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Manganese modified structural and optical properties of bismuth silicate glasses

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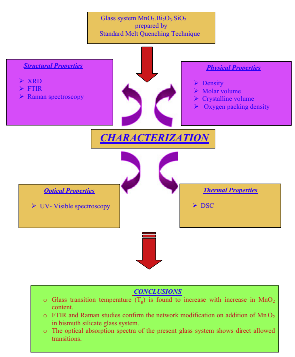
HIGHLIGHTS

- SiO_2 is present in SiO_4 tetrahedral structural units with two NBOs per silicon.
- Conversion of BiO_3 structural units into BiO_6 units with increase in MnO_2.
- MnO_2 acts as network modifier and exists in MnO_6 structural units.
- On addition of MnO_2, Bi–O–Si linkages are replaced by Bi–O–Mn linkages.

GRAPHICAL ABSTRACT



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ABSTRACT

Glass system with compositions xMnO$_2$–(60−x) Bi$_2$O$_3$–40SiO$_2$ have been synthesized by standard melt quench technique. X-ray diffraction patterns confirm the amorphous nature of as-prepared glass samples. The values of density have been measured and molar volume determined is found to decrease with increase in MnO_2 content. Theoretical calculations of crystalline volume (V_c) have also been made. The glass transition temperature (T_g) determined using differential scanning calorimetry (DSC) is observed to increase with increase in MnO_2 content. The structural analysis has been carried out using FTIR and Raman spectroscopy. In the present glass system, MnO_2 acts as network modifier and exists in MnO_6 structural units. Bismuth acts both as network former with BiO_3 pyramidal units as well as network modifier with BiO_6 octahedral units in the present glass system. SiO_2 exists in form of SiO_4 tetrahedral structural units with two non-bridging oxygens (NBO's). The optical band gap energy (E_g) has been estimated from Tauc's plot for direct transitions, it decreases with increase in manganese content.
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Introduction

Glasses containing Bi_2O_3 in combination with SiO_2 have been studied for their possible use in optical waveguides in the infrared region or as active medium of Raman fiber optical amplifiers and oscillators [1]. Transition metal ions (TMIs) containing glasses have attracted a great attention because of their numerous applications in memory switching, electrical threshold, and optical switching devices, etc. [2–4]. TMIs are considered as effective and useful dopant ions in the glass materials owing to the fact that they exist in different valence states with different coordinations simultaneously in the glass network, which is mainly responsible for bringing significant changes in the physical properties and structural modifications in the glass system [5]. Manganese ions have strong bearing on optical, electrical and magnetic properties [6] and have been widely studied due to their technological importance for catalytic and electrochemical applications [7]. Therefore, addition of MnO_2 to the bismuth silicate glasses, is expected to give new

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possibilities to extend the properties of these glasses by modifying their structure. The structural and electronic transport properties of Ti based bismuth silicate glasses have been reported recently [8–10] but there is hardly any report on the structural characterization of MnO_2–Bi_2O_3–SiO_2 glass system. Therefore, it is desired to carry out the detailed study of the effect of manganese on the physical, optical and structural properties of bismuth silicate glasses.

Experiment

Glass samples of compositions $x$$MnO_2$–(60−$x$) Bi_2O_3–40SiO_2; x = 0, 5, 10, 15 and 20 were prepared using analar grade MnO_2, Bi_2O_3 and SiO_2 chemicals by conventional rapid melt quench technique. In this method the appropriate amounts of MnO_2, Bi_2O_3 and SiO_2 were first thoroughly mixed in an agate pestle–mortar. Silica crucible containing the mixture was then put in an electrically heated muffle furnace and the temperature was raised slowly to a temperature between 1000 and 1150 °C depending on the composition. The same temperature was maintained for 1 h and meanwhile the melt was shaken frequently to ensure proper mixing and homogeneity. The melt was poured onto a stainless steel block and subsequently pressed by another similar block at room temperature. The glass samples thus obtained were found black in colour.

Density (ρ) of the samples was measured by Archimedes' principle using SI-234 Denver Instrument and xylene as buoyant liquid. X-ray diffraction studies of the samples were performed using Rigaku Table-Top X-ray diffractometer with Cu Kα radiation (λ = 1.54 Å) at 30 KV and 15 mA with scanning rate of 4° per minute. The glass transition temperature (T_g) of samples was measured by the DSC technique using TA Instruments, Model No. Q600 SDT, at a heating rate of 10 °C/min in nitrogen atmosphere. The Raman spectra of the polished samples were recorded using Renishaw Invia Reflex Micro Raman Spectra with Ar ion laser (514 nm) under back scattering configuration in the spectral range of 50–1200 cm^{-1}. The Fourier Transform Infra Red (FTIR) spectra of the glass samples were recorded using Shimadzu IR affinity-I 8000 FTIR spectrophotometer in the spectral range 400–1600 cm^{-1}. The powdered glass samples were thoroughly mixed with dry KBr and then pellets were formed under a pressure of 9–10 tons. The FTIR and Raman spectra were found to be consisting of large and asymmetric broad bands that in turn are comprised of a number of overlapping peaks. Therefore, deconvolution of the experimental data of FTIR and Raman spectra was necessary and was performed using the inbuilt "multiple peaks fit" module of Origin Pro 8.6 software. The procedure for deconvolution of the spectra used has already been published elsewhere [8]. The statistical validation of fitting was tested by applying *F*-test [11]. The room temperature optical absorption spectra of the glass samples were recorded using Carry 5000 double beam UV–Visible spectrophotometer in the wavelength range 200–1400 nm.

Results and discussion

XRD

The X-ray diffraction patterns of the as-prepared glass samples show only broad diffuse scattering at low angles. This type of scattering reveals the absence of long range structural orders of the prepared glass samples as shown in Fig. 1.

Density

The density is one of the tools to reveal the degree of structural changes of the glass network with composition [8]. The values of density (ρ) measured for all the samples using Archimedes's principle are given in Table 1. Perusal of the data presented in Table 1 shows that the density of glass samples decreases from 6.80 to 6.14 g/cm^3 with increase in MnO_2 content corresponding x = 0 to x = 20. The decrease in density with increase in MnO_2 content is expected in the present system as heavier Bi_2O_3 is being replaced by the lighter MnO_2. The same type of behaviour has also been reported by several other researchers for glass compositions [8,12,13]. The molar volume (V_m) of samples was calculated using the following relation [14]

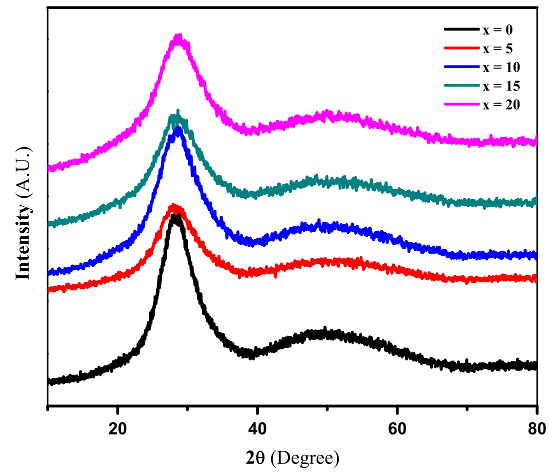

Fig. 1. XRD of different $x$$MnO_2$–(60–$x$) Bi_2O_3–40SiO_2 glass compositions.

$$V_m = \sum x_i M_i / \rho \tag{1}$$

where x_i is the molar fraction and M_i molecular weight of the ith component and ρ is the density of the sample. The values of V_m so calculated are given in Table 1. The molar volume decreases with increase in manganese content. The decrease in V_m may be due to the smaller values of radii (r = 0.91 Å) of manganese ions (Mn) in MnO_2 as compared to that of Bi_2O_3 (r = 1.20 Å) [15]. Crystalline volume (V_c) of the glass samples is given by formula [13]

$$V_c = \sum x_i V_i \tag{2}$$

where V_i is the molar volume of ith component in crystalline phase and its value for Bi_2O_3, SiO_2 and MnO_2 are taken as 52.36, 25.79 and 17.30 cm^3/mol, respectively. The calculated values of V_c are also included in Table 1 and the compositional dependence of molar volume (V_m) and crystalline volume (V_c) for various compositions are shown in Fig. 2. Perusal of the data plotted in Fig. 2 show that the values V_m of the glasses (for x = 0, 5, 10, 15 and 20) are always greater than the corresponding values of V_c, indicating the presence of excess structural volume in these samples. This is characteristic of their glassy nature [13] and also supports the result of XRD patterns.

Table 1
Density (ρ), molar volume (V_m), crystalline volume (V_c), oxygen packing density (*OPD*), glass transition temperature (T_g), optical energy band gap (E_g) of $x$$MnO_2$·(60−$x$) Bi_2O_3·40SiO_2 glasses with different values of x.

Parameters	x = 0	x = 5	x = 10	x = 15	x = 20
ρ (g cm^{-3})	6.796	6.412	6.198	6.162	6.142
V_m (cm^3 mol^{-1})	44.71	44.40	42.87	40.05	37.09
V_c (cm^3 mol^{-1})	40.49	38.74	36.98	35.23	33.48
OPD (gm $atml^{-1}$)	58.15	57.44	58.31	61.18	64.71
T_g (°C)	468	503	508	509	516
E_g (eV)	2.76	2.20	2.03	1.83	1.27

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