Glass-forming region, electrical and structural properties of BiPO4-NbOPO4-P2O5 (Bi2O3-Nb2O5-P2O5) glasses

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Abstract

The glass forming region has been determined in the ternary system BiPO4-NbOPO4-P2O5. Glasses with compositions xBiPO4-(90-x)P2O5-10NbOPO4 ($20{\leq}x{\leq}35$ mol%) and 20BiPO4-(80-x)P2O5-xNbOPO4 ($5{\leq}x{\leq}30$ mol%) were prepared. Their physical, electrical and structural such as density, molar volume, ionic conductivity and FT-IR spectroscopy have been studied in order to understand the structural role of Bi2O3 and Nb2O5 in these glasses. The density of these glasses increases and their molar volume decreases with Bi2O3 and Nb2O5 contents. FT-IR study shows absorption peaks around 1200 cm^{-1}, 1100 cm^{-1}, 1000 cm^{-1}, 900 cm^{-1}, 780-730 cm^{-1}, and 520-480 cm^{-1} corresponding to (PO2)s, (PO3)as, (PO3)s, (P-O-P)as, (P-O-P)s and the bending vibration (δ) of P-O bonds, respectively. The ionic conductivity σ diminishes substantially with increasing concentration of either Bi2O3 or Nb2O5. The variation in σ is related to the decrease in O^{2-} concentration, their mobilty and in the glass network polarization. A correlation between electrical and structurl properties of these glasses has been established.

1. Introduction

P2O5 glasses have several advantages over conventional silicate and borate glasses due to their superior physical properties. However the poor chemical durability, high hygroscopic and volatile nature of phosphate glasses prevented them from replacing the conventional glasses in a wide range of technological applications. In recent years there have been enormous amounts of research on improving the physical properties and the chemical durability of phosphate glasses by introducing a number of glass formers and modifiers such as: Al2O3, MoO3, As2O3, Fe2O3, Sb2O3, Ta2O5, etc… into P2O5 glass network [1, 2].
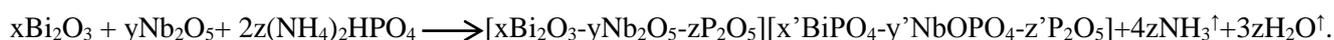
Among various glass systems, the bismuth are considered to be stable and found to be more suitable for the presence of several ions like Li$^+$, Na$^+$, Pb^{2+}, etc. [3-5]. From another view point, the effect of Bi2O3 on the different properties of phosphate glasses has been investigated [6, 7]. In recent years many investigators have reported electrical properties of bismuth-containing phosphate glasses [5, 8, 9]. The obtained results show that the electrical conductivity diminishes with increasing concentration of Bi2O3, and they found that Bi2O3 is present in the octahedral coordination (BiO6). However, Bismuth oxide is not traditional glass former and cannot form glass by itself. In the presence of strong polarizing cations, Bi (III) can reduce its coordination number from six to the three and the glass networks may consist of both [BiO6] highly distorted octahedral and [BiO3] pyramidal units [10, 11]. Because of its dual role, as modifier with [BiO6] octahedral and glass former with [BiO3] units, bismuth ions may influence the electrical properties of glasses.

On the other hand, the glasses containing Nb2O5 are of great interest because of their application as nonlinear photonic materials [12, 13], and as laser hosts having high simulated emission parameters [14]. However, the investigation on the role played by Nb2O5 in the structure of phosphate glass, the coordination state of Nb^{5+}, and the interaction with other elements in the glass network is the subject of many researches. Rachkovskaya and Bubkova [15] have studied glasses P2O5-Nb2O5-V2O5-TiO2 and P2O5-Nb2O5-V2O5-Fe2O3 by infrared spectroscopy. They have found evidence of the existence of NbO4 and NbO6 units. Fukumi and Sakka [16], using Raman spectroscopy, confirmed that there are NbO6 polyhedral in the glass network of SiO2-Nb2O5-K2O. de Aroujo et al. [17, 18] have studied the structure and the electrical properties of lithium niobophosphate glasses and have found that Nb2O5 is present in the octahedral coordination NbO6.

Recently, thermal, structural and ionic conduction of lithium niobophosphate glasses have been studied by Prashant and Hariharan [19]. The authors have observed a significant modification in the structure of lithium metaphosphate glasses, due to the incorporation of Nb_2O_5, such as evolution of NbO_6 octahedral and reduction in the number of non-bridging oxygen in the glass matrix. The main purpose of this work is to investigate the influence of bismuth and niobium oxides contents on the structural and properties, mainly the infrared spectroscopy and electrical measurements, of the glasses with compositions xBiPO$_4$-(90-x)P$_2$O$_5$-10NbOPO$_4$, where x = 20, 25, 30 and 35 in mol%, and 20BiPO$_4$-(80-x)P$_2$O$_5$-xNbOPO$_4$, where x = 5, 10, 20 and 30, in mol %. Other properties such as density and molar volume are also studied in order to understand the structural role of these oxides in the studied glasses.

2. Materials and methods

The glasses investigated had molar compositions x'BiPO$_4$–y'NbOPO$_4$–z'P$_2$O$_5$ (xBi$_2$O$_3$–y Nb$_2$O$_5$-zP$_2$O$_5$). The glasses were prepared from bismuth oxide Bi_2O_3, niobium oxide Nb_2O_5, and diammonium hydrogen phosphate according to the reaction scheme:

$$xBi_2O_3 + yNb_2O_5 + 2z(NH_4)_2HPO_4 \longrightarrow [xBi_2O_3\text{-}yNb_2O_5\text{-}zP_2O_5][x'BiPO_4\text{-}y'NbOPO_4\text{-}z'P_2O_5] + 4zNH_3^{\uparrow} + 3zH_2O^{\uparrow}.$$

The corresponding ground mixtures were introduced in a alumina crucible and heated for 12 h at a temperature varying between 200 and 500°C in order to expel NH_3, and H_2O. The temperature was then progressively raised to 1100°C and held constant at this value for 15 min. the molten glasses were then quenched to room temperature under air atmosphere in order to produce vitreous samples.

Powder X-Ray diffractometry (XRD) was used to examine all the as-quenched melts to confirm the amorphous state of the samples.

Density was measured at room temperature, using with diethyl phthalate as then immersion fluid. The relative error in these measurements was about ±0,03g/cm^3.

FT-IR Characterization of the samples was performed using a JAXO FT/IR 4600 spectrometer equipped with a JAXO PRO ONE module. The sample was scanned in transmission mode 4 cm^{-1} resolution at the range 4000-400 cm^{-1}.

The electrical conductivity of the glass was measured by conductance method at 16 kHz using an automatic PHILIPS PM 6302 LCR bridge. The temperature range explored is ranging from 50 to 500°C.

All the measurements were undertaken along the two lines denoted N and B (Figure 1 and Table 1), which correspond xBiPO$_4$-(90-x)P$_2$O$_5$-10NbOPO$_4$, where x = 20, 25, 30 and 35 in mol%, and 20BiPO$_4$-(80-x)P$_2$O$_5$-xNbOPO$_4$, where x = 5, 10, 20 and 30, in mol %%), respectively.
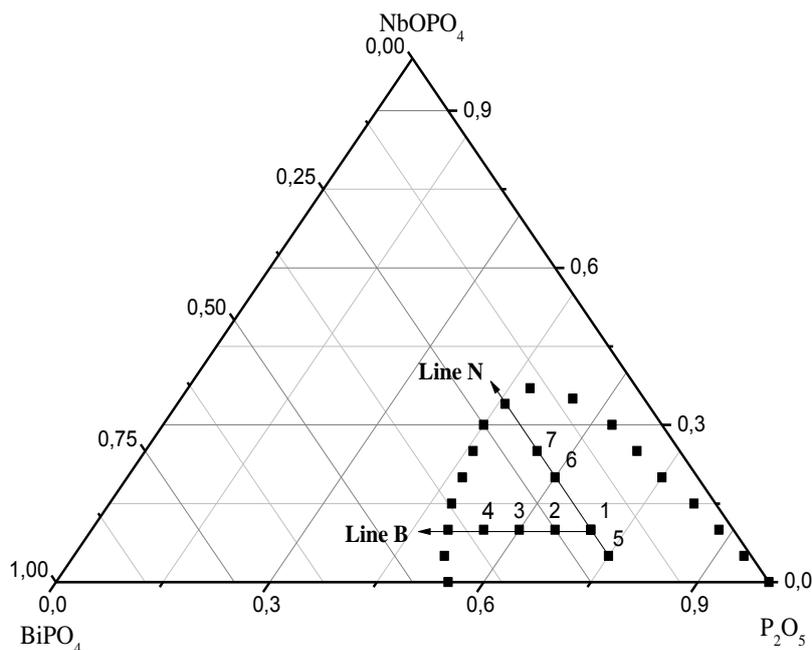
3. Results and discussion

3.1. Glass forming region

The prepared composition, that appeared to be amorphous by X-ray diffraction (absence of diffraction peaks), was classified as being within the forming region.

The nominal compositions of the studied specimens are indicated in Table 1. Figure 1 shows the glass-forming region inside the ternary system reported. The composition of any point inside the diagram is given by the following formula: x'BiPO$_4$–y'NbOPO$_4$–z'P$_2$O$_5$, where x', y' and z' are the molar fractions of BiPO$_4$, NbOPO$_4$ and P$_2$O$_5$, respectively.

Table 1: Glass composition (mol %), density ρ (g.cm^{-3}), molar volume V$_m$ (cm^3.mol^{-1}) and activation energy E$_a$ (eV) of the studied glasses.
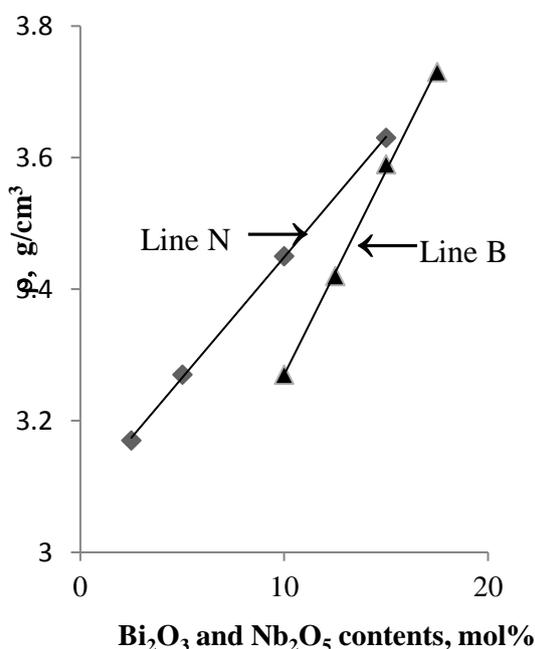
Glass no.	Ternary system BiPO$_4$-P$_2$O$_5$-NbOPO$_4$			Ternary system Bi$_2$O$_3$-Nb$_2$O$_5$-P$_2$O$_5$			ρ	V$_m$	E$_a$
	BiPO$_4$	P$_2$O$_5$	NbOPO$_4$	Bi$_2$O$_3$	Nb$_2$O$_5$	P$_2$O$_5$			
1	20	70	10	10	5	85	3.27	78.11	4.10
2	25	65	10	12.5	5	82.5	3.42	76.34	4.28
3	30	60	10	15	5	80	3.59	74.32	4.76
4	35	55	10	17.5	5	77.5	3.73	73.22	5.20
5	20	75	5	10	2.5	87.5	3.17	80.21	2.99
6	20	60	20	10	10	80	3.45	74.03	5.79
7	20	50	30	10	15	75	3.63	71.34	7.10

Figure 1: Glass-forming region in the ternary system $BiPO_4$-P_2O_5-$NbOPO_4$ at 1100°C.

3.2. Density and molar volume

The molar volume of the $xBiPO_4$-$(90-x)P_2O_5$-$10NbOPO_4$ and $20BiPO_4$-$(80-x)P_2O_5$-$xNbOPO_4$ glasses were calculated from their densities ρ, and their molecular weights, M ($V_m = M/\rho$). The obtained results are collected in Table 1 and are graphically presented in Figures 2 and 3, respectively.

Figure 2: Variation of density with glass compositions for $BiPO_4$-P_2O_5-$NbOPO_4$ glasses

Figure 3: Variation of molar volume with glass compositions for $BiPO_4$-P_2O_5-$NbOPO_4$ glasses

The replacement of P_2O_5 by Bi_2O_3 or Nb_2O_5 results in a linear increase in density. The increase in density indicates that the bismuth and niobium ions reticule the network of the glass. In order to confirm this result, we are interested in the evolution of molar volume in both series of glasses as a function of Bi_2O_3 and Nb_2O_5

(Figure 2). With increasing Bi_2O_3 or Nb_2O_5 contents, the molar volume decreases linearly confirming that both oxides participate in the crosslinking of the vitreous network. Indeed, Rani et al. [20] ascribed the decrease in molar volume V_m with increase in density (ρ) and Bi_2O_3 content, to the formation of Bi—O bonds at the expense of P—O bonds, which reticule the phosphate network and lead to the close structure of the glasses. Similar view point was also used to interpret the formation of Bi—O bonds in Li_2O-Bi_2O_3-P_2O_5 [21] and ZnO-Bi_2O_3-P_2O_5 [22] phosphate glasses.
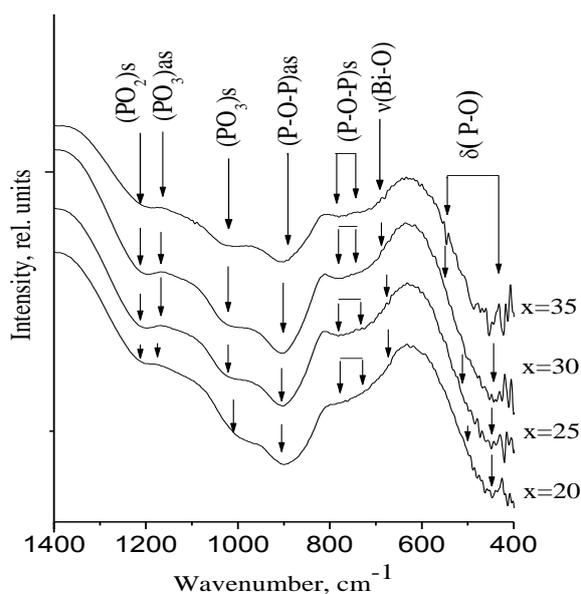
When P_2O_5 increasingly is replaced by Nb_2O_5, the molar volume decreases monotonically with the increase of Nb_2O_5 content. These results indicate a more compact and cross-linked glass network by the formation of Nb—O bonds at the expense of P—O bonds.

The more dense and integrated glass network with increasing Nb_2O_5 is also evidenced by the increases in the glass density (although the contribution of the larger molecular of Nb_2O_5 to the density cannot be negliged).
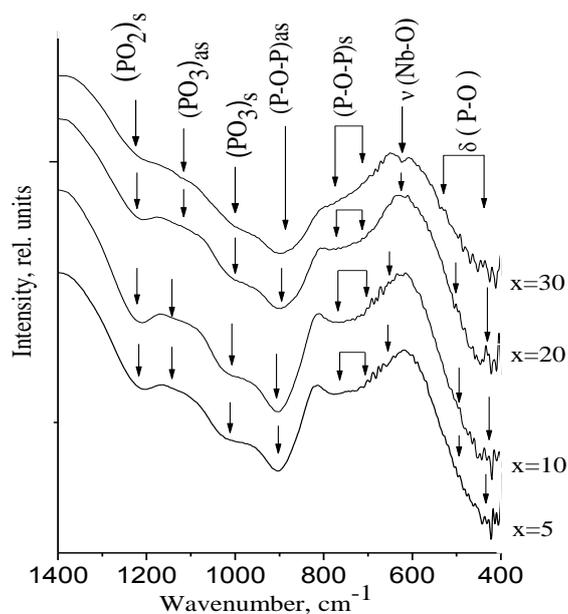
3.3. FT-IR study

Generally, the properties of glass depend upon its composition and its structure to some extent. Phosphate glasses containing bismuth or niobium oxides have a complex composition of network formers, intermediates, modifiers. P_2O_5 is well known network former with PO_4 is doubly bonded to the phosphorus with a substantial π–bonds character to account for the pentavalency phosphorus [23].

FT-IR transmission spectra of $xBiPO_4$-$(90-x)P_2O_5$-$10NbOPO_4$ and $20BiPO_4$-$(80-x)P_2O_5$ -$xNbOPO_4$ glasses with various contents of bismuth or niobium oxides in the frequency range 400 and 1400 cm^{-1} are presented in Figure 4 and 5, respectively.

Figure 4: FT-IR spectra of xBiPO$_4$-(90-x)P$_2$O$_5$-10NbOPO$_4$ glasses at room temperature.

Figure 5: FT-IR spectra of 20BiPO$_4$-(80-x)P$_2$O$_5$-xNbOPO$_4$ glasses at room temperature.

The band near 1200 cm^{-1} is assigned to the PO_2 symmetric stretching mode motion$(PO_2)_s$ [24, 25], the vibration band at 1100 cm^{-1} is attributed to υ_{as} of PO_3 groups (chain end groups). The absorption around 1000 cm^{-1} has been assigned to υ_s of PO_3 [26]. The absorption bands near 900 cm^{-1} are assigned to (P-O-P)$_{as}$, the asymmetric strechnig motion of oxygen atoms bridging two phosphorus atoms in Q^3 phosphate tetrahedron [27], these bands shift to a higher frequency as Bi_2O_3 (or Nb_2O_5) replaces P_2O_5. The modes around 780 and 730 cm^{-1} are assigned to the strechnig modes of the P-O-P linkages, (P-O-P)$_s$ in Q^2 and Q^1 phosphate tetrahedron, respectively [27, 28]. The bands around 520 and 480 cm^{-1} are attributed to the bending vibration (δ) of P-O bonds [28-30].

The substitution of P_2O_5 by Nb_2O_5 (line N) induces a significant changes in the FT-IR spectra. The intensties vibrations associated with the bridging oxygen (P-O-P) around 780 cm^{-1} decrease and a new bands appear
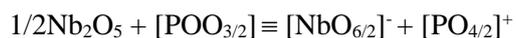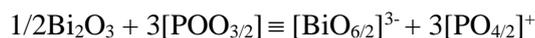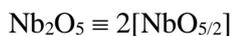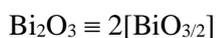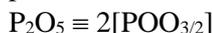
around 650 cm^{-1}. The absence of a band near 1250 cm^{-1} in the studied glasses indicates the absence of the double bonded P=O. The vibrations associated with the non-bridging oxygen (PO$_3$) also decrease with the presence of Nb$_2$O$_5$. This suggestes that the nobium oxygen octahedra are using the NBO associated with the phosphorus to form the glass network structure.

Similarly, such a view point was used to interpret the formation of covalent Nb—O bonds in ternary lithium niobophosphates glasses [19] and in two quaternary systems P$_2$O$_5$-Nb$_2$O$_5$- Fe$_2$O$_3$-PbO [31], and P$_2$O$_5$-Nb$_2$O$_5$-Fe$_2$O$_3$-Li$_2$O [18] phosphate glasses.
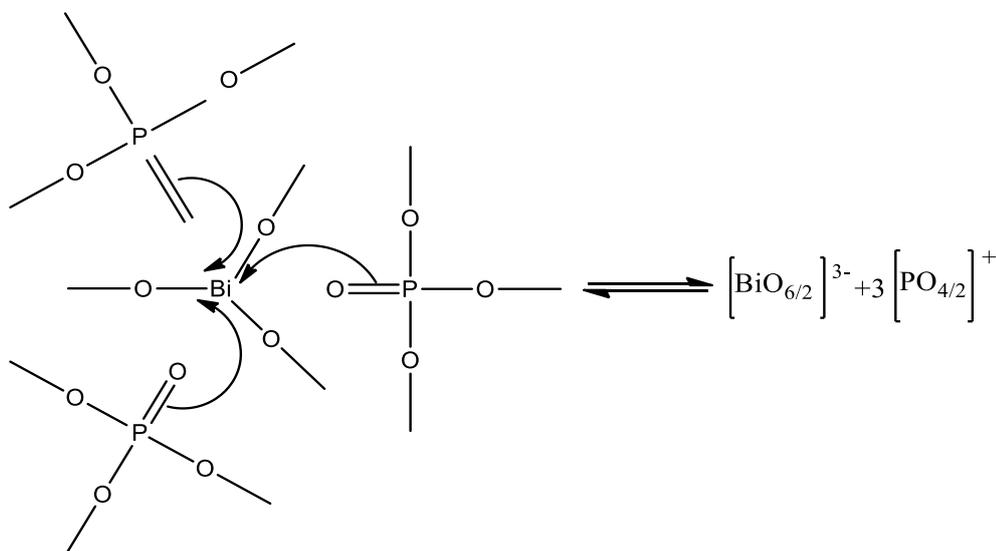
In the case of glassy materials in which P$_2$O$_5$ is replaced by Bi$_2$O$_3$ (line B), same structural change was observed by infrared spectroscopy. A decrease in the amplitude of the vibration band at 1000 cm^{-1} and the appearance of a new band at about 650 cm^{-1} appears. The vibration band around 630 cm^{-1} can be attributed to vibrations of Bi—O bonds of distorted BiO$_6$ octahedral [4, 32].
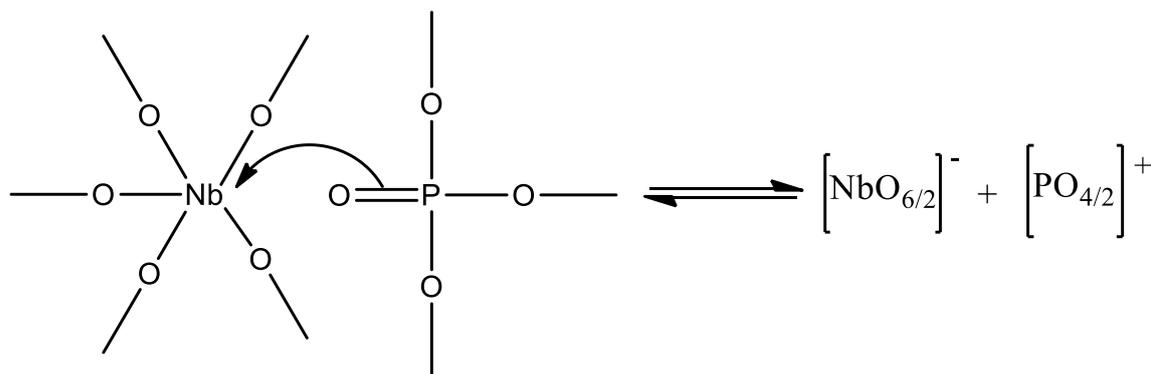
In both lines, the simultaneous occurrence of the two bands characteristic of the P-O-P bridge may be considered as a good indication of the existence of pyrophosphate groups [33]. Pyro-and meta-phosphate compositions give bands in the 900 and 750 cm^{-1} regions; but the meta-phosphate glass is characterized by two modes at around 700$\pm$800 cm^{-1}, which are attributed to the symmetric stretching of P-O-P groups [34], and a strong absorption in 1300 cm^{-1} regions, this absorption in typical of meta-phosphate chains, and its absence in the spectra of the both lines glasses is a good indication that this latter does not contain important amounts of chain structure. In Bi$_2$O$_3$ and Nb$_2$O$_5$ containing glasses it is assumed that in such glasses Bi$_2$O$_3$ and Nb$_2$O$_5$ exist mostly as BiO$_6$ [4, 32] and NbO$_6$ [17-19]. Bi and Nb are located in octahedral sites of type [BiO$_{6/2}$] and [NbO$_{6/2}$] respectively. These units can act as building blocks in the structure of these glasses, along with [POO$_{3/2}$] types of tetrahedral units arising from P$_2$O$_5$ by the corner sharing of oxygen [35].

When Bi$_2$O$_3$ (or Nb$_2$O$_5$) is added to phosphate glasses, the structure chains is broken into pyrophosphate groups (P$_2$O$_7$)$^{4-}$ [34] and the P-O-P bonds are depolymerized by the incorporation of distorted Bi(6) (or Nb(6)) units through P-O-Bi bonds (P-O-Nb). These results agree with a closer structure and act in a manner that Bi$_2$O$_3$ or Nb$_2$O$_5$ enter the glassy matrix as a network former character. It is assumed that bismuth (or niobium) to be present as corner-sharing [BiO$_{6/2}$]$^{3-}$ and [NbO$_{6/2}$]$^-$ octahedral units. The formula [BiO$_{6/2}$]$^{2-}$ and [NbO$_{6/2}$]$^{2-}$ suggests that the additional oxygen atoms are required for the coordination of bismuth and niobium (since Bi$_2$O$_3$ and Nb$_2$O$_5$ themselves can almost generate [BiO$_{3/2}$] and [NbO$_{5/2}$] in the network ans it has be provided by the host network and the electrical neutrality is achieved by the conversion of [POO$_{3/2}$] into [PO4/2]$^+$ units. The processes of incorporation of Bi$_2$O$_3$ and Nb$_2$O$_5$ into the network can be represented as:

P$_2$O$_5$ $\equiv$ 2[POO$_{3/2}$]

Bi$_2$O$_3$ $\equiv$ 2[BiO$_{3/2}$]

Nb$_2$O$_5$ $\equiv$ 2[NbO$_{5/2}$]

1/2Bi$_2$O$_3$ + 3[POO$_{3/2}$] $\equiv$ [BiO$_{6/2}$]$^{3-}$ + 3[PO$_{4/2}$]$^+$

1/2Nb$_2$O$_5$ + [POO$_{3/2}$] $\equiv$ [NbO$_{6/2}$]$^-$ + [PO$_{4/2}$]$^+$
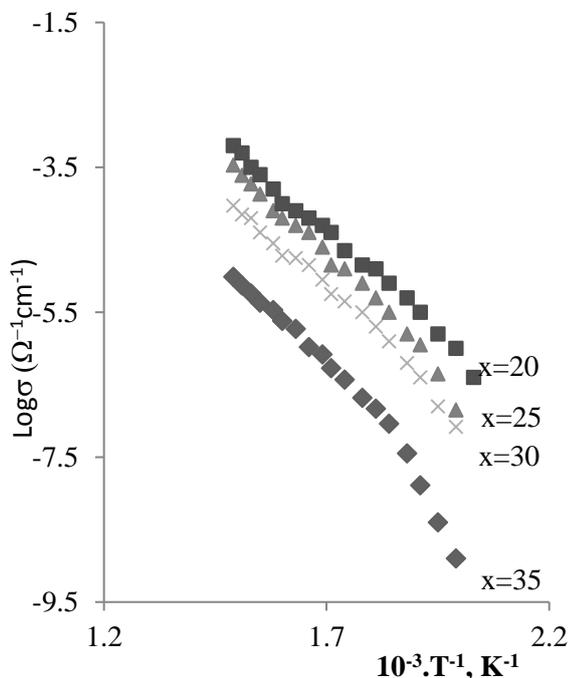
This process can be represented schematically as shown below.

3.4. Ionic conductivity

We have investigated the ionic conductivity of two lines of glasses with composition xBiPO$_4$-(90-x)P$_2$O$_5$-10NbOPO$_4$ with 20≤x≤35 mol% and 20BiPO$_4$-(80-x)P$_2$O$_5$-xNbOPO$_4$ with 5 ≤x≤30 mol%. The temperature dependence in the temperature range studied is given in figures 6 and 7 for two lines, respectively as plots of Logσ versus reciprocal temperature in the temperature range 100–500°C, since no significant variation has been observed below 100°C.
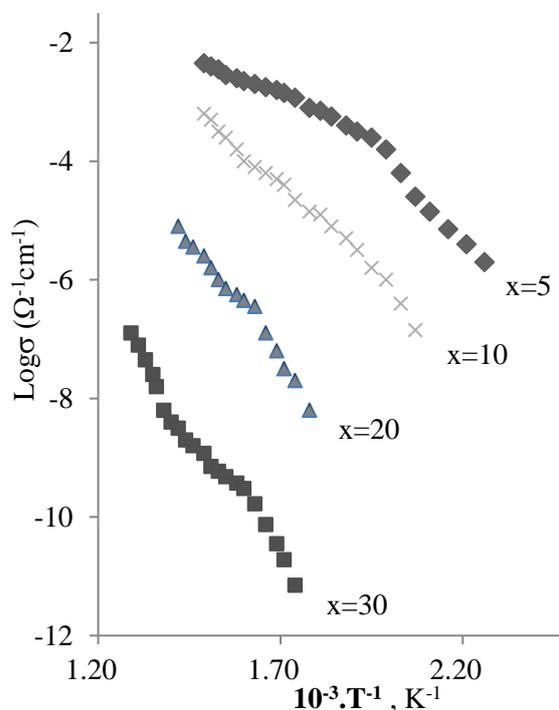
The temperature dependence of conductivity for the glass series, increase with increasing temperature, this can be described by typical Arrhenius, governed by the relation: $\sigma = \sigma_0\exp(\frac{-E_a}{KT})$ where σ_0 is the pre-exponential factor, E_a is the activation energy for ionic conduction, K is Boltzmann's constant and T is absolute temperature in Kelvin.

From the figures 6 and 7, it can be seen that the conductivity decreases with the replacement of P$_2$O$_5$ by Bi$_2$O$_3$ or Nb$_2$O$_5$.

The variation of ionic conductivity with concentration of bismuth or niobium oxides at different temperatures is illustrated in figures 8 and 9. The values of the activation energy for conduction, calculated from the slop of the graphs of logσ against T^{-1} are summarized in Table 1.

Figure 6: Variation of Logσ versus 10^3.T^{-1} for xBiPO$_4$-(90-x)P$_2$O$_5$-10NbOPO$_4$ glass compositions at a fixed frequency (16 kHz).

Figure 7: Variation of Logσ versus 10^3.T^{-1} for 20BiPO$_4$-(80-x)P$_2$O$_5$-xNbOPO$_4$ glass compositions at a fixed frequency (16 kHz).

Figure 8: Variation of σ with Bi_2O_3 content for xBiPO$_4$-(90-x)P$_2$O$_5$-10NbOPO$_4$ glasses at different temperatures.

Figure 9: Variation of σ with Nb_2O_5 content for 20BiPO$_4$-(80-x)P$_2$O$_5$-xNbOPO$_4$ glasses at different temperatures.

The decrease of conductivity with increasing concentration of bismuth or niobium oxides can be explained by: 1) a decrease in the number of carriers O^{2-} and their mobility (in the case of the line B); 2) a decrease in the glass network polarization (in both lines). When Bi_2O_3 or Nb_2O_5 replaces P_2O_5, P—O$^{\delta-}\cdots$Bi$^{\delta+}$ and P—O$^{\delta-}\cdots$Nb$^{\delta+}$, are formed [22, 29] with stronger covalent Bi—O and Nb—O bonds than P—O bond. Thus, the glass is expected to possess a more close structure, this means that the glass will show a decrease in molar volume (Table 2). The decrease of molar volume should narrow the paths of mobile ions and this reduces their mobility. Analogous results have been observed in many other glassy materials [6, 25, 36-38]. Thus, the increase in Ea and the decrease in σ may be consistent with the partially-forming character of the bismuth and niobium oxides. Similar results have been observed in many other oxide glasses [25, 36-38]. These results confirm those observed in infrared spectra.

Conclusions

In the present work, the density, molar volume, infrared spectroscopy and ionic conductivity have been studied for xBiPO$_4$-(90-x)P$_2$O$_5$-10NbOPO$_4$ with $20 \leq x \leq 35$ mol% and 20BiPO$_4$-(80-x)P$_2$O$_5$-xNbOPO$_4$ with $5 \leq x \leq 30$ mol% glasses. Results of study on physical properties are in good agreement with FT-IR analyses. When Bi_2O_3 and Nb_2O_5 are added to phosphate glasses, P-O-Bi and P-O-Nb bonds are formed with a strong covalent Bi-O and Nb-P bands. This suggests that both Bi_2O_3 and Nb_2O_5 act as the network former. The dercrease in conductivity and the increase in activation energy with the substitution of Bi_2O_3 and Nb_2O_5 for P_2O_5 are attributed to the decrease in O^{2-} concentration, their mobilty and in the glass network polarization.

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