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Effect of swift heavy ion irradiation on structural, optical and luminescence properties of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} nanophosphor

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HIGHLIGHTS

- The effect of energy deposition in long persistent $SrAl_2O_4:Eu^{2+}$, Dy^{3+} nanophosphor have been discussed.
- The decrease in PL intensity after irradiation confirms the introduction of additional deep defect levels.
- The TL glow curve of the irradiated phosphors showed a broad band with intermediate kinetics.

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ABSTRACT

The effect of energy deposition by swift heavy ion (SHI) irradiation on the structural, optical and luminescence properties of the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} nanophosphor synthesized by a combustion method has been presented. The samples were irradiated with 120 MeV Ag^{9+} SHIs at fluences in the range of 1×10^{12} ions cm^{-2} to 1×10^{13} ions cm^{-2}. The X-ray diffraction results revealed that the obtained powder corresponds to the monoclinic-phase with space group $P2_1$ and the results also indicate that the SHI irradiation did not cause any change in the crystal structure of the phosphor. However, a decrease in the crystallinity was observed. Under 330 nm excitation, the PL emission spectra show a broad band centered at 516 nm which corresponds to the $4f^65d\rightarrow4f^7(^8S_{7/2})$ transition of the Eu^{2+} ion. The PL intensity of the phosphors was found to decrease with an increase in the ion fluences, which may be due to the enhancement in the non-radiative recombination via additional deep level traps introduced by the SHI irradiation. SHI irradiation enhanced the phosphorescence life time of the phosphors. After SHI irradiation, a blue shift in the diffuse reflectance spectra was observed. The thermoluminescent (TL) glow curve of the SHI irradiated phosphors showed a broadband with a shift in the peak position from 375 K to 391 K with an increase in the ion fluence. Also, the TL intensity has increased with an increase in the ion fluences.

1. Introduction

For the last few decades, Long Lasting Phosphors (LLPs) captured the attention of the research community because of their fundamental importance in day to day life. These phosphors had been widely used in applications such as decorative items, luminous watches, emergency passageway illumination, exit signs, traffic signs, low level lighting, military applications, and lighting equipment (Shionoya and Yen, 1999; Shankar et al., 2003). In addition, LLPs also depicts huge potential for applications such as fiber-optic thermometers, radiation detection and in energy saving devices (Aizawa et al., 2002; Kowatari et al., 2002). Formerly, Cu doped ZnS was the most widely used LLP which is very responsive to moisture and had quite short afterglow duration. Hence, rare earth ion-doped alkaline earth aluminate LLPs such as $SrAl_2O_4:Eu^{2+}$ and its derivatives had been developed due to its long duration phosphorescence characteristics and high quantum efficiency (Aizawa et al., 2011; Zhang et al., 2006; Smets et al., 1989; Mothudi et al., 2012; Ngaruiya et al., 2008). Matsuzawa et al. (1996), successfully synthesized $SrAl_2O_4:Eu^{2+}$, Dy^{3+} for the first time, which is one of the typical rare earth ions doping in alkaline earth aluminates. Subsequently, many researchers had worked on this long lasting strontium aluminate-based phosphor to increase its luminescence intensity and lifetime (Katsumata et al., 1998; Lu et al., 2004; Bartwal et al., 2010). The mechanism of afterglow is

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still not fully understood, however the afterglow process for LLPs is generally attributed to the thermal release of electrons and holes trapped in lattice defects (traps) and their recombination at the emission centers (Clabau et al., 2005, 2006).

Modifications in the luminescence properties of phosphors are recently the current area of investigation (Clarke et al., 1996). The important parameters of the phosphor used in display devices and solid state lighting such as brightness, resolution of color emission and optical parameters are clearly dependent on the factors such as chemical composition, defects, degree of structural disorder and the presence of dopants/impurities. Heavy ions moving with the Bohr velocity i.e. Swift Heavy Ion (SHI) is an efficient tool to tailored the above factors. SHI can modify the structural, morphological, optical, and transport properties of materials by high energy deposition in the material (Fukuoka et al., 2006; Leszek et al., 2004). Interaction of SHI with the phosphor material causes, electronic excitation or ionization in the materials which results in an increase in the temperature around the path of the ion beam. This hike in temperature generates a shock wave so called pressure wave which passes around the heat radially inside the target and results in reduced crystallinity or amorphization of the materials (Kamarou et al., 2008; Wesch et al., 2004). In case of insulators/phosphors SHI can modify the material properties by generating point defects, new color centers, reshuffling of the trapping/luminescent centers and creating stress and strain in the structure (Schwartz et al., 2008; Sattonnay et al., 2007; Kanagasekaran et al., 2008). Zang et al. reported the enhancement of afterglow in $SrAl_2O_4:Eu^{2+}$ with SHI (Zhan et al., 2012). However, no reports have been found in the literature on the SHI induced modification of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphor. By considering the above factors it is worthful to examine the radiation induced modification in the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphor as irradiation results in the creation and reshuffling of the color centers which may modify the luminescence properties of the phosphor. The second part of the work is to examine the thermoluminescence response of the phosphor against 120 MeV Ag^{9+} SHIs, for its application high dose radiation dosimetry, as luminescent nanomaterials have a potential application in dosimetry for the measurements of high doses as compared to conventional microcrystalline phosphor.

Therefore, in this investigation, an effort has been made to see the effect of energy deposition by SHI irradiation on the structural, optical and luminescence properties of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} nanophosphor synthesized by combustion method. The samples were irradiated with 120 MeV Ag^{9+} SHIs at fluences in the range of 1×10^{12} ions cm^{-2} to 1×10^{13} ions cm^{-2}. X-ray diffraction (XRD), diffuse reflectance (DR), thermoluminescence (TL) and photoluminescence (PL) studies of the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphors were carried out before and after irradiation, to determine the change in the structure and spectral properties of the phosphors. In addition, comparative TL analysis has been done for the 120 MeV Ag^{9+} ion and γ-rays of ^{60}Co irradiated for $SrAl_2O_4:Eu^{2+}$, Dy^{3+} nanophosphors.

2. Experimental details

2.1. Synthesis

$SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphors were synthesized by using the combustion method. Nitrates of analytical reagent grade purchased from MERCK Chemicals, i.e. strontium nitrate [$Sr(NO_3)_2$], aluminum nitrate [$Al(NO_3)_3$], europium nitrate [$Eu(NO_3)_3$] and dysprosium nitrate [$Dy(NO_3)_3$]; were used as the initial materials and urea (H_2NCONH_2) was utilized as fuel. In a typical formulation, the stoichiometric composition of the metal nitrate (oxidizer) and urea (fuel) was calculated (as per the balanced chemical equation) and were dissolved in a modest amount of distilled water with vigorous stirring until a thick paste was formed. The thick paste was moved into the crucible and was kept in a preheated muffle furnace at 550 °C. Initially the paste gets boiled followed by drying up and finally decomposed with the evolution of the great quantity of gases such as CO_2, N_2 and H_2O (Patil et al., 2008). The final foamy product was cooled to room temperature and were ground thoroughly using a pestle and mortar into a fine powder. The powder was annealed in air at 800 °C for crystallinity.

The balanced chemical equation for the $Sr_{1-x-y}Eu_xDy_yAl_2O_4$ is as follows:

$$(1-x-y)Sr(NO_3)_2+xEu(NO_3)_2+yDy(NO_3)_2+2Al(NO_3)_3+6.66H_2NCONH_2\rightarrow Sr_{1-x-y}Eu_xDy_yAl_2O_4+13.33H_2O+6.66CO_2+10.66N_2 \quad (1)$$

2.2. SHI irradiation

The samples were irradiated with 120 MeV Ag^{9+} SHI irradiation by using the 15UD pelletron facility available at Inter University Accelerator Center (IUAC), New Delhi. The samples were irradiated with fluences of 1×10^{12} ions cm^{-2}, 5×10^{12} ions cm^{-2} and 1×10^{13} ions cm^{-2}. "The Stopping and Range of Ions in Matter (SRIM)" computer program (Ziegler, 1984) was used to calculate the projectile range of the 120 MeV Ag^{9+} ions through the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphor pellets and were found to be in the micrometer range. The corresponding electronic stopping power and nuclear stopping power are 43.04 MeV/(mg/cm^2) and 0.19 MeV/(mg/cm^2), respectively. The powder samples of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} were pressed into pellets of 10 mm width and thickness less than the projectile range, so that the ions transferred its energy into the samples without residing inside it. The pellets were mounted on the rectangular ladder (sample holder) with six samples on each side. The ladder was then placed in the scattering chamber with a pressure of 10^{-6} Torr and the ladder could be rotated vertically or moved up and down to bring the samples into the path of the ion beam.

2.3. Characterization

The powder X-ray diffraction (PXRD) patterns of the long lasting $SrAl_2O_4:Eu^{2+}$,Dy^{3+} nanophosphors were recorded by a Bruker D8 Advance diffractometer, operating at 40 kV and 40 mA using Cu Kα radiation ($\lambda=1.5406$ Å) in the range of $20^{\circ}\le 2\theta\le 70^{\circ}$, to analyze the phase and crystallinity of the phosphors before and after SHI irradiation. The photoluminescence and life time measurements were recorded at room temperature on a Varian Cary-Eclipse spectrofluorometer equipped with a 150 W Xenon lamp as an excitation source. The Diffuse Reflectance Spectrum measurements were carried on a Shimadzu UV–vis-2600 double beam spectrophotometer equipped with ISR (Integrating Sphere Assembly) using Barium Sulfate as standard. HARSHAW QS 3500 TLD reader was used for TL measurements.

3. Results and discussion

3.1. Structural studies

The XRD patterns of the unirradiated and 120 MeV Ag^{9+} ion irradiated $SrAl_2O_4:Eu^{2+}$, Dy^{3+} nanophosphors along with the standard data file are shown in Fig. 1. All the XRD patterns match well with the JCPDS data file (No. 00-074-0794), which belongs to