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Study of photoluminescence and thermoluminescence properties of $BaAl_2O_4$ (Eu^{2+}, Dy^{3+}) phosphor synthesized by solution combustion method

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HIGHLIGHTS

- $BaAl_2O_4(Eu^{2+},Dy^{3+})$ phosphor synthesized by solution combustion technique.
- The estimated particle size was found to be around 34.62 nm.
- TL behaviour was studied after irradiation with Co-60, 6 MV and 16 MV photon beams.
- Glow peaks obey second order kinetic with 0.413 eV activation energy.
- Used in display devices, monitoring ionizing radiations in nuclear industries.

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ABSTRACT

Eu and Dy co-doped barium aluminate phosphor was successfully synthesized by combustion method using urea as a fuel. Phase formation was confirmed by powder X-ray diffraction (PXRD) analysis. The calculated average crystallite size was found to be ~34.62 nm. Scanning electron microscopy (SEM) images acquired at different (low and high) magnifications reveal that the crystallites have no uniform shape and size. This was due to the non-uniform distribution of temperature and mass flow in the combustion technique. Fourier Transform Infra-red (FTIR) spectrum was recorded to confirm the phase formation and also to identify any impurity if present in the prepared phosphor. Photoluminescence (PL) measurement was carried out to investigate the incorporation of dopant into the host lattice. Thermoluminescence (TL) behaviour of synthesized phosphor was studied after the irradiation with Cobalt-60 gamma rays (E_{avg} = 1.25 MeV) as well as 6 and 16 MV (Mega Voltage) X-ray photons, at various dose levels. The glow curves of irradiated samples exhibit only one peak at 115 °C at each dose level. With the increases of radiation dose an increase in total intensity has been observed. No appreciable shift in peak positions has been observed. Trapping parameters were evaluated to understand the characteristics of prepared phosphor. A simple glow peak with relatively high intensity is one of the important factors, which make this phosphor useful for monitoring the ionizing radiations in nuclear industries, gamma irradiators, high energy accelerators, nuclear reactors etc. where medium and high level of exposure is involved. It could also be applicable for accidental and retrospective dose assessment.

1. Introduction

Rare earth (RE) doped alkaline earth aluminates are considered as promising phosphors for various optoelectronics applications. Phosphors doped with RE ions are best known trichromatic luminescent materials. For general lighting and ultra-violet (UV) devices, the phosphors based on borate, silicate, aluminates etc. are being utilised and play a very important role. The rare earths (lanthanides) have an unfilled 4f shell in which electrons are shielded from the atomic environment by 5d and 5p shells. Due to these unique properties, such phosphors have wide range of applications. Phosphors strontium aluminates ($SrAl_2O_4$: Eu,Dy) and barium aluminates ($BaAl_2O_4$: Eu,Dy) are the important materials for long after-glow phosphorescence (Suriyamurthy and Panigrahi, 2007; Stefani et al., 2009; Sakai et al., 1999; Xiao et al., 2010). Rare

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earth doped aluminate based polycrystalline phosphors have several applications in fluorescent lamp, plasma display unit, electroluminescence panels, light emitting diodes, X-ray imaging plates, Infra-red sensors, luminescence paints etc. (Suriyamurthy and Panigrahi, 2007; Stefani et al., 2009; Sakai et al., 1999; Xiao et al., 2010; Yerpude and Dhoble, 2012; Peng and Hong 2007; Tanno et al., 2010). Apart from these, other important applications of the long lasting afterglow phosphors are in radiation dosimetry, archaeological dating, determination of natural radiation levels, environmental and retrospective dosimetry (McKeever, 1985; Furetta, 2003; Zhydachevskii et al., 2007; Ranogajee-Komor and Osvay, 1986; Arellano-Tanori et al., 2008; Sangeeta and Sabharwal, 2004). The above mentioned applications are based on efficient conversion of incident radiation energy into the visible or near visible region of the electromagnetic spectrum.

Presently, several methods are being used to produce efficient and good phosphors for various applications. Phosphors produced by solid state reaction method require high temperature and long reaction time (Chen et al., 2006; Aitasalo et al., 2001). The solution combustion technique has been used since long time to produce the technically challenging powder phosphor for various applications (Patil, 1993; Doull et al., 2013; Dincer and Ege, 2013). The combustion synthesis method requires shorter reaction time relatively at low temperature as compared to solid state and other methods. This method has also been used to produce technically challenging, homogenous and ultrafine nano-phosphors. This technique is self sustaining and involves highly exothermic reaction in aqueous solution between an organic fuel and metal nitrates (oxidizers). High concentration of surface atoms and defects at nano-grain boundaries may be regarded as one of the fundamental properties of nano-phosphors (Yukihara et al., 2013; Berger and Hajek, 2008; Kortov and Ustyantsev, 2013; Kortov, 2010). In nano-phosphors, a large number of charge-carrier trapping centers have been created at various energy depths in contrast to their bulk counterparts. Due to its high radiation resistance properties, the nano-phosphors play a very significant role for the dosimetry of ionizing radiations.

Thermoluminescence (TL) is one of the methods used in solid state dosimetry of ionizing radiation, archaeological dating, temperature sensor etc. It is also used for study the nature of defect in solids. It is the phenomenon of emission of light caused by heating of a pre-irradiated TL phosphor materials. Thermoluminescence technique is widely used for the monitoring of ionizing radiations applied in medical, research and many other fields (Chawla et al., 2010; Manam and Sharma, 2005; Chen, 1969; Singh et al., 2011; Pathak and Kurchania, 2015; Pathak and Kurchania, 2016). In the present work barium aluminate phosphor doped with Eu and Dy ions ($BaAl_2O_4$:Eu^{2+},Dy^{3+}) is synthesized, using solution combustion method. Photoluminescence (PL) and TL properties of the prepared phosphor have been investigated.

2. Materials and methods

2.1. Synthesis of material

To synthesize europium (Eu) and dysprosium (Dy) co-doped barium aluminate ($BaAl_2O_4$) phosphor, the solution combustion method has been employed. The stoichiometric amounts of ultra pure and analytical (AR) grade $Ba(NO_3)_2$, $Al(NO_3)_3 \cdot 9H_2O$ (Himedia), $Eu(NO_3)_3 \cdot 6H_2O$, $Dy(NO_3)_3 \cdot 5H_2O$ (Biochemika, Otto) and urea (NH_2CONH_2) from s.d.fiNE-Chem Ltd., were calculated according to the total oxidizing and reducing valences of the components such that the equivalence ratio (O/F) is unity and the energy release is maximum (Patil, 1993). Here the metal nitrates act as oxidizer (O) and urea as a fuel (F). All the starting materials were thoroughly mixed in an agate mortar using minimum amount of de-ionized water. The resulting homogeneous thick paste was transferred in a borosilicate beaker of 500 ml and placed into a muffle furnace which was pre-heated at around 550 °C. Initially paste boils and undergoes dehydration, followed by decomposition and evolution of gases. The mixture then froths and swells forming foam, which ruptures with a flame and glows to incandescence. During incandescence the foam further swells to the capacity of container. The entire combustion process was over within 5 min. The obtained combustion product was then gently crushed and thoroughly mixed in an agate mortar. Prepared powder was then transferred into a silica crucible and placed in the furnace for calcination at 700 °C for 1 h. After calcination the powder was thoroughly mixed again to homogenize the final product. The obtained final powder sample was then stored in dark for further studies.

2.2. Characterization

To confirm the phase formation and also to determine the size of crystallites, powder X-ray diffraction (PXRD) study was performed using Rigaku Miniflex-II diffractometer with Cu-Kα (λ = 1.5406 Å) radiation. The surface morphology of the sample was examined by using JEOL/EO JSM-6390 scanning electron microscope (SEM). The Fourier transform infra-red (FTIR) spectrum of sample was recorded by Perkin Elmer Spectrophotometer, using KBr pellet technique. Photoluminescence (PL) measurements were performed by using F-7000, Fluorescence Spectrophotometer and 450 W Xenon lamps as an excitation source. The emission spectrum was recorded at room temperature. Before performing the TL analysis, samples were irradiated with 10, 20, 50, 100 and 200 Gy of doses by Co-60 source (gamma rays of 1.25 MeV average energy) installed in tele-therapy machine (Theratronics 780 C, Canada) with the dose rate of 1.8 Gy/min for the standard (10 cm × 10 cm) field size and depth. Samples were also exposed to 6 MV and 16 MV X-rays photons of 100 Gy dose, generated from medical linear accelerator (Varian medical systems, USA). TL measurements were performed using a thermoluminescence dose (TLD) reader (Harshaw, Model 3500) in the temperature range between 50–400 °C with linear heating rate of 5 °C s^{-1}. Build-up material with appropriate thicknesses was applied over the phosphor samples during the irradiation to deliver desired dose in the sample. The doses were verified by using the reference class 0.6 cc ion chamber (FC-65G, IBA Dosimetry Germany) calibrated at national standard calibration laboratory (BARC, India). The dose measurements were performed according to International Atomic Energy Agency (IAEA) TRS-398 protocol (TRS-398, 2000). In each case, approximate 5 mg of powder sample was used for TL measurement. All the TL measurements were carried out at room temperature.

3. Results and discussion

The X-ray diffraction patterns of prepared $BaAl_2O_4$ (Eu^{2+},Dy^{3+}) phosphor is shown in Fig. 1 (Top). The sharp peaks in the PXRD pattern suggest the formation of crystalline single phase compound. Some traces of $Ba(NO_3)_2$ were observed in XRD spectra, due to the low temperature synthesis route (Stefani et al., 2009). As in the combustion synthesis route, unequal distribution of heat occurs and due to which some amount of barium nitrate is left in the mixture without decomposition. The dominant diffraction peaks of PXRD patterns matches with the standard JCPDS file no. 82-1350 as shown in Fig. 1 (Bottom). The crystallite size of the prepared sample was estimated using Debye Scherer's formula, $D = 0.9\lambda/\beta \cos\theta$ where D is the average grain size of the