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Citation: AIP Conference Proceedings **1665**, 070029 (2015); doi: 10.1063/1.4917893
View online: http://dx.doi.org/10.1063/1.4917893
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1665?ver=pdfcov
Published by the AIP Publishing

Optical Properties of Borotellurite Glasses Containing Metal Oxides

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Abstract. Glass samples of the system: $5M_xO_y$-$20B_2O_3$-$75TeO_2$: M_xO_y = WO_3, Nb_2O_5, PbO, Nd_2O_3, Y_2O_3, Eu_2O_3 were prepared by melt quenching and characterized by X-ray diffraction, density, Differential Scanning Calorimetry, UV-visible and FTIR spectroscopy. XRD patterns confirmed the amorphous structure of all samples. Glass transition temperature was maximum in borotellurite glass containing Y_2O_3. Refractive index, atomic polarizability and basicity increased in the following order of ions: Y^{3+}< Eu^{3+} < Pb^{2+} < Nd^{3+} < Nb^{3+} < W^{6+}. FTIR studies showed that PbO is outstanding in enhancing the concentration of tetrahedral borons in the borotellurite network.

Keywords: Borotellurite glasses, XRD, DSC, FTIR and UV-Visible spectroscopy.
PACS: 81.05.Kf, 61.05.cp, 65.60.+a, 63.50.-x and 78.40.-q

INTRODUCTION

Tellurite glasses have a wide range of applications. One of the commercial applications of tellurite glasses is in the field of optical communication due to their outstanding properties like high refractive index, high optical non-linearity and good infrared transmittance [1-5]. Tellurite glasses have been reported to exhibit 30 times higher Raman gain coefficients than silica glass and find application in Raman amplifiers and non-linear optical waveguides [6, 7]. Many studies are reported on the technological importance of tellurite glasses containing transitional metal and/or rare earth ions in memory switching devices and as cathode materials for batteries [8].

In this work, we report the study of short-range structure and optical and thermal properties of borotellurite glasses doped with W^{6+}, Nb^{3+}, Pb^{2+}, Nd^{3+}, Y^{3+} and Eu^{3+}. Glasses were characterized by density, X-ray diffraction (XRD), Differential Scanning Calorimetery (DSC) and UV-visible and FTIR spectroscopy.

EXPERIMENTAL METHODS

Glasses of the system: $5M_xO_y$-$20B_2O_3$-$75TeO_2$: M_xO_y = WO_3, Nb_2O_5, PbO, Nd_2O_3, Y_2O_3, Eu_2O_3 were prepared using H_3BO_3 (Sigma Aldrich Inc., USA, 99.5%), TeO_2 (Sigma Aldrich Inc., USA, 99%), and WO_3, Nb_2O_5, PbO, Nd_2O_3, Y_2O_3 and Eu_2O_3 as starting materials. The chemicals in the above mentioned compositions were weighed and sintered at 300°C for 24 h and then melted in a temperature range of 800°C to 900°C in a platinum crucible. Glass samples were prepared by normal quenching technique in which a small amount of melt was quenched on a brass block and a button shaped sample was obtained and immediately transferred to a furnace kept at a temperature of about 80°C lower than the glass transition temperature. Samples were annealed for 30 min and then slowly cooled to room temperature.

RESULTS AND DISCUSSION

X-ray diffraction measurements were performed on Bruker D8 Focus X-ray diffractometer with Cu K_α radiation (λ =1.54056 Å) in the 2θ range of 10°-70°. Figure 1 shows the XRD patterns of borotellurite

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AIP Conf. Proc. 1665, 070029-1–070029-3; doi: 10.1063/1.4917893

glasses doped with metal oxides. These patterns do not show any sharp peaks, but the characteristic broad humps due to short-range order in glasses.

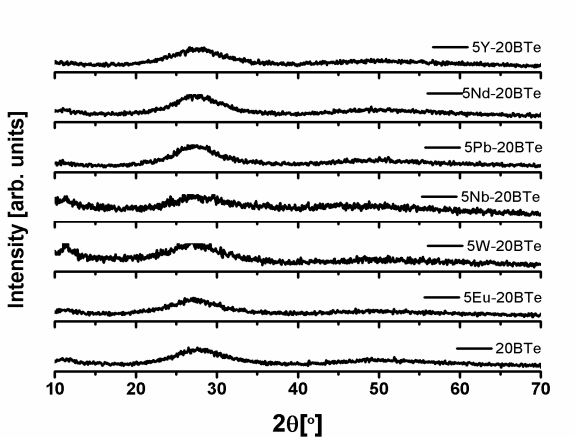

FIGURE 1. XRD patterns of borotellurite glasses doped with different metal oxides.

calculated by dividing the absorbance A, with sample thickness and is plotted in figure 3.

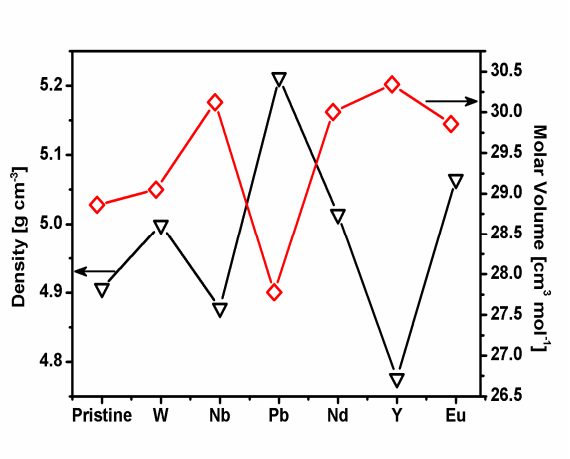

FIGURE 2. Density and molar volume variation in borotellurite glasses containing metal oxides.

TABLE 1. Molecular weight, density, molar volume and glass transition temperature of borotellurite glasses doped with metal oxides.

Sample Code	Composition	Molecular Weight [g mol^{-1}]	Density [g cm^{-3}]	Molar Volume [cm^3 mol^{-1}]	T_g [^{o}C]
20BTe	0.20 B_2O_3-0.80 TeO_2	141.61	4.906	28.86	352
5W-20BTe	0.05 WO_3-0.20 B_2O_3-0.75 TeO_2	145.21	4.999	29.05	358
5Nb-20BTe	0.05 Nb_2O_5-0.20 B_2O_3-0.75 TeO_2	146.92	4.877	30.12	369
5Pb-20BTe	0.05 PbO-0.20 B_2O_3-0.75 TeO_2	144.78	5.212	27.78	340
5Nd-20BTe	0.05 Nd_2O_3-0.20 B_2O_3-0.75 TeO_2	150.45	5.014	30.00	385
5Y-20BTe	0.05 Y_2O_3-0.20 B_2O_3-0.75 TeO_2	144.91	4.776	30.34	393
5Eu-20BTe	0.05 Eu_2O_3-0.20 B_2O_3-0.75 TeO_2	151.22	5.065	29.86	388

Density of glasses were measured by Archimedes principle using an electronic balance with an accuracy of 10^{-4} g. Turpentine oil was used as an immersion liquid. Density and molar volume values are given in Table 1. Density increases on adding metal oxides in the glass network and is maximum for glass containing PbO [Figure 2].

Thermal studies were performed on SETARAM SETSYS Evolution-1750 system in the temperature range of 200-850^{o}C at a heating rate of 10^{o}C/min, in air flow rate of 20 ml/min in Pt pans. From DSC scans, glass transition temperature, T_g was determined [Table 1]. T_g is maximum for the sample having 5-mol% of Y_2O_3 and minimum for glass containing Pb^{2+} ion. All metal ions except Pb^{2+} strengthened the binary borotellurite glass network due to the incorporation of metal oxide bonds with higher bond enthalpies.

Optical absorption spectra of polished disk shaped borotellurite glasses were measured at room temperature on Shimadzu 1601 double beam UV-visible spectrophotometer in wavelength range of 200-1100 nm. The optical absorption coefficient α(λ) was

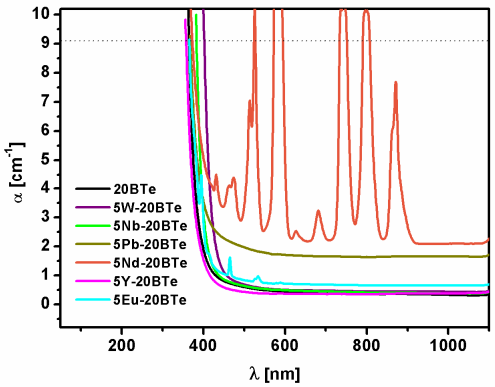

FIGURE 3. Absorption spectra (α vs λ) of borotellurite glasses.

From α vs λ plots, absorption edge, λ_o was determined as the wavelength at which α = 9 cm^{-1} [Table 2]. The absorption edge shifted towards longer wavelengths on adding metal oxides. Optical band gap, E_g of glasses was determined from λ_o. E_g was used to calculate the optical electronegativity χ, refractive index n,

electronic polarizability α_o and optical basicity Λ, of glasses using the formulae reported in the literature [9]. The calculated values are given in table 2.

that N_4 is nearly the same for the undoped borotellurite sample: 20BTe and the glasses doped with Nd^{3+} and Nb^{3+}. Maximum N_4 is in the sample containing Pb^{2+} and the minimum is observed in the glass with W^{6+}.

TABLE 2. Optical energy gap and N_4 in borotellurite glasses containing metal ions.

Sample Code	Absorption edge λ_o, [nm]	Energy gap E_o [eV]	χ	n	α_o	Λ	N_4
20BTe	365	3.4	0.915	2.28	2.68	1.24	0.27
5W-20BTe	402	3.1	0.831	2.35	2.75	1.28	0.17
5Nb-20BTe	383	3.3	0.872	2.32	2.71	1.26	0.27
5Pb-20BTe	368	3.4	0.908	2.29	2.68	1.25	0.38
5Nd-20BTe	373	3.3	0.896	2.30	2.69	1.25	0.27
5Y-20BTe	357	3.5	0.936	2.27	2.66	1.23	0.21
5Eu-20BTe	366	3.4	0.913	2.28	2.68	1.24	0.24

Optical energy gap of glasses containing metal ions was lower than undoped borotellurite glass (i.e. sample 20BTe) except for the sample containing Y^{3+}. The optical electronegativity was lowest for glass having W^{6+}. Values of refractive indices follow the trend: 5Y-20BTe < 20BTe < 5Eu-20BTe < 5Pb-20BTe < 5Nd-20BTe < 5Nb-20BTe < 5W-20BTe.

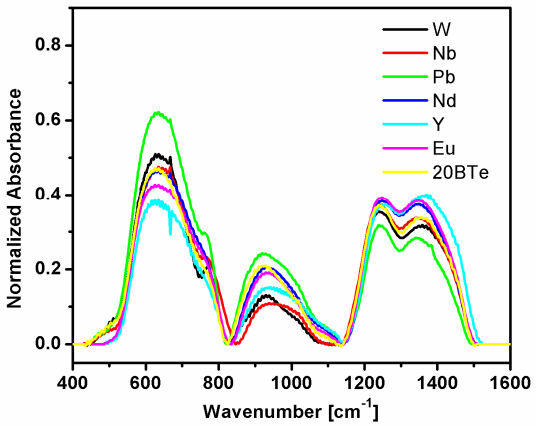

FIGURE 4. FTIR absorption spectra of borotellurite glasses doped with metal ions.

The FTIR absorption spectra show three bands in the wavenumber ranges of 500-800 cm^{-1}, 800-1150 cm^{-1} and 1150-1550 cm^{-1} [Figure 4]. The first band in the wavenumber range of 500-800 cm^{-1} is due to Te-O vibrations in different Te-O units. The bands in the wavenumber ranges of 820-1140 cm^{-1} and 1150-1550 cm^{-1} are due to B-O stretching vibrations in BO_4 and BO_3 units respectively [4]. Areas under the second and third bands i.e. A_4 and A_3 are calculated and the ratios of these areas $A_4/(A_4+A_3)$ is considered proportional to the fraction of tetrahedral borons (N_4) in the glass network. It is clear from the data presented in table 2

CONCLUSIONS

Borotellurite glasses were prepared with 5-mol% of W^{6+}, Nb^{3+}, Pb^{2+}, Nd^{3+}, Eu^{3+}, Y^{3+} and their properties were compared with undoped borotellurite glass. Glass transition temperature is maximum for 5Y-20BTe sample. Refractive index, atomic polarizability and basicity increases in the following order of dopant ions: Y^{3+} < 20BTe < Eu^{3+} < Pb^{2+} < Nd^{3+} < Nb^{3+} < W^{6+}. Conversely optical energy gap is lowest for glass containing WO_3 and is highest for the glass with Y_2O_3. Also, PbO produces a maximum increase in N_4 while WO_3 suppresses it.

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