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Optical properties of sol–gel derived Sr_2SiO_4:Dy^{3+} – Photo and thermally stimulated luminescence

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ABSTRACT

Trivalent dysprosium-doped strontium silicate (Sr_2SiO_4) phosphors were prepared by sol–gel synthesis using tetra ethyl orthosilicate (TEOS) as precursor. The synthesis temperature could be brought down to 600 °C for formation of a single phase sample. The material was characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), photoluminescence (PL), and thermally stimulated luminescence (TSL). The luminescence study revealed strong $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition at 577 nm (yellow), strong $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition at 482 nm (blue) and weak $^4F_{9/2} \rightarrow {}^6H_{11/2}$ transition at 677 nm (red), when excited by 250 nm (Charge transfer band, CTB) or 352 nm (f–f band). The concentration of the dopant ion and the temperature of annealing were optimized for maximum PL intensity. The critical energy-transfer distance for the Dy^{3+} ions was evaluated based on which, the quenching mechanism was verified to be a multipole–multipole interaction. The thermally stimulated luminescence studies of Sr_2SiO_4:Dy^{3+} sample showed main TSL glow peak at 413 K. The trap parameters namely activation energy (E), order of kinetics (b), and frequency factor (s) for this peak were determined using glow curve shape method.

1. Introduction

Rare earths (REs) doped inorganic systems have wide range of application in the field of display devices, lamp phosphors, white light generation, etc. [1–4]. In particular, the remarkable narrow-band emission properties of trivalent rare-earth (RE) ions have been utilized to the maximum extent in the development of efficient phosphors for lamps, plasma display panels, and light-emitting diodes (LEDs) [5–7]. These materials, when excited by a suitable wavelength, give high luminescence yield with desirable chromaticity. The photoluminescence (PL) observed in these materials are attributed to the f–f or f–d transitions of rare-earth ions and the intensity depends on the site symmetry and the nature of the host matrix. In general, Dy^{3+} exhibits three visible emission bands including the blue emission at 480 nm corresponding to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition, the yellow emission at 577 nm corresponding to the hypersensitive transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition ($\Delta J = 2$) and the feeble red emission at 670 nm corresponding to the transition $^4F_{9/2} \rightarrow {}^6H_{11/2}$ [4]. The hypersensitive transition of Dy^{3+} ion is easily influenced by microscopic environment; so the different ratios of yellow-to-blue (Y/B) can be obtained by selecting host materials.

Oxide-based hosts have received considerable attention for use in flat-panel displays due to their luminescent characteristics, stability in high vacuum, and the absence of corrosive gas emission under electron bombardment, as compared to currently used sulfide-based phosphors [8]. Therefore, oxide-based phosphors are likely to emerge as the choice for field emission diodes (FED) green or red phosphors. Among these, strontium silicate is an excellent matrix due its stable crystal structure, good mechanical strength and high thermal stability provided by the tetrahedral silicate $(SiO_4)^{2-}$ group [9]. Sr_2SiO_4 has attracted current interest due to its special structural features and potential application in developing white light-emitting-diodes (LEDs), because a GaN (400 nm chip) coated with Sr_2SiO_4:Eu^{2+} exhibits better luminous efficiency than that of industrially available products such as InGaN (460 nm chip) coated with YAG:Ce [10].

Deposition of energy in a material by ionizing radiation results in generation of charge carriers (electrons or holes) and subsequently they are trapped at vacancies and interstitials. These trapped charge carriers are localized in the lattice. Thermoluminescence (TL) is a powerful technique to study these charge carriers.

Sr_2SiO_4 has been prepared by several synthetic routes including conventional solid-state reaction [10]; liquid phase reaction [11] and microwave assisted sintering [12]. Few reports are also available on the sol–gel synthesis of strontium silicate [13–15]. The conventional solid state reaction route requiring temperatures in excess of 1400 K suffers from inhomogeneous and coarse sample formation with nonuniform size distribution. Large and non-uniform phosphor particles are more likely to be prone to poor adhesion to the substrate and loss of coating. For good luminescence

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characteristics, phosphors should have fine size, narrow size distribution, non-aggregation and spherical morphology. Similarly, several disadvantages have also been noted with other synthetic techniques such as the evaporation of solvents resulting in phase segregation, alteration of the stoichiometry due to incomplete precipitation, expensive chemicals and time consuming processes. This process provides molecular level of mixing, high degree of homogeneity and short reaction time which leads to reduction in crystallization temperature and prevents from segregation during heating. Most of the earlier luminescence reports on this ceramic host have been obtained with 'Eu^{3+}/Eu^{2+}' as the activator ion to yield 'red' or blue–green emission depending on the oxidation state of the rare earth [16–25]. Few groups have also reported on the luminescence of Dy^{3+} in Sr_2SiO_4 [26,27] and $SrSiO_3$ [28] mostly w.r.t white light generation. Nishioka and co-workers [29] have investigated effect of the Dy addition on the crystal structure and the luminescence properties of Sr_2SiO_4:Eu^{2+}.

In the present work, we have synthesized the alkaline earth silicate host doped with varying amounts of dysprosium ion via a sol–gel route. Effect of concentration and annealing temperature on luminescence was investigated. To the best of our knowledge, no report is available on the thermally stimulated luminescence of trivalent dysprosium in strontium silicate matrix.

2. Experimental

2.1. Sample preparation

The alkaline earth silicate samples were prepared via a sol–gel route using tetraethyl orthosilicate (TEOS) as a precursor. Detailed synthesis procedure is already reported in our previous work [18]. At first, hydrolysis reaction of TEOS (Sigma–Aldrich, Reagent Grade, 98%) and ethanol (Thomas Baker, Analytical Reagent, 99.4%) catalyzed by dilute nitric acid (Merck, Guaranteed reagent) was carried out. Appropriate quantity of strontium nitrate solution, prepared by dissolving strontium carbonate (SD fine-Chem Ltd, 99%) in dilute nitric acid, was added to the hydrolyzed solution drop wise with vigorous stirring at 60 °C. After 2 h of stirring the solution was allowed to cool and settle down. After a cooling period of about 2 h, a gel like compound was formed. This gel type mass was dried under infra red (IR) lamp for 1 h and then at room temperature (RT) so as to get a white crystalline solid. This solid mass was repeatedly washed with liquid ammonia (SD fine-Chem Ltd, 25% Extrapure) and quartz double distilled water to get a white mass. This mass was ground thoroughly in agate mortar pestle and heated at 400 °C for 4 h and at 600 °C for 2 h. The final product obtained was a free flowing white crystalline powder. For preparation of Dy doped sample, appropriate quantities of Dy $(NO_3)_3$ (Fluka, >98%) were added to the hydrolyzed TEOS solution.

Heating rate was kept 10 °C/min for each annealing step. All the annealing treatments were done on the as-formed sample (finally heated at 600 °C) at 700, 800 and 900 °C for 2 h. Amount of dysprosium studied is 0.1, 0.5, 1.0 and 2.0 mol%.

2.2. Instrumentation

The phase purity of the prepared phosphors was confirmed by X-ray diffraction (XRD). The measurements were carried out on a STOE X-ray diffractometer equipped with Ni filter, scintillation counter and graphite monochromator. The diffraction patterns were obtained using monochromatic Cu Kα radiation (λ = 1.5406 Å) keeping the scan rate at 1 s/step in the scattering angle range (2θ) of 10–60°. The $K_{\alpha 2}$ reflections were removed by a stripping procedure to obtain accurate lattice constants. To get an idea about the morphology, scanning electron microscope (SEM) studies were done on the as prepared phosphors. SEM was done on an instrument having both Everhart–Thornley secondary electron detector and solid state back scattered electron detector. The micrographs were taken at 20–30 kV acceleration voltages. TSL studies were carried with a home-built unit. Sr_2SiO_4:Dy^{3+} samples were irradiated in a ^{60}Co gamma source (dose rate 2.7 kGy/h) prior to TSL experiments. PL data were recorded on an Edinburgh CD-920 unit equipped with Xe flash lamp as the excitation source. The data acquisition and analysis were done by F-900 software provided by Edinburgh Analytical Instruments, UK.

3. Results and discussion

3.1. Structural analysis: XRD results

Strontium silicate exists in monoclinic (β-Sr_2SiO_4) phase at low temperatures and in orthorhombic (α'-Sr_2SiO_4) phase at high temperatures with a transition temperature of ~85 °C [30]. It has been reported that the crystal structures of α-Sr_2SiO_4 (orthorhombic), and β-Sr_2SiO_4 (monoclinic) are very similar. The XRD peaks are therefore also similar in the JCPDS cards of both phases and structures can co-exist [30,31]. The XRD patterns of the undoped and 0.1 mol% Dy doped strontium silicate sample calcined at 600 °C are shown in Fig. 1 from which it can be seen that all the diffraction peaks of both samples could be indexed to the orthorhombic phase of α'-Sr_2SiO_4 (JCPDS card No. 39-1256). Incorporation of dysprosium has not changed the XRD pattern which confirms that doping is proper has not distorted the structure of strontium silicate. Since no impurity peaks were observed, it is feasible to suggest that both samples are a single phase of α'- Sr_2SiO_4.

XRD data was indexed on an orthorhombic system with space group *Pnma* having cell parameters a = 7.08 Å, b = 5.67 Å and c = 9.74 Å as represented in Table 1. Grain size from X-ray line broadening is obtained from Scherer's formula.

$$B(2\theta) = \frac{0.94\lambda}{L\cos\theta} \tag{1}$$

where L is the crystallite size, λ is the wavelength (for Cu Kα, λ = 1.5418 Å) and $B = \sqrt{(B_M^2 - B_S^2)}$ (B_M is the full width at half maximum of the sample and B_S is that of a standard grain size of around 2 μm). One noteworthy point here is that, the synthesis of this alkaline earth silicate via the conventional solid state reaction route necessitates heating of the sample at temperatures in the range ~1200 °C for several hours [21]. However by sol–gel route, we could bring down the temperature required for formation of single phase

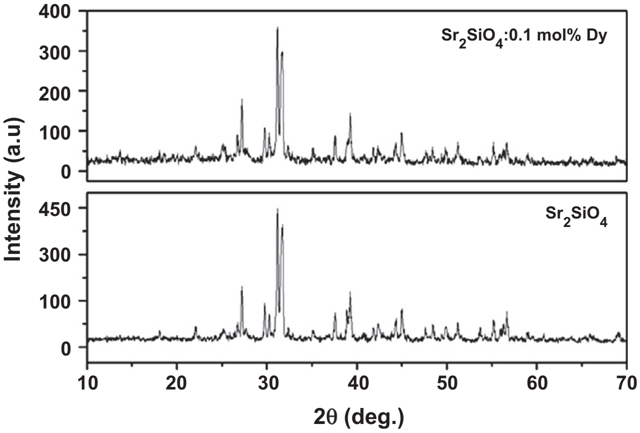

Fig. 1. XRD pattern of the undoped and 0.1 mol% dysprosium doped strontium silicate powder calcined at 600 °C.