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Synthesis and spectral analysis of Sm:BaB_4O_7 microfibers embedded in borate glass

Y. Dwivedi [a,b,*], S.C. Zilio [a], S.B. Rai [c]

[a] Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970 São Carlos, SP, Brazil
[b] Physics Department, National Institute of Technology Kurukshetra, Kurukshetra, Haryana 136119, India
[c] Laser and Spectroscopy Laboratory, Physics Department, Banaras Hindu University, Varanasi, UP221005, India

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ABSTRACT

The present article reports synthesis and spectroscopic analysis of Sm:BaB_4O_7 microfibers embedded in borate glass. Structural analysis, using TEM, XRD techniques, revealed the formation of fibre shaped BaB_4O_7 crystals. A bright red dominated orange–red emission was observed, on 355 nm and 532 nm excitations, in ceramic sample. Higher emission and absorption higher cross-sections were observed in the ceramic sample than its glass counterpart. We have monitored 45% enhancement in emission intensity ratio ($^4G_{5/2}\rightarrow{}^6H_{9/2}/G_{5/2}\rightarrow{}^6H_{5/2}$) in glass–ceramic sample due to significant increment in electric dipole transition. Time resolved analysis explored a significant alteration in the excited state relaxation process due to annealing. Several radiative parameters like stimulated emission cross-section, branching ratio, quantum efficiency etc. were estimated to explore lasing possibility in glass and ceramic samples. We found that the quantum efficiency increases from 60.4% in glass to 62.7% in Sm:BaB_4O_7 microfibers embedded in glass.

1. Introduction

In the last two decades lanthanide (Ln) elements have extensively been studied not only due to their excellent magnetic properties but also due to exceptional optical properties. These properties opened new avenues of applications in various diverse fields e.g. biomedical, lasers, energy generation, telecommunications, display devices, sensors and so on [1]. Among Ln ions, the Sm^{3+} ion is one of the interesting ions to explore its emissive properties due to its possible applications in optical data storage in high-density memory, colour displays etc [2]. Another most exploited field of Sm doped materials is the lasing action. Sm:CaF_2 crystals [3] were reported to lase at ~708 nm while Sm plasma is being used as the active medium for saturated X-ray laser operating at wavelength <10 nm [4].

Several workers have investigated the spectroscopic properties of triply ionized Samarium ion and their energy levels are relatively well established in glasses [5–14]. Nonlinear optical properties of borosilicate glass containing Sm ion have been reported by Hussain et al. [11]. Jayasankar et al. has carried out detailed energy level calculations of Sm^{3+} ion in borosulphate glass [13]. Despite several reports of spectroscopic characterizations in different oxide glasses, detailed analysis in transparent glass–ceramic hosts were still not well discussed. Glass–ceramics are polycrystalline materials formed by controlled crystallization of specially formulated glasses. Glass–ceramic hosts are two phase systems consist of small crystallites embedded in the glass host. Segregation of doped Ln ion in crystallites may provide a lower phonon vibration field which improve absorption and subsequent emission characteristics. Glass ceramics contain generally a higher mechanical and chemical stability [15,16]. Especially, borate glass–ceramics are attractive due to their vast commercial applications in scintillators and tissue-equivalent materials for thermoluminescence (TL) dosimeters, γ and neutron detectors [17–19], and nonlinear optical ceramic properties [20,21]. Changmin et al. reported various optical properties of Sm^{3+} in fluoroborate ceramic [22]. Particularly, to grow a tetraborate single crystal is itself a complicated job due to complex, time consuming procedures. Keeping this view synthesizing tetraborate micro-crystallites in glass host may be an interesting perspective in comparison with their crystalline analogies.

In the present paper we have reported synthesis of fibre shaped Sm^{3+} doped BaB_4O_7 crystals specifically distributed on glass surface and explored various spectroscopic properties with different concentration and annealing time intervals. Stimulated emission cross-section, branching ratio, quantum efficiency etc. radiative parameters were estimated to explore lasing possibility.

* Corresponding author at: Physics Department, National Institute of Technology Kurukshetra, Kurukshetra, Haryana 136119, India. Tel./fax: +91 1744 233 503.
E-mail address: yashjidwivedi@gmail.com (Y. Dwivedi).

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2. Materials and measurements

The chemical compositions $(80-x)$ H_3BO_3+20 BaF_2+x Sm_2O_3 where $x=0$, 0.25, 0.75, 1, 1.25, 1.5 and 1.75 mol% were used to prepare barium borate glass. All regents (H_3BO_3, BaF_2, and Sm_2O_3) used was of high purity (~99.95%). Glasses were prepared using conventional melt and quench synthesis process, similar to the one described earlier [23]. Initially, precisely weighed ingredients were mixed together and annealed at 120 °C to remove moisture from powder. The well mixed starting materials were first melted at 900 °C in a platinum crucible for 30 min in an electric furnace. The molten mixture (free from air bubbles) was quenched by squeezing it into a rectangular steel cast preheated to 200 °C. The glasses were then gradually cooled to room temperature. The obtained glass samples were transparent and of good optical quality. The glass samples were cut and used without polishing for heating. However, the annealed sample was polished, to get a uniform thickness of 2 mm, before optical measurements. Glass ceramic was obtained by two steps thermal treatment of the 'as prepared' glass sample. Glasses were first annealed at 410 °C for 3 h and thereafter at fix 540 °C, near crystallization temperature ~575 °C [24], for different time durations of 8, 10, 15, 20 and 24 h while the heating rate was 15 °C/min. After annealing, tiny crystallites with the same stoichiometric composition of the as-prepared glass were precipitated inside samples. Samples annealed for >15 h gradually become translucent due to growth of larger crystalline size which effectively scattered ambient light and reduces transmittance. Hereafter, glass ceramic samples are referring as GC8, GC10, GC15, GC20 and GC24.

Powder X-ray diffraction (XRD) measurements were carried out using Cu, K_α radiation from a RINT/DMAX 2200H/PC (Rigaku, Japan) machine having a scan speed 2°/min. Data from International Centre for Diffraction Data (ICDD) sheet were used to identify the crystallized phases. Optical microscopy (OM) was performed with a Nikon™ Eclipse L150 microscope equipped with a Nikon™ Coolpix 4.0 MP digital camera. Thickness of the crystallized layer was estimated from a cross-sectional observation of the crystallized glass layer using the same microscope. SEM measurement was carried out on a JEOLTM Model JSM 5410 machine operated at 15 kV. High resolution transmission electron microscopy was carried out by means of a FEI Tecnai G_2F20 electron microscope.

Density of the samples was calculated by the Archimedes principle while using Hexane (density=0.655 g/cm^3 at room temperature) as an immersion liquid. Density of glass–ceramic samples was found to be 2.38, 2.39, 2.43, 2.47, and 2.50 g/cm^3 for GC8, GC10, GC15, GC20, and GC24 samples, respectively, which is higher than the as-prepared glass 2.36 g/cm^3. Refractive indices were determined by Brewster's angle method using red (632.9 nm) He:Ne lasers which were interference free from Sm^{3+} ion absorption peaks. The absorption spectra of the samples were recorded using Lambda 950 (Perkin Elmer, USA) in the range of 200–2300 nm. The luminescence spectra of the samples were recorded on excitation with 532 and 355 nm radiations from a Nd:YAG laser. An iHR320 monochromator equipped with a photomultiplier tube (model no. 1424M) was used to record the dispersed luminescence. The optical resolution of luminescence system was ~0.2 nm. Photoluminescence decay curves have been recorded using 355 nm pulsed radiation (50 mJ, ~10 Hz, pulse width ~7 ns) of Nd:YAG laser and 325 nm of He–Cd laser. The collected signal was fed to a 1 GHz digital oscilloscope and the decay curves were obtained for further analysis. Lifetimes of the radiative levels were estimated by fitting as exponential function to the recorded curves.

3. Results and discussion

3.1. Structural characterizations

Prepared glass samples were undergone through heat treatment at fix temperature (540 °C) for different time durations. Due to annealing, near crystallization temperature, structural relaxation occurs to achieve most stable microstructures. We analyses evolution of microstructure at different growth stages using a Confocal microscope. Samples heated for >15 h became translucent and on further annealing it converted glasses of milky white colour and opaque. Microstructure precipitate for GC15 clearly shows the crystallization preferably occurs near the surface [Fig. 1 (A)]. We measure thickness of crystallized layer ~0.2 mm however it increased to ~0.5 mm in case of GC24. It has been reported that the crystallization of glasses containing BaO and B_2O_3 preferably favour surface crystallization, and in some cases only the BaB_4O_7 crystals were nucleated [25]. In case of non-stoichiometry glass phase with respect to crystal, surface crystallization preferably takes place near the glass surface since nucleation at the surface of the glasses occurs more easily than inside the matrix. Scanning electron microscope image of the crystallized layer shows inhomogeneously distributed, dense stacks of long fibrous and lamellar microstructures with length >20 μm and uniform diameter ~0.28 μm [Fig. 1].

We also monitor transmission electron microscope images of crushed GC15 sample [see Fig. 2]. Image reveals formation of tiny

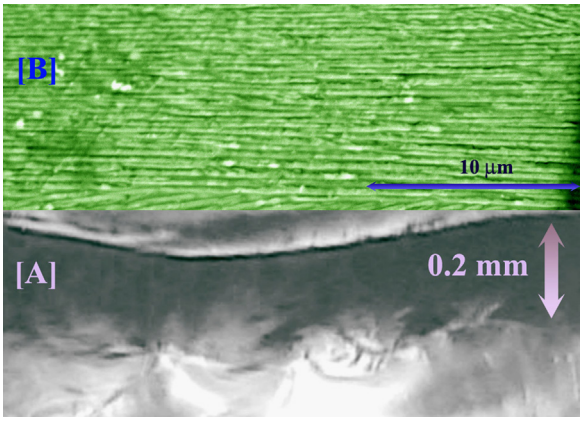

Fig. 1. Optical microscope image of unpolished glass–ceramic GC15 (A) and scanning electron microscope image (B) of the same glass.

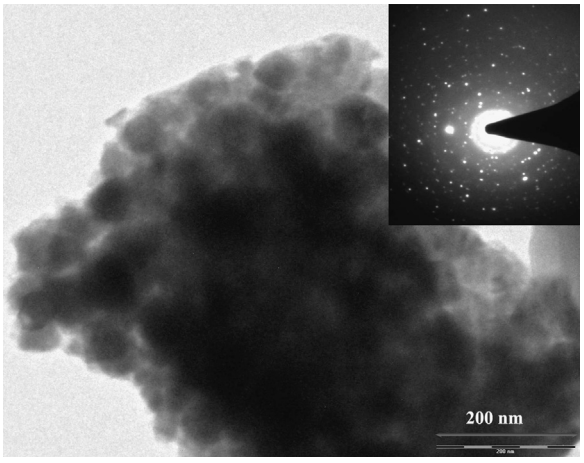

Fig. 2. Transmission electron microscope image of GC15 and diffraction pattern (inset).