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Luminescence characteristics of blue emitting $ZnAl_2O_4$: Ce nanophosphors

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ABSTRACT

Photoluminescence (PL) and Thermally stimulated luminescence (TSL) properties of both virgin and Ce doped $ZnAl_2O_4$ phosphors were investigated. The phosphors were synthesized via sol–gel route using the respective metal nitrates and citric acid. The nano particle nature of the phosphor was confirmed by X ray diffraction and dynamic light scattering techniques. Time resolved photoluminescence and photo-acoustic spectroscopic techniques were used to characterize the emission and excitation properties of the system. TSL properties of the nanophosphor showed a single glow peak at 468 K. Various trap parameters and the kinetics for the glow peak were evaluated assuming the Arrhenius behavior for the system. Electron spin resonance (ESR) technique was used to identify the chemical nature of the traps/defects responsible for the glow peak. The emission spectrum of the nanophosphor was plotted on a standard CIE diagram which suggested a strong bluish violet emission from the phosphor system. Further, the intensity of the phosphor was compared with that of commercial blue phosphor to know the commercial utility of the prepared phosphors.

1. Introduction

Zinc aluminate ($ZnAl_2O_4$) is a member of the spinel family with the general formula $A^{2+}B_2^{3+}O_4$. This material has wide range of applications in optical and ceramic industries [1,2]. With an optical band gap of 3.8–3.9 eV, this compound is reported to be transparent and electroconductive as result of which it can be used for ultraviolet (UV) photoelectronic devices. Further, the material is also employed in various catalytic reactions such as cracking, dehydration, hydrogenation and dehydrogenation in chemical and petrochemical industries [3]. Many reports are available in the literature on the luminescent properties of rare earth ions incorporated in this matrix. Due to the simple electronic structure and allowed nature of transitions, Ce^{3+} ($4f^1$) becomes an interesting rare earth dopant ion of choice in this matrix. Ce^{3+} ion undergoes a parity and spin allowed transition, resulting in a broad PL emission band whose position depends on the host matrix as well as synthetic conditions of the sample. It exhibits a 5d–4f emission band with a large absorption band position in the UV region with a short luminescence decay time.

The luminescent properties are greatly dependent on the grain size of sample, leading to attractive properties when the grain size decreases. A number of preparation methods of samples are reported in literature such as (i) sol–gel method (ii) solid state reaction (iii) hydrothermal reaction and (iv) combustion process etc. to achieve nanocrystalline materials. It is important to develop a simple route for the synthesis of $ZnAl_2O_4$. The sol–gel route is an efficient route for this purpose as it offers high purity, homogeneity, single phase and small and uniform particles size at relatively lower processing temperature in comparison with other conventional methods.

It is well known that nano particles do not possess conduction band consisting of a plethora of energy levels but have specific and explicit energy level distribution. Due to this quantization, the band gap in semiconductor nano-clusters increase by an amount inversely related to the crystallite size. Nano crystalline powders of $ZnAl_2O_4$ prepared by the sol–gel method have been investigated extensively in recent years [1,4,5]. Several research groups have devoted significant efforts towards the synthesis, characterization and investigations of luminescent properties of rare earth doped $ZnAl_2O_4$. The results obtained have proved that the $ZnAl_2O_4$ is a promising host matrix with transparent, electroconductive properties, high thermal stability, low acidity, hydrophobic behavior, stability and high efficiency [4–9].

In this context, PL studies of Ce^{3+}-doped Cs_2NaYF_6 sample have been reported at room temperature and ~10 K using synchrotron radiation [6]. The $5d^1$ (T_{2g}) state of Ce^{3+} have been located from the excitation spectrum, whereas the E_g state is placed above the band gap of Cs_2NaYF_6. The decay curve measurements of the Ce^{3+}

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emission using selective excitation indicated the occupation of more than one type of site by Ce^{3+} in the host lattice. In another report, the luminescence of $Y_3Al_5O_{12}$:Ce,Tb sample was analyzed by PL and time-resolved cathodoluminescence [7]. The energy transfer from Tb^{3+} to Ce^{3+} in the $Y_3A1_5O_{12}$ host crystal was demonstrated by both techniques. Kadam et al. [8] have discussed formation of gamma radiation induced defect centers in Ce^{3+} doped $BaBPO_5$ sample and reported results of electron spin resonance (ESR) signal due to Ce^{3+}. Based on the ESR and thermally stimulated luminescence (TSL) results, these authors have proposed probable mechanisms for the observed glow peaks. We have earlier reported results on $ZnAl_2O_4$:Eu^{3+} sample using PL and TSL techniques [10].

The present work deals with the preparation and characterization of $ZnAl_2O_4$ and Ce^{3+}-doped $ZnAl_2O_4$ nanophosphors by sol–gel process. The synthesized product was characterized for its luminescence properties via PL, Photo-acoustic (PAS), ESR and TSL techniques. ESR gives the static nature of the defects and traps whereas TSL investigation leads to understanding of the dynamic processes involving detrapping and subsequent reactions occurring in the system. While an ESR-TSL correlation study helps us to understand the nature of traps, their energies and detrapping probabilities along with the mechanism of the glow peaks, PAS and PL techniques throw light on the oxidation state of the dopant and emission and absorption properties of the system.

2. Experimental

Virgin $ZnAl_2O_4$ and samples doped with Ce (1 mol %) were synthesized using a citrate sol–gel method. The starting materials used were of AR (analytical reagent) grade. Stoichiometric quantities of nitrates of Zn and Al were dissolved in distilled water and one mole percent of cerium nitrate was added to it. Requisite amounts of citric acid was added to the solution mixture and then heated on a hot plate at 353 K to form a highly viscous gel. This resultant gel was calcined at 1173 K to obtain fine powder of the final product [11]. The chemical reaction occurring in the synthesis process can be described as follows.

$$Zn(NO_3)_2+2Al(NO_3)_3+C_6H_8O_7\cdot H_2O\rightarrow ZnAl_2O_4+4N_2\uparrow+6CO_2\uparrow +1/2\ 11O_2\uparrow+5H_2O$$

The as-synthesized products were characterized by X-ray diffraction (XRD) using Cu K_α-radiation with $\lambda=1.5418$ Å. The XRD data were recorded in a step scan mode with step size of 0.5° and hold time of 5 s thus ensuring minimal error in the recorded diffraction pattern. Dynamic light scattering (DLS) technique was also employed to confirm the particle size distribution of the samples. The light scattering experiments were performed on a Nano ZS90 (Malvern instruments, Wores, UK) model size analyzer. PL excitation and emission spectra were recorded on an Edinburgh F-900 fluorescence spectrometer equipped with M-300 monochromators. The acquisition and analysis of the data were carried out using F-900 software supplied by Edinburgh Analytical Instruments, UK [12]. Photo-acoustic spectra were recorded between 300 and 700 nm region using indigenously developed automated photoacoustic spectrometer with 5 nm resolution [13]. TSL glow curves were recorded using home-built unit in the temperature range 300–550 K with a heating rate of 1 K/s [14]. ESR spectra were recorded at room temperature using a Bruker EMX series spectrometer (EMM1843) operated at X-band frequency. The 'g' values were calibrated relative to a 2,2 diphenyl-1 picryl hydrazil (DPPH) standard and the ESR data was simulated using SIMFONIA program from Bruker.

The phosphors were gamma irradiated using a ^{60}Co source having dose rate of 1 kGy/h.

3. Results and discussion

3.1. Physical characterizations

To study the crystalline structure and estimate the grain size of the $ZnAl_2O_4$:Ce^{3+}, XRD technique was used. The recorded XRD pattern of $ZnAl_2O_4$:Ce^{3+} phosphor is shown in Fig. 1. All the observed peaks could be indexed as given in Table 1. The refined lattice parameters were calculated using a least square method. The X-ray data with cell parameter 'a'=8.059 Å was found to be in good agreement with those given in ICDD Card no. 05-0669 [15]. Subsequently, the grain size of the phosphor was calculated using Scherer's equation $\tau=0.90\lambda/\beta\cos\theta$, where λ is wavelength of X-ray used and β is full width at half-maximum (FWHM) of a diffraction line used for calculation [16]. With increase of calcining temperature, the crystallite size of the Ce^{3+}-doped $ZnAl_2O_4$ phosphor was observed to increase. Using the most intense X-ray line ($2\theta=36.83$) broadening, the average crystallite size for 1173 K heated sample was calculated to be 40 nm.

The average particle size was also estimated by performing DLS measurements on the samples which gives a rough estimate of the hydrodynamic radius of the samples considering each particle as a separate sphere. The results are given in Fig. 2 which suggests a narrow size distribution of around 40 nm for the aluminate system confirming the findings of the diffraction data.

$ZnAl_2O_4$ can be crystallized in a cubic normal or inverse spinel structure depending on the preparation procedure. In the normal spinel structure, the 3^+ ions of Al occupy the octahedral site, while

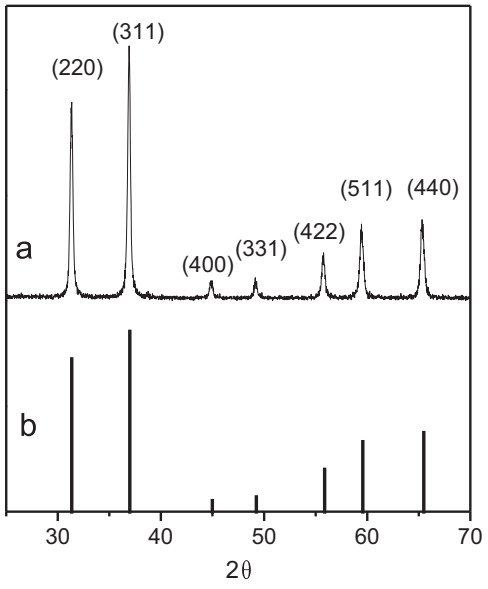

Fig. 1. (a) XRD pattern of Ce^{3+}-doped $ZnAl_2O_4$ phosphor; for comparison, the standard ICDD pattern no. 05–0669 (b) is also shown below the XRD pattern.

Table 1
XRD data of $ZnAl_2O_4$:Ce^{3+}.

2θ values	d_{Obs} (Å)	d_{Cal} (Å)	I/I_0	h k l
31.235(7)	2.862	2.858(6)	85	220
36.840(5)	2.438	2.433(5)	100	311
44.810(5)	2.021	2.019(4)	8	400
49.070(4)	1.855	1.851(3)	10	331
55.655(3)	1.650	1.652(3)	25	422
59.345(2)	1.556	1.556(1)	40	511
65.235(1)	1.429	1.428(1)	45	440