Journal of Luminescence 135 (2013) 105–112

Contents lists available at SciVerse ScienceDirect

Journal of Luminescence

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

Synthesis, characterization, EPR, photo and thermoluminescence properties of $YAlO_3:Ni^{2+}$ nanophosphors

H.B. Premkumar [a], D.V. Sunitha [a], H. Nagabhushana [a,*], S.C. Sharma [a], B.M. Nagabhushana [b], C. Shivakumara [c], J.L. Rao [d], R.P.S. Chakradhar [e]

[a] Prof. C.N.R. Rao Centre for Advanced Materials, Tumkur University, Tumkur-572103, India
[b] Department of Chemistry, M.S. Ramaiah Institute of Technology, Bangalore-560054, India
[c] Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560012, India
[d] Department of Physics, S.V. University, Tirupathi-517502, India
[e] CSIR-National Aerospace Laboratories (CSIR), Bangalore-560017, India

ARTICLE INFO

Article history:
Received 12 May 2012
Received in revised form
27 August 2012
Accepted 5 September 2012
Available online 14 September 2012

Keywords:
Phosphor
X-ray diffraction
$YAlO_3$
Ni^{2+}
EPR
Thermoluminescence

ABSTRACT

$YAlO_3:Ni^{2+}$ (0.1 mol%) doped nanophosphor was synthesised by a low temperature solution combustion method. Powder X-ray diffraction (PXRD) confirms the orthorhombic phase of yttrium aluminate ($YAlO_3$) along with traces of $Y_3Al_5O_{12}$. Scanning Electron microscopy (SEM) shows that the powder particles appears to be spherical in shape with large agglomeration. The average crystallite sizes appeared to be in the range 45–90 nm and the same was confirmed by transmission electron microscopy (TEM) and Williamson–Hall (W–H) plots. Electron Paramagnetic Resonance (EPR) and photoluminescence (PL) studies reveal that Ni^{2+} ions are in octahedral coordination. Thermoluminescence (TL) glow curve consists of two peaks with the main peak at ~224 °C and a shouldered peak at 285 °C was recorded in the range 0.2–15 kGy γ-irradiated samples. The TL intensity was found to be increasing linearly for 224 °C and 285 °C peaks up to 1 kGy and thereafter it shows sub-linear (up to 8 kGy) and saturation behavior. The trap parameters namely activation energy (E), order of kinetics (b), frequency factor (s) at different γ-doses were determined using Chens glow peak shape and Luschiks methods then the results are discussed in detail. Simple glow peak structure, the 224 °C peak in $YAlO_3:Ni^{2+}$ nanophosphor can be used in personal dosimetry.

1. Introduction

Phosphor nanomaterials with different shapes and sizes are of special interest not only for basic research, but also for interesting applications in different fields such as displays, catalysts, solar energy converters and optical amplifiers [1–3]. These materials show special properties such as high surface to volume ratio and local phenomenon such as absorption or change in the surface electronic state. The development of transition and rare earth based perovskite type materials found wide applications as host for solid-state lasers, luminescent systems, solid electrolytes, chemical sensors, magnetic refrigeration materials, substrates for high-temperature superconductor deposition, catalyst supports and thermal barrier coatings [4,5].

Among perovskites, $YAlO_3$ (YAP) is one of the three yttrium aluminium double oxides, together with the $Y_3Al_5O_{12}$ garnet (YAG) and $Y_4Al_2O_9$ monoclinic (YAM) structures. It is well known that all the Y–Al–O compounds show interesting optical properties, especially when they are doped with metal cations [6,7]. It has high refractive index, optical transparency, chemical inertness and mechanical resistance, which make it suitable as host material in lasers, fast scintillator, and ceramic pigment. Till date manganese, cerium-doped $YAlO_3$ was studied extensively for its applications in holographic recording, optical data storage [8]. This phosphor is highly useful in thermoluminescent (TL) dosimetry of ionizing radiation due its properties such as high effective atomic number (Z_{eff}=31.4), relatively high sensitivity, linear response in the dose range 10^{-4} to10^{3} Gy [9].

Conventionally, $YAlO_3$ is produced by solid state reaction of yttrium and alumina powders which essentially involves extensive mechanical mixing followed by lengthy heat treatments and sintering at relatively high temperatures (~1200 °C) [10]. To circumvent the problems associated with solid state synthesis of $YAlO_3$ powder, several wet-chemical techniques, such as the polymerized complex route, combustion synthesis, sol–gel have been utilized to synthesize $YAlO_3$ [11–13]. Most of these methods suffer from the complex and time consuming procedures and/or mismatch in the solution behaviour of the constituents. As a

* Corresponding author. Tel.: +91 9945954010.
E-mail address: bhushanvlc@gmail.com (H. Nagabhushana).

0022-2313/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jlumin.2012.09.004

consequence, gross inhomogeneities may be present in the obtained product. Combustion synthesis is one of the important processing technique used for the synthesis of advanced nanopowders, where the exothermicity of the redox chemical reaction is utilized to produce powders with desired phase and morphology. This process is characterized by high-temperatures, and fast heating rates with rapid reaction times; these features are attractive for the production of technologically important materials as compared to the conventional synthesis methods.

Zhydachevskii et al. [14] studied the TL properties of pure and doped $YAlO_3$ in single crystals. However, sufficient work on the TL and EPR studies of $YAlO_3$ in nano form up to now has not been done. In the present paper, we report $YAlO_3$:Ni^{2+} nanophosphor prepared by a low temperature solution combustion method for the first time and the phosphor was well characterized by PXRD, Fourier transform infrared (FTIR), SEM, TEM, UV–visible spectroscopy (UV–vis), EPR and TL studies. From TL, the kinetic parameters at different γ-doses namely activation energy (E), order of kinetics (b), and frequency factor (s) were determined using Chens glow peak shape method and the results are discussed in detail.

2. Experimental

Analar grade Yttrium nitrate ($Y(NO_3)_3$. H_2O; purity 99.9%), Aluminium nitrate ($Al(NO_3)_3 \cdot 9H_2O$; purity 99.9%), Nickel nitrate ($Ni(NO_3)_2$; purity 99.9%) and oxalyl dihydrazide (ODH, $C_2H_6N_4O_2$) fuel were used as starting materials for the preparation of $YAlO_3$:Ni^{2+} nanophosphors. $YAlO_3$:Ni^{2+} nanophosphor was prepared by taking aluminum/yttrium nitrates in stoichiometric quantity along with ODH. The stoichiometric amount of fuel to oxidizer (Aluminum and nickel nitrate) ratio is considered to be unity ($\Phi=1$). The detailed calculations have been described elsewhere [15]. The corresponding nitrates and ODH was dissolved in double distilled water in a Pyrex dish and then mixed uniformly using magnetic stirrer for ~5 min. Thereafter, the Pyrex dish was placed in a preheated muffle furnace maintained at temperature $\sim 400 \pm 10$ °C. The mixture underwent dehydration with liberation of large amount of gases. Finally a foam type product was left behind in the petridish. The dish was then taken out from the furnace and the foamy product was crushed into a fine powder using pestile and mortor. This powder was used for different characterizations.

The phase purity and the crystallinity of the nanophosphors were examined by powder X-ray diffractometer (PANalytical X′Pert Pro) using CuK_α (1.541 Å) radiation with a nickel filter. The surface morphology of the product was examined by SEM (JEOL JSM 840 A). TEM analysis was performed on a Hitachi H-8100 (accelerating voltage up to 200 kV, LaB_6 filament) equipped with EDS (Kevex Sigma TM Quasar, USA).The FT-IR studies were performed on a Perkin Elmer Spectrometer (Spectrum 1000) with KBr pellets. The UV–vis absorption of the samples was recorded on SL 159 ELICO UV–vis Spectrophotometer. TL measurements were carried out at room temperature using Nucleonix TL reader by using γ-irradiation as excitation source in the dose range 0.2–15 kGy. The EPR spectrum was recorded at room temperature using a JEOL-FE-1X EPR spectrometer operating in the X-band frequency (≈ 9.205 GHz) with a field modulation frequency of 100 kHz. The magnetic field was scanned from 0 to 500 mT and the microwave power used was 20 mW. A powder sample of 100 mg was taken in a quartz tube for EPR measurements.

3. Results and discussion

The powder X-ray diffraction patterns of the un-doped and 0.1 mol% Ni^{2+}doped $YAlO_3$ nanopowders are shown in Fig. 1(a) and (b) respectively. The PXRD patterns exhibit dominant diffraction peaks due to the orthorhombic phase of $YAlO_3$ (JCPDS File no. 70-1677) along with $Y_3Al_5O_{12}$ phase [16]. The crystallite size (d) of un-doped and Ni^{2+} doped $YAlO_3$ samples were estimated using Debye–Scherer's formula [17]. $D=0.9\lambda/\beta$ Cos θ where D is the average grain size of the crystallites, λ is the incident wavelength, θ is the Bragg angle and β is the diffracted full width at half maximum (FWHM; in radian) caused by the crystallites. The average crystallite size of these nanophosphors was observed to be ~45–80 nm.

It is known that the FWHM can be expressed as a linear combination of the contribution from the lattice strain and crystallite size [18]. The effects of the strain and crystallite size on the FWHM can be expressed by the following equation: $\beta \cos\theta/\lambda = 1/\varepsilon + \eta \sin\theta/\lambda$ where 'β' is the measured FWHM (in radians), 'θ' is the Bragg angle of the peak, 'λ' is the X-ray diffraction wavelength, 'ε' is the effective crystallite size and 'η' is the effective strain (Fig. 2). The effective crystallite size for the doped sample was found to be in the range 45–90 nm and it is comparable with that of calculated from Scherrer's equation. The lattice strain was observed to be 2.29×10^{-3} for un-doped and 1.72×10^{-3} for Ni^{2+} doped $YAlO_3$.

Fig. 3 shows the Rietveld analysis pattern of Ni^{2+} doped $YAlO_3$ nanopowders. The major reflections correspond to $YAlO_3$ phase along with $Y_3Al_5O_{12}$. The line marks below the patterns represent the positions of all possible Bragg reflections. The lower solid line represents the difference between the observed and calculated intensities. In general, the Rietveld method utilizes the least-squares refinement for obtaining the best fit between the experimental data and the calculated pattern based on the simultaneously refined models. In the present study, a Thomson–Cox–Hasting

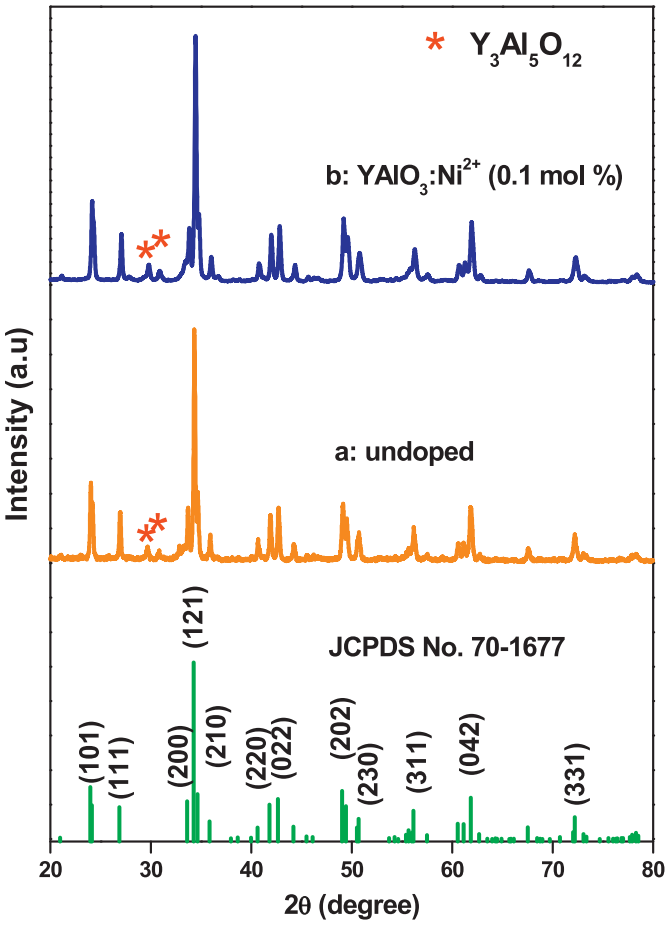

Fig. 1. PXRD patterns of (a) un-doped $YAlO_3$ and (b) $YAlO_3$:Ni^{2+} nanophosphors.