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Ultraviolet B emitting Gd doped Al_2O_3 phosphor – A photoluminescence and electron paramagnetic resonance study

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ABSTRACT

$Al_2O_3:Gd^{3+}$ phosphor was prepared using single step urea combustion method. The prepared phosphor was characterized by X-ray diffraction (XRD), photoluminescence (PL) and electron paramagnetic resonance (EPR) techniques. The formation of the combustion products was confirmed by the XRD analysis. PL studies showed that the $Al_2O_3:Gd^{3+}$ phosphor could be excited at 273/276 nm, while an ultraviolet (UV) emission centered at ~ 314/317 nm was exhibited. The EPR spectrum of sample exhibited resonance signals due to Gd^{3+} ion at low symmetry sites in the host lattice. Both PL as well as EPR studies of the sample confirmed the presence of Gd^{3+} in the Al_2O_3 matrix.

1. Introduction

Alumina is known as important refractory material due to its high melting point and hardness [1–3]. In addition to these properties, its excellent thermal shock resistance makes it a perfect candidate for several applications [3,4]. α-Al_2O_3 is a handy material with a high chemical stability, high band gap, high level of strength, tribological properties, and hence this material is a good choice for various applications [5–9]. α-Al_2O_3 has been investigated as a suitable host for rare earth and transition metal ions [10–12]. Singh et al. [13] reported electron paramagnetic resonance (EPR) and photoluminescence (PL) properties of α-$Al_2O_3:Cr^{3+}$ phosphors. Prakash et al. [14] reported PL investigation of Dy^{3+} doped α-Al_2O_3 phosphor. Mokoena et al. [15] studied cooperative luminescence from α-$Al_2O_3:Yb^{3+}$ phosphor. Rakov et al. [16] reported PL analysis of α-Al_2O_3 powders doped with Eu^{3+} and Eu^{2+} ions.

From decades ultraviolet (UV) radiation has been increasingly used in controlling skin diseases and has become an important part of modern dermatological therapy. Various investigations show that the most effective range for the treatment of psoriasis vitiligo, atopic dermatitis (eczema) and other photo-responsive skin disorders is in the long-wavelength part of the UVB spectrum, i.e., in between 305–320 nm [17–19].

The luminescence properties of Gd^{3+} ion-doped compounds have been of great interest in recent years [20–22]. It is well known that phosphors doped with Gd^{3+} ion had strong ultraviolet emission. Light sources in the UV region are useful in several applications such as biological agents, medical fields, sterilization and covert communications [23–25]. Gd^{3+} ions transition from $^6P_{7/2}$ to $^8S_{7/2}$

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gives rise a narrow band emission at around 311–320 nm which is useful for the treatment of several kind of skin diseases [26,27]. In addition, these Gd^{3+} ions co-doped with other rare-earth ions have been used for energy transfer processes, which yield high luminescence efficiencies. Many researchers have reported the use of Gd^{3+} doped inorganic phosphor materials for phototherapy lamp applications [28–30]. Recently, Singh et al. [31] reported luminescence and EPR studies of ultraviolet light emitting $La_2Zr_2O_7$:Gd^{3+} phosphor. Tamboli et al. [32] reported UV-emitting Gd^{3+}-doped $LiCaBO_3$ phosphor. Okamoto et al. [33] reported luminescent properties of Pr^{3+}-sensitized $LaPO_4$:Gd^{3+} phosphor. Chauhan et al. [26] reported synthesis and PL study of narrow band UVB emitting $LiSr_4(BO_3)_3$:Gd^{3+}, Pr^{3+} phosphors. Pathak et al. [34] studied ultraviolet B emission from Gd^{3+} doped $Y_3Ga_5O_{12}$ garnets. Singh et al. [35] reported ultraviolet B emitting Gd^{3+} doped ZrO_2 phosphor.

One of the most convenient structure-sensitive spectroscopy techniques is EPR which provides valuable information concerning the structural details for the environment of the Gd^{3+} ions in phosphor lattice. In our previous work, detailed EPR investigation on Gd^{3+} ions was reported in different host materials such as $MgAl_2O_4$, [36] $CaAl_{12}O_{19}$, [37] $BaZrO_3$ [38] and ZrO_2 [35]. In continuation of our interest on UV emitting phosphors, in this work, we have prepared Gd^{3+} doped α-Al_2O_3 phosphor. In order to prepare Gd^{3+} doped α-Al_2O_3 phosphor, solution combustion method was adopted and studied XRD, PL and EPR spectroscopy.

2. Experimental

The α-Al_2O_3:$Gd_{0.01}$ phosphor was prepared utilizing the combustion process. To prepare α-Al_2O_3:$Gd_{0.01}$, 2.0 g of $Al(NO_3)_3 \cdot 9H_2O$, 0.8005 g of CH_4N_2O, and 0.0120 g $Gd(NO_3)_3 \cdot 6H_2O$ were used. To perform the combustion reaction, the stoichiometric amounts of starting materials were placed in a China dish and mixed with minimum amount of deionized water. The resulting solution was allowed to react at 95 °C for 20 min to obtain a homogeneous solution. Then the solution was introduced into a muffle furnace preheated to 500 °C. The products obtained by combustion process were fluffy masses and these were crushed into a fine powder using a mortar and pestle and placed in clean plastic tubes. The prepared powder was further used for characterization.

X-ray diffraction data were recorded at room temperature on an X'Pert Pro Diffractometer (Panalytical) using CuKα radiation in the 2θ range of 10°–80°. The photoluminescence measurements were carried out at room temperature using a Shimadzu RF-5301PC, spectrofluorophotometer equipped with a Xenon flash lamp. The EPR spectra of the sample were recorded on a JEOL FE1X ESR Spectrometer, operating in the X-band frequencies, with a field modulation of 100 kHz.

3. Results and discussion

3.1. X-ray diffraction studies

The phase purity of prepared α-Al_2O_3:Gd was investigated using XRD analysis. The resulting XRD pattern of α-Al_2O_3:Gd is shown in Fig. 1. The XRD results show that most of the diffraction peaks are in accord with α-Al_2O_3 (JCPDS card No. 78-2427) confirming the hexagonal structure. The observed XRD pattern indicated that there are presences of some minor phases in the sample marked as (●) which belong to θ-Al_2O_3. Fujita et al. [39] also observed θ-Al_2O_3 peaks, when they prepared α-Al_2O_3 by sol-gel method at 1100 °C. To obtain a pure phase of α-Al_2O_3 they annealed the sample at 1200 °C. It may be noted that we have prepared crystalline phase of α-Al_2O_3 even at 500 °C furnace temperature within 5 min. Scherer's equation was used to estimate the crystallite size from the main (113) diffraction XRD peak. $D = 0.9\ \lambda/\beta\cos\theta$, where λ is the wavelength of incident X-ray, θ is the corresponding Bragg's diffraction angle, and β is the FWHM of the (113) peak. The crystallite size calculated from this method was found to be 37.33 nm.

3.2. Photoluminescence studies

Fig. 2 shows the excitation spectra of Al_2O_3:Gd^{3+} monitored at different emission wavelength. When monitored at 314 nm, the

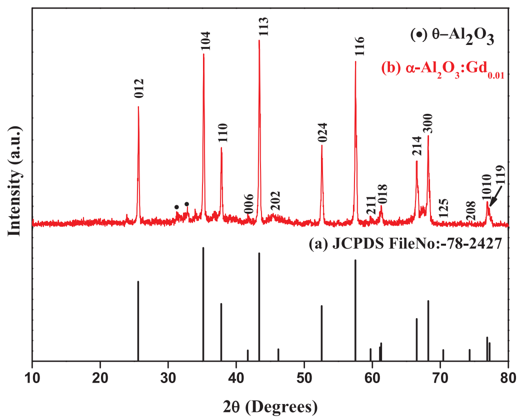

Fig. 1. Powder XRD pattern of (a) α-Al_2O_3 (JCPDF No. 78-2427) and (b) Al_2O_3:$Gd_{0.01}$ phosphor.