

Highly Luminescent Red Emission Harvesting from ZnAl₂O₄: Eu³⁺ Phosphors for Solid State Lighting Applications

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Abstract—Rare earth doped aluminates have been emerged as a new class of luminescent materials, showing brightness, high stability and easy processing technique that are suitable for phosphor converted light emitting diode and field emission display applications. Rare earth dopants exhibit very narrow line emission bands due to their characteristic intra 4f transitions which are independent of the host matrix. In the current report, the Eu³⁺ doped ZnAl₂O₄ phosphor have been synthesized by low temperature sol-gel route. The synthesized phosphors display intense red luminescence with high color purity under UV excitation which has been detected via naked eye. The proposed phosphor may be established as an ultimate choice for next generation solid state lighting and field emission display devices.

1. INTRODUCTION

Among the family of spinel structured metal aluminate, ZnAl₂O₄ (ZNA) ceramic is often used in the field of catalytic and electronic applications [1]. ZNA is a wide band gap semiconductor with an optical band gap of 3.8 eV, which makes it useful for optoelectronic devices. Rare earth doped ZNA compounds have been widely studied for various potential applications such as field emission displays (FEDs) vacuum fluorescent displays (VFDs) and Light emitting diode (LEDs) devices due to their higher thermal stability than commonly used sulfide phosphor [2]. Various methods were used to prepare Eu³⁺ doped ZnAl₂O₄ phosphors by different route. Chen et al. [3] synthesized the spherical porous Eu³⁺ doped ZnAl₂O₄ phosphor through PEG-assisted hydrothermal route followed by post annealing. At the same time ZnAl₂O₄:Eu³⁺ hollow nanophosphors using carbon nanosphere as hard template was also reported by Chen et al. [4]. Kumar et al.[5] prepared the Eu³⁺ doped Phosphor in air atmosphere at 900°C. Yang et al.[6] developed ZnAl₂O₄/Eu core-shell structure by hydrolyzing a mixture of aluminum chloride hexahydrate and zinc chloride in deionized water and studied their photoluminescence properties. ZnAl₂O₄:Eu³⁺ nanorods with spinel structure were synthesized by homogeneous co-precipitation method [7].

In this paper, we have reported the preparation of Eu³⁺ doped ZnAl₂O₄ phosphor through citrate nitrate sol-gel route. The steady state and the time resolved spectroscopic characterizations were carried out to investigate the photo luminescence property in detail.

2. EXPERIMENTAL PROCESS

2.1 Synthesis of ZnAl₂O₄:Eu³⁺ phosphor:

Eu³⁺ doped ZNA phosphor powders were synthesized by citrate-nitrate sol-gel route. Analytical reagent grade Zn(NO₃)₂·6H₂O (Merck, 99.9%), Al(NO₃)₃·9H₂O (Merck,99.9%), Eu(NO₃)₃ (prepared by dissolving Eu₂O₃, Sigma Aldrich 99.99% in dilute HNO₃ solution), citric acid (Merck, 99.9%) and ethylene-di-amine (Merck, 99.9%) were used as raw materials. For Eu_x:Zn_(1-x)Al₂O₄ samples, the concentration of Eu were varied from 0 to 2% (x=0, 0.01, 0.02). In a typical reaction stoichiometric amounts of Zinc nitrate, aluminium nitrate, europium nitrate were dissolved in 40 ml deionized water (DI) and stirred for 30 minutes. Then citric acid aqueous solution was added in the precursor solution and stirred for another 30 minutes, resulting in a homogeneous transparent solution. Ethylenediamine was added into solution and the solution pH adjusted to 5. Afterwards the solution mixture was heated at 80° C to form highly viscous colloidal gel and the dried gel was then heated at 480°C to remove the organic compounds. Finally, the obtained powders were ground in a mortar and heat treated at 980°C for 5 h in a box furnace to obtain ultrafine pure and Eu³⁺ doped Zinc aluminate powders.

2.2 Characterizations

The as-synthesized powders were characterized through X-ray diffraction (XRD) for purity and phase identification, using a Bruker D8 ADVANCE ECOX-ray powder diffractometer with monochromatized CuK α radiation, (λ =1.5404 Å). The FTIR spectra were taken in the mid IR region, (i.e. 400–4000

cm⁻¹) by using a Shimadzu IR Affinity-1 spectrometer. The steady state photoluminescence spectra were taken on Shimadzu RF 5301 spectrofluorometer and time-resolved photoluminescence was measured using an Edinburgh luminescence spectrometer (Model No. FLSP-980) equipped with microsecond xenon flash lamp as the source of excitation.

3. RESULT AND DISCUSSION

The X-ray diffraction pattern of pure ZNA and Eu³⁺ doped ZNA are shown in the Fig. 1. The peaks at 31.2, 36.75, 44.77, 49.0, 55.55, 59.2, and 65.2 2θ values, which corresponds to reflection from (220), (311), (400), (331), (422), (511) and (440) plane of ZNA respectively [5]. Presence of no impurity peaks confirms the formation of single phase spinel structured ZNA having space group Fd-3m.

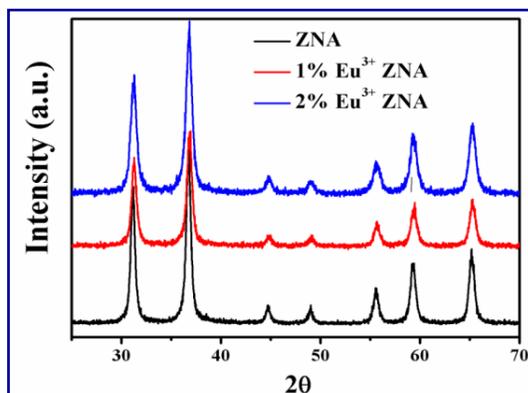


Fig. 1: XRD pattern of pure ZNA and Eu³⁺ doped ZNA phosphors

Fig. 2 represents the FTIR spectra of pure and Eu³⁺ doped ZNA phosphor. The peak observed at 495 cm⁻¹ is related to the bending mode of AlO₆. The peaks at 556 and 660 cm⁻¹ are found due to the stretching modes of AlO₆. The broad peak at 3500 cm⁻¹ is found due to the stretching vibration of H₂O [8].

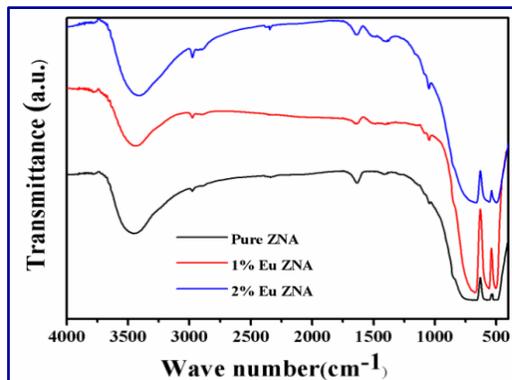


Fig. 2: FTIR spectra of pure, 1% Eu³⁺ and 2% Eu³⁺ doped ZNA phosphor

The photoluminescence (PL) measurement of the 1% Eu³⁺ and 2% Eu³⁺ doped ZNA phosphors were characterized by PL excitation and emission spectra. In this experiment same amount of samples were taken each time during measurement. Fig. 3 shows the PL excitation spectra of 1% Eu³⁺ doped ZNA and 2% Eu³⁺ doped ZNA phosphors which were taken by monitoring the emission of Eu³⁺ at 616 nm. The charge transfer band at 254 nm arises due to the electron transfer from fully filled 2p-orbitals of O²⁻ to partially filled 4f levels of Eu³⁺. The excitation peaks in the longer wave length between 350 to 480 nm are found due to intra-configuration f-f transitions of Eu³⁺ ions. In the photoluminescence spectrum, the four main peaks at 594, 616, 652 and 700 nm are attributed due to ⁵D₀ → ⁷F_j (1-4) transitions of Eu³⁺ ions, respectively [9].

The CIE chromaticity coordinate (shown in Fig. 5) calculated from the PL spectrum is (x=0.65222, y=0.34747) which means that Eu³⁺ doped phosphor could be used as a red light emitting material in LEDs and display devices.

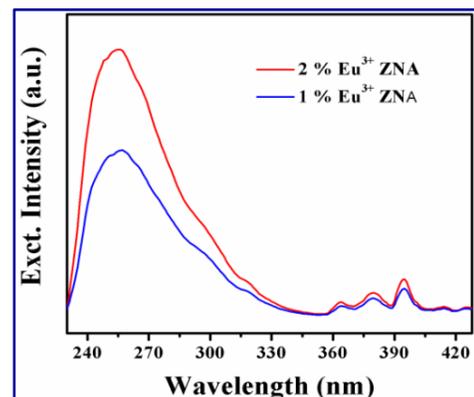


Fig. 3: Excitation spectra of 1% Eu³⁺ doped and 2% Eu³⁺ doped ZNA phosphors monitored at 616 nm emission

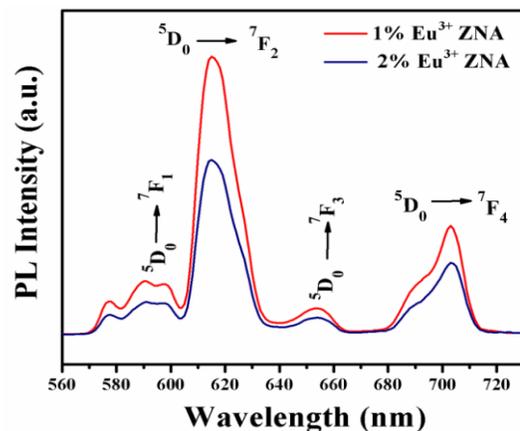


Fig. 4: PL emission spectra of 1% Eu³⁺ doped and 2% Eu³⁺ doped ZnAl₂O₄ phosphors recorded at 254 nm excitation

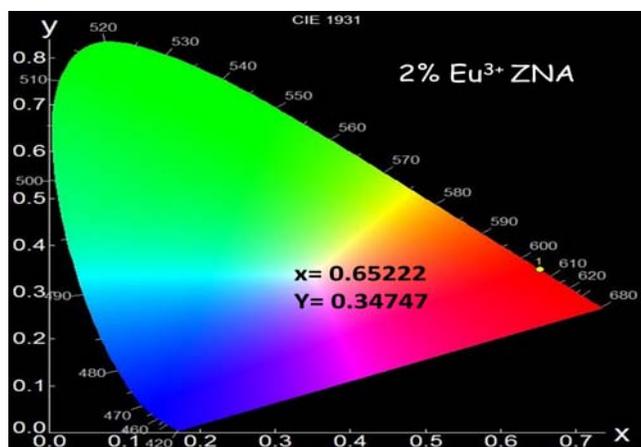


Fig. 5: Color co-ordinate of the 2% Eu^{3+} doped ZNA phosphor

The time resolved spectroscopic technique was performed to determine the radiative lifetime of the 616 nm emission of the synthesized phosphors. The decay curve was well fitted to a double-exponential decay equation as $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$. Where parameters A_1 and A_2 are the fitting constants and τ_1 and τ_2 are the decay components. The average life time (τ_{av}) is calculated by the following equation.

$$\tau_{av} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

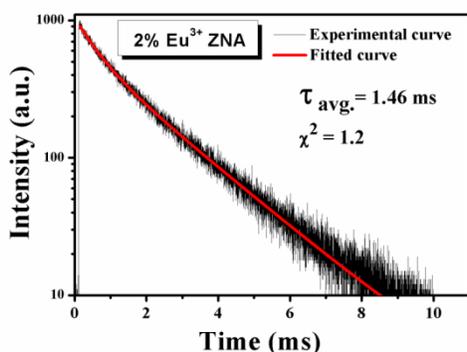


Fig. 5: Photoluminescence decay curve of 2% Eu^{3+} doped ZNA phosphor

The calculated average lifetime of 2% Eu^{3+} doped ZNA is found to be 1.46 ms that confirms the suitability of the phosphor for using in many solid state lighting applications.

4. CONCLUSION

We have successfully synthesized the pure and Eu^{3+} doped ZnAl_2O_4 phosphors by simple sol-gel technique. The as synthesized samples were well characterized by XRD and FTIR spectroscopy. The synthesized phosphors showed the intense red luminescence property with high colour purity which could be used in solid state lighting applications.

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