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Spectroscopic and luminescence studies of thulium doped strontium borate glass

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ABSTRACT

Un-doped as well as Tm doped strontium borate glasses were prepared and characterized by different spectroscopic techniques. ^{11}B MAS-NMR studies on the glass samples have shown the presence of BO_3 structural units in addition to the tetrahedrally coordinated BO_4 structural units confirming glass formation. Optical absorption and photoluminescence studies of these samples showed stabilization of thulium as Tm^{3+} ions in the virgin sample, while, on γ-irradiation, partial reduction to Tm^{2+} was observed. EPR investigations of virgin and γ-irradiated samples showed the presence of BO_3^{2-} centered radicals in the latter samples only. TSL studies of γ-irradiated Tm doped strontium borate glass showed two glow peaks around 423 and 528 K. Tm^{3+} was identified as the luminescent center from spectral studies. Temperature dependence studies of EPR spectra have shown the thermal destruction of BO_3^{2-} radical ion to be associated with the TSL glow peak at 423 K. Based on these investigations, the mechanism for the processes occurring during γ-irradiation and subsequent thermal treatment is proposed.

1. Introduction

Research in the area of luminescent phosphors has always been very active and activities are directed towards development of new materials, synthesis processes and devise developments for application purpose. Rare-earth ions, like Ce^{3+} and Eu^{2+} have luminescence life-times in ns–μs range with broad emission whose wave-length position changes with host characteristics, while, other trivalent ions such as Eu^{3+}, Tb^{3+}, Dy^{3+}, Sm^{3+}, Tm^{3+} etc. have luminescence life-times in a few hundreds of μs–ms range with sharp emission almost insensitive to host matrix as regards wave-length position. Because of such widely varying properties, the materials containing rare-earth ions have application in fields as varied as illumination device, display devices, nuclear radiation measurements and monitoring, medical diagnostics and optical amplification. Optical properties of rare-earth ions in crystalline and glassy environments are still the subject of intense studies from application point of view [1–6] and also for fundamental understanding of the underlying process.

For commercial phosphors hosts based on borates, phosphates, aluminates, silicates, vanadates, etc. are generally exploited. In borate related phosphors, the boron atom has two types of hybridized orbitals, the planar sp^2 and the three-dimensional sp^3 in order to coordinate with three/four oxygen atoms, respectively, and leads to different co-ordination and environment for B_xO_y complex anionic groups. Rare earth doped borate materials have found application in Plasma Display Panels as red emitting phosphor ($(Y,Gd)BO_3$:Eu), UV emitting medical lamps (SrB_4O_7:Eu), as green-emitting phosphor in fluorescent lamps ($GdMgB_5O_{10}$:Ce, Tb) [7]. For dosimetric application, alkali borates (Li, K) and magnesium borates have been extensively investigated [8–13]. Strontium tetraborate, SrB_4O_7, has a unique structural framework consisting of a three-dimensional (B_4O_7) network of BO_4 tetrahedra, with Sr^{2+} cations participating in SrO_9 polyhedra [14–17]. In this host lattice, the lanthanide ions Eu^{3+}, Sm^{3+}, Yb^{3+} and Tm^{3+} can be reduced to their corresponding divalent states in air at high temperature without the introduction of reducing agents [15,16,18,19]. Luminescence investigations are reported for SrB_4O_7:Eu [20,21], while, thermally stimulated luminescence studies are reported for SrB_4O_7:Dy [22,23]. However, no detailed investigations are reported to understand mechanism involved in the thermally stimulated luminescence processes. Present work deals with the spectroscopic investigations of strontium borate glass doped with thulium ions to identify the oxidation state of the thulium ions and to understand the mechanism of the TSL process. X-ray diffraction (XRD), nuclear magnetic resonance (NMR) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) were used for the chemical characterization of the glass samples.

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2. Experimental procedures

Stoichiometric amounts of $SrCO_3$ (A.R. grade) and H_3BO_3 (G.R. grade) together with 3 mol% excess of H_3BO_3 (to compensate for B_2O_3 evaporation losses), were thoroughly mixed and ground. The samples were prepared via a two stage heating in air atmosphere using crystalline alumina crucible. In the first stage, the samples were heated at 875 K for 3 h and subsequently at 1150 K for 4 h after through mixing and grinding. A transparent glassy sample was obtained. Thulium doped samples were prepared in a similar manner using high purity Tm_2O_3. The concentration of Tm in the samples was varied between 0.5 and 2 mol%. The X-ray diffraction patterns were recorded to check the non-crystallinity of the glass sample using a Philip X-ray diffractometer with monochromatic Cu Kα radiation. The pattern (shown in Fig. 1) revealed broad humps characteristic of the amorphous materials and did not reveal any sharp peaks. The chemical compositions of the samples were obtained by emission spectrometric method using Inductively Coupled Plasma as an excitation source. Chemical analysis have shown that Sr and B are in the molar ratio of 1:4 indicating that strontium borate glasses have the composition $SrO{:}2B_2O_3$. Optical absorption studies were carried out using a JASCO-V 530 Spectrophotometer. Photoluminescence studies were carried out using an Edinburgh time resolved fluorescence spectrometer (F-900). For PL measurements, the glass samples were mounted on a holder kept at 45° to the incident beam. This resulted in most of the emission measurements being done from the front surface. ^{11}B magic angle spinning nuclear magnetic resonance (MAS-NMR) studies were carried out using a 300 MHz Bruker Avance DPX 300 machine with a basic frequency of 96.25 MHz. Samples were packed inside zirconia rotor and spun at 5 kHz. 90° pulse duration employed for ^{11}B NMR experiments was 2 μs, with a delay times of 3 s. With a view to find out the effect of 90° pulse duration on the ^{11}B NMR line shapes, experiments were carried out with pulse durations as low as 0.2 μs. However, it was observed that the line shapes were unaffected with variation in the pulse duration. ^{11}B MAS NMR patterns were simulated using the WINFIT program supplied by Bruker. All the ^{11}B NMR patterns were corrected for the boron nitride (BN) background arising from the Bruker MAS NMR probe. The chemical shift values are reported with respect to 1 M aqueous solution of H_3BO_3. The thermally stimulated luminescence studies (TSL) were carried out in the high temperature (300–700 K) region on a home built TSL unit coupled to a personal computer. A ^{60}Co source was used for gamma irradiation of the samples. Electron Paramagnetic Resonance (EPR) measurements were carried out on a Varian E-112 E-line Century series X-band EPR spectrometer. TCNE ($g = 2.00277$) was used as a standard for g-factor measurements. Step heat treatments were performed to follow the decay and evolution of the defect centers. These were carried out in situ in the EPR cavity using the Varian variable temperature accessory. PL, OAS, NMR, TSL and EPR studies were carried out on 1 mol% Tm doped samples, though for preliminary investigations 0.5 and 2 mol% Tm doped samples were also used.

3. Results

3.1. NMR Studies

^{11}B MAS-NMR patterns of Tm doped $SrO{:}2B_2O_3$ glass samples is shown in Fig. 2. The pattern consists of a sharp peak superimposed over a broad peak, which appears as shoulders symmetrically placed on either side of the sharp peak. Based on the previous ^{11}B MAS-NMR studies on boron containing glasses [24], the broad peak can be attributed to the trigonally coordinated BO_3 structural units and the sharp peak to the tetrahedrally coordinated BO_4 structural units. As ^{11}B is a quadrupolar nuclei ($I = 3/2$), due to the lack of cubic symmetry, boron nuclei in BO_3 structural units suffers from significant quadrupolar interaction resulting in a broad resonance peak. Unlike this, boron in BO_4 structural units, due to its highly symmetric cubic environment, has got negligible quadrupolar interaction and hence gives rise to a sharp peak. Based on the relative intensities of the broad and sharp peaks in the ^{11}B MAS NMR patterns, the ratio of BO_3 and BO_4 structural units present in the sample is found to be around 1:1. It is worthwhile to mention here that in most of the B_2O_3 containing glasses boron exists in both BO_3 and BO_4 structural units. Based on XRD and ^{11}B NMR results, it can be inferred that the prepared sample is glassy in nature.

3.2. Optical absorption studies

The optical absorption studies were carried using a Jasco-V 530 Spectrophotometer. The spectra recorded in 200–1100 nm region for 1 mol% Tm doped sample are shown in Fig. 3 as the plot of absorption coefficient versus wavelength. The sample of 1.25 mm

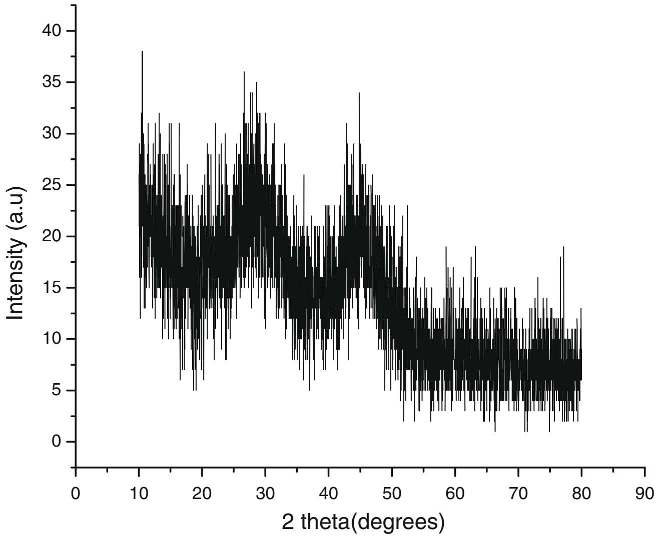

Fig. 1. X-ray diffraction pattern of $SrO{\cdot}2B_2O_3$ glass sample.

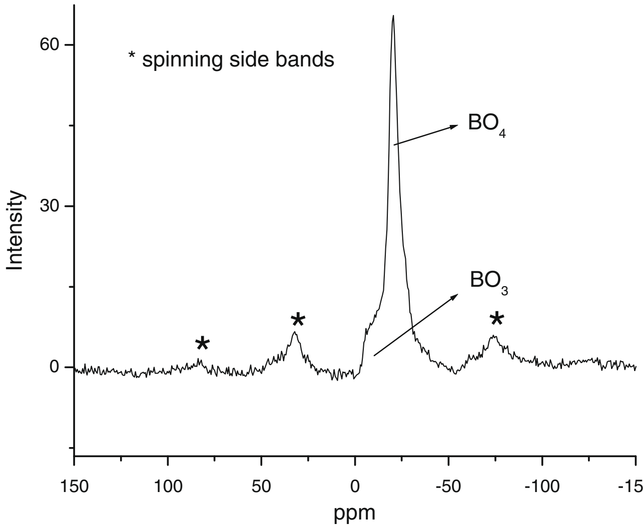

Fig. 2. NMR scan for strontium borate glass.