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Structural role of BaO and PbO in BaO-PbO-B_2O_3 glasses

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ABSTRACT

FTIR spectra of three BaO-PbO-B_2O_3 glass series have been analyzed xBaO (30-x)PbO 70B_2O_3 ($0 \leq x \leq 30$ mol%), xBaO (40-x)PbO 60B_2O_3 ($0 \leq x \leq 40$ mol%) and xBaO (50-x)PbO 50B_2O_3 (0x ≤ 50 mol%). The fraction N_4 of four coordinated boron is constant with increasing the BaO content, at the expense of PbO in the first two series and then N_4 decreases in the third series. By using Doweidar's Differential change model to make use of the N_4 data and follow the change in the modifier and nonbridging fractions of BaO and in the modifier and former fractions of PbO. These fractions change markedly, at different rates, with the glass composition.

KEYWORDS

Borate;
FT-IR;
Oxide glass.

INTRODUCTION

Recently, glasses containing barium oxide have attracted considerable attention due to their interesting properties leading to different applications. Oxide glasses containing significant concentrations of transition metal ions or low mobility metal ions such as Zn^{2+} or Ba^{2+} exhibit electronic conductivity and may be regarded as high resistivity semiconductors[1]. Addition of barium to borate glasses has provided a suitable glass matrix for immobilization of sulphate bearing HLW[2]. Glasses containing barium are also proved to be good radiation shielders[3].

B_2O_3 forms, with modifier oxides, glassy networks consisting of symmetric BO_3 triangles, BO_4 tetrahedra and asymmetric BO_3 units. The concentration and the form of these units depend on the modifier oxide content in glass. These units may arise either as separated units or in the form of groupings such as boroxol, penta-, tri-, di-, meta-, pyro- and orthoborate[4,5].

PbO is known to enter PbO-B_2O_3 glasses as only a modifier oxide up to 15 mol%. In this case PbO is entirely consumed to convert triangular BO_3 units into BO_4 tetrahedra[6,7]. Above 15-20 mol% PbO some lead atoms start to be network former in the form of PbO_4 units. The fraction of PbO_4 units undergoes a monotonic increase when increasing the PbO content up to the glass formation limit[8]. On the other hand, there is an increase in the concentration of BO_4 units and thus in the fraction N_4 of four coordinated boron atoms up to a maximum around 50 mol% PbO. Non-bridging oxygen ions (NBOs) do not form in this composition region[5-7]. Bray et al.[6] ruled out formation of NBOs in the borate network above 50 mol% PbO. In contrary, Meera et al.[5] indicated that for PbO>50 mol% NBOs would be formed at the expense of BO_4 units.

NMR investigation by Greenblatt and Bray[9] in barium borate glasses revealed that until R=0.5 symmetric BO_3 units with three bridging oxygens convert to BO_4 tetrahedra at a rate approximately equal to two tetrahedra per added oxygen. This occurs with essentially no formation of non-bridging oxygens (NBOs). Above R=0.5 and until their data run out near R=1, the tetrahedra convert to asymmetric BO_3 with one or two non-bridging oxygens. These results are essentially the same as those found in the lithium and sodium borates[9-10].

The present work aims to investigate BaO–PbO–B_2O_3 glasses. It is a trial to explore the structure of this type of glass, by taking in consideration the dual structural role of PbO.

EXPERIMENTAL

Three series of glass, of the formulae xBaO (30-x)PbO 70B_2O_3 ($0 \leq x \leq 30$ mol%), xBaO (40-x)PbO 60B_2O_3 ($0 \leq x \leq 40$ mol%) and xBaO (50-x)PbO 50B_2O_3 ($0 \leq x \leq 50$ mol%), were prepared using high quality H_3BO_3, PbO and $BaCO_3$. The glasses were prepared under normal atmospheric conditions by melting the well-mixed raw materials in porcelain crucibles in an electric furnace at temperatures ranged between 900 °C and 1300 °C, depending on the glass composition. The melt was swirled frequently to insure the homogeneity. The melt was then poured and pressed between two stainless steel plates to form discs of 1 to 2 mm thickness. All the obtained samples were visually homogeneous and transparent.

The FTIR absorption spectra were obtained, by KBr pellets technique, at room temperature in the range 400-2000 cm^{-1} using Mattson 5000 FTIR spectrometer with a spectral resolution of 2 cm^{-1}. The spectrum of each sample represents an average of 20 scans, which was normalized to the spectrum of blank KBr pellet; i.e. a pure KBr spectrum was subtracted from each glass spectrum. Also, the spectra were corrected to the background and dark currents using two-point baseline correction.

RESULTS

The infrared spectra of the glass series having the molar formulae xBaO (30-x)PbO 70B_2O_3 ($0 \leq x \leq 30$ mol%), xBaO (40-x)PbO 40B_2O_3 ($0 \leq x \leq 40$ mol%) and xBaO (50-x)PbO 50B_2O_3 ($0 \leq x \leq 50$ mol%), are shown in Figure 1(a), (b) and (c), respectively. All the spectra show two broad intense bands in the regions ~770–1170 cm^{-1} and ~1170– 1800 cm^{-1}. In addition, there is a relatively smaller band centered around 700 cm^{-1}. These features are characteristic for borate glasses. Bands in the region ~770–1170 cm^{-1} are generally attributed to B–O stretching vibration of BO_4 units in various borate groups, like pentaborate, triborate and diborate groups[11,12]. On the other hand, absorption bands in the region ~1170–1800 cm^{-1} are related to B–O stretching vibration of trigonal BO_3 units only. The

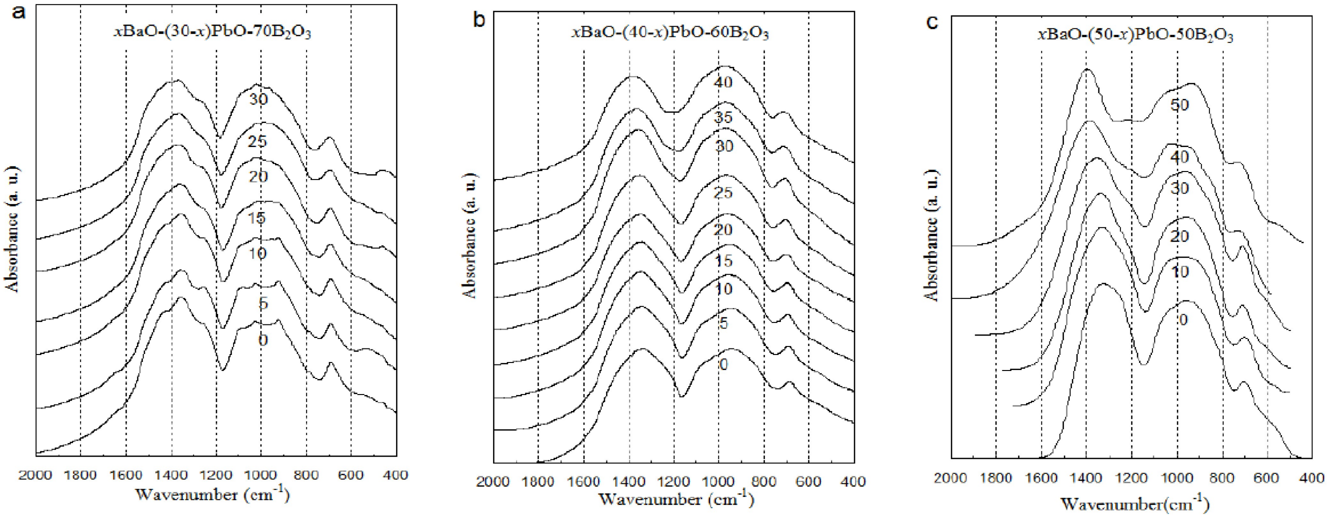

Figure 1 : FTIR spectra of the glasses xBaO•(30-x)PbO•70B_2O_3 (a), xBaO•(40-x)PbO•60B_2O_3 (b) and xBaO•(50-x)PbO’”50B_2O_3 (c). Numbers at the plots refer to BaO content in mol%.

latter are incorporated in various borate groups containing non-bridging oxygen ions such as metaborate, pyroborate and orthoborate groups[5,13]. The small band at 700 cm^{-1} is assumed to be due to bending vibration of B–O–B in symmetric BO_3 triangles[12].

DISCUSSION

xBaO (30-x)PbO 70B_2O_3 glasses

The spectra in Figure 1(a–c) can be used to calculate the fraction (N_4) of four-coordinated boron atoms in the studied glasses. N_4 is taken as the ratio (concentration of BO_4 units) /(concentration of BO_3+BO_4 units). This can be done by obtaining the area under the absorption envelops in the IR spectra. The area under an absorption peak is considered to be proportional to the concentration of structural units emerging it. The deconvolution technique used in[14,15] can be applied to analyze the IR spectra of the studied glasses. Figure 2 presents an example of the deconvoluted spectra.

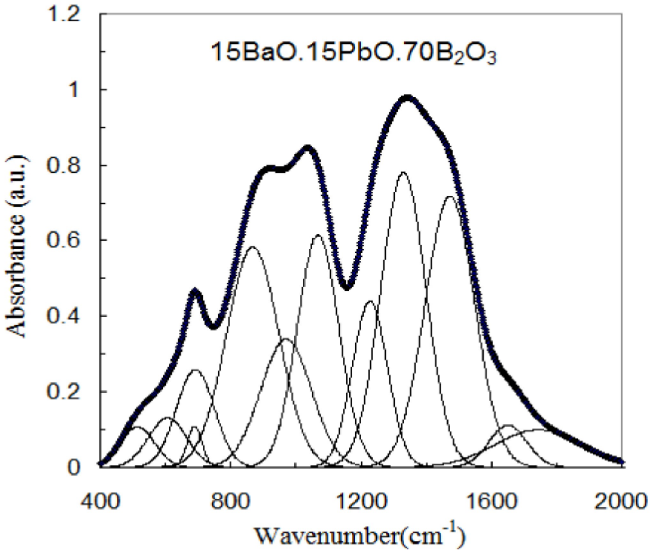

Figure 2 : Deconvolution of the IR spectrum of the glass 15BaO•15PbO•70B_2O_3. The symbol (×) represents the experimental data and the light solid lines represent the individual bands corresponding to different structural groups. The heavy solid line is the predicted spectrum.

Figure 3 shows that N_4 is constant with increasing the BaO content in xBaO (30-x)PbO 70B_2O_3 glasses. The N_4 value of the glass free of BaO is consistent with the values obtained from reported NMR results[6,8,16]. Also the N_4 value of the glass free of PbO is consistent with the values obtained from reported IR results[17]. Since BaO increases at the expense of PbO, it is then deduced that the contribution of BaO in modifying the borate network is nearly equal to that of PbO.

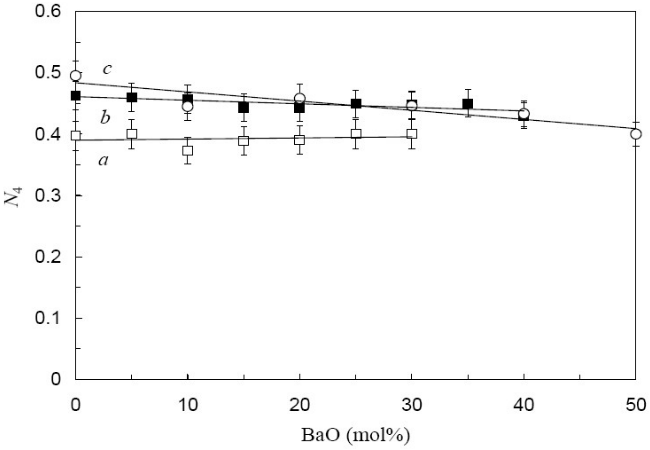

Figure 3 : N_4 of the glasses xBaO·(30-x)PbO·70B_2O_3 (a), xBaO·(40-x)PbO·60B_2O_3 (b)and xBaO·(50-x)PbO·50B_2O_3 (c), as a function of BaO content. The lines are fitting plots of the data. Relative error limits are estimated as ±5%.

As known, PbO[6,7] can play a dual role in the glassy networks. Under certain conditions, it enters the structure as only network modifiers or both network modifiers and network formers. When playing the role of modifier, PbO enters the structure in a similar way as the alkaline earth oxides, i.e. they may form BO_4 units or asymmetric BO_3 units with NBOs, depending on the glass composition. As network former, it builds PbO_4 tetrahedral units. Whereas BaO[9] enters the structure as only network modifier i.e. it may form BO_4 units or asymmetric BO_3 units with NBOs, depending on the glass composition.

The B_2O_3 content (70 mol%) is not yet fully saturated with BO_4 units. These units are assumed to increase in PbO–B_2O_3 glasses up to N_4=0.5[6,16] and increase in BaO-B_2O_3 glasses up to N_4= 0.45[17] so the constancy of N_4 with increasing the BaO content in xBaO (30-x)PbO 70B_2O_3glasses might be attributed to that the rate at which PbO converts symmetric BO_3 to tetrahedral BO_4 is equal to that of BaO.

This conclusion is supported with the observed constant rate in the intensity of the absorption beak at 700 cm^{-1} (Figure 1a) that is attributed to bending vibration of B–O–B in symmetric BO_3 triangles[12],in the intensity of the absorption beak in the region ~770–1170 cm^{-1} (Figure 1a) that is attributed to B-O stretching vibration of BO_4 units in various borate groups, like pentaborate, triborate and diborate groups[11,12,18] and in the intensity of the absorption beak in the region ~1170-1800 cm $^{-1}$ (Figure 1a) that is attributed to B-O stretching vibration of asymmetric BO_3 triangles[5,13].

Advanced techniques, such as NMR spectroscopy, are required to determine the modifier fraction of both BaO and PbO. However, a simple technique can be applied to attain this aim. This technique makes use of Doweidar's "Differential change model - that has been applied to analyze density, molar volume[19], refractive index, molar refraction[20] and thermal expansion[21] of various types of glass. The basis of that model is that certain properties of glass can be expressed by additive relations. The latter can be given in terms of the concentration of structural units and a factor for each type of units. The factor of a unit may change with composition, such as the volume of structural units in borate glasses[22] or has a constant value as the volume found for the structural units in silicate glasses[19]. According to this technique, N_4 might be related to the contribution of each type of modifier oxide in the conversion process from symmetric BO_3 units to BO_4 tetrahedra.

$$\mathbf{N_4=N_{4(Ba)}+N_{4(Pb)}} \qquad (1)$$

where $N_{4(Ba)}$ is the part of N_4 that arises from the modifier BaO and $N_{4(Pb)}$ is that due to the modifier PbO. The constancy of N_4 in Figure (3) (at a mean value 0.394) reveals that, in xBaO (30-x)PbO $70B_2O_3$ glasses, PbO and BaO glasses convert BO_3 units into BO_4 units at the same rate. This means that the contribution of a modifier oxide to N_4 depends on its relative fraction in glass, and thus

$$\mathbf{N_4 = 0.394[(30\text{-}x)/30] + 0.394(x/30)} \qquad (2)$$

In this relation

$$\mathbf{N_{4(Pb)} = 0.394[(30\text{-}x)/30]} \qquad (3)$$

and

$$\mathbf{N_{4(Ba)} = 0.394(x/30)} \qquad (4)$$

The terms [(30-x)/30] and (x/30) represent the relative fraction of $30PbO{\cdot}70B_2O_3$ and $30BaO{\cdot}70B_2O_3$ matrices, respectively. Equations (3) and (4) reveal that there would be a linear decrease in $N_{4(Pb)}$ (between 0.394 and 0) and an opposite increase in $N_{4(Ba)}$ with increasing BaO content from 0 to 30 mol%, these features are shown in (Figure 4).

$N_{4(Pb)}$ and $N_{4(Ba)}$ values obtained from equations (3) and (4) can be used to obtain the portions (molar fraction) of PbO and BaO that form BO_4 units. These are given as

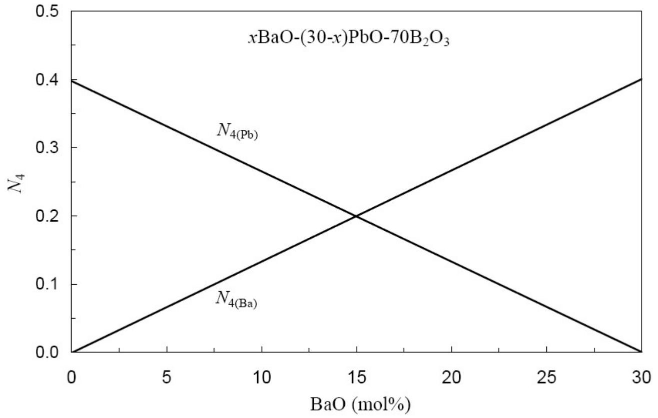

Figure 4 : Composition dependence of the N_4 fractions ($N_{4(Ba)}$ and $N_{4(Pb)}$) created, respectively, by BaO and PbO in xBaO·(30-x)PbO·$70B_2O_3$ glasses.

$$\mathbf{C_{Pb(B4)} = N_{4(Pb)}\ C_B} \qquad (5)$$

and

$$\mathbf{C_{Ba(B4)} = N_{4(Ba)}\ C_B} \qquad (6)$$

In these relations, $C_{Pb(B4)}$ and $C_{Ba(B4)}$ refer, respectively, to the molar fraction of PbO and BaO consumed in the conversion of symmetric BO_3 units to BO_4 tetrahedra. C_B is the molar fraction of B_2O_3 in glass.

The rest of BaO that forms asymmetric BO_3 units ($C_{Ba(as)}$) can be given by

$$\mathbf{C_{Ba(as)} = C_{Ba} - C_{Ba(B4)}} \qquad (7)$$

and the rest of PbO that may act as network former and build PbO_4 tetrahedra is

$$\mathbf{C_{Pb(f)} = C_{Pb} - C_{Pb(B4)}} \qquad (8)$$

Therefore, the molar fraction of residual symmetric BO_3 units ($C_{B(s)}$) can then be obtained as

$$\mathbf{C_{B(s)} = C_B - (C_{Pb(B4)} + C_{Ba(B4)}) - (C_{Pb(f)} + C_{Ba(as)})} \qquad (9)$$

Figure 5 presents the change in $C_{Ba(B4)}$, $C_{Pb(B4)}$, $C_{Ba(as)}$ and $C_{Pb(f)}$ with the concentration of BaO. It is shown that, with increasing the BaO content, there is a decrease in $C_{Pb(B4)}$ and a slight decrease in $C_{Pb(f)}$. These effects are expected due to the decrease in PbO content. Figure 5 shows an opposite change of $C_{Ba(B4)}$ and $C_{Pb(B4)}$. The values of $C_{Pb(B4)}$ and $C_{Pb(f)}$ for the glass free of BaO are nearly consistent with those predicted from NMR results of PbO–B_2O_3 glasses[8]. It is to notice that the nonbridging fraction of BaO $C_{Ba(as)}$ and former fraction of PbO $C_{Pb(f)}$ is lower than the modifier fraction. Figure (3) also shown that, for the studied xBaO (30-x)PbO $70B_2O_3$ glasses, N_4 is constant with increasing BaO content because $C_{Pb(B4)}$ is nearly equal to $C_{Ba(B4)}$.

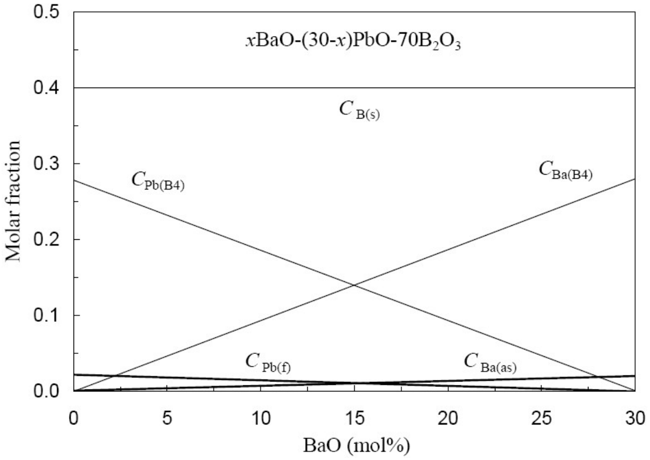

Figure 5 : Molar fraction of, respectively, PbO and BaO that form BO_4 tetrahedra ($C_{Pb(B4)}$, $C_{Ba(B4)}$),asymmetric BO_3 units ($C_{Ba(as)}$) and tetrahedra PbO_4 units as a function of BaO content in xBaO·(30-x)PbO·70B_2O_3glasses.$C_{B(s)}$ refers to the molar fraction of symmetric BO_3 units.

xBaO (40-x)PbO 60B_2O_3 glasses

The infrared spectra of xBaO (40-x)PbO 60B_2O_3 glasses are presented in Figure 1(b). Figure 3 shows that there is a small linear decrease in N_4 with increasing the BaO content in xBaO (40-x)PbO 60B_2O_3 glasses, which depends on the values for the start and end glass composition. N_4 varies from 0.463 for the glass 40PbO·60B_2O_3 to 0.439 for 40BaO·60B_2O_3. The N_4 value of the glass free of BaO is consistent with the values obtained from reported NMR results[6,8,16]. Also the N_4 value of the glass free of PbO is nearly consistent with the values obtained from reported IR results[17].

Since BaO increases at the expense of PbO, it is then deduced that the rate that N_4 decreases with increasing the BaO content in xBaO (40-x)PbO 60B_2O_3 glasses might be attributed to that the rate at which PbO converts symmetric BO_3 to tetrahedral BO_4 is higher than to that of BaO and that the B_2O_3 content (60 mol%) is not yet fully saturated with BO_4 units.

As above, N_4 data can be analyzed using Eqs. ((1)–(9)). The change with composition of $N_{4(Ba)}$ and $N_{4(Pb)}$ of xBaO (40-x)PbO 60B_2O_3 glasses is given in Figure 6. It is observed that $N_{4(Pb)}$ decreases nearly with a rate that is small greater than the rate that $N_{4(Ba)}$ increases. The resultant effect is a decease in N_4 when increasing the concentration of BaO. The change in $C_{Ba(B4)}$, $C_{Pb(B4)}$, $C_{Ba(as)}$ and $C_{Pb(f)}$ with BaO content is given in Figure (7). The values of $C_{Pb(m)}$ and $C_{Pb(f)}$ for the glass free of BaO (40PbO•60B_2O_3) are nearly consistent with those predicted from NMR results of PbO–B_2O_3 glasses[8].

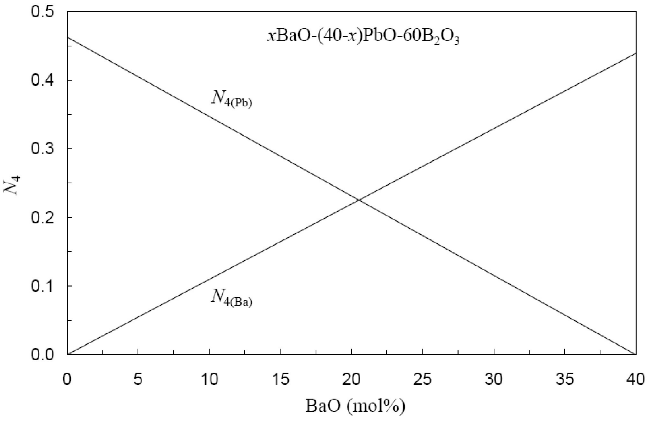

Figure 6 : Composition dependence of the N_4 fractions ($N_{4(Ba)}$ and $N_{4(Pb)}$) created, respectively, by BaO and PbO in xBaO·(40-x)PbO·60B_2O_3 glasses.

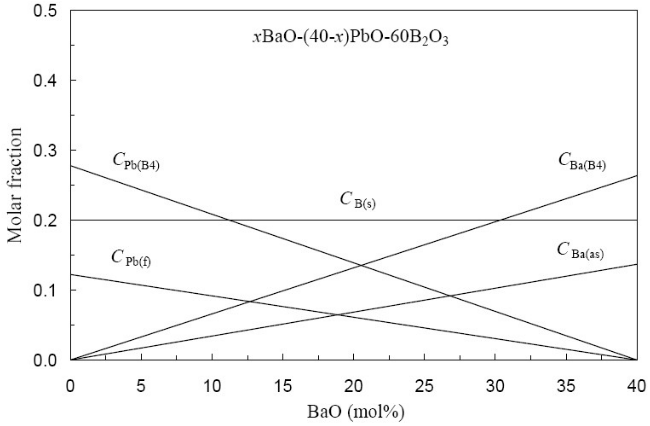

Figure 7 : Molar fraction of, respectively, PbO and BaO that form BO_4 tetrahedra ($C_{Pb(B4)}$, $C_{Ba(B4)}$),asymmetric BO_3 units ($C_{Ba(as)}$) and tetrahedra PbO_4 units as a function of BaO content in xBaO·(40-x)PbO·60B_2O_3 glasses. $C_{B(s)}$ refers to the molar fraction of symmetric BO_3 units.

It appears that the fraction of modifier PbO, $C_{Pb(B4)}$ is always greater than that of the former PbO,$C_{Pb(f)}$ also the fraction of modifier BaO, $C_{Ba(B4)}$, is always greater than that of the nonbridging BaO $C_{Ba(as)}$. It is observed that $C_{Pb(f)}$ decreases nearly with a rate that is small less than the rate that $C_{Ba(as)}$ increases and this is one of the factors that make N_4 decreases with increasing BaO content.

xBaO (50-x)PbO 50B_2O_3 glasses

The infrared spectra of this series of glasses are presented in Figure 1(c). It shows that with increasing the BaO content, at the expense of PbO, the intensity of the the band in the region ~770-1770 cm^{-1} decreases. Figure 3 shows a continuous decrease of N_4 when increasing the concentration of BaO. It follows that the decrease in N_4 (Figure 3) might be due to lower contribution of BaO as a modifier oxide, with respect to PbO.

Figure 8 shows a continuous decrease in $N_{4(Pb)}$ and an increase in $N_{4(Ba)}$ when increasing the concentration of BaO. The values of $N_{4(Pb)}$ and $N_{4(Ba)}$ are limited between 0 and the value for the corresponding PbO-B_2O_3 and BaO-B_2O_3glasses.

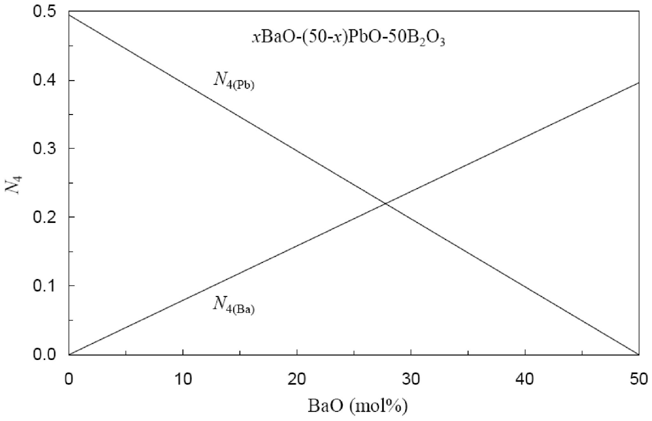

Figure 8 : Composition dependence of the N_4 fractions ($N_{4(Ba)}$ and $N_{4(Pb)}$) created, respectively, by BaO and PbO in xBaO·(50-x)PbO·50B_2O_3 glasses.

The change with BaO content, of $C_{Ba(B4)}$, $C_{Pb(B4)}$, $C_{Ba(as)}$ and $C_{Pb(f)}$ in xBaO (50-x)PbO 50B_2O_3 glasses is presented in Figure 9. This figure shows that, over the entire region of composition, the former fraction of PbO $C_{Pb(f)}$ is nearly equal to its modifier fraction $C_{Pb(m)}$ and the nonbridging fraction of BaO $C_{Ba(as)}$ is greater than the modifier fraction $C_{Ba(m)}$. These features are in contrast to those shown in Figures 5 and 7. Furthermore, from the start up, BaO tends preferentially to form asymmetric BO_3. Also the nonbridging fraction of BaO $C_{Ba(as)}$ for a glass with specific BaO content is greater than the former fraction of PbO $C_{Pb(f)}$ of the glass having the same PbO content whereas the modifier fraction of BaO $C_{Ba(m)}$ for a glass with specific BaO content is smaller than the modifier fraction of Pb $C_{Pb(m)}$ of the glass having the same PbO content so all these results leads to a decrease in N_4 with increasing BaO concentration.

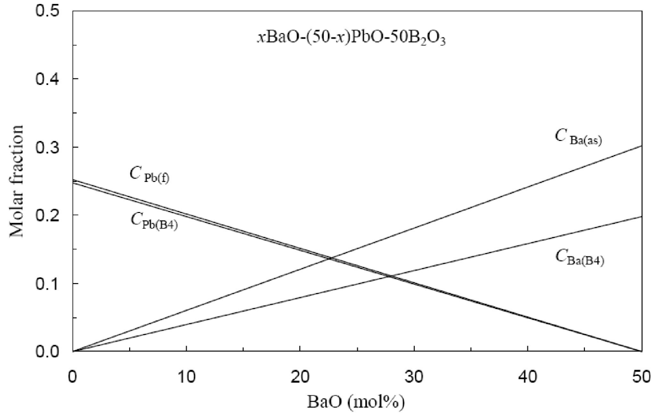

Figure 9 : Molar fraction of, respectively, PbO and BaO that form BO_4 tetrahedra ($C_{Pb(B4)}$, $C_{Ba(B4)}$),asymmetric BO_3 units ($C_{Ba(as)}$) and tetrahedra PbO_4 units as a function of BaO content in xBaO·(50-x)PbO·50B_2O_3 glasses.

CONCLUSION

Infrared spectroscopy can be used to get quantitative information about the contribution of both BaO and PbO to the structure of BaO–PbO–B_2O_3 glasses. A decrease in N_4 with increasing BaO content, at the expense of PbO, in the studied glasses reveals that BaO modifies the borate network to a lower extent with respect to PbO. The fraction of modifier BaO, and thus the nonbridging part, depends on the start PbO content.

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