Journal of Luminescence 178 (2016) 407–413

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Full Length Article

Structural and photophysical investigations of bright yellow emitting Dy: $ZnAl_2O_4$ nanophosphor

Pushpa Kumari, Y. Dwivedi *

Department of Physics, National Institute of Technology Kurukshetra, Haryana 136119, India

ARTICLE INFO

Article history:
Received 14 February 2016
Received in revised form
12 June 2016
Accepted 13 June 2016
Available online 16 June 2016

Keywords:
$ZnAl_2O_4$:Dy^{3+}
Nanophosphor
Spinel
Photoluminescence

ABSTRACT

$ZnAl_2O_4$:Dy nanophosphors were synthesized using co-precipitation and hydrothermal methods. Various structural and optical characterizations were made using X-ray diffraction (XRD), Transmission electron microscopy, Scanning electron microscopy, UV-Visible absorption, Infrared absorption, photoluminescence and time resolved luminescence techniques. Dy^{3+} doped samples showed yellow dominating multicolour emission on excitation with 348 nm. We have estimated J–O parameters and other various radiative parameters like quantum efficiency, Stimulated emission cross-section etc. Considerable effect of SiO_2 was noticed on crystalline size and emission intensity of Dy ions. A comparison between the samples synthesized by different methods, and Dy concentration has been made and detail report presented in the article.

1. Introduction

In recent years, the nanocrystals with unique morphology and promising optical properties attracted researcher attention due to their potential application in variety of appliances [1]. Spinel type materials are interesting topics of research since they exhibit different sizes depending properties. Zinc aluminate ($ZnAl_2O_4$) is a spinel type oxide, where Zn and Al are divalent and trivalent ions, respectively [2]. $ZnAl_2O_4$ nanophosphors exhibit merits of high thermal and chemical stability which is prerequisites for various applications such as host matrix optical coating, photo catalysis degradation and high temperature ceramic material [3]. Zinc aluminate may find its application in ultraviolet photoelectronic devices, as catalytic support, to improve wear resistance, to preserve whiteness etc. [4].

Zinc aluminate nanocrystals commonly prepared by high temperature calcination of mixed aluminum and zinc oxides which may be classified further according to their framework geometries, spinels, perovskites or garnets [5]. High temperature is necessary to improve the crystallinity and thus greatly limit their application [6]. $ZnAl_2O_4$ with cubic spinel structure having 3.8 eV optical bandgap, which indicates in $ZnAl_2O_4$ is transparent for light possessing wavelength greater than 326 nm [7]. Over the last decade, many methods for the synthesis of $ZnAl_2O_4$ have been reported including co-precipitation [8], hydrothermal [9], sol–gel and solution combustion technique [10,11]. Various studies reveal optical and catalytic properties of zinc aluminate nanoparticles [12].

Doping of hetro atom/ion may influences the growth process of nanocrystals and provide control over the crystallite phase, size and optical emission properties [13]. Rare earths (RE) doped inorganic solids are often used as laser material, optical amplifier, optical memory, photocatalytic activity, white light and temperature sensing [14–20] etc. Several groups have reported a variety of RE doped aluminate oxide phosphors reporting efficient optical properties in the visible region [21]. $ZnAl_2O_4$ doped with RE ions has been investigated most frequently because of unique luminescent properties. Photoluminescence of the trivalent RE ions are mainly due to electronic and magnetic dipole transitions within $4f^n$ energy manifolds. Trivalent Dy ion is one of the most studied RE ions, due to unique emission peaks spreading in blue to IR regions. Emission spectrum of Dy^{3+} ion, consist of $^4F_{9/2} \rightarrow {}^6H_j$ (j=7/2, 9/2, 11/2, 13/2 and 15/2) transition. Among all lanthanide ions, Dy^{3+} ($4f^9$) ion gives most intense emission in yellow region [22,23]. Research on trivalent Dy ion doped materials is important because these materials have high potential in lighting industry. The Dy ion is one of the most efficient RE ions for laser, telecommunication amplifier and Q-switch device.

In the present work, we have attempted to explore structural and optical properties of Dy doped $ZnAl_2O_4$ and also to monitor the effect of SiO_2 on $ZnAl_2O_4$ nanocrystals growth. Efforts were made to observed the effect of atleast two synthesis methods namely, co-precipitation and hydrothermal methods. We have

* Corresponding author.
E-mail address: yashjidwivedi@nitkkr.ac.in (Y. Dwivedi).

http://dx.doi.org/10.1016/j.jlumin.2016.06.027
0022-2313/

reported bright yellow dominating multicolor emission on 348 nm excitation having different transition, the $^4F_{9/2}$ level gives radiative transition to the ground state ^6H_j (j=15/2, 13/2, 11/2, 9/2 and 7/2 levels).

2. Synthesis and characterizations

2.1. Chemicals

The following chemicals were used for sample synthesis: Aluminium Nitrate [$Al(NO_3)_3.9H_2O$](99%), Zinc Nitrate [$Zn(NO_3)_2.6H_2O$], Tetraethylorthosilicate [$SiC_8H_{20}O_4$] (99%), Dysporsium Oxide [Dy_2O_3] (99.9%), Ethanol (99.9%), Hydro Chloric acid (HCl) and Ammonia Hydroxide [NH_4OH]. These chemicals were purchased from Sigma Aldrich Company and used as it was received.

2.2. Synthesis

$ZnAl_2O_4$ and Dy doped $ZnAl_2O_4$ nanophosphors were prepared by using Coprecipitation and Hydrothermal methods. Bulk solution of Dysprosium chloride was prepared by dissolution of Dy_2O_3 in Hydrochloric acid. Prepared Dysprosium chloride solution was dried and re-crystallized in desiccator. Initially, stoichiometric proportion of Aluminium Nitrate and Zinc Nitrate was dissolved in 5 ml of distilled water separately and stirred for 1 h at 40 °C. Another solution of TEOS was prepared in mixture of water and ethanol solution for 2 h for better hydrolysis. Later on, both the nitrate solutions were added to TEOS solution drop by drop whilst stirring. After stirring for an hour Ammonium hydroxide solution (25%) was added drop-wise reducing the pH value 09. A white precipitate appear immediately which was collected by centrifuge. Collected material was washed with double distilled water and ethanol for 3–4 times and then dries in oven at 70 °C temperature in air overnight. To prepare Dy doped sample, required amount of re-crystallized Dysprosium chloride was added in the solution of TEOS and Zinc Nitrate solution, slowly. Then the solution was stirred for an hour and pH value was set at 09 with the help of Ammonium Hydroxide solution. Precipitate, thus obtained was separated by centrifuge at 500 rpm and washed with distilled water and ethanol and dried in oven at 70 °C for overnight. For hydrothermal synthesis precipitate was diluted to 80 ml with double distilled water and then poured into a Teflon-lined stainless steel autoclave. After hydrothermal treatment at 220 °C for 8 h, the resultant solid was collected by centrifugation and dried at 70 °C. We have prepared samples for Dy 0.5, 0.75, 1, 1.25, and 1.5% molar concentrations. Undoped and doped samples were annealed at different temperature 800 °C, 900 °C, 1000 °C and 1100 °C to obtain the desired phase.

2.3. Characterizations

The crystalline phases of the prepared sample were identified by a Rigaku mini diffractometer using Graphite filtered Cu-Kα Radiation (λ=1.54 A°) operated at 40 kV and 100 mA with a scanning rate of 2°/min in the range 10–80°. Crystallite sizes were estimated from Debye Scherrer's relation D=Kλ/β Cosθ where, λ is the X-Ray wavelength, θ is the angel of the Bragg diffraction peak (in radian) and β is the line width at half maximum. Surface morphology was investigated on JSM-6390LV, Scanning Electron Microscope. Transmission Electron Microscope image were recorded on a (H-7500)-120 kV machine from JEOL Ltd., Japan. Absorption spectra of powder samples were recorded on T+90 Double beam scanning UV-Visible absorption spectrophotometer. Linear refractive index of the samples was estimated using Dimitrov and Sakka method [24] and found to be 2.1 for bangdap 4.3 eV. The Fourier Transform Infrared spectra of the samples were recorded on Carry eclipse 6300 machine in the range of 400–4000 cm^{-1}. Excitation and photoluminescence spectra of prepared samples were carried out on RF-530 Spectrofluorophotometer (Shimadzu, Japan) in the range of 200–800 nm. Photoluminescence decay measurements were recorded with pulsed 355 nm laser (7 ns pulse width) radiation of Nd: YAG laser as an excitation source and the collected luminescence signal was fed to a 150 MHz digital oscilloscope (model no. HM 1507, Hameg Instruments). Lifetimes of the radiative levels were estimated by fitting as exponential function to the decay curves.

3. Results and discussion

3.1. Crystalline Phase analysis

The XRD patterns of the undoped and Dy doped samples, annealed at 1000 °C/2 h and prepared by different methods, were monitored in the range of 10–80° angle and depicted in Figs. 1 and 2. In case of undoped sample pattern obtained was found to be match well with cubical spinel system of $ZnAl_2O_4$ (JCPDS No. 82-1043) [7,25]. The mean crystallite size was estimated by taking average of atleast three non-interfering planes and found to be ~12 nm using Debye-Scherrer's equation. We have also monitored the effect of Dy ion in crystalline phase. We have not observed any major change in the crystalline phase though small shift towards the higher angle side and broadening of the peak was evident (see Fig. 1).

Effect of annealing temperature on the crystalline parameters and synthesis methods are compared in Table 1. It has been observed that the crystallite size and lattice parameter increases while strain decreases with increasing annealing temperature. It was also observed that when SiO_2 is also present in the host, the crystallite size of $ZnAl_2O_4$ reduces, significantly.

Efforts were made to analysis the Bragg's peak using Debye-Scherrer formula and Williamson-Hall (W-H plot), and detail obtained is tabulated in Tables 1 and 2. Slight peak shift and peak broadening indicates the minor change in the crystalline structure of $ZnAl_2O_4$. The ionic radius of Zn^{+2}, Dy^{+3}, Al^{+3} and Si^{+4} was

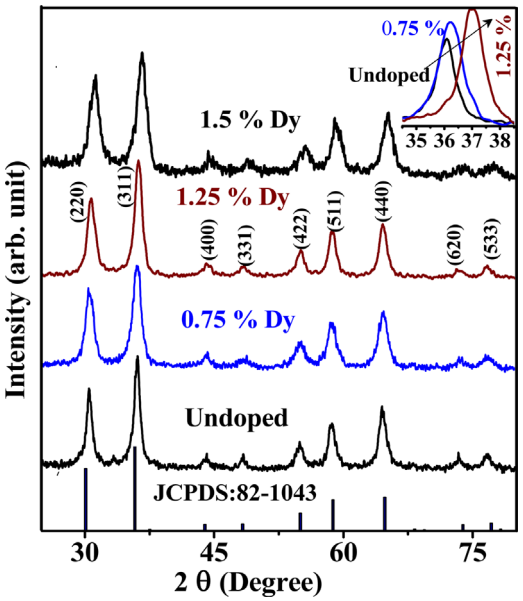

Fig. 1. X-Ray diffraction patterns of undoped $ZnAl_2O_4$ nanophosphor, 0.75 mol%, 1.25 mol%, and 1.5 mol% Dy doped samples. Comparison of peak shift in pure, 0.75 and 1.25 mol% Dy doped $ZnAl_2O_4$ samples in given in inset.