

# Classification of oxide glasses: A polarizability approach

Vesselin Dimitrov<sup>a</sup>, Takayuki Komatsu<sup>b,\*</sup>

<sup>a</sup>Department of Silicate Technology, University of Chemical Technology and Metallurgy, 8 Kl. Ohridski Blvd., Sofia 1756, Bulgaria

<sup>b</sup>Department of Chemistry, The Nagaoka University of Technology, 1603-1 Kamitomioka-cho, Nagaoka-shi, Niigata-ken 940-2188, Japan

Received 19 October 2004; accepted 10 December 2004

## Abstract

A classification of binary oxide glasses has been proposed taking into account the values obtained on their refractive index-based oxide ion polarizability  $\alpha_{\text{O}^{2-}}(n_0)$ , optical basicity  $A(n_0)$ , metallization criterion  $M(n_0)$ , interaction parameter  $A(n_0)$ , and ion's effective charges as well as O1s and metal binding energies determined by XPS. Four groups of oxide glasses have been established: glasses formed by two glass-forming acidic oxides; glasses formed by glass-forming acidic oxide and modifier's basic oxide; glasses formed by glass-forming acidic and conditional glass-forming basic oxide; glasses formed by two basic oxides. The role of electronic ion polarizability in chemical bonding of oxide glasses has been also estimated. Good agreement has been found with the previous results concerning classification of simple oxides. The results obtained probably provide good basis for prediction of type of bonding in oxide glasses on the basis of refractive index as well as for prediction of new nonlinear optical materials.

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**Keywords:** Oxide glasses; Refractive index; Electronic polarizability; Optical basicity; Metallization; Chemical bonding; XPS spectra; Nonlinear optical materials

## 1. Introduction

The estimation of the electronic polarizability of ions is subject of the so-called polarizability approach in materials science, which is well known especially in the field of glass science as done by Kordes [1], Fajans and Kreidl [2], and Weil and Marboe [3]. The most familiar and widely used relationship in this approach is Lorentz–Lorenz equation. Recently, Dimitrov and Sakka [4,5] have applied by means of this equation the polarizability approach to various simple oxides estimating the oxide ion polarizability  $\alpha_{\text{O}^{2-}}$  and optical basicity  $A$  of the oxides based on their refractive index  $n_0$  and energy gap  $E_g$ . The polarizability approach was systematically developed in our recent investigations concerning the origin of electronic ion polarizability and optical basicity of numerous simple oxides [6–8]. Classification of simple oxides has been made from the

viewpoint of polarizability [9]. Three groups of oxides have been proposed taking into consideration the values obtained on refractive index or energy gap-based oxide ion polarizability, cation polarizability, optical basicity, O1s binding energy, metal (or nonmetal) binding energy, and Yamashita–Kurosawa's interaction parameter of the oxides. The group of semicovalent predominantly acidic oxides includes BeO, B<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, GeO<sub>2</sub>, and Ga<sub>2</sub>O<sub>3</sub>. Some main group oxides such as CaO, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, and TeO<sub>2</sub> as well as the most transition metal oxides are included in the group of ionic or basic oxides. The group of very ionic or very basic oxides consists of CdO, SrO, and BaO as well as PbO, Sb<sub>2</sub>O<sub>3</sub>, and Bi<sub>2</sub>O<sub>3</sub>.

Since the simple oxides are usually initial components for synthesis of different multi-component glasses with practical interest, an estimation of the role of individual oxides from the viewpoint of their electronic polarizability in glass formation and in glass structure is extremely necessary. The binary oxide glass-forming systems are very suitable objects in this connection. That

\*Corresponding author. Fax: +81 258 47 9300.

E-mail address: [komatsu@chem.nagaokaut.ac.jp](mailto:komatsu@chem.nagaokaut.ac.jp) (T. Komatsu).

is why we have extended the polarizability approach for investigation of different binary oxide glasses. Suitable relationships between refractive index-based oxide ion polarizability  $\alpha_{\text{O}^{2-}}(n_0)$ , optical basicity  $A(n_0)$ , metallization criterion  $M(n_0)$ , interaction parameter  $A(n_0)$ , and O1s and metal binding energies determined from XPS spectra have been found [10–19]. Four groups of binary oxide glasses have been examined: glasses formed by two acidic oxides; glasses formed by acidic and modifier's basic oxides; glasses formed by acidic and conditional glass-forming basic oxide; glasses formed by two basic oxides [16,19].

With a view to corroborate such classification of oxide glasses we have tried in this article to show some chemical bonding arguments such as interaction parameter and effective charges borne by oxide and metal ions as well as experimental results recently obtained by XPS approving the applicability of the polarizability approach in glass chemistry. In result, a more detailed classification of oxide glasses is made and its application for nonlinear optical glasses is discussed.

## 2. Results and discussion

### 2.1. Refractive index-based oxide ion polarizability of oxide glasses

The Lorentz–Lorenz equation relates molar refraction to refractive index and molar volume of a glass as done by Kordes [1], Fajans and Kreidl [2], and Weil and Marboe [3]:

$$R_m = [(n_0^2 - 1)/(n_0^2 + 2)]V_m, \quad (1)$$

where  $R_m$  is the molar refraction,  $V_m$  the molar volume and  $n_0$  the linear refractive index. This equation gives the average molar refraction for isotropic substances, i.e., for liquids, glasses, and cubic crystals. By introducing Avogadro's number  $N_A$  the molar refraction  $R_m$  can be expressed as a function of molar polarizability  $\alpha_m$

$$R_m = 4\pi\alpha_m N_A/3. \quad (2)$$

With  $\alpha_m$  in ( $\text{\AA}^3$ ) this equation can be transformed to

$$R_m = 2.52\alpha_m. \quad (3)$$

Assuming that  $R_m$  and  $\alpha_m$  of a binary glass with common formula  $xA_pO_q \cdot (1-x)B_rO_s$  are additive quantities, we can calculate the electronic ion polarizability of an average oxide ion in glass  $\alpha_{\text{O}^{2-}}(n_0)$  using the equation

$$\alpha_{\text{O}^{2-}}(n_0) = [(V_m/2.52)(n_0^2 - 1)/(n_0^2 + 2) - \Sigma\alpha_i](N_{\text{O}^{2-}})^{-1}, \quad (4)$$

where  $\Sigma\alpha_i$  denotes molar cation polarizability given by  $xp\alpha_A + (1-x)r\alpha_B$  and  $N_{\text{O}^{2-}}$  denotes the number of oxide ions in the chemical formula given by  $xq +$

$(1-x)s$ . Dimitrov and Komatsu [10] have calculated by means of Eq. (4) the oxide ion polarizability of various binary oxide glasses including borate, phosphate, silicate, germanate, tellurite, and titanate. The obtained data for  $\alpha_{\text{O}^{2-}}(n_0)$  taken from Ref. [10] are shown in Tables 1–4, column 4. Data for the refractive index  $n_0$  of the glasses are also given in Tables 1–4, column 3. Recently, Honma et al. [13–15] have determined in similar way  $\alpha_{\text{O}^{2-}}(n_0)$  of  $\text{Sb}_2\text{O}_3\text{--B}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3\text{--B}_2\text{O}_3$ , and  $\text{La}_2\text{O}_3\text{--P}_2\text{O}_5$  glasses, and the obtained values are also shown in Tables 2 and 3, column 4. As can be seen, in general electronic oxide ion polarizability increases with increasing refractive index of the glasses. Largest values of  $\alpha_{\text{O}^{2-}}(n_0)$  between 2 and  $3\text{\AA}^3$  were obtained for tellurite and titanate glasses as well as for phosphate, borate, silicate and germanate glasses containing large amount  $\text{Sb}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$  or  $\text{V}_2\text{O}_5$ . The results are in agreement with similar calculations made recently by Vithal et al. [20] and Reddy et al. [21] for binary oxide glasses as well as with previous results concerning oxide ion polarizability of simple oxides [9].

### 2.2. Refractive index-based bulk optical basicity of oxide glasses

The bulk optical basicity ( $A$ ) of an oxide medium is a numerical expression of the average electron donor power of the oxide species constituting the medium and it is used as a measure of the acid–base properties of oxides, glasses, alloys, slags, molten salts, etc. [22,23]. According to the pioneering study by Duffy and Ingram [23], the optical basicity of glasses can be determined experimentally from frequency shift observed in the  $^1\text{S}_0\text{--}^3\text{P}_1$  band in UV spectra of probe ions such as  $\text{Tl}^+$ ,  $\text{Pb}^{2+}$ , or  $\text{Bi}^{3+}$  with  $6s^2$  electron configuration incorporated in the glass matrix. But the applicability of this method is rather limited because of the ultraviolet impairment of many glasses.

Simultaneously, it is possible to calculate the so-called “theoretical” optical basicity  $A_{\text{th}}$  of multi-component glass on the basis of the following equation proposed by Duffy and Ingram [24]:

$$A_{\text{th}} = X_1A_1 + X_2A_2 + \dots + X_nA_n, \quad (5)$$

where  $X_1, X_2, \dots, X_n$  are equivalent fractions based on the amount of oxygen each oxide contributes to the overall material stoichiometry and  $A_1, A_2, \dots, A_n$  are basicities assigned to the individual oxides.

An alternative approach for determination of optical basicity seems to be the relationship between basicity and refractivity. On the basis of refraction data Duffy [25] has established that an intrinsic relationship exists between electronic polarizability of the oxide ions  $\alpha_{\text{O}^{2-}}$  and optical basicity of the oxide medium  $A$ , as

Table 1

Linear refractive index  $n_0$ , oxide ion polarizability  $\alpha_{O_2-}(n_0)$ , optical basicity  $A(n_0)$ , interaction parameter  $A(n_0)$ , metallization criterion  $M(n_0)$ , effective charge  $q_o$ , mean O1s binding energy and metal binding energies Me(1) and Me(2) of binary oxide glasses formed by two acidic oxides

System	Mol%	$n_0$	$\alpha_{O_2-}(n_0)$ ( $\text{\AA}^3$ )	$A(n_0)$	$A(n_0)$ ( $\text{\AA}^{-3}$ )	$M(n_0)$	$q_o$	O1s (eV)	Me(1) (eV)	Me(2) (eV)
GeO <sub>2</sub> -SiO <sub>2</sub>	6	1.466	1.465	0.529	0.206	0.723	-0.61	—	—	—
	11	1.482	1.560	0.600	0.186	0.715	-0.69	—	—	—
	18	1.484	1.583	0.614	0.180	0.714	-0.71	—	—	—
	24	1.490	1.567	0.605	0.182	0.711	-0.70	—	—	—
	61	1.552	1.710	0.693	0.153	0.681	-0.80	—	—	—
B <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	10	1.459	1.457	0.524	0.210	0.727	-0.60	—	B1s	Si2p
	20	1.458	1.434	0.506	0.216	0.727	-0.58	—	—	—
	30	1.459	1.434	0.506	0.216	0.727	-0.58	—	—	—
	50	1.460	1.414	0.489	0.223	0.726	-0.56	532.88	193.52	103.52
	75	1.461	1.394	0.473	0.230	0.726	-0.54	—	—	—
	90	1.462	1.383	0.463	0.233	0.725	-0.53	—	—	—
P <sub>2</sub> O <sub>5</sub> -SiO <sub>2</sub>	8.70	1.471	1.480	0.541	0.205	0.721	-0.62	—	—	—
	14.25	1.480	1.422	0.496	0.218	0.716	-0.57	—	—	—
	21.4	1.507	1.389	0.468	0.226	0.702	-0.54	—	—	—
	25.10	1.533	1.382	0.461	0.228	0.69	-0.53	—	—	—
	29.90	1.537	1.335	0.419	0.240	0.688	-0.48	—	—	—
GeO <sub>2</sub> -B <sub>2</sub> O <sub>3</sub>	5	1.480	1.430	0.503	0.221	0.716	-0.58	—	—	—
	10	1.502	1.574	0.609	0.189	0.705	-0.70	—	—	—
	15	1.516	1.525	0.574	0.192	0.698	-0.66	—	—	—
	20	1.531	1.554	0.595	0.191	0.691	-0.68	—	—	—
	40	1.562	1.663	0.666	0.168	0.676	-0.77	—	—	—
	60	1.579	1.703	0.690	0.157	0.668	-0.79	—	—	—
	80	1.598	1.777	0.730	0.142	0.659	0.84	—	—	—
	90	1.604	1.804	0.745	0.136	0.656	-0.86	—	—	—
Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	5	—	—	0.489 <sup>a</sup>	0.215 <sup>a</sup>	—	-0.56 <sup>a</sup>	532.19	—	—
	10	—	—	0.497 <sup>a</sup>	0.214 <sup>a</sup>	—	-0.57 <sup>a</sup>	532.15	—	—
	15	—	—	0.505 <sup>a</sup>	0.213 <sup>a</sup>	—	-0.58 <sup>a</sup>	532.07	—	—
	20	—	—	0.513 <sup>a</sup>	0.212 <sup>a</sup>	—	-0.59 <sup>a</sup>	532.17	—	—
	25	—	—	0.520 <sup>a</sup>	0.212 <sup>a</sup>	—	-0.60 <sup>a</sup>	532.07	—	—

<sup>a</sup>The data are for theoretical optical basicity and theoretical interaction parameter.

given by Eq. (6):

$$A = 1.67(1 - 1/\alpha_{O_2-}) \quad (6)$$

Eq. (6), as shown by Dimitrov and Sakka [4] in the case of simple oxides, gives the opportunity of calculating the optical basicity of the medium on the basis of experimental data for refractive index  $n_0$  or for the energy gap  $E_g$  of the solids and of obtaining the so-called refractive index-based optical basicity  $A(n_0)$  or energy gap-based optical basicity  $A(E_g)$ .

Dimitrov and Komatsu [10] extended the optical basicity approach to binary oxide glasses. For various binary oxide glasses including phosphate, borate, silicate, germanate, tellurite, and titanate, the theoretical optical basicity  $A_{th}$  was calculated using Eq. (5) on the basis of the optical basicity data for the simple oxides obtained by Duffy [24] and Dimitrov and Sakka [4]. Also by means of Eq. (6), the optical basicity of the glasses  $A(n_0)$  was estimated using data of oxide polarizability based on the refractive index,  $\alpha_{O_2-}(n_0)$ . A good agreement has been observed between the

optical basicity data obtained using different initial quantities. Data for  $A(n_0)$  according to Ref. [10] are listed in Tables 1–4 (column 5). Recently, Honma et al. [13–15] determined in similar way  $A(n_0)$  of Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>, and La<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> glasses and the obtained values are shown also in Tables 2 and 3, column 5. The data on theoretical optical basicity  $A_{th}$  for SrO-V<sub>2</sub>O<sub>5</sub>, and PbO-V<sub>2</sub>O<sub>5</sub> glasses are calculated in the present study by means of Eq. (5) and are also included in Table 4, column 5. As can be seen the basicity of phosphate, borate, and silicate glasses with large amount glass-forming oxide is low and it is below 0.75. They are more acidic glasses because the main component is a strong acidic oxide such as P<sub>2</sub>O<sub>5</sub> (0.33), B<sub>2</sub>O<sub>3</sub> (0.42) or SiO<sub>2</sub> (0.48) [4,9]. The optical basicity  $A(n_0)$  of borate glasses increases when the content of oxides such as Sb<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub> is large. The increase of the basicity correlates with the high optical basicity of Sb<sub>2</sub>O<sub>3</sub> (1.18) and Bi<sub>2</sub>O<sub>3</sub> (1.19). The basicity of tellurite glasses is also significant. It is of the same order as that of CaO and it varies in a very narrow range. TeO<sub>2</sub> (0.93) as conditional

Table 2

Linear refractive index  $n_0$ , oxide ion polarizability  $\alpha_{O_2-}(n_0)$ , optical basicity  $A(n_0)$ , interaction parameter  $A(n_0)$ , metallization criterion  $M(n_0)$ , effective charges  $q_o$ ,  $q_{Me+}$  and  $q_{Men+}$ , mean O1s binding energy, metal binding energies Me(1) and Me(2) of binary oxide glasses formed by acidic and modifier's basic oxides

System	Mol%	$n_0$	$\alpha_{O_2-}(n_0)$ ( $\text{\AA}^3$ )	$A(n_0)$	$A(n_0)$ ( $\text{\AA}^{-3}$ )	$M(n_0)$	$q_o$	$q_{Me+}$	$q_{Men+}$	O1s (eV)	Me(1) (eV)	Me(2) (eV)
Li <sub>2</sub> O–P <sub>2</sub> O <sub>5</sub>	19.9	1.496	1.454	0.521	0.212	0.708	–0.60	0.75	1.46	—	—	—
	26.6	1.501	1.438	0.509	0.216	0.706	–0.59	0.75	1.28	—	—	—
	39.7	1.504	1.432	0.504	0.217	0.704	–0.58	0.76	1.14	—	—	—
	50.1	1.512	1.436	0.508	0.216	0.700	–0.58	0.75	0.99	—	—	—
	59.4	1.525	1.457	0.524	0.216	0.694	–0.60	0.74	0.86	—	—	—
Na <sub>2</sub> O–P <sub>2</sub> O <sub>5</sub>	17.2	1.492	1.456	0.523	0.210	0.709	–0.60	0.88	1.38	—	—	—
	30.4	1.487	1.450	0.518	0.211	0.712	–0.60	0.88	1.25	—	—	—
	43.9	1.485	1.466	0.531	0.206	0.713	–0.61	0.87	1.08	—	—	—
	50.1	1.484	1.477	0.539	0.202	0.714	–0.62	0.87	0.99	—	—	—
	60.6	1.482	1.531	0.579	0.189	0.714	–0.67	0.86	0.87	—	—	—
SrO–P <sub>2</sub> O <sub>5</sub>	25	1.539	1.345	0.429	0.232	0.687	–0.49	—	—	—	—	—
	30	1.546	1.351	0.434	0.228	0.683	–0.50	—	—	—	—	—
	35	1.549	1.389	0.468	0.217	0.682	–0.54	—	—	—	—	—
	40	1.551	1.422	0.495	0.207	0.681	–0.57	—	—	—	—	—
	45	1.554	1.465	0.529	0.196	0.680	–0.61	—	—	—	—	—
	50	1.561	1.492	0.551	0.188	0.676	–0.63	—	—	—	—	—
	55	1.575	1.492	0.551	0.185	0.669	–0.63	—	—	—	—	—
ZnO–P <sub>2</sub> O <sub>5</sub>	25.45	1.527	1.502	0.558	0.199	0.692	–0.64	—	—	—	—	—
	29.04	1.531	1.497	0.554	0.199	0.691	–0.64	—	—	—	—	—
	40.78	1.532	1.505	0.561	0.195	0.690	–0.65	—	—	—	—	—
	49.72	1.519	1.537	0.583	0.188	0.697	–0.67	—	—	—	—	—
	60.26	1.577	1.572	0.608	0.178	0.668	–0.70	—	—	—	—	—
	64.85	1.606	1.589	0.620	0.174	0.655	–0.71	—	—	—	—	—
CdO–P <sub>2</sub> O <sub>5</sub>	4.9	1.505	1.479	0.541	0.206	0.703	–0.62	—	—	—	—	—
	21.2	1.522	1.474	0.538	0.202	0.695	–0.62	—	—	—	—	—
	32.9	1.552	1.476	0.540	0.198	0.681	–0.62	—	—	—	—	—
	40.9	1.565	1.495	0.553	0.190	0.674	–0.64	—	—	—	—	—
	49.7	1.607	1.513	0.566	0.182	0.655	–0.65	—	—	—	—	—
	57.2	1.630	1.531	0.579	0.174	0.645	–0.67	—	—	—	—	—
PbO–P <sub>2</sub> O <sub>5</sub>	7.6	1.521	1.484	0.544	0.203	0.696	–0.63	—	—	—	—	—
	18.8	1.557	1.470	0.534	0.200	0.678	–0.61	—	—	—	—	—
	30.3	1.604	1.469	0.533	0.195	0.656	–0.61	—	—	—	—	—
	35.4	1.633	1.471	0.534	0.191	0.642	–0.61	—	—	—	—	—
	40.0	1.659	1.470	0.534	0.188	0.632	–0.61	—	—	—	—	—
	55.2	1.768	1.464	0.530	0.174	0.585	–0.61	—	—	—	—	—
	60.5	1.812	1.465	0.530	0.168	0.568	–0.61	—	—	—	—	—
	61.6	1.826	1.477	0.540	0.165	0.563	–0.62	—	—	—	—	—
La <sub>2</sub> O <sub>3</sub> –P <sub>2</sub> O <sub>5</sub>	10	1.527	1.358	0.441	0.227	0.693	–0.51	—	—	532.45	134.20	836.14
	15	1.534	1.394	0.473	0.214	0.689	–0.54	—	—	532.18	134.18	836.12
	20	1.544	1.419	0.493	0.204	0.684	–0.57	—	—	531.96	134.02	836.03
	25	1.569	1.477	0.539	0.187	0.672	–0.62	—	—	531.88	133.91	836.01
Li <sub>2</sub> O–B <sub>2</sub> O <sub>3</sub>	4.14	1.472	1.374	0.454	0.236	0.720	–0.52	0.79	0.76	—	—	—
	10.23	1.494	1.366	0.448	0.237	0.709	–0.52	0.80	0.72	—	—	—
	14.21	1.507	1.360	0.443	0.239	0.703	–0.51	0.80	0.67	—	—	—
	20.27	1.525	1.355	0.438	0.240	0.694	–0.50	0.80	0.61	—	—	—
	25.98	1.542	1.351	0.434	0.242	0.685	–0.50	0.81	0.55	—	—	—
Na <sub>2</sub> O–B <sub>2</sub> O <sub>3</sub>	5.12	1.481	1.371	0.452	0.236	0.716	–0.52	0.90	0.75	—	—	—
	10.33	1.491	1.370	0.451	0.235	0.710	–0.52	0.90	0.71	—	—	—
	15.20	1.497	1.371	0.452	0.234	0.707	–0.52	0.90	0.67	—	—	—
	20.23	1.502	1.374	0.454	0.234	0.705	–0.52	0.90	0.62	—	—	—
	25.13	1.509	1.380	0.460	0.231	0.701	–0.53	0.90	0.58	—	—	—
	29.85	1.516	1.392	0.471	0.227	0.698	–0.54	0.89	0.55	—	—	—
	34.20	1.517	1.417	0.493	0.220	0.697	–0.57	0.88	0.54	—	—	—

Table 2 (continued)

System	Mol%	$n_0$	$\alpha_{O_2}(n_0)$ ( $\text{\AA}^3$ )	$A(n_0)$	$A(n_0)$ ( $\text{\AA}^{-3}$ )	$M(n_0)$	$q_0$	$q_{Me+}$	$q_{Men+}$	O1s (eV)	Me(1) (eV)	Me(2) (eV)
K <sub>2</sub> O–B <sub>2</sub> O <sub>3</sub>	4.09	1.479	1.372	0.453	0.235	0.716	−0.52	0.95	0.75	—	—	—
	10.17	1.488	1.378	0.458	0.230	0.712	−0.53	0.95	0.72	—	—	—
	14.11	1.488	1.386	0.464	0.227	0.712	−0.53	0.95	0.68	—	—	—
	19.97	1.488	1.401	0.478	0.220	0.712	−0.55	0.95	0.66	—	—	—
	25.83	1.495	1.415	0.489	0.214	0.709	−0.56	0.95	0.61	—	—	—
	29.96	1.499	1.437	0.508	0.207	0.706	−0.58	0.94	0.59	—	—	—
	34.00	1.502	1.468	0.533	0.199	0.705	−0.61	0.94	0.59	—	—	—
Ag <sub>2</sub> O–B <sub>2</sub> O <sub>3</sub>	10	1.512	1.368	0.449	0.232	0.700	−0.52	—	—	—	—	—
	20	1.584	1.417	0.490	0.214	0.665	−0.56	—	—	—	—	—
	30	1.631	1.551	0.593	0.178	0.644	−0.68	—	—	—	—	—
BaO–B <sub>2</sub> O <sub>3</sub>	20	1.535	1.326	0.410	0.236	0.690	−0.47	—	—	—	—	—
	30	1.578	1.345	0.430	0.223	0.668	−0.49	—	—	—	—	—
	40	1.607	1.408	0.484	0.200	0.655	−0.56	—	—	—	—	—
CdO–B <sub>2</sub> O <sub>3</sub>	40.5	1.672	1.454	0.521	0.194	0.626	−0.60	—	—	—	—	—
	46.6	1.705	1.501	0.558	0.180	0.611	−0.64	—	—	—	—	—
	51.5	1.732	1.539	0.585	0.170	0.600	−0.63	—	—	—	—	—
	56.5	1.750	1.574	0.610	0.159	0.593	−0.70	—	—	—	—	—
PbO–B <sub>2</sub> O <sub>3</sub>	30	1.699	1.347	0.431	0.217	0.614	−0.50	—	—	—	—	—
	40	1.768	1.342	0.426	0.206	0.585	−0.49	—	—	—	—	—
	50	1.842	1.376	0.456	0.185	0.556	−0.52	—	—	—	—	—
	60	1.918	1.469	0.533	0.153	0.528	−0.61	—	—	—	—	—
	70	2.001	1.606	0.630	0.116	0.500	−0.72	—	—	—	—	—
La <sub>2</sub> O <sub>3</sub> –B <sub>2</sub> O <sub>3</sub>	10	1.673	1.389	0.468	0.219	0.625	−0.54	—	—	—	—	—
	20	1.678	1.520	0.571	0.180	0.622	−0.66	—	—	—	—	—
	30	1.721	1.617	0.638	0.153	0.605	−0.73	—	—	—	—	—
Li <sub>2</sub> O–SiO <sub>2</sub>	20.0	1.500	1.520	0.571	0.196	0.706	−0.66	0.71	1.13	—	—	—
	30.3	1.524	1.572	0.608	0.185	0.694	−0.70	0.68	1.11	—	—	—
	41.7	1.549	1.586	0.616	0.182	0.682	−0.71	0.68	0.96	—	—	—
	50.0	1.559	1.621	0.640	0.176	0.677	−0.74	0.66	0.90	—	—	—
Na <sub>2</sub> O–SiO <sub>2</sub>	15	1.482	1.540	0.586	0.190	0.715	−0.67	0.85	1.16	531.9	Si2p 102.5	Na1s 1071.5
	20	1.490	1.565	0.603	0.184	0.711	−0.69	0.85	1.12	531.6	102.6	1071.5
	25	1.498	1.591	0.621	0.179	0.707	−0.71	0.84	1.09	531.2	101.9	1071.5
	30	1.504	1.627	0.643	0.171	0.704	−0.74	0.83	1.08	530.9	101.9	1071.1
	33	1.506	1.648	0.656	0.167	0.703	−0.75	0.83	1.05	530.6	101.8	1071.2
	40	—	—	—	—	—	—	—	—	530.3	101.3	1070.9
	45	—	—	—	—	—	—	—	—	530.1	100.8	1070.9
50	—	—	—	—	—	—	—	—	529.8	100.6	1070.6	
K <sub>2</sub> O–SiO <sub>2</sub>	15	1.488	1.562	0.601	0.180	0.712	−0.69	0.93	1.17	—	Si2p —	K2p —
	20	1.493	1.589	0.620	0.173	0.709	−0.71	0.93	1.14	531.25	102.3	292.7
	25	1.498	1.630	0.646	0.163	0.707	−0.74	0.92	1.11	—	—	—
	30	1.503	1.675	0.673	0.154	0.704	−0.77	0.92	1.08	—	—	—
	33	1.507	1.700	0.688	0.148	0.702	−0.79	0.92	1.06	530.45	101.3	292.2
Rb <sub>2</sub> O–SiO <sub>2</sub>	15	1.494	1.548	0.593	0.180	0.709	−0.68	0.95	1.17	—	Si2p —	Rb3d <sub>5/2</sub> —
	20	1.502	1.590	0.621	0.169	0.705	−0.71	0.95	1.12	—	—	—
	25	1.510	1.708	0.693	0.147	0.701	−0.80	0.94	1.24	—	—	—
	30	1.517	1.695	0.685	0.146	0.698	−0.79	0.94	1.11	—	—	—
	33	1.521	1.675	0.673	0.146	0.696	−0.77	0.94	0.99	529.98	100.9	108.9
Cs <sub>2</sub> O–SiO <sub>2</sub>	5.0	1.481	1.485	0.546	0.199	0.715	−0.63	0.99	1.19	—	—	—
	12.2	1.510	1.529	0.578	0.184	0.701	−0.67	0.99	1.06	—	—	—
	20.0	1.530	1.584	0.616	0.167	0.691	−0.71	0.99	1.10	—	—	—
	26.7	1.548	1.649	0.658	0.150	0.681	−0.76	0.99	1.08	—	—	—
CaO–SiO <sub>2</sub>	39.0	1.590	1.648	0.656	0.160	0.662	−0.75	—	—	—	—	—
	44.6	1.612	1.680	0.676	0.152	0.652	−0.78	—	—	—	—	—

Table 2 (continued)

System	Mol%	$n_0$	$\alpha_{O_2-(n_0)} (\text{\AA}^3)$	$A(n_0)$	$A(n_0) (\text{\AA}^{-3})$	$M(n_0)$	$q_0$	$q_{Me+}$	$q_{Men+}$	O1s (eV)	Me(1) (eV)	Me(2) (eV)
	50.0	1.629	1.718	0.698	0.144	0.645	−0.80					
	52.9	1.635	1.740	0.710	0.140	0.642	−0.82					
	57.5	1.645	1.778	0.731	0.133	0.637	−0.84					
PbO–SiO <sub>2</sub>											Si2p	Pb5d <sub>3/2</sub>
	25	—	—	—	—	—	—			531.6	102.6	19.7
	30	1.749	1.442	0.513	0.181	0.593	−0.59			531.5	102.5	19.8
	40	1.811	1.516	0.568	0.155	0.568	−0.65			531.2	102.2	19.7
	50	1.859	1.608	0.631	0.129	0.550	−0.73			530.6	101.7	19.3
	60	1.942	1.650	0.658	0.110	0.520	−0.76			530.1	101.2	19.1
	66	1.996	1.740	0.710	0.092	0.501	−0.82			529.9	101.0	18.8
Li <sub>2</sub> O–GeO <sub>2</sub>	6.4	1.651	1.862	0.773	0.128	0.635	−0.89	0.57	1.76			
	13.1	1.693	1.837	0.762	0.131	0.617	−0.88	0.58	1.72			
	18.3	1.715	1.837	0.762	0.131	0.607	−0.88	0.58	1.70			
	23.2	1.715	1.842	0.763	0.131	0.607	−0.88	0.57	1.68			
Na <sub>2</sub> O–GeO <sub>2</sub>	10	1.670	1.874	0.778	0.126	0.626	−0.89	0.79	1.70	—		
	12.5	—	—	—	—	—	—	—	—	530.7		
	15	1.681	1.889	0.787	0.124	0.621	−0.90	0.79	1.68	—		
	17.5	—	—	—	—	—	—	—	—	530.5		
	20	1.678	1.900	0.792	0.122	0.622	−0.91	0.78	1.66	530.2		
	25	1.660	1.956	0.817	0.116	0.630	−0.94	0.77	1.68	—		
	30	1.640	1.994	0.832	0.111	0.640	−0.96	0.77	1.67	530.1		
K <sub>2</sub> O–GeO <sub>2</sub>	4.49	1.642	1.926	0.803	0.118	0.639	−0.92	0.90	1.80			
	10.53	1.661	1.902	0.793	0.119	0.630	−0.91	0.90	1.72			
	17.59	1.652	1.932	0.805	0.114	0.635	−0.93	0.90	1.67			
	26.69	1.620	2.016	0.842	0.103	0.650	−0.97	0.89	1.65			

glass-former is the main component of these glasses and obviously its acid–base property has a significant effect.

### 2.3. Refractive index-based metallization criterion of oxide glasses

According to the theory on metallization of the condensed matter proposed by Herzfeld [26], for the condition  $R_m/V_m = 1$  in the Lorentz–Lorenz equation the refractive index becomes infinite, which corresponds to the metallization of covalent solid materials. In other words the electron becomes itinerant and the system acquires metallic status. The necessary and sufficient condition for predicting the nonmetallic or metallic nature of solids are:  $R_m/V_m < 1$  (nonmetal) and  $R_m/V_m > 1$  (metal). The difference from 1 is the so-called metallization criterion [5]

$$M = 1 - R_m/V_m. \quad (7)$$

Eq. (7) indicates that when  $(1 - R_m/V_m)$  becomes zero the transition to the metal state takes place. In the tight binding approach to the band theory the nonmetal to metal transition of a binary compound, such as simple oxide, occurs when the energy gap  $E_g$  becomes zero [5]. Taking into account the similarity in both approaches based on a particular quantity tending to zero, Duffy [27] has suggested that a good correlation exists between the energy gap of the oxides and their molar refraction.

On this basis the metallization criterion  $M(n_0)$  and  $M(E_g)$  of numerous simple oxides has been calculated by Dimitrov and Sakka [5] using data of their refractive index  $n_0$  and energy gap  $E_g$ , respectively. It was established that the oxides with large refractive index and small energy gap such as PbO, TiO<sub>2</sub>, Sb<sub>2</sub>O<sub>3</sub>, CdO, Ta<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, CeO<sub>2</sub>, etc. possess a metallization criterion in the 0.35–0.45 range, while alkaline and alkaline-earth oxides, as well as B<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, have a small refractive index, large energy gap and a metallization criterion ranging from 0.50 to 0.70.

By means of Eqs. (1) and (7) Dimitrov and Komatsu [10] have calculated metallization criterion  $M(n_0)$  for different binary oxide glasses. The obtained values are picked up from Ref. [10] and collected in Tables 1–4 (column 7) for different binary oxide glasses. Good agreement can be found between the present results for the binary oxide glasses and those for the simple oxides [4,10]. As can be seen, tellurite glasses containing Nb<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>, MoO<sub>3</sub>, and lead-titanate glasses as well as borate glasses containing large amount of Sb<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub> possess a metallization criterion  $M(n_0)$  in the 0.42–0.5 range. On the other hand, borate, silicate, and germanate glasses containing large amount of glass-forming oxide have metallization criterion ranging from 0.50 to 0.75. The small metallization criterion means that the width of both valence and conduction bands becomes large, resulting in a narrow

Table 3

Linear refractive index  $n_0$ , oxide ion polarizability  $\alpha_{O_2-}(n_0)$ , optical basicity  $A(n_0)$ , interaction parameter  $A(n_0)$ , metallization criterion  $M(n_0)$ , effective charges  $q_o$ , mean O1s binding energy and metal binding energy Me(2) of binary oxide glasses formed by acidic and conditional glass forming basic oxides

System	Mol%	$n_0$	$\alpha_{O_2-}(n_0) (\text{\AA}^3)$	$A(n_0)$	$A(n_0) (\text{\AA}^{-3})$	$M(n_0)$	$q_o$	O1s (ev)	Me(2) (eV)
Sb <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub>	15.5	1.619	1.612	0.635	0.170	0.650	-0.73	—	—
	21.1	1.651	1.670	0.670	0.156	0.635	-0.77	—	—
	28.7	1.693	1.741	0.711	0.141	0.617	-0.82	—	—
	31.4	1.705	1.777	0.730	0.135	0.611	-0.84	—	—
	36.3	1.730	1.821	0.753	0.126	0.601	-0.87	—	—
	40.5	1.755	1.854	0.770	0.119	0.591	-0.88	—	—
	79.5	2.015	2.663	1.042	0.041	0.495	-1.20	—	—
	86.4	2.065	2.865	1.087	0.031	0.479	-1.25	—	—
Bi <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub>	10.0	1.591	1.761	0.721	0.148	0.662	-0.83	—	—
	14.5	1.623	1.700	0.688	0.155	0.647	-0.79	—	—
	20.5	1.752	1.808	0.746	0.135	0.592	-0.86	—	—
	30.0	1.870	2.026	0.847	0.127	0.546	-0.97	—	—
	35.0	1.950	2.084	0.868	0.123	0.517	-1.00	—	—
V <sub>2</sub> O <sub>5</sub> -P <sub>2</sub> O <sub>5</sub>	25.0	1.682	1.657	0.663	0.167	0.621	-0.76	—	—
	33.3	1.720	1.738	0.710	0.153	0.605	-0.82	—	—
	42.8	1.765	1.845	0.765	0.137	0.587	-0.88	—	—
	53.8	1.815	1.979	0.827	0.118	0.567	-0.95	—	—
	66.7	1.890	2.156	0.895	0.098	0.538	-1.03	—	—
Sb <sub>2</sub> O <sub>3</sub> -B <sub>2</sub> O <sub>3</sub>	10	1.474	1.365	0.447	0.224	0.719	-0.51	532.86	Sb3d <sub>3/2</sub> 540.27
	20	1.570	1.570	0.606	0.169	0.672	-0.70	532.27	540.19
	30	1.707	1.877	0.780	0.117	0.611	-0.90	532.27	540.01
	40	1.767	2.010	0.839	0.097	0.586	-0.97	532.13	539.85
	50	1.820	2.153	0.894	0.079	0.565	-1.03	531.97	539.67
	60	1.853	2.317	0.949	0.063	0.552	-1.09	531.77	539.57
	70	1.881	2.417	0.979	0.054	0.542	-1.12	531.61	539.52
Bi <sub>2</sub> O <sub>3</sub> -B <sub>2</sub> O <sub>3</sub>	25	1.818	1.480	0.542	0.176	0.566	-0.62	531.45	Bi4f <sub>5/2</sub> 159.31
	30	1.836	1.626	0.643	0.146	0.559	-0.74	531.18	159.30
	40	1.976	1.970	0.822	0.097	0.508	-0.95	530.94	158.76
	50	2.074	2.171	0.901	0.073	0.476	-1.04	530.72	158.73
	60	2.097	2.284	0.939	0.061	0.469	-1.08	530.42	158.75
	65	2.129	2.370	0.965	0.053	0.459	-1.11	530.32	158.74
Bi <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	26.4	1.75	2.245	0.932	0.074	0.593	-1.07	—	—
	31.0	1.83	2.448	0.989	0.059	0.561	-1.14	—	—
	36.4	1.89	2.432	0.984	0.057	0.539	-1.13	—	—
	41.3	1.97	2.622	1.034	0.045	0.510	-1.19	—	—
	46.5	1.99	2.773	1.067	0.036	0.503	-1.23	—	—
	49.6	2.07	2.623	1.034	0.042	0.477	-1.19	—	—
Bi <sub>2</sub> O <sub>3</sub> -GeO <sub>2</sub>	9.16	1.715	2.020	0.843	0.101	0.607	-0.97	—	—
	18.14	1.873	2.230	0.922	0.076	0.545	-1.06	—	—
	24.59	1.910	2.278	0.937	0.069	0.531	-1.08	—	—
	32.95	2.050	2.549	1.015	0.049	0.484	-1.17	—	—
	39.24	2.070	2.608	1.030	0.044	0.477	-1.18	—	—
Sb <sub>2</sub> O <sub>3</sub> -GeO <sub>2</sub>	9.56	1.675	2.059	0.860	0.098	0.625	-0.99	—	—
	14.69	1.715	2.131	0.885	0.088	0.608	-1.02	—	—
	22.67	1.780	2.287	0.940	0.073	0.580	-1.08	—	—
	32.13	1.820	2.360	0.962	0.064	0.565	-1.11	—	—
	34.86	1.840	2.406	0.977	0.060	0.557	-1.12	—	—
	41.15	1.950	2.667	1.044	0.044	0.517	-1.20	—	—
V <sub>2</sub> O <sub>5</sub> -GeO <sub>2</sub>	10	1.680	2.035	0.850	0.108	0.622	-0.98	—	—
	20	1.750	2.173	0.902	0.093	0.593	-1.04	—	—
	40	1.900	2.351	0.960	0.078	0.535	-1.10	—	—
	50	1.960	2.388	0.970	0.075	0.514	-1.12	—	—

Table 4

Linear refractive index  $n_0$ , oxide ion polarizability  $\alpha_{O^{2-}}(n_0)$ , optical basicity  $A(n_0)$ , interaction parameter  $A(n_0)$ , metallization criterion  $M(n_0)$ , effective charges  $q_o$ ,  $q_{Me+}$  and  $q_{Men+}$ , mean O1s binding energy and metal binding energy Me(1) of binary oxide glasses formed by two basic oxides

System	Mol%	$n_0$	$\alpha_{O^{2-}}(n_0)$ ( $\text{\AA}^3$ )	$A(n_0)$	$A(n_0)$ ( $\text{\AA}^{-3}$ )	$M(n_0)$	$q_o$	$q_{Me+}$	$q_{Men+}$	O1s (eV)	Me(1) (eV)	Me(2) (eV)
Li <sub>2</sub> O–TeO <sub>2</sub>	15	1.99	2.246	0.927	0.044	0.504	−1.07	0.46	2.17	530.13	Te3d <sub>5/2</sub> 575.96	—
	20	1.98	2.254	0.929	0.045	0.507	−1.07	0.46	2.18	529.98	575.82	—
	25	1.95	2.211	0.915	0.049	0.517	−1.05	0.47	2.14	529.95	575.79	—
	30	1.92	2.21	0.915	0.051	0.528	−1.05	0.47	2.15	529.82	575.68	—
Na <sub>2</sub> O–TeO <sub>2</sub>	5	2.13	2.366	0.964	0.037	0.459	−1.11	0.73	2.20	—	Te3d <sub>5/2</sub> —	—
	10	2.07	2.346	0.959	0.038	0.477	−1.10	0.73	2.16	530.07	575.92	—
	13	2.03	2.381	0.969	0.038	0.490	−1.11	0.72	2.17	—	—	—
	15	—	—	—	—	—	—	—	—	529.96	575.83	—
	17	2.001	2.444	0.987	0.036	0.500	−1.13	0.72	2.20	—	—	—
	20	1.93	2.415	0.979	0.038	0.524	−1.13	0.72	2.18	529.76	575.61	—
	23	1.887	2.442	0.985	0.038	0.540	−1.13	0.72	2.17	—	—	—
	25	—	—	—	—	—	—	—	—	529.76	575.63	—
	30	—	—	—	—	—	—	—	—	529.53	575.45	—
	35	—	—	—	—	—	—	—	—	529.34	575.26	—
	K <sub>2</sub> O–TeO <sub>2</sub>	4.85	2.11	2.383	0.969	0.035	0.465	−1.11	0.87	2.19	—	Te3d <sub>5/2</sub> —
9.40		2.05	2.436	0.985	0.034	0.484	−1.13	0.87	2.20	—	—	—
10		—	—	—	—	—	—	—	—	529.90	575.73	—
12.90		2.005	2.494	1.000	0.032	0.498	−1.15	0.87	2.21	—	—	—
15		—	—	—	—	—	—	—	—	529.74	575.57	—
15.60		1.964	2.526	1.010	0.032	0.512	−1.16	0.87	2.21	—	—	—
17.30		1.925	2.504	1.004	0.032	0.526	−1.16	0.87	2.20	—	—	—
20		—	—	—	—	—	—	—	—	529.55	575.45	—
25		—	—	—	—	—	—	—	—	529.53	575.38	—
Ag <sub>2</sub> O–TeO <sub>2</sub>	20	2.18	2.408	0.977	0.034	0.444	−1.12	—	—	—	—	—
	25	2.16	2.386	0.970	0.035	0.450	−1.12	—	—	—	—	—
	30	2.15	2.381	0.969	0.035	0.453	−1.11	—	—	—	—	—
MgO–TeO <sub>2</sub>	10	2.106	2.297	0.943	0.040	0.467	−1.08	—	—	—	—	—
	15	2.063	2.231	0.923	0.044	0.480	−1.06	—	—	—	—	—
	20	2.053	2.257	0.930	0.045	0.483	−1.07	—	—	—	—	—
SrO–TeO <sub>2</sub>	10	2.118	2.327	0.952	0.038	0.462	−1.10	—	—	—	—	—
	15	2.073	2.324	0.952	0.038	0.476	−1.10	—	—	—	—	—
BaO–TeO <sub>2</sub>	10	2.119	2.352	0.960	0.036	0.462	−1.10	—	—	—	—	—
	15	2.106	2.409	0.977	0.034	0.466	−1.12	—	—	—	—	—
	20	2.063	2.399	0.974	0.036	0.480	−1.12	—	—	—	—	—
ZnO–TeO <sub>2</sub>	10.1	2.13	2.318	0.950	0.039	0.459	−1.09	—	—	—	—	—
	20.0	2.08	2.275	0.935	0.043	0.474	−1.08	—	—	—	—	—
	30.0	2.03	2.258	0.930	0.046	0.490	−1.07	—	—	—	—	—
	40.0	1.982	2.212	0.915	0.051	0.506	−1.05	—	—	—	—	—
	45.0	1.954	2.205	0.912	0.053	0.516	−1.05	—	—	—	—	—
PbO–TeO <sub>2</sub>	5	2.20	2.374	0.967	0.035	0.439	−1.11	—	—	—	—	—
	10	2.20	2.358	0.962	0.035	0.439	−1.11	—	—	—	—	—
	15	2.20	2.356	0.962	0.035	0.439	−1.11	—	—	—	—	—
	20	2.21	2.348	0.959	0.034	0.436	−1.10	—	—	—	—	—
TiO <sub>2</sub> –TeO <sub>2</sub>	5	2.190	2.341	0.957	0.039	0.441	−1.10	—	—	—	—	—
	10	2.214	2.363	0.964	0.042	0.435	−1.11	—	—	—	—	—
	15	2.227	2.356	0.962	0.045	0.431	−1.11	—	—	—	—	—
ScO <sub>1.5</sub> –TeO <sub>2</sub>	5	2.121	2.335	0.955	0.038	0.462	−1.10	—	—	—	—	—
	10	2.085	2.271	0.935	0.042	0.472	−1.08	—	—	—	—	—
NbO <sub>2.5</sub> –TeO <sub>2</sub>	10	2.172	2.342	0.957	0.041	0.447	−1.10	—	—	—	—	—
	20	2.182	2.402	0.975	0.042	0.444	−1.12	—	—	—	—	—
	30	2.192	2.453	0.989	0.043	0.441	−1.14	—	—	—	—	—



Table 4 (continued)

System	Mol%	$n_0$	$\alpha_{O_2}(n_0)$ ( $\text{\AA}^3$ )	$A(n_0)$	$A(n_0)$ ( $\text{\AA}^{-3}$ )	$M(n_0)$	$q_0$	$q_{Me+}$	$q_{Men+}$	O1s (eV)	Me(1) (eV)	Me(2) (eV)
MoO <sub>3</sub> –TeO <sub>2</sub>	10	2.115	2.237	0.923	0.046	0.463	–1.06	—	—	—	—	—
	20	2.132	2.310	0.947	0.051	0.458	–1.09	—	—	—	—	—
	30	2.092	2.272	0.935	0.056	0.470	–1.08	—	—	—	—	—
WO <sub>3</sub> –TeO <sub>2</sub>	5	—	—	—	—	—	—	—	—	530.8	—	—
	10	2.166	2.344	0.957	0.047	0.448	–1.10	—	—	—	—	—
	20	2.169	2.349	0.959	0.047	0.448	–1.10	—	—	—	—	—
	30	2.172	2.387	0.970	0.050	0.446	–1.12	—	—	530.7	—	—
K <sub>2</sub> O–TiO <sub>2</sub>	33.3	1.810	2.700	1.052	0.048	0.569	–1.21	0.86	2.17	—	—	—
	50.0	1.684	2.640	1.037	0.050	0.620	–1.19	0.86	1.85	—	—	—
Rb <sub>2</sub> O–TiO <sub>2</sub>	33.3	1.820	2.642	1.039	0.050	0.565	–1.20	0.91	2.09	—	—	—
	50.0	1.725	2.974	1.109	0.031	0.603	–1.27	0.9	2.04	—	—	—
	60.0	1.700	3.377	1.176	0.016	0.614	–1.35	0.89	2.05	—	—	—
PbO–TiO <sub>2</sub>	20	2.268	2.924	1.099	0.036	0.420	–1.26	—	—	—	—	—
	30	2.239	2.266	0.934	0.071	0.428	–1.07	—	—	—	—	—
	40	2.030	2.032	0.848	0.084	0.490	–0.98	—	—	—	—	—
SrO–V <sub>2</sub> O <sub>5</sub>	20	—	—	1.043 <sup>a</sup>	0.055 <sup>a</sup>	—	–1.20	—	—	530.65	V2p <sub>3/2</sub> 517.6	Sr3p <sub>3/2</sub> 269.47
	30	—	—	1.045 <sup>a</sup>	0.054 <sup>a</sup>	—	–1.20	—	—	530.54	517.52	269.30
	40	—	—	1.047 <sup>a</sup>	0.053 <sup>a</sup>	—	–1.20	—	—	530.43	517.47	269.22
	50	—	—	1.050 <sup>a</sup>	0.051 <sup>a</sup>	—	–1.21	—	—	530.39	517.45	269.20
PbO–V <sub>2</sub> O <sub>5</sub>	22	—	—	1.047 <sup>a</sup>	0.054 <sup>a</sup>	—	–1.20	—	—	530.27	V2p <sub>3/2</sub> 517.08	Pb4f <sub>7/2</sub> 138.62
	35	—	—	1.054 <sup>a</sup>	0.052 <sup>a</sup>	—	–1.21	—	—	530.14	517.14	138.58
	43	—	—	1.058 <sup>a</sup>	0.050 <sup>a</sup>	—	–1.22	—	—	530.15	517.10	138.43
	54	—	—	1.069 <sup>a</sup>	0.046 <sup>a</sup>	—	–1.23	—	—	530.15	517.05	138.33

<sup>a</sup>The data are for theoretical optical basicity and theoretical interaction parameter.

optical band gap and increased tendency for metallization of the glasses. Really a systematic decrease of the apparent optical band gap has been established in lead-containing borate and silicate glasses [28], alkali-borate glasses [29], BaO–B<sub>2</sub>O<sub>3</sub> glasses [30], Sb<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> glasses [14], and Bi<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> glasses [15].

#### 2.4. Refractive index-based interaction parameter of oxide glasses

Fifty years ago, Yamashita and Kurosawa [31] have proposed a general theory of the dielectric constant of simple ionic crystals based on quantum-mechanical treatment of the electronic structure of constituent ions in order to take into account the effect of charge overlapping between neighboring ions. In that theory the perturbed wave function of 2*p* electrons of a negative ion such as F<sup>–</sup> and O<sup>2–</sup> was used. The total energy change of the crystal due to the applied electric field was expressed by sum of three components:

$$\Delta E = \Delta E_0 + \Delta E_1 + \Delta E_2, \quad (8)$$

where  $\Delta E_0$  is the energy change of the positive and negative ions in free state,  $\Delta E_1$  the change of the electrostatic mutual interaction energy between them

and  $\Delta E_2$  the change of the exchange energy between the ions. The polarization of ionic pair in high frequency field can be regarded as a simplest model of such energy change neglecting the polarization of the positive ion. In that case the quantum mechanical equation describing  $\Delta E$  contains terms assigned to the energy changes  $\Delta E_1$  and  $\Delta E_2$  due to the possible interionic interaction of a negative ion only with its nearest neighbors. According to Yamashita and Kurosawa [31], a quantitative measure of this complex interaction can be given by the so-called interaction parameter *A*. The physical meaning of the parameter *A* relates to the charge overlapping between neighboring ions. For a chosen cation-oxide ion pair, it represents the charge overlapping of the oxide ion with its nearest positive neighbor and expresses the decrease in polarizability of oxide ion placed in crystal lattice in respect to the free-ion polarizability. From chemical point of view such overlapping arises in chemical bonding. According to the fundamental theory [32], the formation of the chemical bond between two ions or atoms is the result of overlapping of their outermost electron clouds. In the case of oxide materials the bonding realizes due to the interaction between 2*p* electrons of the oxide ions and outermost valence electrons

of the cation. The product of that interaction is ionic–covalent chemical bond.

Following the approach developed by Dikshit and Kumar [33] for halide crystals and some simple oxides Dimitrov and Komatsu [8,11] applied the interaction parameter  $A$  to describe the polarizability state of an average oxide ion in numerous simple oxides and binary oxide glasses and its ability to form an ionic–covalent bond with the cation. It was found that in the case of binary glass with general formula  $xApOq(1-x)BrOs$  the so-called refractive index-based interaction parameter  $A(n_0)$  can be expressed as a sum from the parts each cation with the given oxide ion contributes to the total interaction for an averaged cation–anion pair in the glass matrix:

$$A(n_0) = X_{ApOq}[(\alpha_f^- - \alpha_{O2-})]/2(\alpha_{f(A)}^+ + \alpha_f^-)(\alpha_{f(A)}^+ + \alpha_{O2-}) + X_{BrOs}[(\alpha_f^- - \alpha_{O2-})]/2(\alpha_{f(B)}^+ + \alpha_f^-)(\alpha_{f(B)}^+ + \alpha_{O2-}), \quad (9)$$

where  $X_{ApOq}$  and  $X_{BrOs}$  are equivalent fractions based on the amount of oxygen each oxide contributes to the overall glass stoichiometry,  $\alpha_f^-$  is the electronic polarizability of the free oxide ion,  $\alpha_{O2-}$  is the average electronic polarizability of the oxide ions in the glass matrix calculated on the basis of refractive index data by means of the Lorentz–Lorenz equation and  $\alpha_{f(A)}^+$  and  $\alpha_{f(B)}^+$  are the electronic polarizabilities of cations  $A$  and  $B$ , respectively.

On the other hand, the so-called theoretical interaction parameter  $A_{th}$  can be given by

$$A_{th} = X_{ApOq}A_{ApOq} + X_{BrOs}A_{BrOs}, \quad (10)$$

where  $A_{ApOq}$  and  $A_{BrOs}$  are the values of the interactions parameters of oxides  $ApOq$  and  $BrOs$ , respectively [9].

Dimitrov and Komatsu [11] have calculated by means of Eqs. (9) and (10) refractive index-based interaction parameter  $A(n_0)$  and theoretical interaction parameter  $A_{th}$  for a large number of oxide glasses. A value of  $3.921 \text{ \AA}^3$  for the electronic polarizability of the free oxide ion  $\alpha_f^-$  was used taking into account the value of ionic refraction of  $O^{2-}$  theoretically determined by Pauling [34]. Honma et al. [13–15] applied the approach to  $La_2O_3$ – $P_2O_5$ ,  $Sb_2O_3$ – $B_2O_3$ , and  $Bi_2O_3$ – $B_2O_3$  glasses. A good correspondence has been observed between data obtained for  $A(n_0)$  and  $A_{th}$  on the basis of different initial quantities using different calculating procedures. The data of  $A(n_0)$  for different binary glasses are taken from Refs. [11,13–15] and are listed in Tables 1–4 (column 6). The data of  $A_{th}$  for  $SrO$ – $V_2O_5$  and  $PbO$ – $V_2O_5$  glasses are calculated in the present study by means of Eq. (10). As can be seen in Tables 1–4, the interaction parameter of glasses formed by two classical glass-formers as well as conventional borate, phosphate, and silicate glasses is large ( $0.15$ – $0.25 \text{ \AA}^{-3}$ ). Phosphate glasses as well as borate, silicate, and germanate glasses

with large amounts  $Sb_2O_3$ ,  $Bi_2O_3$ , and  $V_2O_5$  exhibit an interaction parameter in the  $0.07$ – $0.15 \text{ \AA}^{-3}$  range approximately. The tellurite glasses present the lowest values of  $A$  around  $0.04$ – $0.05 \text{ \AA}^{-3}$ . Simultaneously, the interaction parameter of the glasses is in good agreement with the values of interaction parameters of simple oxides. According to Ref. [8], the interaction parameter of acidic glass-forming oxides such as  $P_2O_5$ ,  $B_2O_3$ , and  $SiO_2$  is very high  $0.238$ ,  $0.244$  and  $0.216 \text{ \AA}^{-3}$ , respectively. In contrast the basic oxides such  $La_2O_3$  ( $0.03 \text{ \AA}^{-3}$ ),  $PbO$  ( $0.005 \text{ \AA}^{-3}$ ),  $V_2O_5$  ( $0.057 \text{ \AA}^{-3}$ ),  $TeO_2$  ( $0.034 \text{ \AA}^{-3}$ ),  $Sb_2O_3$  ( $0.011 \text{ \AA}^{-3}$ ), and  $Bi_2O_3$  ( $0.008 \text{ \AA}^{-3}$ ) possess low interaction parameter. Briefly, it seems that the results presented in Tables 1–4 for interaction parameter  $A$  are probably good ground for predicting the interionic interactions in different oxide glasses on the basis of their refractive index.

### 2.5. Correlation between interaction parameter and effective charges of oxide and metal ions in oxide glasses

A molecular orbital treatment of the basicity of oxyanion units has been performed by Binks and Duffy [35] showing that the optical basicity value is directly proportional to the negative charge borne by the oxide ions. It has been found also that the effective charge of the oxide ion  $q_o$  rises and the cationic charge  $q_{M+}$  falls with increasing basicity of the glass [36]. Following the approach proposed in Refs. [35–37], we calculated the effective charges of oxide ions  $q_o$  of the glasses listed in Tables 1–4 as well as that of alkali ions  $q_{M+}$  in the case of alkali containing glasses discussed in Tables 2 and 4 by means of Eqs. (11) and (12),

$$q_o = -1.15A \quad (11)$$

$$q_{M+} = 1 - [1 - 0.5(1.15A_{R2O})](A - 0.16)/(A_{R2O} - 0.16), \quad (12)$$

where  $A_{R2O}$  is optical basicity of the corresponding alkali oxide and  $A$  is refractive index-based optical basicity as shown in Tables 2 and 4. The results are given in Tables 1–4. The values of effective charges borne on the second metal ion  $q_{Mn+}$  are also presented, based on stoichiometry and charge neutrality. As can be seen in Tables 1–4, in general with increasing refractive index-based optical basicity  $\Lambda(n_0)$  of the glasses  $q_o$  increases but  $q_{M+}$  and  $q_{Mn+}$  decrease. This is in accordance with pioneering results obtained by Duffy et al. on this phenomenon [36,37].

As was pointed out in Part 2.4, interaction parameter represents the interaction along an averaged cation–oxide ion pair in a view to formation of ionic–covalent chemical bond in the glass. Small interaction parameter means weak interionic interaction resulting in large unshared electron density [8,11]. In contrast, large value of the interaction parameter corresponds to strong

interionic interaction resulting in small amount unshared electron density at an averaged oxide ion.

On the other hand the effective charge borne by an averaged oxide ion  $q_o$  in fact represents also the amount of the unshared electron density at an average oxide ion available for donation. Therefore, it is of interest to check the correlation between refractive index-based interaction parameter  $A(n_0)$  and effective charge borne by oxide ion  $q_o$  taking into consideration the similarity in the physical nature of these quantities. We have plotted the data of refractive index-based interaction parameter of the glasses against the data of effective charge of oxide ion in Figs. 1–4. As can be seen in Figs. 1–4, a good agreement exist between  $A(n_0)$  and  $q_o$  of the glasses. In general, the interaction parameter decreases with increasing effective charge borne by oxide ion in the sequence: glasses formed by two acidic oxides; glasses formed by glass-forming acidic and modifier basic oxides; glasses formed by glass-forming acidic and conditional glass-forming basic oxides and glasses formed by two basic oxides. This means that in this direction the amount of the unshared electron density

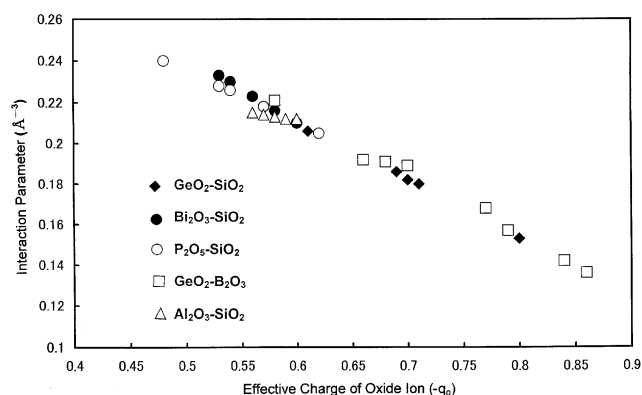


Fig. 1. Interaction parameter as a function of effective charge of oxide ion for oxide glasses formed by two acidic oxides.

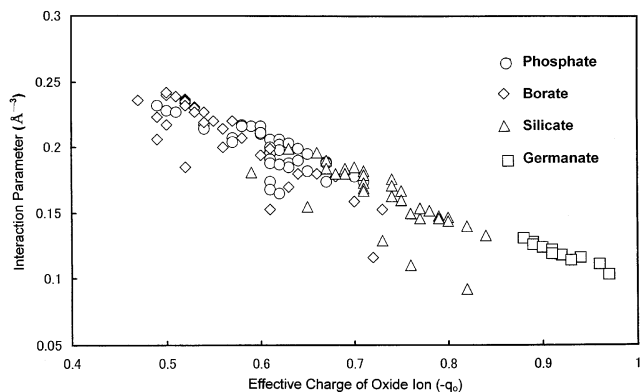


Fig. 2. Interaction parameter as a function of effective charge of oxide ion for oxide glasses formed by glass-forming acidic and modifier basic oxides.

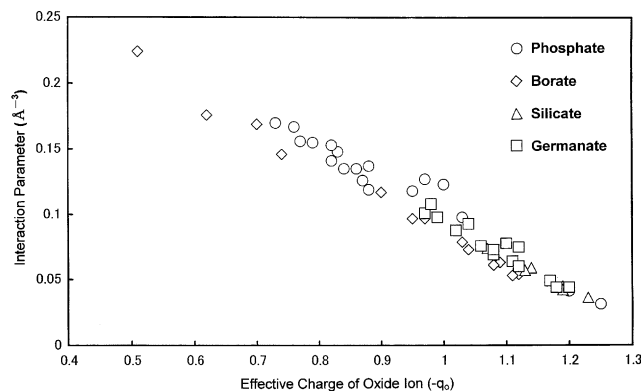


Fig. 3. Interaction parameter as a function of effective charge of oxide ion for oxide glasses formed by glass-forming acidic and conditional glass-forming basic oxides.

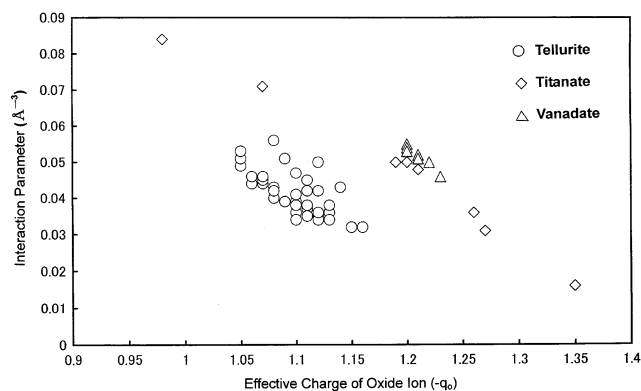


Fig. 4. Interaction parameter as a function of effective charge of oxide ion for oxide glasses formed by two basic oxides.

increases and ionicity of an averaged cation-oxide ion chemical bond increases.

## 2.6. Correlation between O1s binding energy and metal binding energy in XPS spectra of oxide glasses

Despite the large number of XPS studies on different oxide glasses, a systematic O1s and metal binding energy chemical shift with varying composition is reported in only a few recent papers [13–15,38–41]. On this basis Dimitrov and Komatsu [18] have reported that correlation exists between O1s and metal binding energy chemical shift in XPS spectra of Na<sub>2</sub>O–SiO<sub>2</sub>, PbO–SiO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>–P<sub>2</sub>O<sub>5</sub>, Sb<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> and R<sub>2</sub>O–TeO<sub>2</sub> (R = Li, Na and K) glasses. It was found that in general the mean O1s binding energy decreases with decreasing metal binding energy of the glasses. More recent data on XPS spectra of SrO–V<sub>2</sub>O<sub>5</sub> and PbO–V<sub>2</sub>O<sub>5</sub> glasses show similar correlations [42,43]. The data on O1s and metal binding energies of Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>–P<sub>2</sub>O<sub>5</sub>, R<sub>2</sub>O–SiO<sub>2</sub> (R = Na and K), PbO–SiO<sub>2</sub>, Sb<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>, R<sub>2</sub>O–TeO<sub>2</sub> (R = Li, Na and K), SrO–V<sub>2</sub>O<sub>5</sub>, and

PbO–V<sub>2</sub>O<sub>5</sub> glasses taken from Refs. [13–15, 38–43] are listed in Tables 1–4. Since excepting O1s XPS spectra of Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> and R<sub>2</sub>O–TeO<sub>2</sub> (R = Li, Na and K) glasses O1s peak of other glasses contains two components of O1s binding energy, we calculated mean O1s binding energy and that value is included in Tables 2 and 3. As can be seen, the introducing of the second oxide to P<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, TeO<sub>2</sub> or V<sub>2</sub>O<sub>5</sub> leads to a decrease of both O1s and metal binding energies. For instance, Na1s, Pb5d, Si2p, La3d, and P2p binding energies decrease with decreasing O1s binding energy in XPS spectra of Na<sub>2</sub>O–SiO<sub>2</sub>, PbO–SiO<sub>2</sub>, and La<sub>2</sub>O<sub>3</sub>–P<sub>2</sub>O<sub>5</sub> glasses (Table 2). Similarly, the Sb3d, Bi4f, Te3d, Sr3p, Pb4f, and V2p binding energies decrease with decreasing O1s binding energy in XPS spectra of Sb<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>, R<sub>2</sub>O–TeO<sub>2</sub> (R = Li, Na and K), SrO–V<sub>2</sub>O<sub>5</sub>, and PbO–V<sub>2</sub>O<sub>5</sub> glasses (Tables 3 and 4). We assume that the observed chemical shift of both O1s and metal binding energies toward lower binding energy with increasing basicity and decreasing interaction parameter can be regarded as experimental proof for interaction between valence orbitals of metal and oxide ions leading to the formation of M–O chemical bonds in the glass structure.

### 2.7. Correlation between refractive index-based interaction parameter and mean O1s binding energy of oxide glasses

A detailed analysis of the O1s XPS spectra of a large number of simple oxides is made by Barr [44]. It was established that O1s binding energy of different oxides is located in the 528.0–533.5 eV range. The observed O1s chemical shift was assigned to the different degree of ionicity in the M–O bonds. Recently, Dimitrov et al. [6] have obtained that a good correlation exists between the experimentally measured O1s peak position in the XPS spectra of simple oxides reported by Barr [44] and their electronic oxide ion polarizability. Gautier-Soyer et al. [45] and Cruguel et al. [46] have found relationship between atomic charges and XPS chemical shift in some complex aluminosilicate and aluminum borosilicate glasses. More recently, Dimitrov and Komatsu [17] have established that in general the O1s binding energy decreases with increasing refractive index-based optical basicity of Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>–P<sub>2</sub>O<sub>5</sub>, R<sub>2</sub>O–SiO<sub>2</sub> (R = Li, Na, K and Rb), PbO–SiO<sub>2</sub>, Na<sub>2</sub>O–GeO<sub>2</sub>, Sb<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>, and R<sub>2</sub>O–TeO<sub>2</sub> (R = Li, Na and K) glasses. The observed chemical shift to lower binding energy was explained by an increase in electron charge density of the oxide ions due to an increase in their electronic polarizability. Since parameter *A* represents the interaction along an average M–O chemical bond we have plotted mean O1s binding energy as a function of interaction parameter of the Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>–P<sub>2</sub>O<sub>5</sub>, R<sub>2</sub>O–SiO<sub>2</sub> (R = Na and K), PbO–SiO<sub>2</sub>,

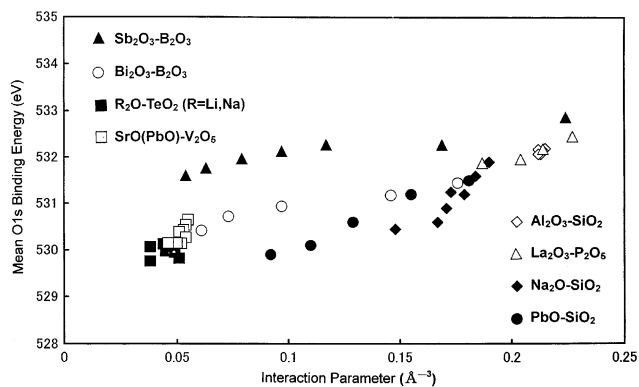


Fig. 5. Mean O1s binding energy as a function of interaction parameter of oxide glasses.

Sb<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>, R<sub>2</sub>O–TeO<sub>2</sub> (R = Li, Na and K), SrO–V<sub>2</sub>O<sub>5</sub>, and PbO–V<sub>2</sub>O<sub>5</sub> glasses (see Tables 1–4) in Fig. 5. In general, there is a systematic trend of decreasing O1s binding energy with decreasing interaction parameter in these glasses. Glasses formed by two acidic oxides (Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>) as well as phosphate, silicate and borate glasses containing small amount of modifier basic oxides possess large interaction parameter (0.15–0.25 Å<sup>–3</sup>) and high values of O1s binding energy at about 533–531 eV. In opposite, tellurite and vanadate glasses as well as borate glasses with a large amount of Sb<sub>2</sub>O<sub>3</sub> or Bi<sub>2</sub>O<sub>3</sub> are characterized by small interaction parameter less than 0.1 Å<sup>–3</sup> and low values of O1s binding energy less than 530.5 eV approximately. Therefore, the results show that generally the mean O1s binding energy correlates with ionic–covalent character of an averaged cation–oxide ion pair and could be ably used for investigation of its change with the composition of oxide glasses.

### 2.8. Classification of oxide glasses

Analysis performed in previous parts (2.1–2.7) on the results accumulated in Tables 1–4 concerning refractive index-based electronic polarizability, optical basicity, metallization criterion, interaction parameter, effective charges of ions as well as data on O1s and metal binding energies allows a more detailed classification of the oxide glasses into four groups.

#### 2.8.1. First group (glasses formed by two glass-forming acidic oxides)

In this group are included B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>–SiO<sub>2</sub>, GeO<sub>2</sub>–SiO<sub>2</sub>, GeO<sub>2</sub>–B<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>, etc. The glasses are characterized by small refractive index (*n*<sub>0</sub> = 1.4–1.6), low oxide ion polarizability (*α*<sub>O<sub>2</sub><sup>–</sup></sub> = 1.3–1.8 Å<sup>3</sup>), low cation polarizability, low optical basicity (*A* = 0.4–0.8), large metallization criterion (*M* = 0.65–0.75), small effective charge of oxide ion (*q*<sub>0</sub> = –0.5–(–0.6)), high O1s binding energy around

532 eV<sub>2,3</sub> and large interaction parameter ( $A = 0.25 - 0.15 \text{ \AA}^{-1}$ ), giving ground for existing of strong covalent bonds in the glass structure such as Si–O–Si, B–O–B, P–O–P, Si–O–Al, etc.

### 2.8.2. Second group (glasses formed by glass-forming acidic and modifier's basic oxides)

In this group are included  $R_2O-P_2O_5$  ( $R = \text{Li, Na}$ );  $RO-P_2O_5$  ( $R = \text{Sr, Zn, Cd, Pb}$ );  $La_2O_3-P_2O_5$ ;  $R_2O-B_2O_3$  ( $R = \text{Li, Na, K, Ag}$ );  $RO-B_2O_3$  ( $R = \text{Ba, Cd, Pb}$ );  $La_2O_3-B_2O_3$ ;  $R_2O-SiO_2$  ( $R = \text{Li, Na, K, Rb, Cs}$ );  $RO-SiO_2$  ( $R = \text{Ca, Pb}$ );  $R_2O-GeO_2$  ( $R = \text{Li, Na, K}$ ) glasses. The glasses possess refractive index in medium range ( $n_0 = 1.5 - 1.9$ ), comparatively low oxide ion polarizability ( $\alpha_{O^{2-}} = 1.3 - 1.9 \text{ \AA}$ ), and optical basicity ( $A = 0.4 - 0.85$ ), comparatively large metallization criterion ( $M = 0.55 - 0.70$ ), effective charge of oxide ion in wide range ( $q_0 = (-0.5) - (-0.9)$ ), O1s binding energy in the 532.5–530 eV range, and comparatively large interaction parameter ( $A = 0.24 - 0.10 \text{ \AA}^{-1}$ ), giving ground to accept the formation of  $M-O-M$  (BO) covalent bonds along with  $M-O-R^{n+}$  (nonbridging oxygens, NBO) bonds with increased ionicity where  $M = \text{P, B, S, Ge, etc.}$  and  $R = \text{Li, Na, K, Ca, Ba, etc.}$

### 2.8.3. Third group (glasses formed by glass-forming acidic and conditional glass-forming basic oxides)

In this group are included  $R_2O_3-P_2O_5$  ( $R = \text{Sb, Bi}$ );  $R_2O_3-B_2O_3$  ( $R = \text{Sb, Bi}$ );  $Bi_2O_3-SiO_2$ ;  $R_2O_3-GeO_2$  ( $R = \text{Sb, Bi}$ );  $V_2O_5-P_2O_5$  ( $GeO_2$ ). The glasses possess high refractive index ( $n_0 = 1.5 - 2.1$ ); high oxide ion polarizability ( $\alpha_{O^{2-}} = 1.5 - 2.8 \text{ \AA}$ ); high optical basicity ( $A = 0.5 - 1.0$ ); medium range metallization criterion ( $M = 0.5 - 0.7$ ); comparatively large effective charge of oxide ion ( $q_0 = (-0.7) - (-1.1)$ ); O1s binding energy in the 532–530 eV range, and low interaction parameter ( $A = 0.17 - 0.05 \text{ \AA}^{-1}$ ), showing the formation of  $M(1)-O-M(1)$  strong covalent bonds and  $M(1)-O-M(2)$  and  $M(2)-O-M(2)$  bonds with increased ionicity where  $M(1) = \text{B, Si, Ge, and } M(2) = \text{Sb, Bi, V, etc.}$

### 2.8.4. Fourth group (glasses formed by two basic oxides)

Tellurite, vanadate, and titanate glasses such as  $R_2O-TeO_2$  ( $R = \text{Li, Na, K, Ag}$ );  $RO-TeO_2$  ( $R = \text{Mg, Sr, Ba, Zn, Pb}$ );  $TiO_2-TeO_2$ ;  $Sc_2O_3-TeO_2$ ;  $Nb_2O_5-TeO_2$ ;  $RO_3-TeO_2$  ( $R = \text{Mo, W}$ );  $R_2O-TiO_2$  ( $R = \text{K, Rb}$ );  $PbO-TiO_2$ ;  $SrO-V_2O_5$ ;  $PbO-V_2O_5$  belong to this group. The glasses possess very high refractive index ( $n_0 = 1.9 - 2.3$ ), high oxide ion electronic polarizability ( $\alpha_{O^{2-}} = 2.2 - 2.3 \text{ \AA}$ ), high optical basicity ( $A = 0.9 - 1.2$ ); small metallization criterion less than 0.5, high effective charge of oxide ions ( $q_0 = (-1.1) - (-1.3)$ ), low O1s binding energy (530–529 eV), and very small interaction parameter  $A = 0.05 - 0.03 \text{ \AA}^{-1}$ , showing that chemical bonds with large ionic contribution are formed in the glass structure.

## 2.9. Validity of the proposed classification of oxide glasses from chemical bonding point of view

The observed relationships in Figs. 1–5 between interaction parameter, effective charge of oxide ion and O1s binding energy as well as the relationship between O1s and metal binding energies shown in Tables 1–4 indirectly represents the degree of interaction between valence orbitals of corresponding cation and  $O^{2-}$  ions in view to the formation of  $M-O$  chemical bonds in glass structure.

Highest interaction parameter and smallest effective charge of oxide ion have been observed in  $B_2O_3-SiO_2$ ,  $P_2O_5-SiO_2$ ,  $GeO_2-SiO_2$ ,  $GeO_2-B_2O_3$  and  $Al_2O_3-SiO_2$  glasses (Table 1, Fig. 1). This indicates very strong influence of the cations on the electron cloud of the oxide ion. In result, strong covalent bonds such as P–O–P, B–O–B, and Si–O–Si are formed in the binary glasses. The formation of mixed bonds Al–O–Si, B–O–Si is also proposed [41,47].

The second group includes glasses formed by glass-forming acidic and modifier's basic oxide. The glasses can be regarded as more acidic than more basic. The interaction parameter in general decreases, but it is comparatively large, while the effective charge of oxide ion increases, but it is comparatively small (Table 2, Fig. 2). Simultaneously, O1s binding energy shifts to lower values with decreasing interaction parameter of the glasses (Table 2, Fig. 5). It is generally accepted that the addition of modifier oxide to  $SiO_2$  or  $P_2O_5$  breaks up the  $M-O-M$  ( $M = \text{Si, P}$ ) network that consists of bridging oxygens (BO) and creates NBO. For instance a formation of two O1s binding energy components is found in the XPS spectra of  $Na_2O-SiO_2$ ,  $PbO-SiO_2$ , and  $La_2O_3-P_2O_5$  glasses where pure discrimination between BO and NBO oxygen atoms could be made [13,39,40]. Therefore the decrease of the interaction parameter with increasing modifier's content could be attributed to the formation of NBOs in the glass structure which possess large polarizabilities, along with BOs affected strongly by two Si or P cations having lower polarizability.

At the same time, the observed metal XPS chemical shift in the XPS spectra of  $Na_2O-SiO_2$ ,  $PbO-SiO_2$ , and  $La_2O_3-P_2O_5$  glasses to lower binding energy, i.e., P2p, La3d, Si2p, Na1s, and Pb5d is also informative (see Table 2). For example, La3d binding energy decreases with decreasing O1s binding energy in XPS spectra of  $La_2O_3-P_2O_5$  glasses. The shift of La3d peaks down to lower binding energy could be explained by charge transfer from the surroundings oxygens to the 4f orbitals of  $La^{3+}$  ions [13,48]. In general,  $La^{3+}$  ions act as network modifiers and La–O chemical bond is basically ionic, but it is considered that the occurrence of a charge transfer effect suggests the formation of covalent like bonding between oxide ions and  $La^{3+}$  ions. Similarly, Matsumoto et al. [39] have proposed that a decreasing

Na1s binding energy in XPS spectra of Na<sub>2</sub>O–SiO<sub>2</sub> glasses is connected with increased electron density of sodium ions, suggesting that the bond order between O2p and Na3s (or 3p) increased with increasing Na<sub>2</sub>O content. In addition, a considerable delocalization of electrons in O2p–Si3d  $\pi$ -bonds is also proposed. Such phenomena could be the reasons for the decrease of Na1s and Si2p binding energy in XPS spectra of Na<sub>2</sub>O–SiO<sub>2</sub> glasses with decreasing O1s binding energy (Table 2). Similarly, the decrease of Pb5d binding energy with decreasing O1s binding energy in XPS spectra of PbO–SiO<sub>2</sub> glasses can be assigned to the formation of Pb–O bonds with increased covalency. That is apparently equivalent to an increase of electron charge density around Pb<sup>2+</sup> ions in the glass structure and decrease in metal binding energy (Table 2). Therefore, the comparatively large interaction parameter and comparatively small values of the effective charge of oxide ion in the glasses from second group could be attributed to increased covalency of bonds such as La–O, Pb–O even to an increase in bond order between alkali ion and NBO.

Third group includes glasses formed by glass-forming acidic and conditional glass-forming basic oxide. It is seen that the interaction between an acidic oxide such as P<sub>2</sub>O<sub>5</sub>, B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and GeO<sub>2</sub> with a basic oxide such as Sb<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> leads to significant increase of electronic oxide ion polarizability and optical basicity as well. The interaction parameter of binary glasses decreases and effective charge of oxide ions increase showing a decreased interionic interaction inside the averaged M–O chemical bond. O1s binding energy decreases with decreasing interaction parameter as it can be seen in the case of Sb<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> glasses (Fig. 5). A reason for the chemical shift of O1s peak could be a repulsive interaction between Sb5s<sup>2</sup> and Bi6s<sup>2</sup> outermost lone pairs and oxygen 2p electrons, resulting in the smaller overlap of the valence orbitals by the formation of mixed Sb–O–B and Bi–O–B bonds along with B–O–B bonds [14,15]. This relates to larger contribution of O2p orbitals in the valence band corresponding to increased effective charge of oxide ions that is decreased interaction parameter of the glasses.

Simultaneously, Sb3d and Bi4f binding energies decreased with decreasing mean O1s binding energy (Table 3). The decrease in the Sb3d binding energy could be related to increased probability of back donation of electron density from oxide ions to Sb<sup>3+</sup> ions in view to form Sb–O bonds rich in p-character. That is apparently equivalent to an increase in the covalency of Sb–O bonds. In contrast, the almost constant value of Bi4f binding energy in the 40–65 mol% Bi<sub>2</sub>O<sub>3</sub> range probably suggest that the degree of equalization of electron charge distribution in Bi–O–B bonds is not so large and the covalency of Bi–O bonds does not change

significantly with the Bi<sub>2</sub>O<sub>3</sub>/B<sub>2</sub>O<sub>3</sub> ratio, giving the formation of relatively ionic Bi–O bonds.

The fourth group includes glasses such as tellurite, titanate and vanadate formed by two basic oxides. They possess highest effective charge of oxide ion and smallest interaction parameter (Table 4, Fig. 4). The low values of the interaction parameter in the case of tellurite glasses can be explained on the basis of very high polarizability of Te<sup>4+</sup> ion (1.595 Å<sup>3</sup>) which decreases its power to polarize the electron cloud density of the oxide ion. At the same time the interaction parameters of tellurite glasses are very close to those of pure TeO<sub>2</sub> (0.034 Å<sup>-3</sup>). Obviously the interaction along Te–O bonds in the structure of tellurite glasses has a significant effect. It is assumed also that in the case of alkali tellurite glasses the introduction of alkali oxides creates Te–NBO bonds along with bridging Te–O–Te bonds [49,50]. Only one symmetric peak at low binding energy is observed in the XPS spectra of alkali-tellurite glasses which is attributed to both kinds of oxide ions [38]. Therefore, the values of interaction parameter obtained in Table 4 can be attributed to the presence of Te–NBO and Te–BO bonds with large ionic contribution in the structure of alkali-tellurite glasses. Simultaneously, as it is seen in Table 4, Te3d binding energy decreases with decreasing O1s binding energy. According to Himei et al. [38], the shift in Te3d binding energy can be explained by the increase in the extent of the  $p\pi$ – $d\pi$  back donation between O2p and empty Te5d orbitals which reduce the charge separation between tellurium and oxygen atoms in Te–O bonds. This leads to a rise of electron charge density around Te<sup>4+</sup> ions and decreasing Te3d binding energy.

On the other hand, the addition of transition metal oxides such as Nb<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub> and WO<sub>3</sub> to TeO<sub>2</sub> leads to formation of mixed Te–O–Nb, Te–O–Mo, and Te–O–W bonds in the structure of tellurite glasses [51–53]. The increasing of the number of those bonds instead of Te–O–Te are probably responsible for the relatively higher values of O1s binding energy of WO<sub>3</sub>–TeO<sub>2</sub> glasses [54] (see Table 4) and for the slight increasing of the interaction parameter  $A(n_0)$  (Table 4) due to the lower cation polarizability of the transition metal than that of Te<sup>4+</sup>.

The interaction parameter of vanadate glasses (0.055–0.046 Å<sup>-3</sup>) is close to that of pure V<sub>2</sub>O<sub>5</sub> (0.057 Å<sup>-3</sup>) which indicates that interaction along V–O bonds has a significant effect. According to IR and XPS results of SrO–V<sub>2</sub>O<sub>5</sub> and PbO–V<sub>2</sub>O<sub>5</sub> glasses bridging (V–O–V), nonbridging (V–O...Sr) and mixed (V–O–Pb) bonds are formed in the glass structure [42,43,55]. The obtained values of interaction parameter and effective charge of oxide ions in the present study show that the discussed bonds possess large ionic contribution. At the same time the shift of Sr3p and Pb4f peaks to lower binding energy with increasing SrO and PbO content

should be interpreted as evidence for increase in covalency of Pb–O bonds even in increase in bond order between  $\text{Sr}^{2+}$  and NBO.

Briefly, the discussion made above show that close correlation exists between effective charges of ions and values obtained for O1s and metal binding energies. As was pointed out above, with increasing basicity of the glasses effective charge of oxide ion rise but that of metal ions falls [36,37]. At the same time both O1s and metal binding energies shift to lower values.  $\text{Na}_2\text{O}$ – $\text{SiO}_2$  glasses are nice example in this connection. As can be seen in Table 2, with increasing refractive index-based optical basicity  $A(n_0)$  of the glasses  $q_o$  increases but  $q_{\text{Na}^+}$  and  $q_{\text{Si}^{4+}}$  decrease. Simultaneously, the O1s, Na1s and Si2p binding energies decrease. Therefore, the indication of rise in negative charge borne by an averaged oxide ion could be the mean O1s chemical shift in XPS spectra to lower binding energies. At the same time a back electron donation from the oxide ions to metal ions is a possible reason for the increase of electron density around metal ions and a decrease of metal binding energy in XPS spectra. This is apparently equivalent to an increase in covalency of bonds such La–O, Pb–O, Sb–O, Bi–O, V–O, and Te–O even to an increase in bond order between  $\text{Na}^+$  and NBO.

### 2.10. Usefulness of the polarizability classification for nonlinear optical glasses

Electronic polarizability of ions is closely related to many properties of materials such as refraction, conductivity, ferroelectricity, electro-optical effect, optical basicity along with optical nonlinearity [9,10,56]. Nonlinear optical glasses have attracted much attention because of their importance for the development of optical information processing technology [57]. For this purpose, glasses of higher optical nonlinearity have to be found or designed on the basis of correlation of the optical nonlinearity with some other electronic properties which are easily understandable and accessible. Since the optical nonlinearity is caused by electronic polarization of the glass upon exposure to intense light beams, polarizability is one of the most important properties which govern the nonlinearity response of the glass. Recently, detailed analysis was made on the relationships between electronic polarizability, optical basicity, metallization criterion and third-order nonlinear optical properties of different oxide glasses [10]. It was established that third-order nonlinear optical susceptibility  $\chi^{(3)}$  of the glasses increases with increasing optical basicity and tendency for metallization of the glasses. This is associated with the high electron donor ability of the oxide ions and the small optical band gap. Conventional borate, silicate and germanate glasses with low refractive index possess low polarizability, low

optical basicity, large metallization criterion and small  $\chi^{(3)}$ . Tellurite and titanate glasses as well as borate glasses containing a large amount of  $\text{Sb}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_3$  with high refractive index show large polarizability, high optical basicity, small metallization criterion and large  $\chi^{(3)}$ . In this connection good correlation could be found between nonlinear optical properties of the glasses and discussed in the present paper classification. For example,  $\text{Na}_2\text{O}$ – $\text{SiO}_2$  glasses which belong to the second group possess low values of  $\chi^{(3)}$  in the  $3.8 \times 10^{-14}$ – $4.9 \times 10^{-14}$  esu range. At the same time  $\text{Sb}_2\text{O}_3$ – $\text{B}_2\text{O}_3$  glasses (third group) show higher values of  $\chi^{(3)}$  between  $4.96 \times 10^{-14}$  and  $76.2 \times 10^{-14}$  esu. Highest values of  $\chi^{(3)}$  among the oxide glasses possess tellurite glasses which belong to the fourth group of the classification. For example, the measured  $\chi^{(3)}$  values of  $\text{WO}_3$ – $\text{TeO}_2$  glasses are in the  $142 \times 10^{-14}$ – $159 \times 10^{-14}$  esu range. As can be seen in Tables 2–4 in the pointed sequence linear refractive index and optical basicity increase and metallization criterion of the glasses decrease. Therefore from polarizability point of view high-refractive index basic glasses from third and fourth groups (Tables 3 and 4) with increased tendency for metallization are promising materials for application as components of nonlinear optical devices.

### 3. Conclusions

Suitable relationships between refractive index-based oxide ion polarizability, optical basicity, metallization criterion, Yamashita–Kurosawa's interaction parameter, charges of ions and binding energies in XPS spectra have been found for different oxide glasses. Classification of oxide glasses on the basis of the obtained relationships has been proposed. The glasses have been divided into four groups: glasses formed by two glass-forming acidic oxides; glasses formed by glass-forming acidic oxide and modifier's basic oxide; glasses formed by glass-forming acidic and conditional glass-forming basic oxide; glasses formed by two basic oxides. Good correspondence has been found between nonlinear optical properties of the glasses and the proposed classification. It has been concluded that high-refractive index basic glasses with increased tendency for metallization possess the highest values of third-order nonlinear optical susceptibility.

### Acknowledgments

One of the authors (V.D.) would like to express his sincere gratitude to the Japan Society for the Promotion of Science (JSPS) for providing him with financial support.

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