GROUP OPTICAL BASICITY AND SINGLE BOND STRENGTH
OF LEAD BORATE GLASSES

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ABSTRACT

Equation providing the calculation of the theoretical optical basicity $\Lambda_{th(1)}$ of PbO-B$_2$O$_3$ glasses is suggested taking into account the contribution of the mole fraction and the group basicity of different structural units, namely BO$_3$ and BO$_4$ groups. It is found that in case of PbO-B$_2$O$_3$ glasses the curves of the refractive index based optical basicity $\Lambda(n_0)$ and the theoretical optical basicity $\Lambda_{th(1)}$ as a function of PbO content follow a similar trend changing their slope at about 50 mol. % PbO. An equation is proposed to calculate the average single bond strength B_{M-O} of PbO containing borate glasses taking into account the mole fractions of PbO$_3$, PbO$_4$, PbO$_6$, BO$_3$ and BO$_4$ groups. It is established that both equations give the possibility for more precisely estimation of the theoretical optical basicity and the single bond strength of the glasses. It is found that the single bond strength of PbO-B$_2$O$_3$ glasses decreases with increasing PbO content. The observed increase of the optical basicity with decreasing single bond strength of lead borate glasses is discussed with increase the number of Pb-O-B and Pb-O-Pb bonds containing oxide ions with increased polarizability.

<u>*Keywords:*</u> *borate glasses, electronic polarizability, optical basicity, average single bond strength.*

INTRODUCTION

The bulk optical basicity Λ of an oxide medium was introduced by Duffy and Ingram as a numerical expression of the average electron donor power of the oxide species constituting the medium and it is used as a measure of acid-base behavior of oxides, glasses, alloys, slags, molten salts etc [1, 2]. An approach for determination of optical basicity seems to be the relationship between basicity and refractivity. In this connection Duffy [3] suggested a correlation among the optical basicity Λ and the electronic oxide ion polarizability α_{O2-} in the form:

$$\Lambda = 1.67\left(1 - \frac{1}{a_{O^{2-}}}\right) \quad (1)$$

Eq. (1) shows that basicity increases with increasing the polarizability. The oxide ion polarizability can be determined with the application of the Lorentz-Lorenz equation using the values of the corresponding linear refractive index and the density of an oxide or glass. In fact such basicity can be designated "experimental" as its evaluation requires experimentally obtained data. Dimitrov and Sakka [4] and Dimitrov and Komatsu [5] using Eq. (1) estimated the refractive index based optical basicity $\Lambda(n_0)$ of a large number of simple oxides and

binary oxide glasses.

On the other hand it was possible to calculate the so-called "theoretical" optical basicity Λ_{th} of multi-component glass on the basis of the following equation proposed by Duffy and Ingram [6]:

$$\Lambda_{th} = X_1\Lambda_1 + X_2\Lambda_2 + \ldots + X_n\Lambda_n \qquad (2)$$

where $X_1, X_2,\ldots,X_n$ were the equivalent fractions based on the oxygen amount contributed by each oxide to the overall glass stoichiometry, while $\Lambda_1, \Lambda_2,\ldots, \Lambda_n$ were the basicities assigned to the individual oxides. Eq. (2) expresses the average bulk basicity on the ground of the bridging and non-bridging oxide species but in the present form it cannot estimate the cations' coordination number changes.

Duffy and Ingram [2] proposed the convenient concept of "microscopic optical basicity" of individual oxide ions in an oxyanion unit. They suggested further that the term "group basicity λ" was a more important parameter if complete charge neutralization occurred within the oxyanion unit. Recently, Dimitrov and Komatsu [7, 8] introduced the concept of group (i.e. microscopic) optical basicity referring to binary R_2O (RO) $-$ TeO_2 (R = Na, Mg, Sr, Ba, Zn and Pb) and ternary $10R_2O.10R'O.80TeO_2$ (R = Li, Na and K, R'= Mg, Ba and Zn) tellurite glasses based on N_4 and N_3 fractions of different TeO_4 and TeO_3 groups. In fact, the group basicity of TeO_4 unit with one non-bridging oxygen ($\lambda_{TeO_4^-}$ = 1.23), TeO_4 unit without non-bridging oxygen ($\lambda_{TeO_4^0}$ = 0.99) and terminal TeO_3 unit with two non-bridging oxygens ($\lambda_{TeO_3^-}$ = 0.82) was evaluated. More recently, Dimitrov et al. [9] applied the concept to sodium borate and sodium silicate glasses using mole fractions of BO_3, BO_4 and SiO_4 units in the glass structure. The following equation for determination of theoretical optical basicity in the case of sodium borate glasses was proposed:

$$\Lambda_{th(1)} = X_{Na_2O}\Lambda_{Na_2O} + X_{B_2O_3}\left[N_3\lambda_{BO_3} + N_4\lambda_{BO_4} \right] \quad (3)$$

where λ_{BO_3} and λ_{BO_4} are the group basicities of BO_3 and BO_4 groups, while N_3 and N_4 are their mole fractions. It was found that Eq. (3) predicts more precisely the basicity of Na_2O-B_2O_3 glasses than Eq. (2).

More than 70 years ago Sun [10] has suggested the bond energy criterion for glass formation based on the dissociation energy of the oxides and has reported data for the single bond strength B_{M-O} of a chemical bond M-O in an oxide MO_x obtained by dividing the dissociation energy of the oxide by the coordination number (CN) of the metal M. Recently, based on Sun's approach Dimitrov and Komatsu [11] have proposed that the average single bond strength B_{M-O} of binary oxide glass with general formula $xA_pO_q.(1-x)B_rO_s$ could be expressed by the following equation,

$$B_{M-O} = xB_{A-O} + (1-x)B_{B-O} \qquad (4)$$

where B_{A-O} and B_{B-O} are single bond strength of M-O in the corresponding individual oxide. The principal use of Eq. (4) is in predicting the "trends" of single bond strength of an averaged M-O chemical bond in glass structure. It cannot estimate the change in coordination number of the cation (CN), namely the presence of BO_3 and BO_4 units in B_2O_3 containing glasses.

It is of scientific and practical interest to check the group basicity concept and approach for single bond strength in case of other glasses too. Among them the lead borate glasses seem promising because they are extra dense flint optical glasses and today they are of interest from optical nonlinearity point of view. For example Dimitrov et al. [12] and Terashima et al [13] have measured by THG method the nonlinear optical susceptibility $\chi^{(3)}$ of series of PbO-B_2O_3 glasses and have established that $\chi^{(3)}$ increases with increasing of PbO content. The present study reports data referring to the application of the concepts of group optical basicity and average single bond strength to PbO-B_2O_3 glasses. The correlation with the glasses structure in terms of single bond strength is also discussed.

RESULTS AND DISCUSSION

Data on group optical basicity of PbO-B_2O_3 glasses

Dimitrov and Komatsu [5] have determined theoretical optical basicity Λ_{th} of lead borate glasses with compositions $xPbO.(1-x)B_2O_3$ (x = 30, 40, 50, 60 and 70 mol % PbO) using Eq. 2 and their refractive index

Table 1. Compositions, refractive index n_0, refractive index based optical basicity $\Lambda(n_0)$, theoretical optical basicity Λ_{th}, BO_4 mol fraction (N_4), BO_3 mol fraction (N_3), theoretical optical basicity $\Lambda_{th(1)}$ based on mol fraction (N_3 and N_4), average single bond strength $B_{M-O(1)}$ based on mol fraction (N_3 and N_4).

PbO, mol %	n_o Ref. 5	$\Lambda(n_o)$ Ref. 5	Λ_{th} Ref. 5	N_4*	N_3	Λ_{th1} Eq. 5	$B_{M-O(1)}$, kJ/mol Eq. 6
30	1.699	0.431	0.486	0.34	0.66	0.433	364
40	1.768	0.426	0.516	0.39	0.61	0.459	330
50	1.842	0.456	0.552	0.41	0.59	0.497	299
60	1.918	0.533	0.595	0.35	0.65	0.553	272
70	2.001	0.630	0.653	0.21	0.79	0.630	247

* N_4 fractions are estimated by us using graphical data reported in Ref. 13.

based optical basicity $\Lambda(n_o)$ by Eq. 1. The data referring to Λ_{th} and $\Lambda(n_o)$ of $PbO-B_2O_3$ glasses are taken from Ref. 5 and are listed in Table 1. The values of the glasses' refractive index required for the basicity determination are also shown in Table 1.

The structure of lead borate glasses is studied by different methods [13, 14 - 16]. Bray et al. [14] measured the NMR spectra of $PbO-B_2O_3$ glasses. They reported that in the lead borate glasses Pb^{2+} is incorporated mainly in the form of PbO_6 groups up to 50 mol % PbO accompanying the formation of BO_4 units, although a certain portion of Pb^{2+} are incorporated in the glass network between 30 and 50 mol % PbO. Above 50 mol % PbO, an increase in PbO content gives rise to the rapid decrease of BO_4 units in number. Bray et al. [14] determined N_4 fractions of borons that were four-coordinated to oxygens. The data on the estimated N_4 fractions of BO_4 groups are taken from Ref. 14 and are listed in Table 2. It is seen that N_4 increases up to 48.3 mol % PbO and then decreases. The fraction of four- coordinated boron (N_4) for series of $PbO-B_2O_3$ glasses have been determined also by Terashima et al. [13] on the basis of ^{11}B MAS NMR spectra. We estimated the fraction of four-coordinated boron (N_4) for each glass using their graphical data of N_4 as a function of the glass composition. The results are presented in Table 1. As can be seen N_4 increases while N_3 decreases up to 50 mol % PbO for the glasses pointed in Table 1. It should be noticed also that the glass-compositions studied in Refs. 5 and 13 are identical and that is why we presented the results

obtained by the two research groups in one common Table 1. ^{11}B and [207]Pb NMR spectroscopy was used by Martin et al. [16] to probe boron and lead coordination environments in the structure of $PbO-B_2O_3$ glasses. We estimated the fraction of 4-coordinated boron (N_4) for glasses containing 35, 45, 55 and 65 mol % PbO using their graphical data of N_4 as a function of the PbO content (see Ref. 16). The results are listed in Table 3. We chose these four glasses since only for them [207]Pb NMR data are published in Ref. 16.

Duffy and Ingram [2] accepted that the theoretical group basicity of the three-coordinated BO_3 unit without nonbridging oxygens was equal to 0.42. Recently, Duffy [17, 18] reported that fourfold coordinated boron atoms possessed polarizing power much greater than that of threefold coordinated atoms. In fact he found that the basicity moderating parameter γ for four-coordinated boron was extraordinarily high (equal to 4.2). This corresponded to a basicity value for the BO_4 unit attached to four BO_3 units, i. e. to the group basicity of such BO_4 units which will be equal to 0.24. According to Duffy [18] this fact could be explained with the absence of π-bonding in the BO_4 units and the presence of four σ-covalent B-O bonds there.

The data on the fractions of BO_3 and BO_4 groups presented in Tables 1, 2 and 3 and those on the group optical basicity $\lambda_{BO3} = 0.42$ and $\lambda_{BO4} = 0.24$ proposed by Duffy provide to suggest an equation for calculating the theoretical optical basicity $\Lambda_{th(1)}$ of lead borate glasses. It is given by:

Table 2. Compositions, BO_4 mol fraction (N_4) according to Ref. 14, BO_3 mol fraction (N_3), theoretical optical basicity $\Lambda_{th(1)}$ based on mol fraction (N_3 and N_4), average single bond strength $B_{M-O(1)}$ based on mol fraction (N_3 and N_4).

PbO mol %	N_4 Ref. 14	N_3	Λ_{th1} Eq. 5	$B_{M-O(1)}$, kJ/mol Eq. 6
28	0.33	0.67	0.428	371
43	0.46	0.54	0.460	316
48.3	0.53	0.47	0.473	296
63.9	0.30	0.70	0.583	263
74.5	0.17	0.83	0.666	234

Table 3. Compositions, PbO_6 mol fraction (P_6), PbO_4 mol fraction (P_4), PbO_3 mol fraction (P_3), BO_4 mol fraction (N_4), BO_3 mol fraction (N_3), theoretical optical basicity $\Lambda_{th(1)}$ based on mol fraction (N_4 and N_3), average single bond strength $B_{M-O(1)}$ based on mol fraction (N_3 and N_4), average single bond strength $B_{M-O(2)}$ based on mol fraction (P_6, P_4, P_3, N_4 and N_3).

PbO mol %	P_6*	P_4*	P_3*	N_4**	N_3	$\Lambda_{th(1)}$ Eq. 5	$B_{M-O(1)}$, kJ/mol Eq. 6	$B_{M-O(2)}$, kJ/mol Eq. 7
35	0.558	0.442		0.454	0.546	0.431	340	330
45	0.244	0.756		0.53	0.47	0.459	305	300
55		0.643	0.357	0.562	0.438	0.502	276	286
65		0.568	0.432	0.497	0.503	0.567	251	265

* P_6, P_4, P_3 fractions are estimated by us using relative area of Gaussian peaks reported in Ref. 16.

** N_4 fractions are estimated by us using graphical data reported in Ref. 16.

$$\Lambda_{th(1)} = X_{PbO}\Lambda_{PbO} + X_{B2O3}[N_3\lambda_{BO3} + N_4\lambda_{BO4}] \qquad (5)$$

where λ_{BO_3} and λ_{BO_4} are group basicities of BO_3 and BO_4 groups and N_3 and N_4 are their molar fractions. The value of 0.95 for basicty of PbO was used. The values of $\Lambda_{th(1)}$ of each glass are calculated by us using Eq. (3) and the results are presented in Tables 1, 2 and 3. The data of $\Lambda_{th(1)}$ listed in Tables 1 and 2 are plotted as a function of the data of PbO content in Fig. 1. For comparison the data of the refractive index based optical basicity $\Lambda(n_0)$ and the theoretical optical basicity calculated by using Eq. (2) (see Table 1) are also plotted in Fig. 1 as a function of PbO content. As can be seen agreement exists between the data obtained especially between $\Lambda_{th(1)}$ and $\Lambda(n_0)$ data. At the same time the curves which present $\Lambda_{th(1)}$ and $\Lambda(n_0)$ as a function of PbO content have the same move and a small change could be observed in the slope of the curves at approximately 50 mol % PbO. It seems that Eq. (5) predicts more precisely the theoretical optical basicity of $PbO-B_2O_3$ glasses than Eq. (2).

Data on single bond strength of $PbO-B_2O_3$ glasses

We mentioned in the Introduction Part that based on Sun's approach Dimitrov and Komatsu [11] have proposed Eq. 4 for calculation of average single bond strength of binary oxide glasses. The data on the fractions of BO_3 and BO_4 groups presented in Tables 1, 2 and 3 provide to estimate the average single bond strength B_{M-O} in the $PbO-B_2O_3$ glasses by introducing of the mole fractions N_3 and N_4. On this basis we suggest the following equation valid in the case of $PbO-B_2O_3$ glasses:

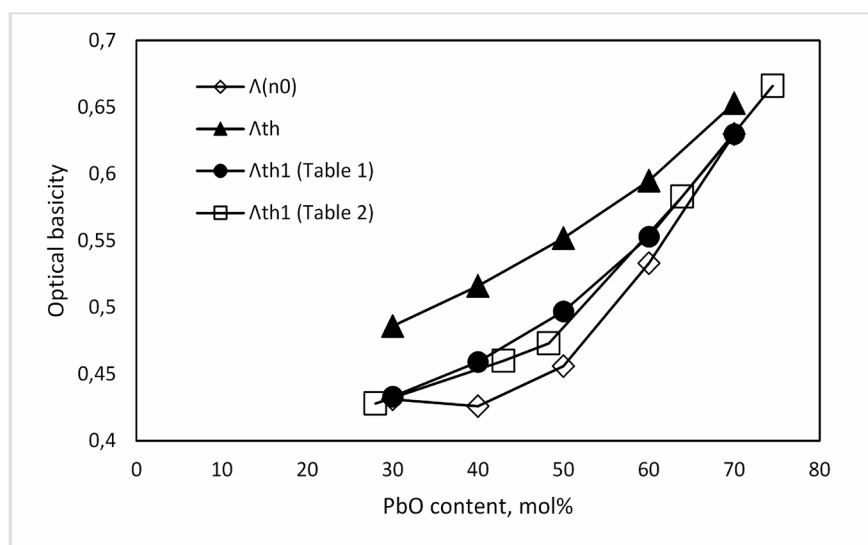$$B_{M-O(1)} = xB_{Pb-O}^{(4)} + (1-x)[N_3 B_{B-O}^{(3)} + N_4 B_{B-O}^{(4)}] \qquad (6)$$

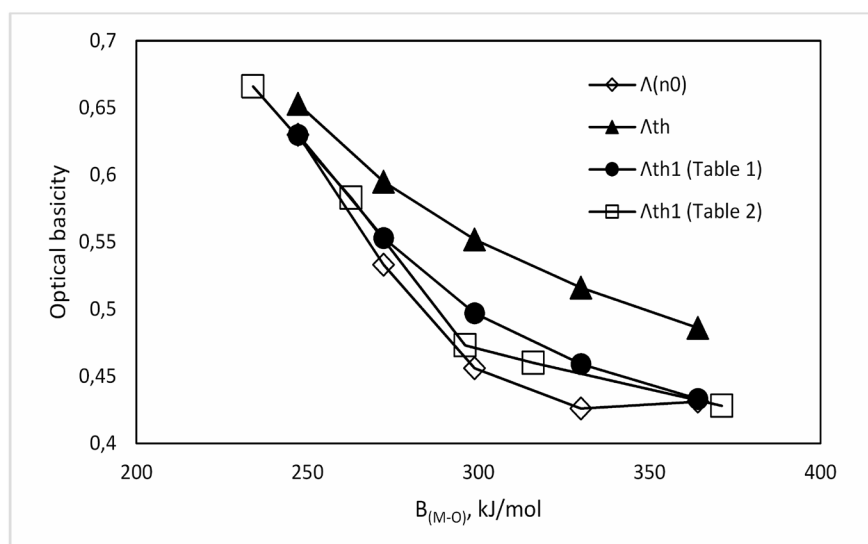Fig. 1. Optical basicity as a function of PbO content.

Fig. 2. Optical basicity as a function of average single bond strength.

where N_3 and N_4 are mole fractions of BO_3 and BO_4 groups in a single glass molecule and $B_{B-O}^{(3)}$ and $B_{B-O}^{(4)}$ are the single bond strength of B-O bonds in the BO_3 and BO_4 groups, respectively. $B_{Pb-O}^{(4)}$ is the single bond strength of Pb-O bond in PbO_4 group. Note that in brackets as superscript is shown coordination number of the cation. Recently, similar equations we suggested also for Sb_2O_3-B_2O_3, Bi_2O_3-B_2O_3 and Na_2O-B_2O_3 glasses [9, 19]. According to Sun [10] the single bond strength of B-O bond in BO_3 group is 119 kcal/mol or 498 kJ/mol, that of B-O bond in BO_4 group is 89 kcal/mol or 373 kJ/mol and that of Pb-O bond in PbO_4 group is 36 kcal/

mol or 151 kJ/mol. We found the values of the average single bond strength B_{M-O} of $xPbO.(1-x)B_2O_3$ (x=30, 35, 40, 45, 50, 55, 60, 65 and 70 mol % PbO) glasses with the application of Eq. (6). They are listed in Tables 1, 2 and 3. It is seen that the addition of PbO leads to B_{M-O} decrease. With a view to investigate the correlation between optical basicity and single bond strength of the glasses we have plotted in Fig. 2 the data of the theoretical optical basicity $\Lambda_{th(1)}$ listed in Tables 1 and 2 as a function of the average single bond strength B_{M-O} of PbO-B_2O_3 glasses. Aiming a comparison the values of the refractive index based optical basicity $\Lambda(n_o)$ and

the theoretical optical basicity Λ_{th} are also plotted in Fig. 2 as a function of average single bond strength. It is evident that in general there is an increase of the optical basicity with the decrease of the single bond strength of the glasses but it should be added that the curves which present $\Lambda_{th(1)}$ and $\Lambda(n_o)$ have an identical shape and small change could be observed in the slope of the curves at about 50 mol % PbO. According to Bray et al. [14] Pb^{2+} ions are incorporated in the structure mainly as PbO_6 groups up to 50 mol% PbO in which Pb-O bonds are ionic. Above 50 mol % PbO PbO_4 and PbO_3 structural units are formed, whose Pb-O bonds are strongly covalent in nature. The observed change in the slope of the curves shown in Figs. 1 and 2 is probably due to such structural transformation.

As it was pointed above Martin et al. [16] probed not only boron but also lead coordination environment by ^{207}Pb NMR spectra. They assigned the coordination number N_c of lead in four glasses from the fitted resonance as follows: for glass containing 35 mol % PbO N_c is 6 - 7 and 3 - 4; for glass with 45 mol % PbO N_c is 6 and 3 - 4; for glass with 55 mol % PbO N_c is 4, 3 - 4 and 3 and for glass with 65 mol % PbO N_c is 3 - 4 and 3. In this connection we assumed that PbO_n (n = 3, 4 and 6) fractions correspond to the relative area of Gaussian peaks used by Martin et al. to fit ^{207}Pb NMR signal. We assumed also that N_c = 6 - 7 corresponds mainly to PbO_6 unit and N_c = 3 - 4 corresponds mainly to PbO_4 unit. Of course this assumption is one approximation but we believe that it is reasonable with a view to look for an approach for more precisely calculation of the average single bond strength of the lead borate glasses. Simultaneously the assumption is in agreement with X-ray diffraction results obtained by Takaishi et al. [15]. On this basis we calculated the mole fractions of PbO_6, PbO_4 and PbO_3 groups designed as P_6, P_4 and P_3 in lead borate glasses containing 35, 45, 55 and 65 mol % PbO using relative area of Gaussian reported in Ref. 16 and the data are presented in Table 3. These data provide to estimate the average single bond strength B_{M-O} of the $PbO-B_2O_3$ glasses by introducing the lead mole fractions P_6, P_4 and P_3 and boron mole fractions N_3 and N_4 and to suggest the following equation valid in the case of lead borate glasses:

$$B_{M-O(2)} = x[P_3B_{Pb-O}^{(3)} + P_4B_{Pb-O}^{(4)} + P_6B_{Pb-O}^{(6)}] + (1-x)[N_3B_{B-O}^{(3)} + N_4B_{B-O}^{(4)}] \qquad (7)$$

where P_3, P_4 and P_6 are mole fractions of PbO_3, PbO_4 and PbO_6 groups and N_3 and N_4 are mole fractions of BO_3 and BO_4 groups in a single glass molecule and $B_{Pb-O}^{(3)}$, $B_{Pb-O}^{(4)}$ $B_{Pb-O}^{(6)}$, $B_{B-O}^{(3)}$ and $B_{B-O}^{(4)}$ are the single bond strength of Pb-O and B-O bonds in the PbO_3, PbO_4, PbO_6, BO_3 and BO_4 groups, respectively. Note that in brackets as superscript is shown coordination number of the cation. According to Sun [10] and Sun and Huggins [20] the dissociation energy of PbO is 145 kcal/mol. The single bond strength of Pb-O bond by using coordination number of Pb^{2+} cation CN = 3 is 48.3 kcal/mol or 202 kJ/mol, and that by using coordination number of Pb^{2+} cation CN = 6 is 24.2 kcal/mol or 101 kJ/.mol. We calculated the values of the single bond strength B_{M-O} of $xPbO.(1-x)B_2O_3$ (x = 35, 45, 55 and 65 mol % PbO) with the application of Eq. (7). The data are presented in Table 3. It is seen that good correspondence exists with the data calculated by Eq. (6) (Tables 1, 2 and 3).

According to the polarizability classification of oxide glasses [21] $PbO-B_2O_3$ glasses belong to the second group glasses formed by glass-forming acidic oxide (B_2O_3) and modifier basic oxide (PbO). From the polarizability point of view B^{3+} cation possess extremely low polarizability (0.002 $Å^3$) and large positive charge. Its unit field strength is very large and B^{3+} affects strongly the electron charge density of the surrounding oxide ions. On this basis, glasses with high B_2O_3 content (60-70 mol %) show lower basicity and higher single bond strength (see Tables 1, 2 and 3). By contrast, the cation unit field strength of Pb^{2+} ion is small. This cation possess very high polarizability (3.623 $Å^3$) and has a lone pair in the valence shell which is also strongly polarizable. These characteristics are responsible for the decreased polarizing effect of Pb^{2+} on the oxide ions. Such oxide ions are freer and their electron donation is increased. In this respect lead borate glasses with high PbO content (60 - 70 mol %) show higher values of the basicity (see Tables 1, 2 and 3). From the chemical bonding point of view, strong covalent B-O-B chemical bonds along with B-O-Pb and Pb-O-Pb bonds with increased iconicity are formed in the structure of $PbO-B_2O_3$ glasses. The

number of B-O-B bonds decreases with increasing PbO content. Such bonds were proposed by Bray et al. [14], Terashima et al. [13] and Takaishi et al. [15] on the basis of data obtained by NMR, Raman spectroscopy and X-ray diffraction studies.

CONCLUSIONS

The theoretical optical basicity of series of PbO-B_2O_3 glasses and the average single bond strength have been estimated by means of proposed equations taking into account the contributions of different structural units namely BO_3, BO_4, PbO_3, PbO_4 and PbO_6 groups in the glass-network. The observed correlation between the optical basicity and the single bond strength of lead borate glasses has been described by presence of B-O-B, Pb-O-B and Pb-O-Pb chemical bonds containing oxide ions with different degree of electronic polarizability.

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