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Study on Glass Parameters in Li₂O-B₂O₃-M₂O₃ Glass (M₂=Sb, Bi)

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ABSTRACT: Glass systems 42.5Li₂O-(57.5-x) B₂O₃-xM₂O₃, (M₂ = Sb, Bi) x=0-57.5 in the step of 5.75 in mol% were prepared by conventional melt-quench technique. The density and molar volume of glasses were determined in order to study their structure. The physical parameters like Boron molar volume, Boron-Boron separation, Number of bonds per unit volume, Oxygen molar volume, Oxygen packing density, Bond ionicity, and Free space volume. Molar volume, oxygen molar volume, boron molar volume, free space volume, bond ionicity and boron-boron separation parameters values are increasing whereas density, oxygen packing density and number of bonds per unit volume parameters values are decreasing; on increasing the mol % of Sb₂O₃ and Bi₂O₃.

KEYWORDS: Density, Molar volume, Boron molar volume, Boron-Boron separation, number of bonds per unit volume, molar volume of oxygen, glass composition, mixed glass former effect.

1. INTRODUCTION

Metal oxide glasses display physical properties. Many well-designed properties of the glass are determined by the elements with mixed valences (in which an element has two or more different valences while forming a compound) in the structure unit ^[1]. Mixed valence effect is required for glasses to stimulate electronic, structural, and chemical progress leading to specific functionality. The valence states of metal cations in glass can be governed chemically using orbital hybridization. Borate glasses are composed of structural groupings as boroxol, tetraborate, diborate, which are linked by bridging oxygens, where the glass consists of microdomains of boroxol rings ^[2]. Near the glass-transition temperature the boroxol rings break up leading to a more open structure which affects strongly the glass behavior as a host material. Furthermore, glasses containing cations (such as Pb²⁺, Sb³⁺, As³⁺, Bi³⁺, or Ge⁴⁺...) with an outer electron shell of 18 + 2 electrons should have higher polarizabilities and lower melting temperatures ^[3]. In the same context, Vanadium, Antimony, and Bismuth oxides possesses interesting semiconducting and photo conducting properties with potential applications in imaging devices, electro photography and laser technology.

Antimony, Bismuth has empty *d*-orbitals which can form three or five bonds by unpairing electrons. Overlap of a *p*-orbital on the oxygen with a *d*-orbital on Sb gives a *pπ-dπ* interaction ^[4]. To obtain effective *pπ-dπ* overlap, the size of the *d*-orbital must be similar the size of the *p*-orbital. Since Sb has a covalent radius of 1.41 Å while for Bi it is 1.46 Å, therefore, an overlap between them might be highly credible. Upon the glass structure, a strong overlap possibly arise providing *2p-3d* orbital hybridization. Such orbital hybridization manifests itself as an increase in glass optical polarizability throughout spin-orbit coupling mechanism ^[5]. Antimony oxide possesses two kinds of structures (SbO4³⁻) acts as a modifier in the glass network with three coordinated oxygen and one lone pair of electrons, whereas (SbO5⁷⁻) with five coordinated oxygen occupies tetrahedral sites in the glass network and acts as a network former ^[6, 7].

The role of an ion in glass environment is largely determined by its ionic radius *a*, and its effective electrostatic field strength *eZ/a²* where *eZ* is the ionic charge. According to stereochemical reasoning, coordination number four is suggested for small ions to be incorporated in interatomic space between four closed-packed oxygens. Octahedron of close-packed oxygens-coordination number 6-or even more is required for larger ions. Transition metals with valences of +3, +4, +5 such as Sb, Bi which having a lower electronegativity, with oxides have a higher electronegativity. Bi₂O₃ as a heavy metal oxide could change the physical properties of phosphate glasses ^[8]. Phosphate glass containing Bi₂O₃ would undergo structural modification when Bi³⁺ cation switched to stable linkage like P-O-Bi ^[9].

Bismuth based glasses have important applications in optoelectronic devices, sensors and superconductors ^[10-15]. Since the release of the first report on 1.3 μm optical amplification in the bismuth-doped silica glasses ^[16] and that on broadband infrared emission properties of bismuth-doped phosphate glasses, the bismuth-doped materials have attracted much attention.

II. EXPERIMENTAL WORK

II.1 GLASS PREPARATION: Glass systems 42.5Li₂O-(57.5-x) B₂O₃-xM₂O₃, (M₂ = Sb, Bi) x=0-57.5 in the step of 5.75 in mol% were prepared by conventional melt-quench technique by using raw materials were of chemically pure. The

initial ingredients were dried at 150°C for about 24 hours before weighing the compositions with an accuracy of 0.00001 gm, using 1E163 Mettler (Switzerland) electronic balance. Raw materials were thoroughly pulverized under acetone in an agate mortar to obtain a homogenous mixture. The homogeneous mixture was melted in porcelain crucible in an electrically programmable heated furnace, type UAF 15/10 Lenton thermal Designs, equipped with automatic temperature controller. The samples were melted at about (1100 ± 20) °C for two hours with heating rate 30°C/min. The molted material were quenched in air and poured at room temperature between two steel plates. The quenched samples were annealed at 300°C for 20 min. The as-made glasses were immediately stored in vacuum desiccators to avoid possible moisture absorption until used for measurements.

III. EXPERIMENTAL DETAILS

III.1 DENSITY AND MOLAR VOLUME: Density of all glass samples are measured at room temperature using toluene as the immersion liquid. Density is generally measured by the fluid displacement method depending on Archimedes principle. According the Archimedes principle, the buoyancy equals the weight of the displaced fluid. Using xylene as the buoyant medium evaluated the density of the glass samples. The density was obtained by employing the relation:

$$\rho = [W_1 / (W_1 - W_2)] * \rho_b$$

Where W_1 is the weight of glass sample in air, W_2 is the weight of glass sample in buoyant liquid, $(W_1 - W_2)$ is the buoyancy, ρ_b is density of buoyant (density of xylene=0.86). All the measurements were made using a digital balance. Then theoretical density of glasses under study are calculated by using the expression

$$\rho_{\text{theo}} = X_{\text{Li}_2\text{O}} * \rho_{\text{Li}_2\text{O}} + X_{\text{B}_2\text{O}_3} * \rho_{\text{B}_2\text{O}_3} + X_{\text{M}_2\text{O}} * \rho_{\text{M}_2\text{O}} \text{ where } M=\text{Sb, Bi}$$

Where $X_{\text{Li}_2\text{O}}$, $X_{\text{B}_2\text{O}_3}$ and $X_{\text{M}_2\text{O}}$ are the molar fraction of Li_2O , B_2O_3 and Sb_2O_3 , Bi_2O_3 and $\rho_{\text{Li}_2\text{O}}$, $\rho_{\text{B}_2\text{O}_3}$ and $\rho_{\text{M}_2\text{O}}$ are the densities of Li_2O , B_2O_3 and Sb_2O_3 , Bi_2O_3

Similarly total molecular weight of the multi-component glass systems are calculated by using the expression

$$M_T = X_{\text{Li}_2\text{O}} * M_{\text{Li}_2\text{O}} + X_{\text{B}_2\text{O}_3} * M_{\text{B}_2\text{O}_3} + X_{\text{M}_2\text{O}} * M_{\text{M}_2\text{O}} \text{ where } M=\text{Sb, Bi}$$

Where $X_{\text{Li}_2\text{O}}$, $X_{\text{B}_2\text{O}_3}$ and $X_{\text{M}_2\text{O}}$ are the molar fraction of Li_2O , B_2O_3 and Sb_2O_3 , Bi_2O_3 and $M_{\text{Li}_2\text{O}}$, $M_{\text{B}_2\text{O}_3}$ and $M_{\text{M}_2\text{O}}$ are the molecular weight of Li_2O , B_2O_3 and Sb_2O_3 , Bi_2O_3

Molar volume of glass samples are calculated by using the expression

$$V_m = M_T / \rho_{\text{theo}}$$

It is clear that density decreases due to increasing fractional mass and molecular weights of Sb_2O_3 , Bi_2O_3 and hence increasing molecular volumes respectively.

III.2 OXYGEN MOLAR VOLUME AND OXYGEN PACKING DENSITY

According to chemical bond approach many additional parameters would also be calculated which are oxygen molar volume and oxygen packing density. Oxygen molar volume is given by ^[17]

$$V_o = V_m / \sum_i X_i * N_i$$

Where N_i is the number of oxygen atoms in each oxide. X_i is mole fraction of oxides and oxygen packing density is calculated by using the expression ^[18]

$$\text{OPD} = n (\rho / M)$$

Where n is the number of oxygen atoms in the composition. ρ is the density and M is total molecular weight of the multi-component.

III.3 BORON MOLAR VOLUME AND BORON-BORON SEPARATION

Boron molar volume is calculated by using the expression ^[19]

$$V_m^B = V_m / 2 (1 - X_B)$$

Where X_B = molar fraction of B_2O_3 oxide in the composition.

The average boron-boron separation (d_{B-B}) is calculated by using the expression ^[19]

$$(d_{B-B}) = [V_m / A_v]^{(1/3)}$$

Where A_v = Avogadro's number (6.0228×10^{23} gm/mol).

III.4 NUMBER OF BONDS PER UNIT VOLUME AND BOND IONICITY

The number of bonds per unit volume is calculated by using the relationship ^[20, 21]

$$n_b = (A_v / V_m) \sum_i (n_{ci} * X_i)$$

Where A_v = Avogadro's number (6.0228×10^{23} gm/mol). n_{ci} and X_i = coordination number and molar fraction of the cation respectively.

Bond ionicity is calculated by using the expression

$$I_b = 1 - \exp [-0.25(\Delta\chi)^2]$$

Where $\Delta\chi$ = electronegativity difference of the glass constituent oxide which is given by ^[22] $\Delta\chi = \chi_{anion} - \chi_{cation}$

Where χ_{anion} and χ_{cation} are Pauling electronegativity of anion and cation.

III.5 FREE SPACE VOLUME

The ions without any spacing between them occupy only a volume equal to V_i which is given by $V_i = \sum_i (4\pi/3)r_i^3$ where r_i is radius of the ion i . Then free space volume V_f is given by ^[19]

$$V_f = V_m - V_i$$

IV. EXPERIMENTAL RESULT AND DISCUSSION

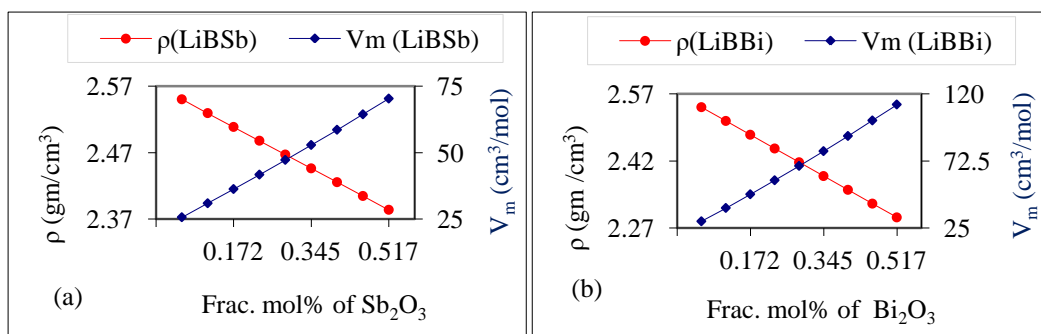


Figure 1(a) ρ , V_m vs. fraction, mol% of Sb_2O_3

Figure 1(b) ρ , V_m vs. fraction, mol% of Bi_2O_3

Figure 1 (a) shows the variation of density for ternary $Li_2O-B_2O_3-Sb_2O_3$ system decreases from (2.55-2.3839) g/cm³. For binary $Li_2O-B_2O_3$ system density is 2.5708 g/cm³ and for binary $Li_2O-Sb_2O_3$ system density decreases to 2.3631 g/cm³. Molar volume for ternary $Li_2O-B_2O_3-Sb_2O_3$ system increases from (25.6819-70.2886) cm³/mol. For binary $Li_2O-B_2O_3$ system it is 20.5114 cm³/mol and for binary $Li_2O-Sb_2O_3$ system molar volume increases to 76.3054 cm³/mol; on increasing the mol% of Sb_2O_3 .

Figure 1 (b) shows the variation of density for ternary $Li_2O-B_2O_3-Bi_2O_3$ system decreases from (2.54-2.2936) g/cm³. For binary $Li_2O-B_2O_3$ system density is 2.5708 g/cm³ and for binary $Li_2O-Bi_2O_3$ system decreases to 2.2628 g/cm³ and

molar volume for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Bi}_2\text{O}_3$ system increases from $(29.7322-112.4126) \text{ cm}^3/\text{mol}$. For binary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system molar volume is $20.5114 \text{ cm}^3/\text{mol}$ and for binary $\text{Li}_2\text{O}-\text{Sb}_2\text{O}_3$ system molar volume is $124.0135 \text{ cm}^3/\text{mol}$; on increasing the mol% of Bi_2O_3 .

Figure 2 shows the variation of Molar volume for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Sb}_2\text{O}_3$ system increases from $(25.6819-70.2886) \text{ cm}^3/\text{mol}$. For binary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system it is $20.5114 \text{ cm}^3/\text{mol}$ and for binary $\text{Li}_2\text{O}-\text{Sb}_2\text{O}_3$ system molar volume increases to $76.3054 \text{ cm}^3/\text{mol}$; on increasing the mol% of Sb_2O_3 .

Variation of molar volume for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Bi}_2\text{O}_3$ system increases from $(29.7322-112.4126) \text{ cm}^3/\text{mol}$. For binary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system molar volume is $20.5114 \text{ cm}^3/\text{mol}$ and for binary $\text{Li}_2\text{O}-\text{Sb}_2\text{O}_3$ system molar volume is $124.0135 \text{ cm}^3/\text{mol}$; on increasing the mol% of Bi_2O_3 .

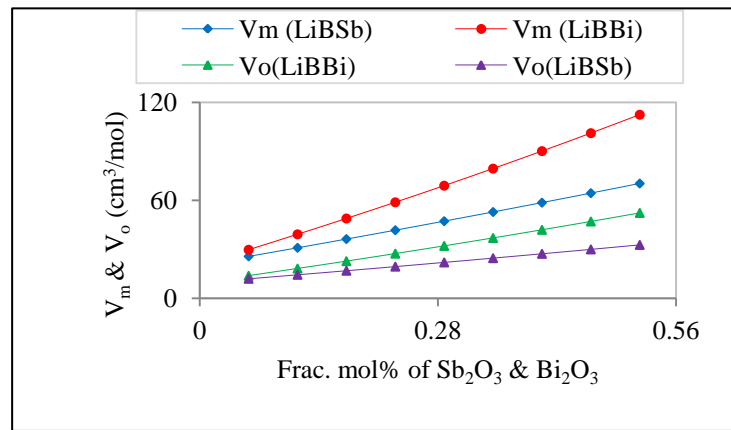


Figure 2 V_m & V_o vs. fraction, mol% of Sb_2O_3 & Bi_2O_3

Variation of oxygen molar volume for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Sb}_2\text{O}_3$ system increases from $(11.9450-32.6923) \text{ cm}^3/\text{mol}$. For binary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system it is $9.5401 \text{ cm}^3/\text{mol}$ and for binary $\text{Li}_2\text{O}-\text{Sb}_2\text{O}_3$ system oxygen molar volume increases to $32.4908 \text{ cm}^3/\text{mol}$; on increasing the mol% of Sb_2O_3 .

Variation of oxygen molar volume for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Bi}_2\text{O}_3$ system increases from $(13.8289-52.2849) \text{ cm}^3/\text{mol}$. For binary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system oxygen molar volume is $9.5401 \text{ cm}^3/\text{mol}$ and for binary $\text{Li}_2\text{O}-\text{Sb}_2\text{O}_3$ system molar volume is $57.6807 \text{ cm}^3/\text{mol}$; on increasing the mol% of Bi_2O_3 .

Molar volumes as well as oxygen molar volumes for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Sb}_2\text{O}_3$ system and for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Bi}_2\text{O}_3$ system similarly for binary $\text{Li}_2\text{O}-\text{Sb}_2\text{O}_3$ and $\text{Li}_2\text{O}-\text{Bi}_2\text{O}_3$ systems are increasing in order. On comparing these two series, molar volumes as well as oxygen molar volumes of ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Sb}_2\text{O}_3$ system is smaller than that of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Bi}_2\text{O}_3$ ternary system; similarly molar volume as well as oxygen molar volume of binary $\text{Li}_2\text{O}-\text{Sb}_2\text{O}_3$ system is also smaller than that of $\text{Li}_2\text{O}-\text{Bi}_2\text{O}_3$ system. Whereas for binary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ molar volume remains constant equal to $20.5114 \text{ cm}^3/\text{mol}$ and oxygen molar volume also remains constant equal to $9.5401 \text{ cm}^3/\text{mol}$; due to common in both systems. Increasing in both molar volumes with increasing in mol % of compositions indicates the extension of network and increasing in non-bridging oxygen bond density.

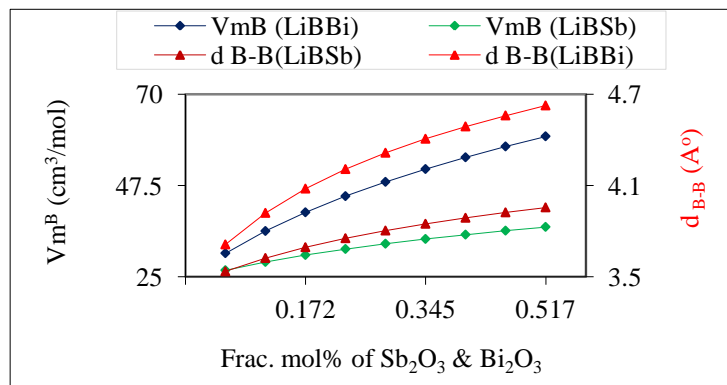


Figure 3 V_m^B & d_{B-B} vs. fraction, mol% of Sb_2O_3 & Bi_2O_3

Figure 3 shows the variation of Boron molar volume for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Sb}_2\text{O}_3$ system increases from (26.6133-37.2883) cm^3/mol . For binary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system boron molar volume is 24.1311 cm^3/mol and for binary $\text{Li}_2\text{O}-\text{Sb}_2\text{O}_3$ system boron molar volume increases to 38.1527 cm^3/mol ; on increasing the mol% of Sb_2O_3 .

Variation of Boron molar volume for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Bi}_2\text{O}_3$ system increases from (30.8106-59.6353) cm^3/mol . For binary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system molar volume is 24.1311 cm^3/mol and for binary $\text{Li}_2\text{O}-\text{Bi}_2\text{O}_3$ system molar volume is 62.0067 cm^3/mol ; on increasing the mol% of Bi_2O_3 .

Variation of Boron-Boron separation for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Sb}_2\text{O}_3$ system increases from (3.5353-3.9561) (A°). For binary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system it is 3.4218 (A°) and for binary $\text{Li}_2\text{O}-\text{Sb}_2\text{O}_3$ system decreases to 3.9863 (A°); on increasing the mol% of Sb_2O_3 .

Variation of Boron-Boron separation for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Bi}_2\text{O}_3$ system increases from (3.7122-4.6263) (A°). For binary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system oxygen molar volume is 3.4218 (A°) and for binary $\text{Li}_2\text{O}-\text{Sb}_2\text{O}_3$ system molar volume is 4.6868 (A°); on increasing the mol% of Bi_2O_3 .

Boron molar volumes as well as Boron-Boron separation for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Sb}_2\text{O}_3$ system and for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Bi}_2\text{O}_3$ system; similarly for binary $\text{Li}_2\text{O}-\text{Sb}_2\text{O}_3$ and $\text{Li}_2\text{O}-\text{Bi}_2\text{O}_3$ systems are increasing in order. On comparing these two system, Boron molar volumes as well as Boron-Boron separation of ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Sb}_2\text{O}_3$ system is smaller than that of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Bi}_2\text{O}_3$ ternary system; similarly Boron molar volume as well as Boron-Boron separation of binary $\text{Li}_2\text{O}-\text{Sb}_2\text{O}_3$ system is also smaller that of $\text{Li}_2\text{O}-\text{Bi}_2\text{O}_3$ system. Whereas for binary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system Boron molar volume remains constant equal to 24.1311 (A°) and Boron-Boron separation also remains constant equal to 3.4218 (A°); due to common in both systems. Increasing in boron molar volumes in both systems correspond to the volume that contains one mol of boron atoms within the specific glass structure. Since Boron molar volumes depends on the cation species, therefore the calculated values of average boron-boron separation are increased from Sb_2O_3 to Bi_2O_3 .

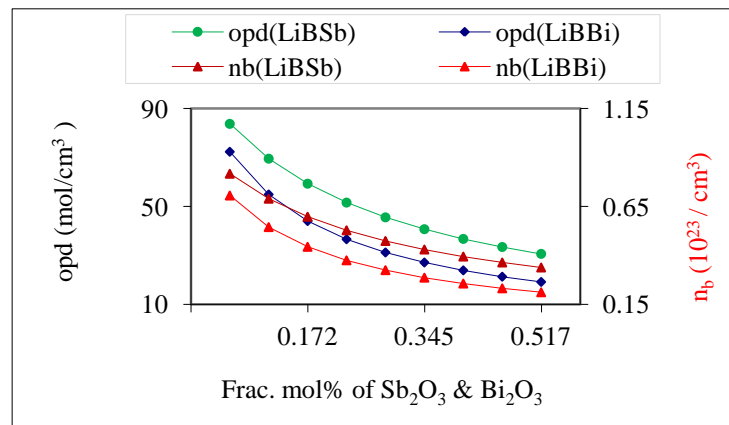


Figure 4 opd & n_b vs. fraction, mol% of Sb_2O_3 & Bi_2O_3

Figure 4 shows the variation of oxygen packing density for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Sb}_2\text{O}_3$ system decreases from (83.7165-30.5881) mol/cm^3 . For binary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system oxygen packing density is 104.8197 mol/cm^3 and for binary $\text{Li}_2\text{O}-\text{Sb}_2\text{O}_3$ system oxygen packing density decreases to 28.1762 mol/cm^3 ; on increasing the mol% of Sb_2O_3 .

Variation of oxygen packing density for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Bi}_2\text{O}_3$ system decreases from (72.3121-19.1259) mol/cm^3 . For binary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system oxygen packing density is 104.8197 mol/cm^3 and for binary $\text{Li}_2\text{O}-\text{Bi}_2\text{O}_3$ system oxygen packing density is 17.3368 mol/cm^3 ; on increasing the mol% of Bi_2O_3 .

Variation of number of bonds per unit volume for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Sb}_2\text{O}_3$ system decreases from (0.8166-0.3378) ($10^{23}/\text{cm}^3$). For binary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system it is 1.0056 ($10^{23}/\text{cm}^3$) and for binary $\text{Li}_2\text{O}-\text{Sb}_2\text{O}_3$ system decreases to 0.3157 ($10^{23}/\text{cm}^3$); on increasing the mol% of Sb_2O_3 .

Variation of number of bonds per unit volume for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Bi}_2\text{O}_3$ system decreases from (0.7054-0.2112) ($10^{23}/\text{cm}^3$). For binary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system it is 1.0056 ($10^{23}/\text{cm}^3$) and for binary $\text{Li}_2\text{O}-\text{Bi}_2\text{O}_3$ system decreases to 0.1942 ($10^{23}/\text{cm}^3$); on increasing the mol% of Bi_2O_3 .

Oxygen packing density as well as number of bonds per unit volume for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Sb}_2\text{O}_3$ system and for ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Bi}_2\text{O}_3$ system; similarly for binary $\text{Li}_2\text{O}-\text{Sb}_2\text{O}_3$ and $\text{Li}_2\text{O}-\text{Bi}_2\text{O}_3$ binary systems are increasing in order. On comparing these two system, Oxygen packing density as well as number of bonds per unit volume of ternary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Sb}_2\text{O}_3$ system is larger than that of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Bi}_2\text{O}_3$ ternary system; similarly Oxygen packing density as

well as number of bonds per unit volume of binary $\text{Li}_2\text{O-Sb}_2\text{O}_3$ system is also larger than that of $\text{Li}_2\text{O-Bi}_2\text{O}_3$ system. Whereas for binary $\text{Li}_2\text{O-B}_2\text{O}_3$ system Oxygen packing density remains constant equal to $104.8197 (10^{23}/\text{cm}^3)$ and number of bonds per unit volume also remains constant equal to $1.0056 (10^{23}/\text{cm}^3)$; due to common in both series.

Decreasing in Oxygen packing density in both systems is associated with decreasing density. Decreasing in number of bonds per unit volume depends up on covalent and ionic radius.

Figure 5 shows the variation of bond ionicity for ternary $\text{Li}_2\text{O-B}_2\text{O}_3\text{-Sb}_2\text{O}_3$ system decreases from (0.5749-0.5731). For binary $\text{Li}_2\text{O-B}_2\text{O}_3$ system bond ionicity is 0.5751 and for binary $\text{Li}_2\text{O-Sb}_2\text{O}_3$ system bond ionicity decreases to 0.5729; on increasing the mol% of Sb_2O_3 .

Variation of bond ionicity for ternary $\text{Li}_2\text{O-B}_2\text{O}_3\text{-Bi}_2\text{O}_3$ system increases from (0.5756-0.5792). For binary $\text{Li}_2\text{O-B}_2\text{O}_3$ system bond ionicity is 0.5751 and for binary $\text{Li}_2\text{O-Bi}_2\text{O}_3$ system bond ionicity is 0.5796; on increasing the mol% of Bi_2O_3 .

Variation of free space volume for ternary $\text{Li}_2\text{O-B}_2\text{O}_3\text{-Sb}_2\text{O}_3$ system increases from (24.5504-67.5128) cm^3/mol . For binary $\text{Li}_2\text{O-B}_2\text{O}_3$ system free space volume is $19.5215 \text{ cm}^3/\text{mol}$ and for binary $\text{Li}_2\text{O-Sb}_2\text{O}_3$ system free space volume decreases to $73.2517 \text{ cm}^3/\text{mol}$; on increasing the mol% of Sb_2O_3 .

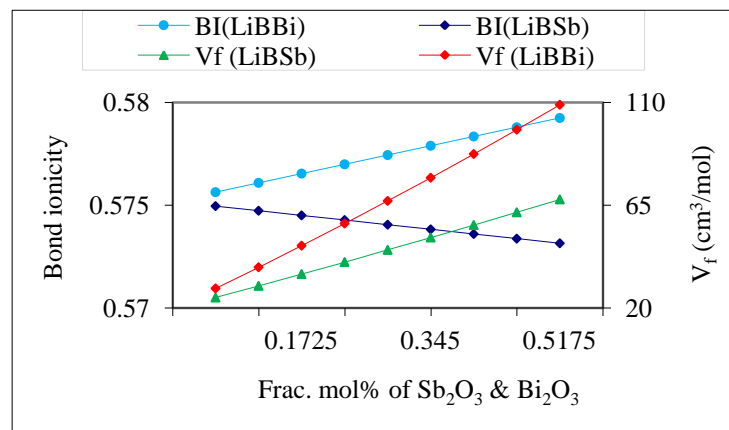


Figure 5 BI & V_f vs. fraction mol% of Sb_2O_3 & Bi_2O_3

Variation of free space volume for ternary $\text{Li}_2\text{O-B}_2\text{O}_3\text{-Bi}_2\text{O}_3$ system increases from (28.5611-108.9434) cm^3/mol . For binary $\text{Li}_2\text{O-B}_2\text{O}_3$ system free space volume is ($19.5215 \text{ cm}^3/\text{mol}$) and for binary $\text{Li}_2\text{O-Bi}_2\text{O}_3$ system free space volume is ($120.1341 \text{ cm}^3/\text{mol}$); on increasing the mol% of Bi_2O_3 .

Free space volume for ternary $\text{Li}_2\text{O-B}_2\text{O}_3\text{-Sb}_2\text{O}_3$ system and for ternary $\text{Li}_2\text{O-B}_2\text{O}_3\text{-Bi}_2\text{O}_3$ system; similarly for binary $\text{Li}_2\text{O-Sb}_2\text{O}_3$ and $\text{Li}_2\text{O-Bi}_2\text{O}_3$ systems are increasing in order. On comparing these two systems, free space volume of ternary $\text{Li}_2\text{O-B}_2\text{O}_3\text{-Sb}_2\text{O}_3$ system is smaller than that of $\text{Li}_2\text{O-B}_2\text{O}_3\text{-Bi}_2\text{O}_3$ ternary system; similarly bond ionicity of binary $\text{Li}_2\text{O-Sb}_2\text{O}_3$ system is also smaller than that of $\text{Li}_2\text{O-Bi}_2\text{O}_3$ system. Whereas for binary $\text{Li}_2\text{O-B}_2\text{O}_3$ system free space volume remains constant equal to $19.5215 (\text{cm}^3/\text{mol})$ and bond ionicity also remains constant equal to 0.5751 (cm^3/mol); due to common in both systems. Bond ionicity of Sb_2O_3 smaller due to large oxygen packing density and bond ionicity of Bi_2O_3 has large values due to small oxygen packing density. Free space volume of Sb_2O_3 and Bi_2O_3 depends up on ionic radius as they have no large difference in ionic radius therefore free space volume increasing is depends on increasing molar volume.

V. CONCLUSIONS

The studied glass materials are alkali metal (Li) and metals (Sb & Bi). The electronic configurations of these metal ions [(Kr) $4d^{10}5s^25p^3$, & (xe) $5d^{10}6s^2-6p^3$] is such that there is a pair of electrons in the outer most (5s,6s) orbital, with an outer electron shell of $18 + 2$ electrons and when small concentrations of the ions are dissolved in glass the 5s 5p & 6s-6p electronic transition take place. Rhombohedral structure and sp^3d (trigonal-bipyramid) belongs to third group of classification of oxide glasses (glasses formed by glass forming acidic and conditional glass-forming basic oxides).

The p - and d - orbitals strongly interact so that the d -states of the transition metal atoms hybridize with the p -bands. Such orbital hybridization is basically corresponding to nonbonding states with more optical polarization. Depending on the nature of valence orbitals, the substitution of p - and d -block elements results as increase in the glass molar volume through creation of nonbridging oxygen bonds. The looked-for mixed valence effect is to replace strong oxygen linkages of trigonal units by weaker anionic tetrahedral unit linkages and the more polarizable state. Due to the weaker

bonding, the molar volume increases and the glass network becomes more open. It provides wide pathways get ways for ions such as Li^+ to be more easily mobile in the glass matrix. The orbital hybridization is proven itself as an active technique to control the glass molar volume and thus to regulate effectively the glass ionic conduction. The gained results are molar volume, oxygen molar volume, boron molar volume, free space volume, bond ionicity and boron-boron separation parameters values are increasing whereas density, oxygen packing density and number of bonds per unit volume parameters values are decreasing; on increasing the mol % of Sb_2O_3 and Bi_2O_3 respectively.

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