red emission for Eu^{3+} doped ZnAl_2O_4 phosphor. However, they found a highly intense band of transition $5D_0 \rightarrow 7F_0$. Moreover, they observed a noticeably increment in the intensity with higher annealing temperature. Afterglow was also noticed for samples prepared by 700 and 800°C. It was attributed to the transfer of Eu^{3+} ions into asymmetrical sites due to high temperature. Osorio et.al. showed red emission band centered at 616nm corresponds to $5D_0 \rightarrow 7F_2$ transition excited at 260 nm[12]. In PL spectra, two broader bands were located at 616nm and 586 nm. The red band at 616 nm was relatively intense originated from electric dipole transition. However, the maximum intensity was observed at 3mol% sample and quenching was observed for a higher concentration of Eu[12]. Similarly, Verma et.al. found an enhancement in the intensity of Eu^{3+} ions was ascribed to cross-relaxation phenomena which are favored by overlapping between donor and acceptor transitions[15]. He et al. [7] observed an asymmetric broad green emission at 532 nm attributed to the $5d-4f$ transition of Eu^{2+} ions. At 1mol% Eu^{2+} , the reported maximum intensity was at only 1% while calculated quantum efficiency was 54.85%. Apart from this, many other peaks associated with impurities were observed at temperature 600°C. Further, an increase in temperature at 1000°C, improvement of photoluminescence was found. Thus, the luminescence spectrum of Eu doped ZnAl_2O_4

influenced by redistribution of electrons into inner 4f shell of dopant ions. Also the local field symmetry and valence state of Eu change the emitting states and resultant emission.

IV. CONCLUSION

The structure of zinc aluminate and luminescence mechanism has been discussed. The analysis shows that zinc aluminate doped with Eu^{3+} ions can be used as a potential orange-red emitting phosphor while Eu^{2+} doped ZnAl_2O_4 phosphor can be used as green emitting phosphor. The strong absorption in the near UV region and intense red emission makes it suitable for near UV-LED-based red-emitting component. Different synthesis methods of phosphor preparation have been briefed. The presented results show Structural, optical, and luminescence properties can be changed with calcination temperature and doping concentration.

V. REFERENCES

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