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Spectroscopic and dielectric investigations on the role of molybdenum ions in lead niobium germanosilicate glasses

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ABSTRACT

Glasses having composition $30PbO–2Nb_2O_5–10GeO_2–(58\text{-}x)SiO_2–xMoO_3$ (where x = 0 to 1 mol%) were prepared by melt quenching technique and characterized. Spectroscopic and dielectric studies are carried out in order to obtain information about the structural disorder of the prepared glasses. The results of the optical absorption, EPR, FTIR and Raman data are analyzed and discussed in view of the glass network structural changes determined by the evolution of molybdenum ions state. These spectroscopic studies have indicated that with increasing the concentration of MoO_3 content a fraction of Mo^{6+} ions convert into Mo^{5+} ions. Accordingly, the formation of square pyramidal structural units having C_{4v} symmetry with Mo═O bond is found to increase. Such modifications cause the structural disorder and depolymerization in the host glass network. Further, the variation of dielectric parameters with temperature has also indicated that the molybdenum ions do exist in Mo^{5+} state with $Mo(V)O^{3-}$ complexes that act as modifiers in these glasses. The analysis of spectroscopic and dielectric studies revealed that the lead niobium germanosilicate glasses doped with MoO_3 exhibiting semiconducting nature and are useful in the electronic devices.

1. Introduction

Germanosilicate glasses are composed of two network-former oxides, have acquired increasing interest and active research because of their potential applications, covering a large variety of fields, such as mechanical, civil, aerospace, electron irradiation and biomedical engineering applications [1]. They are photosensitive to ultraviolet radiation, which allows for photo-induced refractive index modulations in the material [2]. But the difficulty which arises in the preparation of these glasses is their chemical homogeneity due to the high viscous and poor reactivity of these melts [3].

It was anticipated that the addition of a heavy metal oxide PbO will overcome the difficulty in the preparation of germanosilicate glasses since, up to nearly 70 mol% of lead can be incorporated in the glass network of both SiO_2 and GeO_2 [4,5]. The dual role played by PbO as a network former as well as a network modifier with different structural units (PbO_3, PbO_4, PbO_5 and PbO_6) is quite interesting. Besides this the anomaly of germanium is more pronounced in lead based germanate glasses in contrast with conventional alkali/alkaline earth oxides mixed germanate glasses [6]. Addition of this metal oxide such as PbO to the germanosilicate glasses, it was found that a great increase of radiation-induced attenuation (RIA) which is suitable for radiation dosimeter application [7].

Nb_2O_5 is a promising cathodic electrochromic material potentially useful for device application such as smart windows, electronic displays and electro-optic devices because of its excellent chemical stability and corrosion resistance. In addition Nb_2O_5 is one of the first materials in which resistive switching effect has been observed [8]. Keeping in view of the potential applications of Nb_2O_5, we have reported [9] earlier the spectroscopic and dielectric properties of Nb_2O_5 doped lead germanosilicate glasses. From the quantitative analysis of these studies, it was established that 2 mol% of Nb_2O_5 doped lead germanosilicate glasses exhibit more conducting nature.

In some of the investigations reported previously it was observed that, glasses doped with transition metal oxides also exhibit semi conducting nature [10]. For such semiconducting behavior of oxide glasses it is necessary that the transition metal ions present should be capable of existing in more than one valance state, so that conduction can take place by the transfer of electron from lower to higher valance state. MoO_3 is one among such transition metal oxide in which molybdenum ions exists in different valance states viz., Mo^{6+}, Mo^{5+}, Mo^{4+} and Mo^{3+}. Among these the electronic conduction can take place by a transfer of electron from Mo^{5+} to Mo^{6+} ions [11]. But in the presence of PbO, molybdenum ions mainly exist in two valance states viz., Mo^{6+} and Mo^{5+} with different structural units like MoO_4 and MoO_6. These lead molybdenum glasses possess a variety of specific features and potential candidates for applications as amorphous semiconductors, waste storage, infrared transmission components, thermal and mechanical sensors, reflecting windows, acousto-optical materials,

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modulator, ion conductors, scintillators in nuclear instruments [10]. Keeping in view of the potential applications, in the present investigations multi-component lead niobium germanosilicate glasses doped with different concentrations of MoO_3 are synthesized. This paper aims to present the influence of molybdenum ions on the local structural disorders in lead niobium germanosilicate glasses by means of spectroscopic and dielectric investigations.

2. Experimental

The glass composition with $30PbO–2Nb_2O_5–10GeO_2–(58\text{-}x)\ SiO_2–x\ MoO_3$ (mol %) ($0 \le x \le 1$) is chosen for the present study. The samples are prepared by a conventional melt-quenching method. The detailed compositions of the glasses together with their nomenclature used in the present study are as follows:

M_0: $30PbO–2Nb_2O_5–10GeO_2–58SiO_2$

M_1: $30PbO–2Nb_2O_5–10GeO_2–57.8SiO_2–0.2MoO_3$
M_2: $30PbO–2Nb_2O_5–10GeO_2–57.6SiO_2–0.4MoO_3$
M_3: $30PbO–2Nb_2O_5–10GeO_2–57.4SiO_2–0.6MoO_3$
M_4: $30PbO–2Nb_2O_5–10GeO_2–57.2SiO_2–0.8MoO_3$
M_5: $30PbO–2Nb_2O_5–10GeO_2–57.0SiO_2–1.0MoO_3$.

The raw materials are analytical reagents of amorphous SiO_2, GeO_2, Nb_2O_5 (Sigma Aldrich 99.99% pure) and PbO, MoO_3 (LOBA). The amount of batch was calculated in order to yield 15 g of final product. The starting materials were weighed using a digital balance (VIBRAHT with an accuracy of ±0.001 g) carefully and thoroughly mixed in an agate mortar for 40 min and transferred into a 25 ml silica crucible (Infusil make) subsequently it is heated at 1400 °C (in air) for 10 min in a PID temperature-controlled furnace until bubble-free liquid was formed. The resultant melt was swirled to ensure the homogeneity and then poured on a pre heated brass mould and subsequently annealed at 400 °C to remove the internal stresses etc., the resultant flakes of translucent glasses were formed with a change in color from yellow-gold to dark brown.

The density, ρ of the glasses is determined with an accuracy ±0.001 g/cm^3 by the standard principle of Archimedes using *O*-xylene (99.99% pure) as the buoyant liquid with a programmable VIBRAHT density measurement kit. X-ray diffraction patterns of the samples are obtained using Philips X'pert system using the step scan method with CuK_α radiation ($\lambda = 1.5406$ Å), a step size of 0.04 Å and a collection time of 2 s per point over 2θ range, 10–100^0. For the optical absorption spectra of the glasses, samples were cut successively with a diamond wheel then the two faces were grounded and polished with cerium oxide slurries. The final thickness of polished samples was 1 mm. Optical absorption spectra were recorded at room temperature in the wavelength range 200–1400 nm with resolution of 1 nm using JASCO Model V-670 UV–Vis–NIR spectrophotometer. The EPR spectra of molybdenum doped glass samples were recorded on JEOL-FE-IX (X-band) EPR spectrometer operating at 9.125 GHz with a field modulation frequency of 100 kHz. The magnetic field was scanned from 0 to 500 mT and the micro wave power used was 10 mW. Infrared transmission spectra were also recorded on JASCO-FTIR-5300 spectrophotometer up to a resolution of 0.85 cm^{-1} in the spectral range of 400–1600 cm^{-1} using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). These pellets were pressed in a vacuum die at ~680 MPa. Besides the above micro Raman spectra were recorded using Lab RAMHR (UV) spectrometer with a 10 mW internal excitation source of laser wavelength 514.5 nm with a spectral resolution of 0.3 cm^{-1}.

For the dielectric measurements, the samples were grounded and polished to 1 cm × 1 cm × 2 mm dimensions and a thin layer of silver paint was applied on both sides (the large faces) of the samples in order to serve as electrodes. These measurements were carried out using LF-impedance analyzer (Hewlett-Packard model 4192 A) in the frequency range 10^3–10^6 Hz. Dielectric constant and dielectric loss were measured in the temperature range 30–300 °C with an accuracy ±0.01 and ±0.001 respectively.

3. Results

3.1. Characterization and physical parameters

From the measured values of the density ρ and average molecular weight M of the samples, various physical parameters such as ion concentration N_i, mean ion separation R_i, polaron radius R_p of MoO_3 doped PbO-Nb_2O_5-GeO_2-SiO_2 glasses were evaluated using the standard equations [12]

The transition metal ion concentration (N_i) could be obtained from:

$$N_i\ (\text{ions/cm}^3) = (N_A\ m\ (\text{mol}\%)\ d)/M \quad (1)$$

where the terms are having meaning of N_A is the Avogadro's number, d is the density, M is the molecular weight of the glass composition and m is the mol percentage of the transition metal oxide. From the N_i values obtained, the inter-ionic distance (R_i) of transition metal ions and polaron radius (R_p) are evaluated

$$\text{Inter} - \text{ionic distance } R_i\ (\text{Å}) = (1/N_i)^{1/3} \quad (2)$$

$$\text{Polaron radius } R_p\ (\text{Å}) = (1/2)(\pi/6N_i)^{1/3} \quad (3)$$

and presented in Table 1. From Table 1, the density of molybdenum free sample M_0 is found to be 4.687 g cm^{-3} subsequently it is observed to decrease with integration of MoO_3. Fig. 1 shows X-ray diffraction pattern of some of MoO_3 doped PbO-Nb_2O_5-GeO_2-SiO_2 glasses; the absence of the sharp Bragg peaks confirms the amorphous nature of the prepared glass samples.

3.2. Optical absorption

The optical absorption spectra of MoO_3 doped PbO-Nb_2O_5-GeO_2-SiO_2 glasses recorded at room temperature are shown in Fig. 2. From the inset of the figure, it is clear that the UV absorption edge or cut–off wavelength, λ_c for M_0 is observed at 334 nm and is red ward shifted to 385 nm by the integration of MoO_3. The absorption band observed around 340 nm in the molybdenum free sample is due to the electronic transition occurs $a'^3\Sigma^+ \leftrightarrow X^1\Sigma^+$ [9,13]. This band is caused by triplet singlet electronic transition of Ge^{2+} state when germania in GeO form in the glass matrix. With the addition of 0.2 mol% of MoO_3 the band due Ge^{2+} is disappeared where as a broad absorption band is observed at 705 nm. As the concentration of MoO_3 is increased gradually to 1 mol% the half-width and intensity of this band is observed to increase with shift in the peak position towards higher wavelength. The optical band gap energy, E_g values were determined for all prepared glasses using the following equation [14].

$$\alpha h\nu = B\ (h\nu - E_g)^n \quad (4)$$

Table 1
Physical parameters of MoO_3 doped PbO-Nb_2O_5-GeO_2-SiO_2 glasses.

Sample	Density ρ (g/cm^3) (±0.001)	Molar volume V_m (cm^3) (±0.001)	Conc. Mo ions N_i ($\times 10^{21}$ ions/cm^3) (±0.01)	Inter ionic distance of Mo ions R_i (Å) (±0.01)	Polaron radius R_p (Å) (±0.01)
M_0	4.687	1.083	–	–	–
M_1	4.634	1.098	4.76	5.94	2.39
M_2	4.623	1.113	9.50	4.72	1.90
M_3	4.612	1.126	14.27	4.12	1.66
M_4	4.606	1.145	19.01	3.74	1.50
M_5	4.593	1.165	23.36	3.49	1.40