

Role of Mixed Valence Effect and Orbital Hybridization on Molar Volume of Heavy Metal Glass for Ionic Conduction Pathways Augmentation

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Abstract Ionic conductivity of glasses can be engineered by understanding the chemical bonding properties and their effect especially on the glass molar volume. Thus, a series of heavy lead borate glass of the composition $0.25\text{B}_2\text{O}_3\text{--}0.75\text{PbO}$ is prepared by the melt quenching technique. The mixed valence effect and orbital hybridization of $3d$ -transition metal oxide and $4p$ -chalcogen combination are used through the co-substitution of Cr_2O_3 and SeO_2 by B_2O_3 to open up the glass network and to increase the glass molar volume. It provides weaker anionic tetrahedral $\text{BO}_{4/2}^-$ unit linkages instead of strong oxygen linkages of trigonal $\text{BO}_{3/2}$ units. Moreover, a gradual conversion of chromium ions from Cr^{6+} state to Cr^{3+} state exists where the Cr^{3+} ion is acting as a modifier to break up the glass local symmetry introducing additional coordinated defects. Among the different negative sites, the existence of nonbridging oxygen bonds and orbital hybridization or $p\pi\text{--}d\pi$ overlaps the molar volume increases and the glass network becomes more open. Thus, it would provide wide pathways for ions like Li^+ to be more easily mobile in the glass matrix. Chemical bond approach is used to explain the obtained results.

Keywords Glass, Molar volume, p - and d -block elements, Orbital hybridization, Ionic conductivity, Nonbridging oxygen, Bond density

1. Introduction

Metal oxides display physical properties ranging from piezoelectricity to superconductivity, from negative thermal expansion to ionic conductivity and transparent conductors. They are used in computers, Li-ion batteries, fluorescent lights, cellular phones, and fuel cells. 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]. High-temperature superconductor [2] was a milestone in the study of metal-oxides and is an effective example for the mixed valence chemistry. 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 [3]. 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. In lead borate glass the extreme difference between the masses of the lead and the boron atom are favorable for spectroscopic investigations. This is because increasing the heavy metal oxide content causes an increase in the glass thermal stability. Furthermore, glasses containing cations (such as Pb^{2+} , As^{3+} , or Bi^{3+}) with an outer electron shell of $18 + 2$ electrons should have higher polarizabilities and lower melting temperatures [4]. In the same context, lead monoxide possesses interesting semiconducting and photo conducting properties with potential applications in imaging devices, electro photography and laser technology.

Selenium has empty d -orbitals which can form four or six bonds by unpairing electrons. Overlap of a p -orbital on the oxygen with a d -orbital on Se gives a $p\pi\text{--}d\pi$ interaction [5]. To obtain effective $p\pi\text{--}d\pi$ overlap, the size of the d -orbital must be similar the size of the p -orbital. Since Se has a covalent radius of 1.14 \AA while for Cr it is 1.17 \AA , therefore, an overlap between them might be highly credible. Upon the glass structure, a strong overlap possibly arise providing $2p\text{--}3d$ orbital hybridization. Such orbital hybridization manifests itself as an increase in glass optical polarizability throughout spin-orbit coupling mechanism [6]. Selenium oxide possesses two kinds of structures as selenite and selenate around Se atom. Selenite (SeO_3^{2-}) acts as a modifier

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in the glass network with three coordinated oxygen and one lone pair of electrons, whereas the selenate (SeO_4^{2-}) with four coordinated oxygen occupies tetrahedral sites in the glass network and acts as a network former [7, 8].

The role of an ion in glass environment is largely determined by its ionic radius a , and its effective electrostatic field strength eZ/a^2 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 or +4 such as Cr, which having a lower electronegativity, with oxides have a higher electronegativity such as SeO_2 are required to design the glass optoelectronic structure such as the glass band gap [9-11].

Existing of chalcogenide elements in glass network provides a number of amorphous semiconductor-like properties [12, 13]. For instance, increasing the relative atomic mass of the chalcogen or its proportion in the glass reduces its average bond strength [14]. Elements such as Se have electronic structure s^2p^4 tend to gain two electrons forming M^{2-} ions, or to share two electrons and thus forming two covalent bonds. Many well-designed properties of the glass are obtained by using elements with mixed valences in the structure network [1]. In the present work, $3d-4p$ orbital replacement of B_2O_3 by a combination of Cr_2O_3 and SeO_2 is used to engineer the molar volume of a heavy metal borate glass. The chemical bond approach is used to analyze and to explain the role of mixed valence effect on the glass molar volume to enhance the expected glass ionic conductivity.

2. Experimental Details

2.1. Glass Preparation

Three series of lead borate glasses of composition $x\text{Cr}_2\text{O}_3-(0.25-x)\text{B}_2\text{O}_3-0.75\text{PbO}$, $x\text{SeO}_2-(0.25-x)\text{B}_2\text{O}_3-0.75\text{PbO}$ and $x(\text{Cr}_2\text{O}_3-\text{SeO}_2)-(0.25-x)\text{B}_2\text{O}_3-0.75\text{PbO}$ are prepared, Table 1, where x is the oxide molar fraction. The used materials were of chemically pure grade, in the form of H_3BO_3 , Cr_2O_3 , SeO_2 and Pb_3O_4 . The amount of the glass

batch was 50 g melt^{-1} . The glass was prepared by melt quenching technique using porcelain crucibles in an electric furnace. The temperature of melting was 1100°C , whereas the duration of melting was one hour after the last traces of batches were disappeared. To avoid the presence of bubbles in the glass melt, the melt was continuing stirred during the glass preparation. Then the melt was poured onto stainless steel mould and annealed at around 350°C to remove the thermal strains. Optical slabs were prepared by grinding and polishing of the prepared samples with paraffin oil and minimum amount of water. The thickness of the glass slabs was about 3 mm. Polishing was completed with stannic oxide and paraffin to reach a minimum surface roughness which was tested by an interferometric method. The homogeneity of the glasses was examined using two crossed polarizers.

2.2. Measurement of Glass Density

The hydrostatic density of the glasses, ρ , at room temperature was measured by the Archimedes principle using a sensitive microbalance. The error in measuring the glass density was 0.001 g/cm^3 .

3. Results and Discussion

3.1. Density and Molar Volume

The molar volume, V_m , of the glass was calculated using the expression:

$$V_m = \sum_i x_i M_i / \rho \quad (1)$$

where ρ is the glass density, x_i is the molar fraction and M_i is the molecular weight of the i th component, respectively. Table 1 illustrates the measured variation in the heavy metal borate glass density and molar volume due to incorporation of small equal molar fractions of SeO_2 and Cr_2O_3 on the expense of B_2O_3 content. This means that the bond length or interatomic spacing between the atoms may be attributed to the variation in the stretching force constants of the bonds inside the glass network.

Table 1. Glass compositions, density and molar volume

No.	Glass compositions	ρ (g/cm ³)	V_m (cm ³ /mol)
1 st Series			
1	0.25 B_2O_3 -0.75 PbO	5.641	34.544
2	0.002 SeO_2 -0.248 B_2O_3 -0.75 PbO	5.694	34.242
3	0.004 SeO_2 -0.246 B_2O_3 -0.75 PbO	5.685	34.313
4	0.006 SeO_2 -0.244 B_2O_3 -0.75 PbO	5.702	34.225
2 nd Series			
5	0.002 Cr_2O_3 -0.248 B_2O_3 -0.75 PbO	5.657	34.478
6	0.004 Cr_2O_3 -0.246 B_2O_3 -0.75 PbO	5.673	34.413
7	0.006 Cr_2O_3 -0.244 B_2O_3 -0.75 PbO	5.627	34.725
3 rd Series			
8	0.001 SeO_2 +0.001 Cr_2O_3 -0.248 B_2O_3 -0.75 PbO	5.640	34.574
9	0.002 SeO_2 +0.002 Cr_2O_3 -0.246 B_2O_3 -0.75 PbO	5.636	34.623
10	0.003 SeO_2 +0.003 Cr_2O_3 -0.244 B_2O_3 -0.75 PbO	5.555	35.151

3.2. Intermolecular Separation and Bond Density

Replacement of Cr_2O_3 or/and SeO_2 into the glass network instead of B_2O_3 makes effective changes for the density and molar volume of the base glass sample (i.e., sample 1). Since the molar masses of Cr_2O_3 and SeO_2 are 99.99 and 110.96 g/mol, respectively, while for B_2O_3 is 69.622 g/mol, so the replacement of SeO_2 by B_2O_3 explains such increase in the glass density of the base sample with increasing SeO_2 content as in samples 5, 6 and 7 (second series). The density and molar volume show opposite behavior (sample 4), where with the same SeO_2 amount ($x = 0.006$) the glass density increased by 1.06% and the molar volume decreased by 1.01%. The behavior of glass density reveals that, with the increase in SeO_2 content a partial reversible transformation occurs for a part of selenite groups (SeO_3^{2-}) into the more densselenate (SeO_4^{2-}) with its four coordinated oxygen occupying tetrahedral sites in the glass network.

In the same context, the fluctuation in the glass density which is seen with samples 1, 2, 3, and 4 (first series) due to replacement of Cr_2O_3 by B_2O_3 may be attributed to the conversion of chromium ions from Cr^{6+} state to Cr^{3+} state and vice versa. Sample 7 with Cr_2O_3 molar fraction 0.006 has the lowest density, second series. It means the conversion of chromium ions from Cr^{6+} state into Cr^{3+} state which has the longest ionic radius (0.65 Å) in compare with Cr^{6+} that has ionic radius 0.36 Å. Also the existing of Cr^{3+} ions acts as modifier which may create an inconsistency in the number of nonbridging oxygen bonds NBO relative to bridging oxygen bonds (BO). Glass samples 8, 9, and 10 (third series), which contain a variable equal share of mole fraction, x , for both Cr_2O_3 and SeO_2 , show a profound decrease in the glass density compared to the base glass sample. Such unexpected density and molar volume behaviors may be attributed to the creation of an excess of nonbridging oxygen bonds which open up the structure of the glass networks.

Analyzing the glass molar volume is more informative by correlate it with the role of SeO_2 and Cr_2O_3 hybridization on the number of bonds per unit volume (n_b). The number of bonds per unit volume of the glass is calculated using the relationship [15, 16]:

$$n_b = \frac{N_A}{V_m} \sum_i (n_c x_i) \quad (2)$$

where n_c is the coordination number of the cation. The used coordination number of B^{3+} , Pb^{2+} , Cr^{3+} and Se^{4+} are 4, 8, 6, and 4, respectively. Thus, the molar volume is found to increase with the decrease in number of bonds per unit volume of the present glass. Molar volume decreases also with increasing the SeO_2 and/or Cr_2O_3 content, as shown in Fig. 1. In comparison between sample 1 (base) and sample 10, the molar volume, V_m , is increased from 34.544 to 35.151 cm³/mol, respectively, accompanying with a decrease in number of bonds per unit volume, n_b , from 12.20 × 10²⁸ m⁻³ to 12.00 × 10²⁸ m⁻³. So the increase in glass molar volume could be ascribed to some structural changes such as the

increase in nonbridging oxygen bond density and in addition the associated decrease in the number of bonds per unit volume of the glass which is recognized with the equal share increase in molar fraction for both SeO_2 and Cr_2O_3 up to $x = 0.006$.

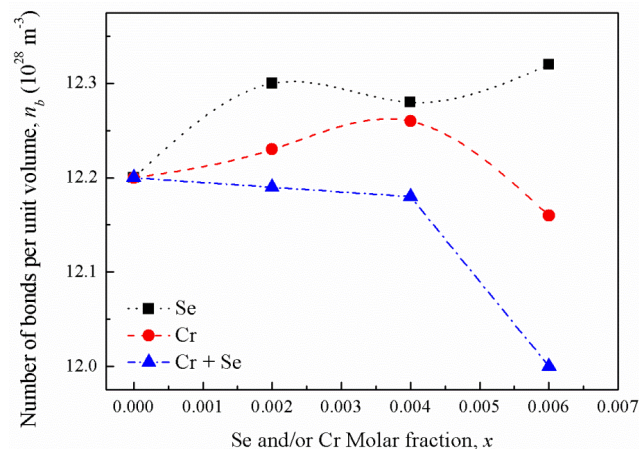


Figure 1. Number of bonds per unit volume versus oxide molar fractions

3.3. Oxygen Molar and Packing Densities

According to chemical bond approach and for further explanation the obtained glass molar volume and density behavior, many additional parameters would also be calculated which are; the volume of glass in which 1 mole of oxygen is contained (the molar volume of oxygen, V_o) and oxygen packing density (OPD). The molar volume of oxygen is given by [17]:

$$V_o = \frac{V_m}{\sum_i x_i n_i} \quad (3)$$

where n_i is the number of oxygen atoms in each oxide. The oxygen packing density is calculated from the density and composition using the formula:

$$\text{OPD} = 1000 C \left(\frac{\rho}{M} \right) \quad (4)$$

where C is the number of oxygens per formula unit. The determined oxygen molar density and oxygen packing density of the glass samples are shown in Figs. 2, 3. Regarding to samples 1 and 10, the obtained increase in oxygen molar volume from 28.20 to 28.74 cm³/mol, respectively, is associated with an increase in oxygen packing density from 115.79 to 256.04 mol/l. It confirms the formation of nonbridging oxygen bonds with the replacement of B_2O_3 by equal share of both SeO_2 and Cr_2O_3 contents up to a molar fraction of 0.006 (sample 10). This finding may be associated with a formation of more negatively charged tetrahedral $\text{BO}_{4/2}^-$ units, which leads to a variation in the ratio between trigonal $\text{BO}_{3/2}$ units and the anionic tetrahedral $\text{BO}_{4/2}^-$ units of the glass network [18, 19].

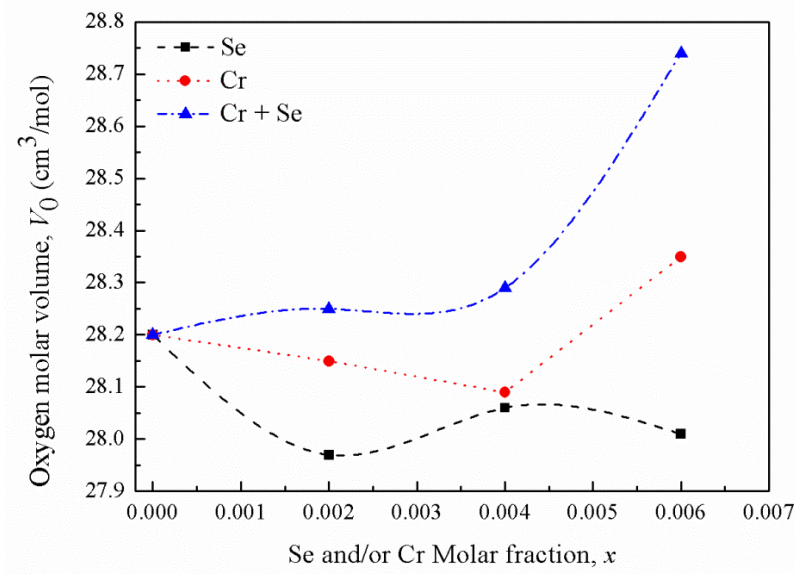


Figure 2. Oxygen molar volume versus oxide molar fractions

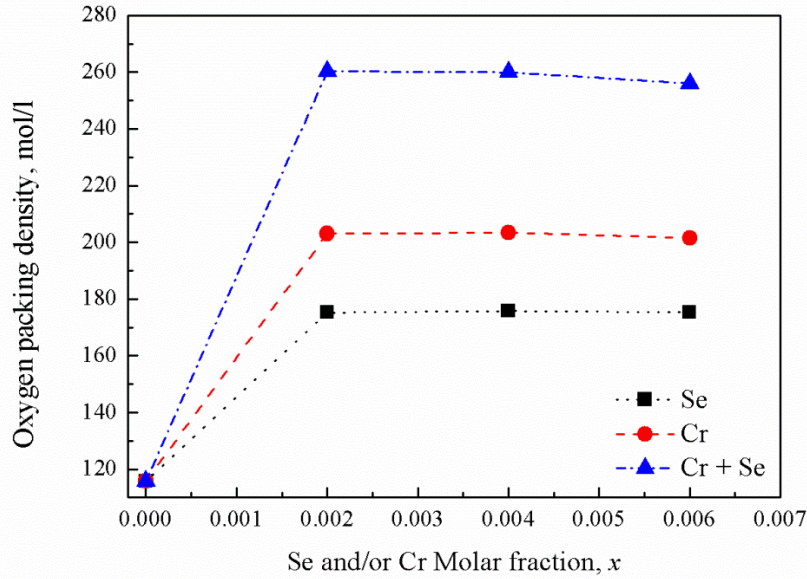


Figure 3. Oxygen packing density versus oxide molar fractions

In addition, conversion of chromium ions from CrO_4^{2-} structural units to predominantly Cr^{3+} state in octahedral environment may occur, taking part in network modifier positions. This situation is also responsible for the increase in nonbridging oxygens due to which an increase in the molar volume is obtained. Absence of CrO_4^{2-} structural units causes an increase in the degree of depolymerization of the glass network. For a chromium and selenium addition, as the case of samples 8, 9 and 10, a gradual conversion of chromium ions from Cr^{6+} state to Cr^{3+} state exists and the Cr^{3+} ion in such case acts as modifiers breaking up local symmetry and introduces coordinated bond defects in these glasses.

3.4. Boron Molar Volume and Glass Network Free Space

The average boron-boron separation $\langle d_{\text{B-B}} \rangle$ is calculated to

give more insight on the modification of the glass network due to the presence of SeO_2 and Cr_2O_3 . The boron atoms are the central atoms with negatively charged tetrahedral $\text{BO}_{4/2}^-$ units. Thus the boron molar volume V_m^{B} which corresponds to the volume that contains one mole of boron atoms within the specific glass structure is fined as [20]:

$$V_m^{\text{B}} = \frac{V_m}{2(1-x_{\text{B}})} \quad (5)$$

where x_{B} is the molar fraction of B_2O_3 oxide. The average boron-boron separation $\langle d_{\text{B-B}} \rangle$ is calculated using the expression:

$$\langle d_{\text{B-B}} \rangle = \left(\frac{V_m^{\text{B}}}{N_A} \right)^{1/3} \quad (6)$$

where N_A is Avogadro's number (6.0228×10^{23} g/mol). Since V_m^B depends on cation species, therefore, the calculated values of average boron-boron separation $\langle d_{B-B} \rangle$ are increased with the increase in the SeO_2 and Cr_2O_3 contents from 0.337 nm (sample 1) to 0.344 nm for sample 10. Thus, the incorporation of SeO_2 and Cr_2O_3 on expense of B_2O_3 leads to a substantial expansion of the glass structural network which confirms the obtained density and molar volume values. Furthermore, the calculated values of boronmolar volume V_m^B illustrate that with increasing both SeO_2 and Cr_2O_3 contents together on the expense of boron oxide, the V_m^B is increased from 23.029 (sample 1) to 23.248 cm^3/mol , respectively, as in case of sample 10. Since V_m^B depends on cation species, therefore, with the increase in the SeO_2 and Cr_2O_3 contents, an increase in the average boron-boron separation may be obtained. Thus, the incorporation of SeO_2 and Cr_2O_3 on expense of B_2O_3 leads to a substantial non densification of the glass structural network which approves the obtained density and molar volume values. The increase in the bond length or inter-atomic spacing between the atoms may be also attributed to a decrease in the stretching force constants of the bonds inside the glass network.

Additionally, the decrease in the number of bonds per unit volume, n_b , can be investigated by the determination of interatomic distance between Se and Cr atoms. For a glass has an oxide component, i , of $x_i\text{A}_b\text{O}_c$, where b and c are the valence of both the anion O and cation A, respectively, then the concentrations of the ions A and O are given by [20]:

$$n(\text{A}) = \frac{bx_i N_A}{V_m}, \quad (7)$$

$$n(\text{O}) = \frac{cx_i N_A}{V_m}, \quad (8)$$

The minimum separation distance, d , between identical ions is given by:

$$d = \left(\frac{1}{n} \right)^{1/3} \quad (9)$$

In comparison of the base sample with sample 10, the interatomic separation between oxygen atoms d_{O-O} of lead oxide increases from 0.425 nm to 0.428 nm with increasing of the combination of SeO_2 and Cr_2O_3 contents on the expenses of boron oxide content. This confirms once again the obtained increase in the glass molar volume. The ions without any spacing between them occupy only a volume equal to V_i which is given by $V_i = \sum_i \frac{4}{3} \pi r_i^3$ where r_i is the radius of the ion i and the summation is taken over all the ions present in one mole of the glass. Then the free space, V_f , in one mole of the glass [20] which is not occupied by the ions is equal to $V_f = V_m - V_i$. As shown in Fig. 4, increasing the mole fraction contents of SeO_2 and Cr_2O_3 together up to 0.006 (sample 10) increases the free space per mole from 21.14 (sample 1) to 21.75 cm^3/mole , respectively. So the conjunct introduction of SeO_2 and Cr_2O_3 enhances the $2p$ electron density of the unshared oxygen ion which in turn increases the ionicity of chemical bonds of glass. Hence it increases the intermolecular free space which leads to increase the glass molar volume [21].

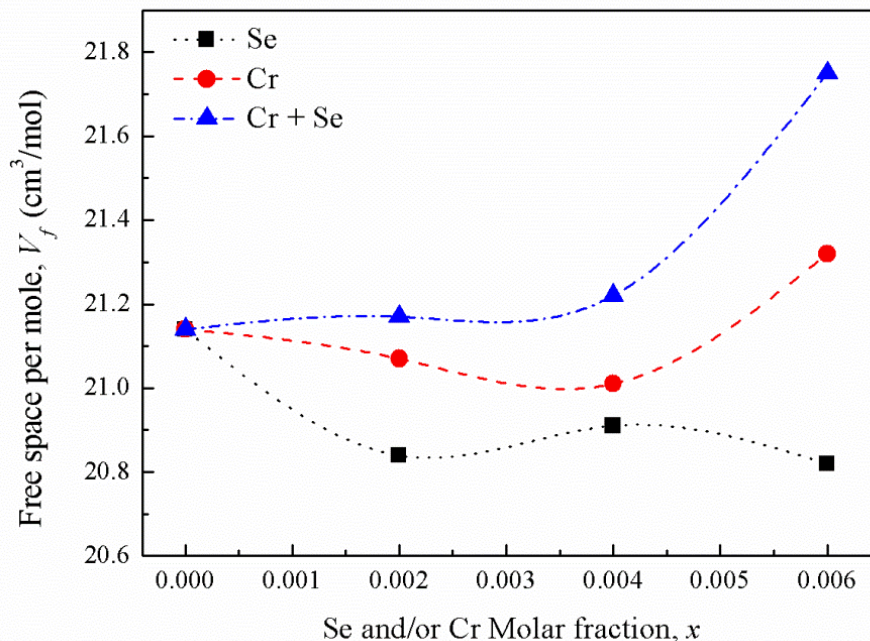


Figure 4. Free space per mole versus oxide molar fractions

3.5. Molar Volume and the Bond Ionicity

Boron has ionic cation radius 0.20 Å while Se and Cr have relative large ionic cation radii 1.84 and 0.65 Å, respectively. Therefore, it is expected that, with the insertion of Se and Cr transformation of a part of BO₃ groups into BO₄ groups is taking place. It produces an assured increase in the number of nonbridging oxygen bonds (NBO) relative to the bridging bonds (BO), which manifests itself by the increase in molar volume. Furthermore, the ionicity of oxides decreases with increasing polarization power of cations [22]. Accordingly, ionic character or bond ionicity (I_b) could describe the bonding nature of the investigated glass [23]. Therefore, the change in the molar volume of the present glass system could be discussed on the basis of a number of parameters such as electronegativity difference and Pauling's ionicity. The glass electronegativity difference, $\Delta\chi$, is calculated using the formula:

$$\Delta\chi = \sum_i x_i \Delta\chi_i \quad (10)$$

The electronegativity difference of the glass constituent oxide which is given by [24]:

$$\Delta\chi = \chi_A - \chi_C \quad (11)$$

where χ_A and χ_C are the Pauling electronegativity of the anion (oxygen) and that of the cation, respectively. Applying Pauling's empirical definition of bond ionicity, I_b , where

$$I_b = 1 - \exp(-0.25(\Delta\chi)^2), \quad (12)$$

gives a value for I_b of the glass. The electronegativity differences of the glass constituent oxide bonds B-O, Cr-O, Se-O and Pb-O are 1.4, 1.89, 0.89 and 1.44, respectively. The calculated bond ionicity, I_b , of the different glass samples exhibits a decrease in its value from 0.4002 with the base sample to 0.398 with 0.006 SeO₂ mole fraction (sample 4). In case of Cr₂O₃ with 0.006 mole fraction (sample 7) the bond ionicity is increased to be 0.402 due to the high electronegativity difference of Cr₂O₃.

With continues replacement of SeO₂ and Cr₂O₃ instead of B₂O₃, the bond ionicity showed almost no variation in its value which was 0.4002. This result could be understood through the change of some amount of Cr³⁺ with ionic radius 0.65 Å to Cr⁶⁺ which has less ionic radius of 0.36 Å. In general, it illustrates that there is a relationship between molar volumes of the glass and ametric atomic scale such as electronegativity differences of the glass constituent oxide bonds [25]. According to the classification for morphology of non-crystalline solids based on bond ionicity [26], the present glass system is considered as modified continuous random networks with increased interstitial spaces.

3.6. Nearest-neighbor Coordination

Because of its large glass forming region, nearest-neighbor coordination in a quaternary glass system is mostly appropriate to explain the obtained glass molar

volume values. The average coordination number, m , in the present glass system is defined by

$$m = \sum_i n_i x_i \quad (13)$$

where n_i is coordination number of the cation. The used coordination number of B³⁺, Pb²⁺, Cr³⁺ and Se²⁺ ions are 4, 8, 6, and 4, respectively. The calculated values of average coordination number of the investigated glasses show an increase upon the partial introducing for both SeO₂ and Cr₂O₃ into the glass network instead of boric acid. The increase in glass average coordination number from 7.00 to 7.006 exhibits the same trend of glass molar volume which is increased from 34.544 to be 35.151 cm³/mol, respectively. This behavior confirms that the average coordination number and molar volume are strongly correlated. Therefore, the induced structural change by SeO₂ and Cr₂O₃ in the glass partially converts BO₃ unit to BO₄ structural unit and the glass network begins to break up producing nonbridging oxygen bonds (NBOs). Such an expansion of the network due to NBOs with weaker BO₄ units (that is less tightly bounded with more polarized excited electrons) explains the obtained increase in the molar volume of sample 10.

Thus the increase in the glass molar volume due to mixed valence effect may result from the competition between three types of negative site with different binding energy.

The first type is due to the BO₄⁻ units where the negative charge is distributed around the boron site. The second is due to the conversion from bridging to nonbridging oxygen bonds which increases the negative charge localized on the B-O bond with a deeper potential well. The third is due to conversion of chromium ions from Cr⁶⁺ state to Cr³⁺ state. Thus through the mixed valence effect, with 3d-4p orbital replacement of B₂O₃ by a combination of small conjoint molar fractions of Cr₂O₃ and SeO₂, the molar volume of a heavy metal glass could be tuned. Thus it is possible to make comparatively cheap junctions with important implications for the economics of solar cells. No doubt, this anionic conduction would motivate the research on chalcogen-oxide glasses for Li-ion batteries, fluorescent lights, cellular phones, and fuel cells. So, increasing the glass molar volume might contribute directly in the production of promising glasses for ionic conduction domain [18, 27-29].

4. Conclusions

Conduction band mainly consists of atomic orbitals of cationic atoms, since anionic atoms are more electronegative than cationic atoms. Upon the structure of investigated glass, the *p*- and *d*- orbitals strongly interact so that the *d*-states of the transition metal atoms Cr hybridize with the chalcogen Se *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 (through

a very small replacement of boron oxide content by an equal share of molar fractions of SeO_2 and Cr_2O_3) is to replace strong oxygen linkages of trigonal $\text{BO}_{3/2}$ units by weaker anionic tetrahedral $\text{BO}_{4/2}^-$ unit linkages and the more polarizable Cr^{3+} state. The projected result would be glass network weakening with a decrease in both the melting temperature and the viscosity of the melt. 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 would encourage and may drive to further prospective researches on the fields of interest related to the present study.

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