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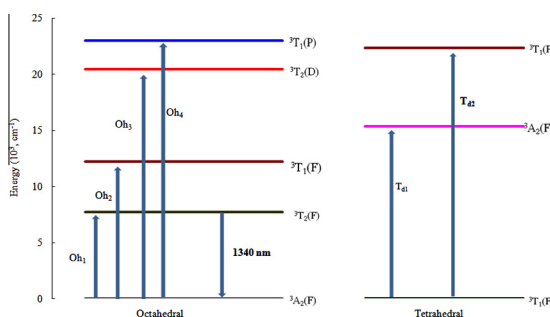
Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saaSpectroscopic features of Ni²⁺ ion in PbO–Bi₂O₃–SiO₂ glass systemB. Suresh^a, M. Srinivasa Reddy^{a,*}, A. Siva Sesha Reddy^c, Y. Gandhi^b, V. Ravi Kumar^c, N. Veeraiah^c^a Department of Physics, Univ. College of Engg and Technology, Acharya Nagarjuna University, Nagarjuna Nagar 522510, A.P., India^b Department of Physics, Kakani Venkata Ratnam College, Nandigama 521185, A.P., India^c Department of Physics, Acharya Nagarjuna University, Nagarjuna Nagar 522510, A.P., India

HIGHLIGHTS

- PbO–Bi₂O₃–SiO₂: xNiO glasses were synthesized.
- IR, Raman optical absorption and luminescence studies have been carried out.
- Analysis of the results indicated that Ni ions occupy octa and tetrahedral positions.
- The photoluminescence (PL) efficiency found to be the highest for the glass N₁₀.
- The reasons for high PL efficiency were analyzed in the light of structural changes.

GRAPHICAL ABSTRACT

Energy level diagram involving absorption and emission transitions of Ni²⁺ ion in the glass N₈.

ARTICLE INFO

Article history:

Received 4 September 2014

Received in revised form 10 January 2015

Accepted 23 January 2015

Available online 2 February 2015

Keywords:

Bismuth silicate glasses

Nickel ions

Spectroscopic studies

ABSTRACT

Glasses of the composition (30-x)PbO–5Bi₂O₃–65SiO₂: xNiO (with x ranging from 0 to 1.0 mol%) were synthesized. A variety of spectroscopic studies, viz., IR, Raman optical absorption and luminescence properties of these glasses have been carried out as a function of NiO concentration. The analysis of results of all these studies has indicated that the nickel ions occupy both octahedral and tetrahedral positions. However, with the increase of NiO concentration the octahedral occupancy of Ni²⁺ ions prevailed over the tetrahedral ions. The luminescence spectra of these glasses have exhibited a broad NIR emission band in region 1100–1500 nm. This band is identified as being due to ³T₂(3F) → ³A₂(3F) octahedral transition of Ni²⁺ ions. The luminescence efficiency and cross section have been found to be the highest for the glass containing the highest concentration of NiO. The reasons for such high luminescence efficiency have been discussed in the light of structural variations taking place in the host glass network.

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Introduction

Heavy-metal oxide glasses and glass ceramics with nonconventional network formers like Bi₂O₃ have received a remarkable attention due to their wide applications e.g., as layers for optical and opto-electronic devices, thermal and mechanical sensors, reflecting windows, etc. [1–5]. With their excellent optical

properties, these glasses are promising candidates for ultra fast optical switches, infrared transmission components and other photonic devices. Because of the small field strength of Bi³⁺ ions, bismuth oxide cannot form glass by itself like other traditional glass formers; however, it participates in the glass formation in the presence of conventional glass formers viz. B₂O₃, SiO₂ and P₂O₅ with BiO₃ pyramidal units and BiO₆ octahedral units [5,6].

Silicate glasses are known due to their excellent physical properties and high chemical resistance [7,8]. The normal silicate glasses are compound glasses which contain other oxides (alkali

* Corresponding author. Tel.: +91 9866612004.

E-mail address: msreddy81@rediffmail.com (M. Srinivasa Reddy).

metal oxides, alkali earth metal oxides, or glass-forming oxides, e.g., B_2O_3 , P_2O_5 , Al_2O_3 , but have SiO_2 as the main component [9]. However, the relatively large phonon energy (about 1200 cm^{-1}) and low refractive index (about 1.5) of the silicate matrix result in high nonradiative transition rate and short luminescence lifetime, which are harmful to population inversion and laser output [10,11]. Introducing Bi_2O_3 into normal silicate glass leads to lower phonon energy, larger refractive index, longer emission lifetime and better gain property and as a result a better $2.0\text{ }\mu\text{m}$ emission. Besides, the addition of Bi_2O_3 to main silicate glasses causes to decrease melting temperature to a larger extent.

Bismuth silicate glasses are of great importance for their industrial and special applications as low-loss fiber optics, infrared transmitting materials or as active medium of Raman fiber optical amplifiers and oscillators [12–14]. The large polarizability and small field strength of Bi^{3+} in oxide glasses the Bi_2O_3 mixed silicate glasses are suitable for optical devices such as ultra fast all optical switches, optical isolators, optical Kerr shutters (OKR) and environmental guidelines [15].

Bismuth containing glasses are also often compared with lead glasses [16]. The Bi^{3+} and Pb^{2+} ions are the group of ions with lone pair electron configurations. They have two electrons outside a closed shell which promotes pyramidal bonding [17]. The pyramidal geometry possesses a dipole moment which may result in spontaneous polarization [18,19].

PbO containing glasses are technologically important and are potential candidates for making ultra low loss wave guides, glass-to-metal seals, infrared transmitting devices and optical gratings [20,21]. One of the advantages of addition of PbO to the silicate glass systems is that it resists the crystallization since it participates in the glass network form with $[PbO_4]$ structural units and play the role of an intermediate due to its own ionic field strength [22,23]. The lead ions may also act as modifiers and participate in the glass network with PbO_6 structural units.

There has been an increasing demand for the development of materials suitable for ultra broadband optical amplifiers to revolutionize telecommunication systems. Although rare earth ion-doped glasses were considered as suitable candidates for such applications, the optical amplification bandwidth in these materials is narrowed, due to the fact that the emission bands of the 4f–4f transition of the rare earth ions are very narrow. One possible way to get high-gain optical amplification with larger bandwidths in the visible region is by introducing Cr^{4+} ions in the glass matrices; nevertheless, the chromium ions exist in multivalent states, i.e. in Cr^{3+} , Cr^{4+} , Cr^{5+} and Cr^{6+} states in the glass network simultaneously [24,25]. Hence, it is too difficult to achieve strict control over the required or suitable valence state of these ions embedded in glasses and glass ceramics. Unlike these ions, nickel ions mostly exist in the divalent state and are extremely stable and there is no need for special care in experimentation in retaining nickel ions in the divalent state. There have been hardly any reports so far about reduction or oxidation of Ni^{2+} ions to lower or higher oxidation states in glasses. Further, Ni^{2+} is an ion with exceptionally large crystal stabilization energies particularly when it is in an octahedral field [26]. Ni^{2+} ions exhibit several strong absorption bands in the visible and near-infrared (NIR) regions where pumping sources are easily available. The octahedrally positioned Ni^{2+} ions in glass networks are expected to exhibit eye-safe laser emission of wavelength about $1.5\text{ }\mu\text{m}$ due to the ${}^3T_2 \rightarrow {}^3A_2$ transition, even at room temperature, which is of great importance in telecommunications [27]. There exist a considerable number of recent studies on the lasing action of nickel ions in various glass and glass–ceramic materials [28,29] including bismuth and silicate based glasses in the literature [30–33]. But the spectral characteristics of Ni ions in high dense and interesting glass systems like $PbO-Bi_2O_3-SiO_2$ glasses are rare. Thus the aim of this paper is to explore the

environment of Ni^{2+} in the $PbO-Bi_2O_3-SiO_2$ glass network by means of spectroscopic properties and to throw some light on the possible use of these glasses in broad band optical amplifiers and for laser emission in NIR region.

Experimental

For the present study, particular compositions $(30-x)PbO-5Bi_2O_3-65SiO_2: xNiO$ (x ranging from 0 to 1.0 in steps of 0.2) were chosen. The details of the compositions are:

N_0 : $30PbO - 5Bi_2O_3 - 65SiO_2$

N_2 : $29.8PbO - 5Bi_2O_3 - 65SiO_2 : 0.2NiO$

N_4 : $29.6PbO - 5Bi_2O_3 - 65SiO_2 : 0.4NiO$

N_6 : $29.4PbO - 5Bi_2O_3 - 65SiO_2 : 0.6NiO$

N_8 : $29.2PbO - 5Bi_2O_3 - 65SiO_2 : 0.8NiO$

N_{10} : $29.0PbO - 5Bi_2O_3 - 65SiO_2 : 1.0NiO$

Analytical-grade reagents of SiO_2 , PbO , Bi_2O_3 and NiO powders in appropriate amounts (all in mol%) were thoroughly mixed in an agate mortar and melted using a thick-walled platinum crucible at $1300 \pm 10\text{ }^\circ\text{C}$ in a PID temperature-controlled furnace for about 30 min. The resultant bubble-free melt was then poured in a brass mold and subsequently annealed at $450\text{ }^\circ\text{C}$ with a cooling rate of $1\text{ }^\circ\text{C}/\text{min}$. The samples prepared were free from visible inhomogeneities, such as inclusions, cracks or bubbles. Differential thermal analysis (DTA) was carried out in the temperature range $30-1300\text{ }^\circ\text{C}$ using Netzsch Simultaneous DSC/TG Thermal Analyzer (STA409C) with 32-bit controller to determine the glass transition temperature. The heating rate was maintained as $10\text{ }^\circ\text{C}/\text{min}$ and the values of T_g (glass transition temperature) and T_c (crystallization temperature) are evaluated to an accuracy of $\pm 1.0\text{ }^\circ\text{C}$. The density d of the glass was measured to an accuracy of $\pm 0.0001\text{ g}$ by the standard principle of Archimedes using *o*-xylene (99.99% pure) as the buoyant liquid with an Ohaus balance (model AR 2140). The mass of the samples was measured to an accuracy of 0.1 mg using this balance. The refractive index n_d of the glasses was measured (at $\lambda = 589.3\text{ nm}$) using Abbe refractometer with monobromo naphthalene as the contact layer between the glass and the refractometer prism to an accuracy of ± 0.001 . Infrared transmission spectra were recorded on a JASCO-FT/IR-5300 spectrophotometer to a resolution of 0.1 cm^{-1} in the spectral range $400-2000\text{ cm}^{-1}$ using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). These pellets were pressed in a vacuum die at $\sim 680\text{ MPa}$. The Raman spectra were recorded with NIR excitation line (1064 nm) using a Bio-Rad spectrometer FTS 175 C equipped with an FT Raman supplementary accessory working in a back-scattering geometry system to an accuracy of 0.1 cm^{-1} . The methods adopted for recording optical absorption and luminescence spectra were similar to those reported in our earlier papers [34,35].

Results

The physical parameters such as nickel ion concentration N_i , mean nickel ion separation R_i , molar volume (V_M) were evaluated from the measured values of density d and calculated average molecular weight M using the conventional formulae [36] and are presented in Table 1. DTA scans recorded for $PbO-Bi_2O_3-SiO_2$ glasses doped with different concentrations of NiO are shown in Fig. 1. All the traces exhibited typical glass transition with the inflection point between 560 and $584\text{ }^\circ\text{C}$; with the growing content

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