GROUP OPTICAL BASICITY AND SINGLE BOND STRENGTH OF OXIDE GLASSES

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ABSTRACT

This paper is a review of our recent results in the field of group optical basicity of the oxide glasses. Dimitrov and Komatsu have recently introduced the concept of group (i.e. microscopic) optical basicity, proposed by Duffy and Ingram, 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 a terminal TeO_3 unit with two non-bridging oxygens ($\lambda_{TeO_3^-}$ = 0.82) is evaluated.

Equations for evaluation of the theoretical optical basicity $\Lambda_{th(1)}$ of Na_2O-B_2O_3, PbO-B_2O_3, Na_2O-SiO_2 and R_2O-RO-TeO_2 glasses are advanced taking into account the contribution of the mole fraction and the group basicity of different structural units, namely BO_3, BO_4 and SiO_4 groups.

Equations providing the calculation of the average single bond strength $B_{M\text{-}O}$ of Na_2O-B_2O_3, PbO-B_2O_3, Na_2O-GeO_2, Bi_2O_3-B_2O_3 and ZnO-Bi_2O_3-B_2O_3 glasses are suggested considering the mole fractions of BO_3, BO_4, GeO_4, GeO_6, PbO_3, PbO_4 and PbO_6 groups.

It is established that there is a general trend of optical basicity increase along with single bond strength decrease in borate-silicate-germanate-tellurite-bismuthate glasses sequence.

Keywords: oxide glasses, optical basicity, bond strength, structure.

INTRODUCTION

According to the pioneering studies of Duffy and Ingram [1] the bulk optical basicity Λ of an oxide medium is a numerical expression of the average electron donor power of the oxide species constituting the medium. It can be used as a measure of the acid-base properties of oxides, glasses, alloys, slags, molten salts, etc. In accordance with Duffy and Ingram [2] it is possible to calculate the average or so-called theoretical optical basicity Λ_{th} of a glass on the basis of the following equation,

$$\Lambda_{th} = X_1\Lambda_1 + X_2\Lambda_2 + \ldots + X_n\Lambda_n \quad (1)$$

where $X_1, X_2, \ldots, X_n$ are the equivalent fractions based on the amount of oxygen contributed by each oxide to the overall glass stoichiometry, while $\Lambda_1, \Lambda_2, \ldots, \Lambda_n$ are the basicities assigned to the individual oxides. The principal use of this equation is in predicting the "trends" in optical basicity rather than the "true" basicity value. It expresses the average basicity determined by oxide species such as

bridging and non-bridging species. In the present form it cannot estimate the changes of cations' coordination number. Irrespective of some limitations the equation can be used as a simple formula for calculating the ideal optical basicity of a glass.

In this connection Duffy and Ingram [1] propose a convenient concept of "microscopic optical basicity" for individual oxide ions in an oxyanion unit. Furthermore, they suggest that the term "group basicity λ" is a more important parameter if complete charge neutralization occurs within an oxyanion unit.

On the other hand, Duffy [3] suggests a correlation between the optical basicity Λ and the oxide ion polarizability $\alpha_{O_{2-}}$ in the form:

$$\Lambda = 1.67\left(1 - \frac{1}{\alpha_{O_{2-}}}\right) \quad (2)$$

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 a 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] estimate the refractive index based optical basicity $\Lambda(n_0)$ of a large number of simple oxides and binary oxide glasses using the equation cited above. They propose polarizability classifications of simple oxides and oxide glasses. Three groups of simple oxides are distinguished: I. Semicovalent predominantly acidic oxides – B_2O_3, P_2O_5, SiO_2, GeO_2; II. Ionic (basic) oxides – 3d transition oxides, CaO, TiO_2, Sc_2O_3, V_2O_5, ZnO, Y_2O_3, ZrO_2, Nb_2O_5, MoO_3, In_2O_3, TeO_2, CeO_2, Ta_2O_5, WO_3; III. Very ionic (very basic) oxides – Na_2O, SrO, CdO, Sb_2O_3, Cs_2O, BaO, PbO, Bi_2O_3

At the same time four groups of oxide glasses are recognized: I. Glasses formed by two glass-forming oxides; II. Glasses formed by glass-forming acidic and modifier's basic oxides; III. Glasses formed by glass-forming acidic and conditional glass-forming basic oxides; IV. Glasses formed by two basic oxides.

More than 70 years ago Sun [6] suggests the bond energy criterion for glass formation based on the dissociation energy of the oxides. He reports data on the single bond strength of a chemical M-O bond in MO_x oxide obtained by dividing the oxide dissociation energy by the coordination number (CN) of metal *M*. Based on Sun's approach Dimitrov and Komatsu [7] propose that the single bond strength B_{M-O} of a binary glass with general formula $xA_pO_q.(1-x)B_rO_s$ can be expressed by the following equation:

$$B_{M-O} = xB_{A-O} + (1-x)B_{B-O} \quad (3)$$

where x is the mole fraction of A_pO_q, B_{A-O} and B_{B-O} refer to the single bond strength of M-O in the corresponding individual oxide.

It is of scientific and practical interest to check the group basicity concept and the approach to single bond strength in case of different oxide glasses.

The aim of this paper is to study the correlation between the group optical basicity and the chemical bonding in: Na_2O-B_2O_3, PbO-B_2O_3, Na_2O-SiO_2, Na_2O-GeO_2, $10R_2O.10R'O.80TeO_2$ (R = Li, Na and K, R'= Mg, Ba and Zn), Bi_2O_3-B_2O_3 and ZnO-Bi_2O_3-B_2O_3 glasses taking into account the mole fractions of BO_3, BO_4, SiO_4, GeO_4, GeO_6, PbO_3 PbO_4 and PbO_6 groups.

RESULTS AND DISCUSSION

B_2O_3 containing glasses

$Na_2O - B_2O_3$ glasses

Bray and O'Keefe [8] record the NMR spectra of M_2O-B_2O_3 (M=Li, Na, K, Rb and Cs) glasses. They determine N_4 fractions of borons that are four-co-ordinated to oxygens. Data for the estimated N_4 fractions of BO_4 groups for Na_2O-B_2O_3 glasses are taken from ref. [8] and are listed in Table 1 (column 2). It is seen that N_4 increases, while N_3 decreases in the glasses included in Table 1.

Duffy and Ingram [1] suggest that the theoretical group basicity of three-coordinated BO_3 unit without non-bridging oxygens amounts to 0.42. Recently, Duffy [9] finds that the basicity moderating parameter γ of the four-coordinated boron is extraordinarily high, equal to 4.2. This value corresponds to basicity of 0.24 for BO_4 unit attached to four BO_3 units. In fact this value refers to the group basicity of such BO_4 units. According to the author the absence of π-bonding in the BO_4 units

and presence of four σ-covalent B-O bonds in them [10] explains this phenomenon.

On the basis of the data of the fractions of BO_3 and BO_4 groups determined by Bray and O'Keefe and group optical basicity $\lambda_{BO_3} = 0.42$ and $\lambda_{BO_4} = 0.24$ proposed by Duffy, Dimitrov et al. [11] suggest an equation for calculation of the theoretical optical basicity $\Lambda_{th(1)}$ of sodium-borate glasses:

$$\Lambda_{th(1)} = X_{Na_2O}\Lambda_{Na_2O} + X_{B_2O_3}\left[N_3\lambda_{BO_3} + N_4\lambda_{BO_4}\right] \quad (4)$$

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 molar fractions. The value of 1.10 referring to Na_2O basicity is used. The values of $\Lambda_{th(1)}$ of each glass are taken from ref. [11] and the results are presented in Table 1 (column 4). Data for the refractive index based optical basicity with upper star according to ref. [5] is given in column 3 for a comparison.

The known data on N_4 mole fractions in the glass structure reported by Bray and O'Keefe give the possibility to estimate more precisely the average single bond strength B_{M-O} of the Na_2O-B_2O_3 glasses by introducing of the mole fractions N_3 and N_4. In this connection the following equation is derived for Na_2O-B_2O_3 glasses in accordance with ref. [11]:

$$B_{M-O} = xB_{Na-O}^{(6)} + (1-x)\left[N_3B_{B-O}^{(3)} + N_4B_{B-O}^{(4)}\right] \quad (5)$$

where N_3 and N_4 are mole fractions of BO_3 and BO_4 groups in one glass molecule, while $B_{B\text{-}O}^{(3)}$ and $B_{B\text{-}O}^{(4)}$ refer to the single bond strength of B-O bonds in BO_3 and BO_4 groups, respectively. The values of $B_{M\text{-}O}$ are taken from ref. [11] and are presented in Table 1 (column 5).

$PbO - B_2O_3$ glasses

Bray et al. [12] record the NMR spectra of PbO-B_2O_3 glasses. They determine N_4 fractions of borons that were four-coordinated to oxygens. The data on the estimated N_4 fractions of BO_4 groups are listed in Table 2 (column 5). They are designated by a star. It is seen that N_4 increases up to 48.3 mol % of PbO and than decreases. The data on the fractions of BO_3 and BO_4 groups presented in Table 2 and those on the group optical basicity $\lambda_{BO3} = 0.42$ and $\lambda_{BO4} = 0.24$ proposed by Duffy provide to suggest

Table 1. Na_2O–B_2O_3 glass system, composition, BO_4 fractions N_4, refractive index based optical basicity $\Lambda(n_0)$, theoretical optical basicity $\Lambda_{th(1)}$, single bond strength B_{M-O}.

First oxide, mol %	N_4	$\Lambda(n_o)$	$\Lambda_{th(1)}$	B_{M-O}, kJ/mol
5.12*		0.452*		
10.33*		0.451*		
10.00	0.116		0.424	444
15.20*		0.452*		
15.00	0.160		0.431	419
20.23*		0.454*		
20.00	0.280		0.425	387
25.13*		0.460*		
25.00	0.380		0.426	359
29.85*		0.471*		
31.00	0.420		0.443	333
34.20*		0.493*		
33.30	0.430		0.450	324

an equation for calculating the theoretical optical basicity $\Lambda_{th(1)}$ of lead borate glasses. According to Dimitrov et al. [13] it is presented in the form:

$$\Lambda_{th(1)} = X_{PbO}\Lambda_{PbO} + X_{B_2O_3}\left[N_3\lambda_{BO_3} + N_4\lambda_{BO_4}\right] \quad (6)$$

where λ_{BO3} and λ_{BO4} are the group basicities of BO_3 and BO_4 groups, while N_3 and N_4 are their molar fractions. The results are picked up from ref. [13] and are listed in Table 2 (column 7). They are designated by a star.

^{11}B and ^{207}Pb NMR spectroscopy is used by Martin et al. [14] to probe boron and lead coordination environments in the structure of PbO-B_2O_3 glasses. We estimate the fraction of 4-coordinated boron (N_4) for glasses containing 35 mol %, 45 mol %, 55 mol % and 65 mol % of PbO using their graphical data of N_4 as a function of PbO content [13]. Martin et al. probe not only boron but also lead coordination environment by ^{207}Pb NMR spectra. In this connection we assume 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. These data provides to estimate the average single bond strength $B_{M\text{-}O}$ of PbO-B_2O_3 glasses by introducing the lead mole fractions P_6, P_4 and P_3 as well as boron mole fractions N_3 and N_4. Furthermore, it leads to an equation valid in the case of lead borate glasses. It is

Table 2. $PbO–B_2O_3$ glass system, composition, PbO_n fractions P_6,P_4,P_3, BO_n fractions N_4, N_3, theoretical optical basicity $\Lambda_{th(1)}$, single bond strength $B_{M–O}$.

First oxide, mol %	P_6	P_4	P_3	N_4	N_3	$\Lambda_{th(1)}$	$B_{M-O(1)}$, kJ/mol	$B_{M-O(2)}$, kJ/mol
28*				0.330*	0.670*	0.428*	371*	
35	0.558	0.442	0	0.454	0.546	0.431	340	330
43*				0.460*	0.540*	0.460*	316*	
45	0.244	0.756	0	0.530	0.470	0.459	305	300
48.3*				0. 530*	0.470*	0.473*	296*	
55	0	0.643	0.357	0.562	0.438	0.502	276	286
63.9*				0.300*	0.700*	0.583*	263*	
65	0	0.568	0.432	0.497	0.503	0.567	251	265
74.5*				0.170*	0.830*	0.666*	234*	

advanced by Dimitrov et al. [13] in the form:

$$B_{M-O(2)} = x\left[P_3 B_{Pb-O}{}^{(3)} + P_4 B_{Pb-O}{}^{(4)} + P_6 B_{Pb-O}{}^{(6)}\right] + \\ + (1-x)\left[N_3 B_{B-O}{}^{(3)} + N_4 B_{B-O}{}^{(4)}\right] \quad (7)$$

where P_3, P_4 and P_6 are the mole fractions of PbO_3, PbO_4 and PbO_6 groups, N_3 and N_4 are the mole fractions of BO_3 and BO_4 groups in a single glass molecule, while $B_{Pb-O}{}^{(3)}$, $B_{Pb-O}{}^{(4)}$ $B_{Pb-O}{}^{(6)}$, $B_{B-O}{}^{(3)}$ and $B_{B-O}{}^{(4)}$ are the single bond strengths of Pb-O and B-O bonds in PbO_3, PbO_4, PbO_6, BO_3 and BO_4 groups, respectively. The obtained results according to ref. [13] are summarized in Table 2 (column 9).

SiO_2 containing glasses

$Na_2O – SiO_2$ glasses

Sprenger et al. [15] elaborate a discrete bond model (DBM) of sodium silicate glasses based on XPS, Raman and NMR results. In sodium silicate glasses, the fraction of differently bound silica-oxygen species $Q^{(i)}$ (i = 0 - 4) is a function of stoichiometry and Na/Si ratio. $Q^{(4)}$ are SiO_4 units without NBO, $Q^{(3)}$ are SiO_4 units with one NBO, $Q^{(2)}$ are SiO_4 units with two NBO, $Q^{(1)}$ are SiO_4 units with three NBO and $Q^{(0)}$ are SiO_4 units with four NBO. On the basis of the data of the fractions of different Si species proposed by Sprenger et al. and group basicities proposed by Duffy and Ingram [1] for differently bound silica-oxygen species $Q^{(i)}$ (i = 0 - 4) Dimitrov et al. [11] advance an equation for calculation of theoretical optical basicity $\Lambda_{th(1)}$ of sodium-silicate glasses:

$$\Lambda_{th(1)} = X_{Na_2O}\Lambda_{Na_2O} + X_{SiO_2}\left[\begin{matrix} Q^{(4)}\lambda_{SiO_4{}^{0}} + Q^{(3)}\lambda_{SiO_4{}^{-}} + Q^{(2)}\lambda_{SiO_4{}^{2-}} + \\ + Q^{(1)}\lambda_{SiO_4{}^{3-}} + Q^{(0)}\lambda_{SiO_4{}^{4-}} \end{matrix}\right] \quad (8)$$

where $\lambda_{SiO_4{}^{0}}$, $\lambda_{SiO_4{}^{-}}$, $\lambda_{SiO_4{}^{2-}}$, $\lambda_{SiO_4{}^{3-}}$ and $\lambda_{SiO_4{}^{4-}}$ are the group basicities of $SiO_4{}^{0}$, $SiO_4{}^{-}$, $SiO_4{}^{2-}$, $SiO_4{}^{3-}$ and $SiO_4{}^{4-}$ units, while $Q^{(4)}$, $Q^{(3)}$, $Q^{(2)}$, $Q^{(1)}$ and $Q^{(0)}$ are their molar fractions expressed as %/100. The values of $\Lambda_{th(1)}$ of Na_2O-SiO_2 glasses are calculated by us [11] using Eq. (8) and the results are presented in Table 3 (column 5). They are compared with refractive index based optical basicity $\Lambda(n_o)$ [5] (column 4). Column 6 shows data for the single bond strength of sodium-silicate glasses calculated by Eq. 3 in accordance with ref. [11].

GeO_2 containing glasses

Na_2O-GeO_2 glasses

It is well known that alkali germanate glasses are characterized by the presence of extrema in their property-composition relationships, a phenomenon known as the "germanate anomaly" effect. It is probably due to the change of the coordination number of Ge^{4+} ions from 4 to 6. The fractions of $[GeO_6]$ groups in Na_2O-GeO_2 glasses are estimated by Sakka and Kamiya [16] on the basis of IR spectra. It is found that the molar fraction of GeO_6 increases with addition of Na_2O instead of bridging $[GeO_4]$. It reaches a maximum at 20 mol. % of Na_2O and than decreases. Takahashi and Yoshio [17] derive the bond energies of three groups,

Table 3. Na_2O-SiO_2 glass system, composition, SiO_4 fractions $Q^{(4)}$, $Q^{(3)}$, refractive index based optical basicity $\Lambda(n_0)$, theoretical optical basicity $\Lambda_{th(1)}$, single bond strength B_{M-O}.

First oxide, mol %	$Q^{(4)}$, %/100	$Q^{(3)}$, %/100	$\Lambda(n_o)$	$\Lambda_{th(1)}$	B_{M-O}, kJ/mol
15	0.65	0.35	0.586	0,534	389
20	0.50	0.50	0.603	0,554	371
25	0.35	0.65	0.621	0,574	353
30	0.15	0.85	0.643	0,601	335
33	0	1.00	0.656	0,614	325

namely $[GeO_6]$ group, all bridging $[GeO_4]_{BO}$ groups and the isolated $[GeO_4]_{NBO}$ group, on the ground of the compositional dependence of the heat of solution of crystalline sodium germinates. They propose equations for calculating the fractions of these three groups (N_1, N_2, N_3) in the structure of Na_2O-GeO_2 glasses as well as one for determination of the dissociation energy of the groups. We determine the single bond strength B_{Ge-O} of GeO_6 and GeO_4 groups for $xNa_2O.(1-x)GeO_2$ (x=5-30 mol %) glasses as follows: 323 kJ/mol for $[GeO_6]$, 343 kJ/mol for all bridging $[GeO_4]$ and 460 kJ/mol for $[GeO_4]_{NBO}$ groups [18] on the basis of the thermodynamic approach of Takahashi and Yoshio.

An equation for estimation of the average single bond strength B_{M-O} of sodium germanate glasses taking into account the contribution of different structural units is suggested by Dimitrov and Komatsu [18]:

$$B_{M-O} = xB_{Na-O} + (1-x)\left[\begin{matrix} N_1 B_{Ge-O}^{(GeO_6)} + N_2 B_{Ge-O}^{(GeO_4)BO} + \\ + N_3 B_{Ge-O}^{(GeO_4)NBO} \end{matrix}\right] \quad (9)$$

The calculated data are presented in Table 4 (column 6). Those referring to the refractive index based optical basicity $\Lambda(n_0)$ [5] are also given in Table 4 (column 5).

TeO_2 containing glasses

Dimitrov and Sakka [4] find that the refractive index based optical basicity of TeO_2, $\Lambda(n_o)$ is equal to 0.99. Since the structure of TeO_2 glass and α-TeO_2 crystal consists of TeO_4 groups without non-bridging oxygens, this means that the group basicity of such TeO_4 group (TeO_4^o) is also 0.99. Dimitrov and Komatsu [5] determine the refractive index based bulk optical basicity $\Lambda(n_o)$ of different tellurite glasses. It is found that tellurite glasses are basic in nature and their basicity is close to that of CaO ($\Lambda(n_o)$=1.0) Aida et al. [19] confirm the high values of the optical basicity even in ternary tellurite glasses. For instance, glasses from R_2O-R'O-TeO_2 systems (R=Li, Na, and K, R'=Mg, Ba, and Zn) possess large oxide ion polarizability 2.1 Å^3 - 2.4 Å^3 and large optical basicities of 0.90 - 0.97. In fact the large oxide ion polarizability and optical basicity could be related to the unique structural peculiarities of the tellurite glasses. The change of the

Table 4. $Na_2O.GeO_2$ glass system, composition, GeO_n fractions N_1, N_2, N_3, refractive index based optical bsicity $\Lambda(n_0)$, single bond strength B_{M-O}.

First oxide, mol %	N_1	N_2	N_3	$\Lambda(n_0)$	B_{M-O}, kJ/mol
10	0.22	0.78	0	0.778	311
15	0.36	0.64	0	0.787	297
20	0.50	0.50	0	0.792	282
25	0.66	0.34	0	0.817	267
30	0	0.79	0.21	0.832	283

tellurium coordination polyhedron from TeO_4 trigonal bipyramids to TeO_3 trigonal pyramids is well recognized for various tellurite glasses (Dimitriev et al.[20], Sekiya et al.[21], Sakida et al. [22, 23]). Sakida et al. [22, 23] report a comprehensive data on the structure of M_2O-TeO_2 (M = Li, Na, K, Rb and Cs) and MO-TeO_2 (M = Mg, Zn, Sr, Ba and Pb) glasses obtained by means of ^{125}Te nuclear magnetic resonance (NMR) spectroscopy. The fractions of several tellurite structural units, namely N_4^0, N_4^-, $N_4^*(=N_4^-+N_4^{2-})$, N_3^- and $N_3^*(=N_3^-+N_3^{2-})$, are determined.

Dimitrov and Komatsu [24, 25] have recently introduced the concept of group (i.e., microscopic) optical basicity proposed for binary R_2O (RO) – TeO_2 (R=Na, Mg, Sr, Ba, Zn, and Pb) and ternary tellurite $10R_2O.10R'O.80TeO_2$ (R=Li, Na, and K, R'O=Mg, Ba, and Zn) glasses. The data available for different N_4 (%) and N_3 (%) fractions of tellurium-oxygen polyhedra in tellurite glasses reported by Sakida et al. provide to assume that the optical basicity of TeO_2 in each glass composition could be expressed as a sum of the group basicities of the different TeO_4 and TeO_3 groups taking into account their molar fraction in the glass structure of the corresponding glass. It is presented as follows:

$$\Lambda_{TeO_2} = N_4^o \lambda_{TeO_4^o} + N_4^- \lambda_{TeO_4^-} + \\ + N_3^- \lambda_{TeO_3^-} + N_3^* \lambda_{(TeO_3^- + TeO_3^{2-})} \quad (10)$$

where $\lambda_{TeO_4^o}$, $\lambda_{TeO_4^-}$, $\lambda_{TeO_3^-}$ and $\lambda_{(TeO_3^- + TeO_3^{2-})}$ are the group basicities of TeO_4^o, TeO_4^-, TeO_3^- and sum of (TeO_3^-+TeO_3^{2-}) groups, while N_4^o, N_4^-, N_3^- and N_3^* are their molar fractions given as %/100. Thus, Dimitrov and Komatsu [25] calculate the theoretical optical basicity of ternary tellurite glases of the compositions given in Table 5. They contain different TeO_n groups, namely TeO_4 unit with one non-bridging oxygen ($\lambda_{TeO_4^-}$ = 1.23), TeO_4 unit without nonbridging oxygen ($\lambda_{TeO_4^o}$ = 0.99) and terminal TeO_3 unit with two non-bridging oxygens ($\lambda_{TeO_3^-}$ = 0.82). The results according to ref. [25] are presented in Table 5 (column 6). The data of the refractive index based optical basicity is also given in Table 5 (column 5) [25] for a comparison. The single bond strength of the glasses according to ref. [25] is listed in Table 5 (column 7).

Bi_2O_3 containing glasses

We calculate the refractive index based optical basicity $\Lambda(n_o)$ using the data of the refractive index and the density of Bi_2O_3-B_2O_3 and ZnO-Bi_2O_3-B_2O_3 glasses [26, 27]. It is found that the basicity increases with Bi_2O_3 content increase. Terashima et al. [28] investigate the structure and nonlinear optical properties of Bi_2O_3-B_2O_3 glasses and find on the basis of ^{11}B MAS NMR spectra that a change of boron coordination number from 3 to 4 is possible in the structure of binary glasses with increasing

Table 5. R_2O-RO-TeO_2 glass systems, compositions, TeO_n fractions, N_4^0, N_4^-, N_3^-, refractive index based optical basicity $\Lambda(n_0)$, theoretical optical basicity $\Lambda_{th(1),}$ single bond strength $B_{M\text{-}O.}$

	N_4^0	N_4^-	N_3^-	$\Lambda(n_o)$	$\Lambda_{th(1)}$	$B_{M\text{-}O}$, kJ/mol
$10Li_2O.10MgO.80TeO_2$	0.500	0.090	0.410	0.905	0.924	259
$10Na_2O.10MgO.80TeO_2$	0.500	0.085	0.415	0.942	0.938	252
$10K_2O.10MgO.80TeO_2$	0.500	0.090	0.410	0.965	0.953	249
$10Li_2O.10BaO.80TeO_2$	0.500	0.950	0.405	0.946	0.955	257
$10Na_2O.10BaO.80TeO_2$	0.500	0.090	0.410	0.961	0.968	250
$10K_2O.10BaO.80TeO_2$	0.500	0.095	0.405	0.962	0.984	247
$10Li_2O.10ZnO.80TeO_2$	0.500	0.085	0.415	0.937	0.941	258
$10Na_2O.10ZnO.80TeO_2$	0.500	0.080	0.420	0.967	0.955	252
$10K_2O.10ZnO.80TeO_2$	0.500	0.085	0.415	0.967	0.971	249

Table 6. $ZnO\text{-}Bi_2O_3\text{-}B_2O_3$ glass system, composition, BO_4 fractions N_4, refractive index based optical basicity $\Lambda(n_0)$, theoretical optical basicity $\Lambda_{th(1)}$, single bond strength B_{M-O}.

Glass System	First oxide, mol %	N_4	Λn_0	$\Lambda_{th(1)}$ 0.24	$\Lambda_{th(1)}$ 0.57	B_{M-O}, kJ/mol
$ZnO.10Bi_2O_3.B_2O_3$	**30**	0.305	0.652	0.551	0.611	331
	40	0.314	0.700	0.597	0.653	300
	50	0.295	0.754	0,656	0.702	270
	60	–	0.819	0.725[a]	0.764[a]	239[a]
	65	–	0.858	0.765[a]	0.800[a]	223[a]
$ZnO.20Bi_2O_3.B_2O_3$	**30**	0.331	0.771	0.652	0.705	294
	40	0.308	0.834	0.711	0.754	265
	50	0.227	0.892	0.785	0.812	237
$ZnO.30Bi_2O_3.B_2O_3$	**20**	0.350	0.850	0.697	0.750	288
	30	0.316	0.906	0.757	0.798	295
	40	0.243	0.951	0.828	0.854	231
Bi_2O_3–B_2O_3						
	25	0.408	0.542	0.557	0.637	361
	30	0.420	0.643	0.598	0.675	343
	40	0.400	0.822	0.685	0.747	310
	50	0.317	0.901	0.776	0.818	280
	60	0.236	0.939	0.865	0.890	249
	65	0.175	0.965	0.909	0.925	233

[a] *These values were calculated under the assumption of* $N_4=0.3$.

Bi_2O_3 content. The fractions of BO_3 and BO_4 units are determined (see Table 6). An equation for evaluation of the average single bond strength B_{M-O} of $Bi_2O_3\text{-}B_2O_3$ glasses is suggested by Dimitrov and Komatsu [26]. It takes into account the contribution of different structural units namely BiO_6, BO_3 and BO_4 groups. Its form is:

$$B_{M-O} = xB_{Bi-O^{(6)}} + (1-x)\left[N_3B_{B-O^{(3)}} + N_4B_{B-O^{(4)}} \right] \quad (11)$$

where N_3 and N_4 are the mole fractions of BO_3 and BO_4 groups in one glass molecule, while $B_{B\text{-}O(3)}$ and $B_{B\text{-}O(4)}$ refer to the single bond strength of B-O bonds in BO_3 and BO_4 groups, respectively. $B_{Bi\text{-}O(6)}$ is the single bond strength of Bi-O bonds in BiO_6 groups. Inoue et al. [27] determine the refractive index based optical basicity $\Lambda(n_o)$ of $ZnO\text{-}Bi_2O_3\text{-}B_2O_3$ glasses on the basis of data referring to the measured refractive index and density. The glasses of a high Bi_2O_3 or ZnO content possess high values of basicity (0.8-1.0), which is indicative of their basic nature. The fraction of 4-coordinated boron (N_4) is determined for a series of $ZnO\text{-}Bi_2O_3\text{-}B_2O_3$ glasses by Ida et al. [29] on the basis of ^{11}B MAS NMR spectra (see Table 6).

An equation for estimation of the average single bond strength B_{M-O} of $ZnO\text{-}Bi_2O_3\text{-}B_2O_3$ glasses is suggested by us [27]. It takes into account the contribution of different structural units namely ZnO_4, BiO_6, BO_3 and BO_4 groups. It is presented by:

$$B_{M-O} = xB_{Zn-O}{}^{(4)} + yB_{Bi-O}{}^{(6)} + \\ +(1-x-y)\left[N_3B_{B-O}{}^{(3)} + N_4B_{B-O}{}^{(4)} \right] \quad (12)$$

where N_3 and N_4 are the mole fractions of BO_3 and BO_4 groups in one glass molecule, while $B_{B\text{-}O}{}^{(3)}$ and $B_{B\text{-}O}{}^{(4)}$ are the single bond strengths of B-O bonds in BO_3 and BO_4 groups. $B_{Zn\text{-}O}{}^{(4)}$ and $B_{Bi\text{-}O}{}^{(6)}$ are the single bond strengths of Zn-O and Bi-O bonds in ZnO_4 and BiO_6 groups, respectively. The obtained data for B_{M-O} of $Bi_2O_3\text{-}B_2O_3$ and $Zno\text{-}Bi_2O_3\text{-}B_2O_3$ glasses is picked up from refs. [26,

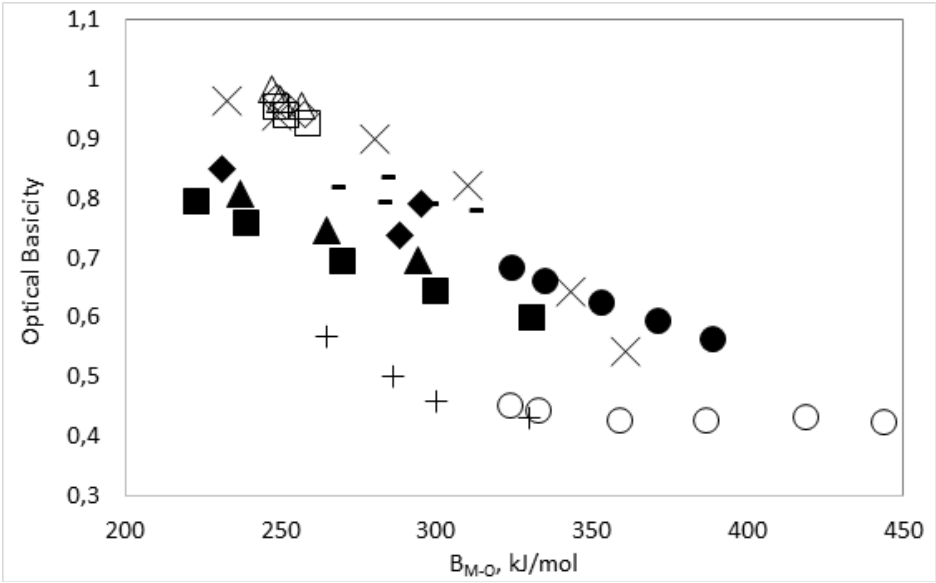

Fig. 1. Optical basicity as a function of the single bond strength of the glasses.
$\circ Na_2O-B_2O_3$; $+ PbO-B_2O_3$; $\bullet Na_2O-SiO_2$; $- Na_2O-GeO_2$,
$\square 10R_2O.10MgO.80TeO_2$; $\triangle 10R_2O.10BaO.80TeO_2$; $\Diamond 10R_2O.10ZnO.80TeO_2$;
$\times Bi_2O_3.B_2O_3$; $\blacksquare ZnO.10Bi_2O_3.B_2O_3$, $\blacktriangle ZnO.20Bi_2O_3.B_2O_3$; $\blacklozenge ZnO.30Bi_2O_3.B_2O_3$.

27] and is presented in Table 6 (column 7).

The obtained results referring to the theoretical optical basicity and the single bond strength of different oxide glasses are presented in Fig. 1. It can be seen that there is a general trend of increase of the optical basicity along with decrease of the single bond strength in the borate-silicate-germanate-tellurite-bismuthate glasses sequence. A high optical basicity means an increased electron donor ability of the oxide ions. On the other hand, small single bond strength can be connected with presence in the glasses structure of chemical bonds of increased iconicity such as Te-O-Te, Zn-O-Bi, Bi-O-Bi.

CONCLUSIONS

A review is presented referring to the correlation between the optical basicity and the single bond strength of oxide glasses. Equations for the calculation of theoretical optical basicity $\Lambda_{th(1)}$ of Na_2O-B_2O_3, PbO-B_2O_3, Na_2O-SiO_2 and R_2O-RO-TeO_2 glasses are advanced. They take into account the contribution of the mole fraction and the group basicity of different structural units, namely BO_3, BO_4 and SiO_4 groups. Equations providing the evaluation of the average single bond strength B_{M-O} of Na_2O-B_2O_3, PbO-B_2O_3, Na_2O-GeO_2, Bi_2O_3-B_2O_3 and ZnO-Bi_2O_3-B_2O_3 glasses are introduced. They take into account the mole fractions of BO_3, BO_4, GeO_4, GeO_6, PbO_3, PbO_4 and PbO_6 groups. It is found that there is a general trend of increase of the optical basicity along with decrease of the single bond strength in the sequence borate-silicate-germanate-tellurite-bismuthate glasses.

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