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Antimony oxide based glasses, novel laser materials

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ABSTRACT

Glasses based on Sb_2O_3 make one of the major classes of heavy metal oxide glasses. This paper concerns two antimonite glasses, $88Sb_2O_3$-$10Na_2O$-$2Bi_2O_3$ (SNB2) and $60Sb_2O_3$-$20WO_3$-$19Na_2O$-$1Bi_2O_3$ (SWNB1), doped with 0.25 mol% Er_2O_3. Bulk samples have been prepared and their absorption and fluorescence spectra have been recorded. Differential scanning calorimeter (DSC) measurements emphasize a thermal stability range $\Delta T > 100$ °C that expresses a good stability against devitrification. Both FTIR and Raman spectra provide information on the structural organization of the glasses. The maximum phonon energies are 700 cm^{-1} and 920 cm^{-1} for SNB2 and SWNB1 glasses, respectively. The spectroscopic analysis of the absorption and emission properties of the Er^{3+} ions in the SNB2 and SWNB1 glasses has been performed. The Judd-Ofelt theory has been applied to interpret the local environment of the Er^{3+} ion site and covalency of the Er–O bond, but also to determine the radiative lifetime (τ_r) for $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission transition. The emission cross-sections for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition (1528 nm) were calculated using McCumber and Füchtbauer-Ladenburg theories. We discuss the potential application of these glasses.

1. Introduction

The demand of suitable glass compositions for optical applications in the near infrared spectral range is in continuous increase. Among substances that produce lasing, optical materials (glasses) doped with rare earth (RE) represent an important group, characterized by a high concentration of active atoms. Glasses based on antimony oxide make one of the major classes of heavy metal oxide glasses. The glasses based on Sb_2O_3 are good candidates, by their proprieties as a good stability against devitrification, and high refractive index ($\geq$2). Antimonite glasses possess low phonon energy [1] which is of interest when combined with other oxides to expand the transparency window up to 6 μm in the infrared. Recently, the glasses of antimony oxide have been the subject of several studies [1–11]. Antimony oxide based glasses have potential for the field of optical amplification in telecommunication C-band (1530–1560 nm) [1,2].

Erbium doped fibers amplifiers (EDFA) are the first to be developed industrially overwhelmingly, in the early 1990's. This special attention given to the erbium ions due to the its emission band at 1.53 μm, which makes it an ideal component for applications in the field of optical data transmission. In a previous papers [1,2] we reported on the spectroscopic properties of erbium doped antimony oxide based glasses. The lifetime of the initial level $^4I_{13/2}$ of the laser transition is about 2.8 m in our glasses, and the maximum cross section of 10×10^{-21} cm^2. These two values provide a significant gain to erbium doped fibers. Although it is possible to pump Er in the $^4I_{11/2}$ manifold at 980 nm laser excitation. In other publications this study was extended to other glasses containing a wide variety of different network modifying ions [12–18].

The aim of this work is to compare the spectroscopic properties of the infrared $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission of Er^{3+} ions in a SNB2 and SWNB1 glasses. The phenomenological intensity parameters Ω_i

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(i = 2, 4, 6) were determined by using the Judd-Ofelt theory, indicate the effect of glass composition. One of the important factors required for optimizing the host material is the cross section for stimulated emission at the laser wavelength. So, the 1.53 μm fluorescence has been observed. We conclude that Er^{3+}-doped SNB2 and SWNB1 are suitable materials in developing infrared laser.

2. Experimental

2.1. Sample preparation

Glasses with chemical composition of (mol%) $88Sb_2O_3$-$10Na_2O$-$2Bi_2O_3$, and $60Sb_2O_3$-$20WO_3$-$19Na_2O$-$1Bi_2O_3$ (referred to as SNB2 and SWNB1, respectively). The starting materials used in the preparation of these glasses are commercial powders of Sb_2O_3 (99+%), ACROS ORGANICS, sodium carbonate (99.8min), Bi_2O_3 (99% Alfa Aesar), Bi_2O_4 Prolabo WWR brand, and Er_2O_3 (99.9% Sigma Aldrich). Two samples doped with 0.25 mol% Er_2O_3 corresponding to the composition SNB2 and SWNB1 were synthetized. After weighing and mixing, batches of 6 g in weight were melted in silica crucibles at a temperature close to 800 °C, for 10–15 min in air. During the synthesis, the tube was shaken to homogenize the melt, while a release of CO_2 was observed, due to the decomposition of sodium carbonate. Vitreous samples were obtained by pouring the melt onto brass molds. This processing corresponds to a moderate quenching rate (<40 K/s), followed by annealing at 300 °C and slow cooling down to room temperature. Polishing was implemented after annealing to obtain samples of shape, thickness and surface quality suitable for optical measurements.

All glass samples are transparent and yellow colored. Characteristic temperatures are measured by the differential scanning calorimeter (DSC) using TA Instruments DSCQ20, with a heating rate of 10 °C/min in the temperature range of 25–500 °C. The estimated error is 2 K for glass transition T_g. Fourier Transform InfraRed (FTIR) measurements of the glass samples were recorded on a Perkin-Elmer FTIR spectrometer with KBr pellet technique from 4000 cm^{-1} to 400 cm^{-1}. Raman spectra of the glass samples were recorded on a Bruker 'SENTERRA' Raman spectrometer, using a diode laser in the near infrared range (NIR) at the wavelength 785 nm with a power of 50 mW, and an exposure time of 30 s.

2.2. Optical measurements

Density was measured by the Archimedes method with water as the immersion liquid. The absorption spectra of the samples were measured by a Perkin Elmer UV-VIS-NIR spectrometer operating between 200 and 3000 nm, with a slit of 1 nm resolution. Photoluminescence (PL) spectra were recorded in the near-infrared (NIR) range between 1400 and 1700 nm, under 980 nm laser excitation from a Ti-sapphire laser. The emission spectra were measured with a CCD iDus near-infrared InGaAs camera from Andor Technology equipped with a 300 line/mm grating blazed at 1000 nm. Decay curves at the peak of the emission spectrum were recorded using 8 ns pulsed laser excitation at 980 nm. This excitation was performed with an NT342 optical parametric oscillator pumped with a pulsed frequency-tripled Nd:YAG laser from Ekspla. The sample luminescence was focused on a cooled InGaAs detector. Judson InGaAs Detector Model J23-18I-R01M-2.2, P/N 435008 has a fast time response, the HWHM (halfwidth at half maximum) of the response to the pulsed nanoseconds laser is about 110 ns? A 1300 nm long pass filter was mounted on the detector to select the luminescence of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of erbium ions. The luminescence decays were recorded by a Lecroy digital oscilloscope.

3. Results and discussion

3.1. Thermal properties

DSC curves for SNB2 and SWNB1 glasses are shown in Fig. 1. The values of the glass transition temperature, T_g, are 271 °C and 312 °C for SNB2 and SWNB1 glasses, respectively. DSC curves emphasize a thermal stability range $\Delta T > 100$ °C that expresses a good stability against devitrification [1]. Thermal analysis shows that the addition of Bi_2O_3 and WO_3 to alkali antimonate glasses increases Tg, this results is agree with others reported in Refs. [1,19]. Tg changes, which suggests a structural evolution.

Once synthesized glasses, it is imperative that they are thermally stable so that they can be exploited, i.e. that $\Delta T = T_x - T_g$ must be superior to 120 °C. This was done in this work.

3.2. FTIR and Raman spectra

The local structure of antimony oxide based glasses was evidenced by FT-IR and Raman spectroscopic techniques.

The IR spectra of SNB2 and SWNB1 glasses are shown in Fig. 2, where three spectral bands centered around 486 cm^{-1} is observed, 604 cm^{-1}, 938 cm^{-1}, and a fourth located on the shoulder of the infrared spectrum centered at 736 cm^{-1}. One can conclude that these bands observed can be attributed to fundamental vibrations bands of pyramidal unit SbO_3 [1]; except the band 938 cm^{-1} which may be due to the vibrations of Si–O bond stretching in SiO_4 tetrahedra [20] which are present in the glass due to contamination of the silica crucible during the synthesis. The peak at 824 cm^{-1} in the red curve of SWNB1 is attributed to stretching vibrations of W-O single bonds or double bonds W=O structural units WO_4 and WO_6, respectively. The addition of WO_3 in the antimony glasses (Sb_2O_3) breaks the network structure formed by SbO_3 units in these compositions, as evidenced by the appearance of structural entities WO_4 and WO_6. This result is consistent with the increase in the glass transition temperature T_g.

To study the evolution of the glass structure with addition of WO_3, Raman measurements were performed on glass samples. Fig. 3 shows the Raman spectrum for SWNB1 glass, which was detected in 50–1520 cm^{-1} frequency region. Several absorption bands are observed. In the antimony glass, there are three distinct modes of vibration of trigonal pyramidal (tp) SbO_3 structural units giving birth to three broad Raman bands are diffuse, and are located

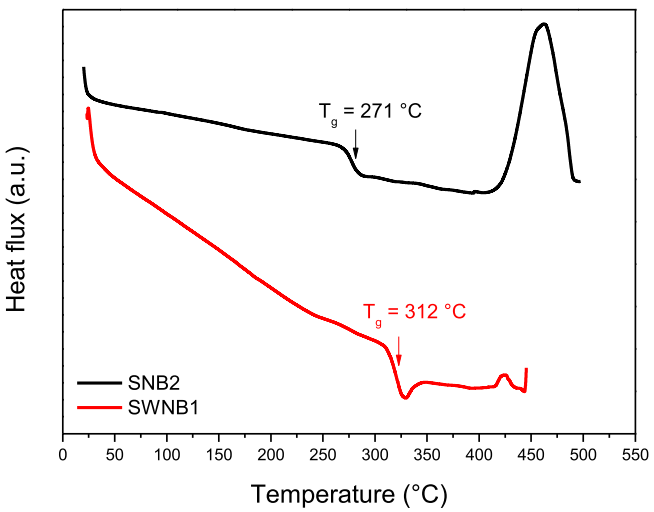

Fig. 1. DSC curves for the SNB2 and SWNB1 glasses (heating rate 10 °C/min).

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