

# Classification of Simple Oxides: A Polarizability Approach

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A simple oxide classification has been proposed on the basis of correlation between electronic polarizabilities of the ions and their binding energies determined by XPS. Three groups of oxides have been considered taking into account the values obtained on refractive-index- or energy-gap-based oxide ion polarizability, cation polarizability, optical basicity, O 1s 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> with low oxide ion polarizability, high O 1s binding energy, low cation polarizability, high metal (or nonmetal) outermost binding energy, comparatively low optical basicity, and strong interionic interaction, leading to the formation of strong covalent bonds. Some main group oxides so-called ionic or basic such as CaO, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, and TeO<sub>2</sub> and most transition metal oxides show relatively high oxide ion polarizability, O 1s binding energy in a very narrow medium range, high cation polarizability, and low metal (or nonmetal) binding energy. Their optical basicity varies in a narrow range and it is close to that of CaO. The group of very ionic or very basic oxides includes 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>, which possess very high oxide ion polarizability, low O 1s binding energy, very high cation polarizability, and very low metal (or nonmetal) binding energy. Their optical basicity is higher than that of CaO and the interionic interaction is very weak, giving rise to the formation of very ionic chemical bonds. © 2002 Elsevier Science

## INTRODUCTION

Electronic polarizability of ions is closely related to many properties of the materials such as refraction, conductivity, ferroelectricity, electro-optical effect, and optical

nonlinearity along with optical basicity (1–3). That is why today's knowledge of the state of polarization of ions in different crystalline and amorphous materials is of significant interest. Simple oxides are usually the initial components for synthesis of such multicomponent oxide materials. From this point of view the estimation of the polarizability of individual species in different simple oxides is an important first step. The estimation of the electronic ion polarizability is the subject of the so-called polarizability approach in materials science, which is well known especially in the field of glass science (4). Recently, the polarizability approach in glass has shown renewed interest because of the need to understand the origin of some new optical behaviors such as third-order optical nonlinearities (5). The polarizability approach has been systematically developed in our recent papers concerning the origin of electronic polarizability and optical basicity in simple oxides (6–10) and oxide glasses (5, 11–15). The most familiar and widely used relationship in this approach is the Lorentz–Lorenz equation. Dimitrov and Sakka (6) calculated by means of this equation the electronic oxide ion polarizability ( $\alpha_{O^{2-}}$ ) of a large number of single-component oxides on the basis of the linear refractive index ( $n_0$ ) and energy gap ( $E_g$ ). On this basis the refractive index based  $\Lambda(n_0)$  and energy gap based  $\Lambda(E_g)$  optical basicity of the oxides has also been estimated. Good agreement has been observed between the optical basicity data obtained using independent initial quantities as well as those reported by Duffy (16). The simple oxides have been classified in three groups on the basis of the average electronic polarizabilities of the oxide ion: (a) oxides with polarizability between 1 and 2 Å<sup>3</sup>; (b) oxides with polarizability between 2 and 3 Å<sup>3</sup>; and (c) oxides with polarizability above 3 Å<sup>3</sup> (6).

On the other hand, a detailed analysis of the O 1s XPS spectra of a large number of simple oxides is made by Barr (17). It was established that O 1s binding energy of different

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oxides varies in the 528.0- to 533.5-eV range and its value corresponds to the different degree of ionicity in the  $M-O$  bonds. The simple oxides have been separated into three groups: (a) *semicovalent oxides with O 1s binding energy in the 530.5- to 533.0-eV range*; (b) *normal ionic oxides with O 1s binding energy at  $530 \pm 0.4$  eV*; and (c) *very ionic oxides with O 1s binding energy in the 529.5- to 528.0-eV range*.

The classifications pointed out above are made on the basis of two different physical properties of the oxide ion: electronic polarizability and O 1s binding energy. Very recently, Dimitrov *et al.* (8) reported that there is good agreement between the classification of simple oxides presented by Dimitrov and Sakka on the basis of oxide ion polarizability and that established by Barr on the basis of O 1s binding energy. The assignment proposed in both classifications for some oxides is probably unexpected from their aqueous solution chemistry point of view. For example, it is necessary to emphasize that most transition metal oxides in both cases are discussed as ionic or basic oxides. Therefore, one more precise analysis is necessary with a view to corroborate or reject the validity of such conclusions. That is why we have tried in this article to show some chemical bonding arguments and experimental results recently obtained approving the applicability of the so-called polarizability approach in the solid state chemistry. A more detailed classification of simple oxides is also made.

## DISCUSSION ON PREVIOUS RESULTS

### *Electronic Oxide Ion Polarizability and O 1s Binding Energy of Simple Oxides*

The most familiar and widely used relationship that relates molar refraction  $R_m$  to refractive index  $n_0$  and molar volume  $V_m$  is the Lorentz-Lorenz equation:

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

When Avogadro's number  $N_A$  is introduced, 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 simple oxide with common formula  $A_pO_q$  are additive quantities, it follows that

$$R_m = 2.52 (p\alpha_i + q\alpha_{O_2-}), \quad [4]$$

where  $\alpha_i$  is the cation polarizability and  $\alpha_{O_2-}$  is the polarizability of the oxide ion.

On the other hand, Duffy (18) has obtained an empirical formula that relates energy gap  $E_g$  to molar refraction  $R_m$  for a large number of simple oxides:

$$E_g = 20(1 - R_m/V_m)^2. \quad [5]$$

This equation gives the explicit expression for  $R_m$ :

$$R_m = V_m(1 - \sqrt{E_g/20}). \quad [6]$$

By subtracting the cation polarizability ( $\alpha_i$ ) from the molar polarizability ( $\alpha_m$ ) using Eqs. [1]–[6], Dimitrov and Sakka (6) proposed the following expressions for calculation of the electronic oxide ion polarizability of a simple oxide ( $\alpha_{O_2-}$ ) on the basis of two independent initial values: linear refractive index ( $n_0$ ) and energy gap ( $E_g$ ):

$$\alpha_{O_2-}(n_0) = [(V_m/2.52)(n_0^2 - 1)/(n_0^2 + 2) - p\alpha_i]q^{-1}. \quad [7]$$

$$\alpha_{O_2-}(E_g) = [(V_m/2.52)(1 - \sqrt{E_g/20}) - p\alpha_i]q^{-1}. \quad [8]$$

The authors (6) calculated  $\alpha_{O_2-}(n_0)$  and  $\alpha_{O_2-}(E_g)$  for a large number of simple oxides. It was established that there is a general trend of an increase of oxide ion polarizability with increasing refractive index and decreasing energy gap. Simultaneously good agreement is observed between data obtained using different independent initial quantities. The obtained values  $\alpha_{O_2-}(n_0)$  and  $\alpha_{O_2-}(E_g)$  for individual simple oxides as well as average values on their basis are presented in Tables 1a–1c (columns 2–4). The simple oxides have been classified into three groups on the basis of the electronic polarizabilities of the oxide ion:

(a) Oxides with polarizability between 1 and 2  $\text{\AA}^3$  (for example,  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{GeO}_2$ , and  $\text{Ga}_2\text{O}_3$ ).

(b) Oxides with polarizability between 2 and 3  $\text{\AA}^3$  (for example, most transition metal oxides).

(c) Oxides with polarizability above 3  $\text{\AA}^3$  (for example,  $\text{CdO}$ ,  $\text{PbO}$ ,  $\text{BaO}$ ,  $\text{Sb}_2\text{O}_3$ , and  $\text{Bi}_2\text{O}_3$ ).

Recently, Barr (17) reported comprehensive data on the O 1s peak position in XPS spectra of a large number of simple oxides. It was established that O 1s binding energy of different oxides varies in the 528.0- to 533.5-eV range. The observed O 1s chemical shift was assigned to the different degree of ionicity in the  $M-O$  bonds. The simple oxides have been separated into three groups:

(a) Semicovalent oxides with O 1s binding energy in the range 530.5–533.0 eV: A few oxides ( $\text{SiO}_2$ ,  $\text{GeO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ , and  $\text{As}_2\text{O}_3$ ) exhibit O 1s binding energy > 530.5 eV, which corresponds to relatively significant but varying covalency. They show also an increase in the size of their cationic shift and increase of widths of their valence bands.

**TABLE 1**  
**Electronic Polarizabilities of Oxide Ion Calculated from Refractive Index ( $\alpha_{O_2-(n_0)}$ ) and Energy Gap ( $\alpha_{O_2-(E_g)}$ ), Their Average ( $\alpha_{O_2-}^{av}$ ), and O 1s Binding Energy ( $E_b$ ) of Simple Oxides**

Oxide	$\alpha_{O_2-(n_0)}$ ( $\text{\AA}^3$ )	$\alpha_{O_2-(E_g)}$ ( $\text{\AA}^3$ )	$\alpha_{O_2-}^{av}$ ( $\text{\AA}^3$ )	$E_b$ (eV)
		(1a)		
BeO	—	—	1290 <sup>a</sup>	—
B <sub>2</sub> O <sub>3</sub>	1.345	—	1.345	533.2
P <sub>2</sub> O <sub>5</sub>	—	—	1.350 <sup>b</sup>	533.5
SiO <sub>2</sub>	1.401	1.454	1.427	532.8
Al <sub>2</sub> O <sub>3</sub>	1.460 <sup>b</sup>	—	1.460 <sup>b</sup>	531.2
MgO	1.699	1.675	1.687	530.9
GeO <sub>2</sub>	1.720	—	1.720	531.3
Ga <sub>2</sub> O <sub>3</sub>	1.732	1.913	1.822	530.6
		(1b)		
Li <sub>2</sub> O	2.090	—	2.090	—
CaO	2.505	2.334	2.420	529.8
Sc <sub>2</sub> O <sub>3</sub>	—	2.075	2.075	—
TiO <sub>2</sub>	2.368	2.188	2.278	529.7
V <sub>2</sub> O <sub>5</sub>	—	2.643	2.643	530.0
MnO	2.303	2.357	2.330	529.8
Fe <sub>2</sub> O <sub>3</sub>	2.647	2.467	2.557	530.0
CoO	—	2.405	2.405	529.9
NiO	2.202	2.218	2.210	530.0
CuO	2.838	2.963	2.900	530.3
ZnO	2.612	3.105	2.859	530.3
Y <sub>2</sub> O <sub>3</sub>	2.458	—	2.458	529.3
ZrO <sub>2</sub>	2.054	1.897	1.975	529.9
Nb <sub>2</sub> O <sub>5</sub>	—	2.679	2.679	—
MoO <sub>3</sub>	2.769	2.769	2.769	530.4
In <sub>2</sub> O <sub>3</sub>	—	2.762	2.762	530.1
SnO <sub>2</sub>	1.908	2.191	2.050	530.1
TeO <sub>2</sub>	2.444	2.358	2.401	530.5
CeO <sub>2</sub>	—	2.522	2.522	529.1
Ta <sub>2</sub> O <sub>5</sub>	—	2.291	2.291	—
WO <sub>3</sub>	2.677	2.662	2.670	530.2
		(1c)		
SrO	2.918	3.382	3.150	529.0
CdO	2.909	3.078	2.993	528.6
Sb <sub>2</sub> O <sub>3</sub>	3.172	3.686	3.429	—
BaO	3.652	3.830	3.741	528.2
PbO	3.450	3.311	3.381	529.7
Bi <sub>2</sub> O <sub>3</sub>	—	3.507	3.507	—

<sup>a</sup> According to Ref. (42).

<sup>b</sup> According to Ref. (16).

(b) Normal ionic oxides with O 1s binding energy at  $530 \pm 0.4$  eV: Many ionic (metallic) group oxides such as Na<sub>2</sub>O, CaO, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, and most transition metal oxides exhibit almost the same  $530.0 \pm 0.4$  eV O 1s binding energy. All these oxides possess ionicity between 76 and 89%.

(c) Very ionic oxides with O 1s binding energy in the range 529.5–528.0 eV: Some oxides (SrO, Cs<sub>2</sub>O, BaO, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, Ag<sub>2</sub>O, and CdO) exhibit very low O 1s

binding energy in the 529.5- to 528.0-eV range. They have ionicity greater than 90%.

Very recently, Dimitrov *et al.* (8) established that a good correlation exists between the experimentally measured O 1s binding energy of simple oxides reported by Barr (17) and their oxide ion polarizability determined by Dimitrov and Sakka (6) as well. To the best of our knowledge, this was the first attempt to correlate O 1s binding energy and the electronic polarizability of the oxide ion. For this purpose the authors (8) used data on O 1s binding energy obtained mainly by Barr (17), except those for TeO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, PbO, and P<sub>2</sub>O<sub>5</sub> reported by (19–22) (see Tables 1a–1c, column 5). In the present paper we demonstrate in Tables 1a–1c, the observed correlation between the two different physical properties of the oxide ion: electronic polarizability and O 1s binding energy. As can be seen in Tables 1a–1c, generally O 1s binding energy decreases with increasing oxide ion polarizability of the oxides. The authors (8) concluded on the basis of the observed correspondence between the two classifications discussed above that oxides such as 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> with low oxide polarizability between 1 and 2  $\text{\AA}^3$  possess high O 1s binding energy between 533.5 and 530.5 eV (see Table 1a). Some main group oxides such as CaO, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, and TeO<sub>2</sub> and most transition metal oxides show O 1s binding energy in a very narrow range between 530.5 and 529.5 eV approximately. They possess relatively high oxide ion polarizability between 2 and 3  $\text{\AA}^3$  (see Table 1b). Few oxides, CdO, SrO, and BaO, possess oxide ion polarizability above 3  $\text{\AA}^3$  and lowest O 1s binding energy below 529.5 eV (see Table 1c).

Briefly, the observed chemical shift to lower binding energy from 533.5 to 528.2 eV in the XPS spectra of simple oxides could be explained with an increase in electron charge density of the oxide ions due to an increase in their electronic polarizability. Therefore, the position of the O 1s peak could be used as a measure of the state of the oxide ion polarizability in different materials. It seems also that a close relationship between oxide ion polarizability and bond ionicity is found.

#### *Optical Basicity and O 1s Binding Energy of the Oxides*

The bulk optical basicity ( $\Lambda$ ) of an oxide medium as proposed by Duffy and Ingram 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. (23, 24).

The optical basicity can be determined experimentally from optical absorption spectra of doped ions such as Tl<sup>+</sup>, Pb<sup>2+</sup>, or Bi<sup>3+</sup> with  $d^{10}s^2$  electron configuration but the applicability of this method is rather limited because of ultraviolet impairment of many materials (24). That is why during the years a couple of methods have been proposed

especially in the field of glass science. In this respect many instrumental methods have been used including visible–NIR spectroscopy (25), far-infrared spectroscopy (26) UV-fluorescence spectroscopy (27), ESR spectroscopy (28, 29), X-ray emission spectroscopy (30), and Mossbauer spectroscopy (31). The contribution of these investigations in the field of optical basicity is significant but more of these methods are not direct in respect to the information obtained for the electron donation ability of oxide ions. The optical basicity of the medium has been discussed on the basis of the behaviors of some individual or complex probe ions, such as  $\text{Tl}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{VO}^{2+}$ , and  $^{151}\text{Er}$ , which act as sensors of the basicity. The main disadvantage of these methods excepting far-infrared spectroscopy (26) is that the probe ion might generate new structural sites not typical for the investigated medium.

On the other hand, an intrinsic relationship exists between the oxide ion polarizability and optical basicity in terms of Jorgensen's  $h$  functions as proposed by Duffy and Ingram (23),

$$\Lambda = h'/h, \quad [9]$$

where  $h$  and  $h'$  are related to a single monoatomic ion in its unpolarized and polarized states. For an oxide material the Jorgensen  $h$  function indicates electron donor power of the oxide ion and shows that the ability to transfer electrons to surrounding cations depends on the degree of its polarization. Duffy (3) has established the correlation

$$\Lambda = 1.67(1 - 1/\alpha_{\text{O}_2^-}) \quad [10]$$

between the optical basicity and the electronic polarizability of the oxide ion. Duffy has concluded that this relationship presents a general trend toward an increase in the oxide ion polarizability with increasing optical basicity. Equation [10] gives the possibility to calculate the optical basicity of the medium on the basis of experimental data for refractive index ( $n_0$ ) or energy gap ( $E_g$ ) of the solids and to obtain the so-called refractive-index-based optical basicity  $\Lambda(n_0)$  or energy-gap-based optical basicity  $\Lambda(E_g)$ .

As was pointed in the Introduction, Dimitrov and Sakka (6) have estimated using the approach proposed by Duffy (Eq. [10]) the optical basicity of numerous simple oxides on the basis of average oxide ion polarizability calculated from the refractive index  $\Lambda(n_0)$  and the energy gap  $\Lambda(E_g)$ . The optical basicity values  $\Lambda(n_0)$  and  $\Lambda(E_g)$  as well as the averaged on their basis values  $\Lambda^{\text{av}}$  are presented in Tables 2a–2c (columns 2–4). The data suggested by Duffy are also shown in Tables 2a–2c (column 5). Good agreement could be observed between the optical basicity data obtained using independent initial quantities and those obtained by Duffy (16).

Simultaneously, it is possible to calculate the so-called theoretical optical basicity  $\Lambda_{\text{th}}$  on the basis of the equation proposed by Duffy and Ingram (32),

$$\Lambda_{\text{th}} = X_1\Lambda_1 + X_2\Lambda_2 + \dots + X_n\Lambda_n, \quad [11]$$

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  $\Lambda_1, \Lambda_2, \dots, \Lambda_n$  are basicities assigned to the individual oxides. As commented by Duffy and Ingram (33), the principal use of Eq. [11] is in predicting the “trends” in optical basicity rather than the “true” basicity value. There is no theoretical justification for expressing optical basicity in terms of Eq. [11] (i.e., that equation represents empirical observations) and Eq. [11] necessarily expresses the average basicity arising from all the oxide species such as bridging or nonbridging. Irrespective of some limitations, Eq. [11] can be used as a simple and nice formula for calculation of the ideal optical basicity of the medium.

An alternative approach for prediction of the theoretical optical basicity of an oxide solid is based on the Pauling-type electronegativity. Duffy and Ingram (32) have suggested that a good relation exists between basicity  $\Lambda$  and electronegativity  $\chi$ :

$$\Lambda = 0.75/(\chi - 0.25). \quad [12]$$

The optical basicity of main group elements holds well with the electronegativity rule but for other elements Eq. [12] must be used with caution, especially with transition metal and heavy metal oxides.

Lebouteiller and Courtine (34) have tried to apply the electronegativity approach using a modifying Pauling-type electronegativity, taking into consideration the valence and the coordination of the ions. They have used an ionic-covalent parameter (ICP), which represents the influence of ionic-covalent bonding in an oxide or oxysalt on the acid strength of cations,

$$\text{ICP} = \log(P) - 1.38\chi + 2.07, \quad [13]$$

where  $P$  is the polarizing power of the cation ( $z/r_i^2$  with formal charge  $z$  and Shannon ionic radius  $r_i$ ) and  $\chi$  is the modifying electronegativity of the cation. On the basis of the correlation between ICP and known data on the optical basicity of the oxides given in Refs. (6) and (16), four straight lines have been obtained, depending on the electronic configuration of the cation. On the other hand, for some transition metal oxides ( $d^0$  configuration)  $\Lambda$  values have been assumed based only on logical considerations and chemical observation, thus giving a fifth correlation line. The reported graph has been used for calculation of optical basicity of mixed oxides taking into account the valence

and coordination of the cation. The data reported by Lebouteiller and Courtine for some simple oxides are given in Tables 2a–2c, column 6. It can be seen that agreement exists between the optical basicity data reported by different research groups shown in Tables 2a and 2c but an obvious disagreement is observed between the optical basicity data reported by Dimitrov and Sakka (6) and Lebouteiller and Courtine (34) in the case of some transition metal oxides (for example,  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{TiO}_2$ , and  $\text{Nb}_2\text{O}_5$ ), namely, the most covalent ones (Table 2b). Because of the observed difference, it is necessary to clarify further the origin and validity of the obtained data collected in Tables 2a–2c.

A new step in the development of experimental techniques for the direct estimation of optical basicity seems to be X-ray photoelectron spectroscopy (XPS). Recently, the O 1s chemical shift in XPS spectra was used intensively in the search for an adequate relation between peak position and optical basicity in some oxides and oxide glasses. Mullins (35) has established that the O 1s binding energy is related to the optical basicity of several simple oxides by the Mulliken occupation number of the metal orbital. The basic oxides are those with the least cationic character in the bonding orbitals. Miura *et al.* (20) and Miura and Nanba (36) found that the decrease in O 1s binding energy in the XPS spectra of a number of alkali phosphate, borate, silicate, germanate, and tellurite glasses corresponds to an increase of the calculated optical basicity. It was shown that the chemical shift parameter could give a new and useful concept for estimating the basicity of glass through the O 1s binding energy. Very recently, Dimitrov *et al.* (8) found that a good correlation exists between the experimentally measured O 1s binding energy of simple oxides reported by Barr (17) and the refractive index based optical basicity  $\Lambda(n_o)$  determined by Dimitrov and Sakka (6) (see Tables 2a–2c). It was established that in general O 1s binding energy decreases with increasing refractive-index-based optical basicity. As can be seen in Tables 2a–2c, oxides such as  $\text{P}_2\text{O}_5$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{GeO}_2$ , and  $\text{Ga}_2\text{O}_3$  with high O 1s binding energy between 533.5 and 530.5 eV possess relatively low optical basicity (see Table 2a). These are more acidic oxides. Some main group oxides such as  $\text{CaO}$ ,  $\text{In}_2\text{O}_3$ ,  $\text{SnO}_2$ , and  $\text{TeO}_2$  and most transition metal oxides show O 1s binding energy in the very narrow range between 530.5 and 529.5 eV approximately. The optical basicity of these oxides varies also in a narrow range and it is close to that of  $\text{CaO}$  (see Table 2b). A few oxides,  $\text{Na}_2\text{O}$ ,  $\text{CdO}$ ,  $\text{SrO}$ ,  $\text{PbO}$ , and  $\text{BaO}$ , possess the lowest O 1s binding energy below 529.7 eV. Their optical basicity is higher than that of  $\text{CaO}$  (see Table 1c).

In short, since oxide ion polarizability is closely related to O 1s binding energy (see Tables 1a–1c), decreased O 1s binding energy means increased oxide ion polarizability, that is, stronger electron donor ability of the oxide ion, and

vice versa. Therefore, the close relation between experimentally measured O 1s binding energy and optical basicity based on experimentally determined values of the refractive index or the energy gap of the simple oxides seems to be an important behavior of the solids. That is why O 1s binding energy can be used for the construction of a common basicity scale of oxide materials. In this respect the low optical basicity values for  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$ , and some other oxide, suggested by Lebouteiller and Courtine (34), are rather unacceptable from the O 1s binding energy point of view (see Tables 2a–2c).

#### *Cation Polarizability and Metal or (Nonmetal) Binding Energy of Simple Oxides*

The state of polarization of the oxide ions in oxide materials strongly depends on the polarizing power of the cations. The polarizing power is determined by several components including size, positive charge, coordination number, and polarizability of the cation. In this sequence the polarizability of the cation is probably one of the most significant properties. In this connection the application of the Lorentz–Lorenz equation allows determination of the oxide ion polarizability of the material under consideration by subtraction of its cation polarizability from the experimental molar polarizability. This approach requires having knowledge of polarizabilities of different ions. Because of the lack of data in real solids as a first approximation, the cation polarizability can be assumed to equal to the free-ion polarizability. A couple of sets of free-ion polarizabilities have been proposed by Fajans and Joos (37), Born and Heisenberg (38), Pauling (39), J. Mayer and M. Mayer (40), and Kordes (41) based on theoretical calculation or experimental results. Crystalline state ion polarizabilities determined by Tessman, Kahn, and Shockley are also well known (42). The most comprehensive sets among them are those reported by Pauling (39) and Kordes (41). In the present paper we show polarizability data reported by Kordes, which we have used in our previous papers (6, 8–10, 12–15), except those for  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Te}^{4+}$ , and  $\text{Bi}^{3+}$ , which are taken from Refs. (37, 43, 44) (Tables 3a–3c, column 5).

Recently, on the basis of the similarity in the physical nature of the ionization energy (IE) and binding energy (BE), Dimitrov and Komatsu (9) have found that in the case of a large number of simple oxides generally cation polarizability increases with decreasing metal (or nonmetal) binding energy. The term metal (or nonmetal) binding energy ( $E_B$ ) was introduced to denote both binding energy of the outermost orbital of a cation in an oxide ( $E_B^o$ ) as well as the binding energy of the same orbital in the corresponding pure element ( $E_B^e$ ). The element binding energies are taken mainly from Briggs and Seah (45) except those for Sb, Cs,

TABLE 2

Optical Basicities According to Dimitrov and Sakka Calculated from Refractive Index ( $\Lambda(n_0)$ ) and Energy Gap ( $\Lambda(E_g)$ ), Their Average ( $\Lambda^{av}$ ), Optical Basicity According to Duffy ( $\Lambda_{Duffy}$ ), Optical Basicity According to Lebouteiller and Courtine ( $\Lambda_{LS}$ ), and O 1s Binding Energy ( $E_b$ ) of Simple Oxides

Oxide	$\Lambda(n_0)$	$\Lambda(E_g)$	$\Lambda^{av}$	$\Lambda_{Duffy}$	$\Lambda_{LS}$	$E_b$ (eV)
(2a)						
BeO	—	—	0.375	—	0.48	—
B <sub>2</sub> O <sub>3</sub>	0.43	—	0.43	0.42	0.42	533.2
P <sub>2</sub> O <sub>5</sub>	—	—	—	0.33 (0.40)	0.33	533.5
SiO <sub>2</sub>	0.48	0.52	0.50	0.48	0.48	532.8
Al <sub>2</sub> O <sub>3</sub>	—	—	—	0.60	0.60	531.2
MgO	0.69	0.67	0.68	0.78	0.78	530.9
GeO <sub>2</sub>	0.70	—	0.70	0.60	0.54	531.3
Ga <sub>2</sub> O <sub>3</sub>	0.71	0.80	0.755	—	—	530.6
(2b)						
Li <sub>2</sub> O	0.87	—	0.87	1.00	0.48	—
CaO	1.00	0.95	0.975	1.00	1.00	529.8
Sc <sub>2</sub> O <sub>3</sub>	—	0.87	0.87	—	—	—
TiO <sub>2</sub>	0.96	0.91	0.97	1.00	0.75	529.7
V <sub>2</sub> O <sub>5</sub>	—	1.04	1.04	—	0.63	530.0
MnO	0.94	0.96	0.95	1.00	0.96	529.8
Fe <sub>2</sub> O <sub>3</sub>	1.04	0.99	1.02	—	0.77	530.0
CoO	—	0.98	0.98	—	0.98	529.9
NiO	0.91	0.92	0.915	—	0.91	530.0
CuO	1.08	1.11	1.10	—	0.56	530.3
ZnO	1.03	1.13	1.08	0.95	0.92	530.3
Y <sub>2</sub> O <sub>3</sub>	0.99	—	0.99	—	0.72	529.3
ZrO <sub>2</sub>	0.86	0.79	0.825	0.90	0.71	529.9
Nb <sub>2</sub> O <sub>5</sub>	—	1.05	1.05	—	0.61	—
MoO <sub>3</sub>	1.07	1.07	1.07	—	0.52	530.4
In <sub>2</sub> O <sub>3</sub>	—	1.07	1.07	—	—	530.1
SnO <sub>2</sub>	0.79	0.91	0.85	—	0.87	530.1
TeO <sub>2</sub>	0.99	0.96	0.975 (0.93) <sup>a</sup>	—	—	530.5
CeO <sub>2</sub>	—	1.01	1.01	—	0.65	529.1
Ta <sub>2</sub> O <sub>5</sub>	—	0.94	0.94	—	—	—
WO <sub>3</sub>	1.05	1.04	1.045	—	0.51	530.2
(2c)						
Na <sub>2</sub> O	—	—	—	1.15	1.15	529.7
SrO	1.10	1.18	1.14	1.10	1.10	529.0
CdO	1.10	1.13	1.115	—	1.12	528.6
Sb <sub>2</sub> O <sub>3</sub>	1.14	1.22	1.18	—	—	—
Cs <sub>2</sub> O	—	—	—	1.70	< 1.70	529.4
BaO	1.21	1.23	1.22	1.15	1.20	528.2
PbO	1.19	1.17	1.18	0.95	—	529.7
Bi <sub>2</sub> O <sub>3</sub>	—	1.19	1.19	—	1.19	—

<sup>a</sup> Corrected value of  $\Lambda$  for TeO<sub>2</sub> according to Ref. (14).

Ba, Pb, and Bi, which are according to Watts (46) and are presented in Tables 3a–3c (column 6). The binding energy of the cations is experimentally measured energy in different simple oxides and is taken from Ref. (47), except for those of V<sub>2</sub>O<sub>5</sub>, In<sub>2</sub>O<sub>3</sub>, BaO, and TeO<sub>2</sub>, which are taken from Refs. (48–51) and presented in Tables 3a–3c (column 7). It is seen

that highly polarizable cations possess low outermost binding energy and vice versa. According to Ref. (9), a systematic periodic change of the polarizability against the binding energy has been observed in the isoelectronic series. It has been suggested that outermost core-level binding energy can be used for relative measure of the cation polarizability.

TABLE 3

Elements, Corresponding Oxides and Cations, Outermost Filled Electron Orbital of the Corresponding Cation, Cation Polarizability ( $\alpha_1$ ), Element Binding Energy ( $E_B^e$ ), Cation Outermost Binding Energy ( $E_B^c$ ), and O 1s Binding Energy ( $E_b$ )

Element	Oxide	Cation	Outermost orbital	$\alpha_1$ ( $\text{\AA}^3$ )	$E_B^e$ (eV)	$E_B^c$ (eV)	$E_b$ (eV)
(3a)							
Be	BeO	Be <sup>2+</sup>	1s <sup>2</sup>	0.007	113	113.5	—
B	B <sub>2</sub> O <sub>3</sub>	B <sup>3+</sup>	1s <sup>2</sup>	0.002	191	193.1	533.2
P	P <sub>2</sub> O <sub>5</sub>	P <sup>5+</sup>	2p <sup>6</sup>	0.021	133	135	533.5
Si	SiO <sub>2</sub>	Si <sup>4+</sup>	2p <sup>6</sup>	0.033	102	103.4	532.8
Al	Al <sub>2</sub> O <sub>3</sub>	Al <sup>3+</sup>	2p <sup>6</sup>	0.054	74	74.7	531.2
Mg	MgO	Mg <sup>2+</sup>	2p <sup>6</sup>	0.094	51	52.2	530.9
Ge	GeO <sub>2</sub>	Ge <sup>4+</sup>	3d <sup>10</sup>	0.137	31	32.5	531.3
Ga	Ga <sub>2</sub> O <sub>3</sub>	Ga <sup>3+</sup>	3d <sup>10</sup>	0.195	20	20.3	530.6
(3b)							
Li	Li <sub>2</sub> O	Li <sup>+</sup>	1s <sup>2</sup>	0.024	56	—	—
Ca	CaO	Ca <sup>2+</sup>	3p <sup>6</sup>	0.469	25	—	529.8
Sc	Sc <sub>2</sub> O <sub>3</sub>	Sc <sup>3+</sup>	3p <sup>6</sup>	0.287	31	—	—
Ti	TiO <sub>2</sub>	Ti <sup>4+</sup>	3p <sup>6</sup>	0.184	37	—	529.7
V	V <sub>2</sub> O <sub>5</sub>	V <sup>5+</sup>	3p <sup>6</sup>	0.122	40	42.1	530.0
Mn	MnO	Mn <sup>2+</sup>	3d <sup>5</sup>	0.544	—	—	529.8
Fe	Fe <sub>2</sub> O <sub>3</sub>	Fe <sup>3+</sup>	3d <sup>5</sup>	0.437	—	—	530.0
Co	CoO	Co <sup>2+</sup>	3d <sup>7</sup>	0.508	—	—	529.9
Ni	NiO	Ni <sup>2+</sup>	3d <sup>8</sup>	0.266	—	—	530.0
Cu	CuO	Cu <sup>2+</sup>	3d <sup>9</sup>	0.437	—	—	530.3
Zn	ZnO	Zn <sup>2+</sup>	3d <sup>10</sup>	0.283	10	10.04	530.3
Y	Y <sub>2</sub> O <sub>3</sub>	Y <sup>3+</sup>	4p <sup>6</sup>	0.544	25	—	529.3
Zr	ZrO <sub>2</sub>	Zr <sup>4+</sup>	4p <sup>6</sup>	0.357	29	—	529.9
Nb	Nb <sub>2</sub> O <sub>5</sub>	Nb <sup>5+</sup>	4p <sup>6</sup>	0.242	35	40.8	—
Mo	MoO <sub>3</sub>	Mo <sup>6+</sup>	4p <sup>6</sup>	0.169	38	—	530.4
In	In <sub>2</sub> O <sub>3</sub>	In <sup>3+</sup>	4d <sup>10</sup>	0.662	19	18.0	530.1
Sn	SnO <sub>2</sub>	Sn <sup>4+</sup>	4d <sup>10</sup>	0.479	25	—	530.1
Te	TeO <sub>2</sub>	Te <sup>4+</sup>	5s <sup>2</sup>	1.595	14	12	530.5
Ce	CeO <sub>2</sub>	Ce <sup>4+</sup>	5p <sup>6</sup>	0.702	18	—	529.1
Ta	Ta <sub>2</sub> O <sub>5</sub>	Ta <sup>5+</sup>	4f <sup>14</sup>	0.185	25	26.4	—
W	WO <sub>3</sub>	W <sup>6+</sup>	4f <sup>14</sup>	0.147	34	35.6	530.2
(3c)							
Na	Na <sub>2</sub> O	Na <sup>+</sup>	2p <sup>6</sup>	0.181	31	—	529.7
Sr	SrO	Sr <sup>2+</sup>	4p <sup>6</sup>	0.861	20	—	529.0
Cd	CdO	Cd <sup>2+</sup>	4d <sup>10</sup>	1.054	11	12.2	528.6
Sb	Sb <sub>2</sub> O <sub>3</sub>	Sb <sup>3+</sup>	5s <sup>2</sup>	1.111	7	—	—
Cs	Cs <sub>2</sub> O	Cs <sup>+</sup>	5p <sup>6</sup>	2.595	12	—	529.4
Ba	BaO	Ba <sup>2+</sup>	5p <sup>6</sup>	1.595	16	13.5	528.2
Pb	PbO	Pb <sup>2+</sup>	6s <sup>2</sup>	3.623	3	—	529.7
Bi	Bi <sub>2</sub> O <sub>3</sub>	Bi <sup>3+</sup>	6s <sup>2</sup>	1.508	8	—	—

*Metal (or Nonmetal) Binding Energy–O 1s Binding Energy Correlation*

Since O 1s binding energy represents polarizability of the oxide ions and, as was discussed above, outermost metal (or nonmetal) binding energy represents cation polarizability, it is of interest to check the correlation between them. Searching for such a relation, Dimitrov and Komatsu (9) have established that a decrease of metal (or nonmetal) binding energy in XPS spectra of simple oxides is accompanied by a decrease of O 1s binding energy that is related to increased basicity. This statement means that generally oxides such as B<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> with high metal (or nonmetal) binding energy in the range 60–200 eV possess high O 1s binding energy between 533.5 and 530.5 eV (see Table 3a). One exception from this group is GeO<sub>2</sub> and Ga<sub>2</sub>O<sub>3</sub>, which possess relatively low metal binding energy, less than 40 eV. Some main group oxides, CaO, In<sub>2</sub>O<sub>3</sub>, TeO<sub>2</sub>, SnO<sub>2</sub>, and Na<sub>2</sub>O, and transition metal oxides with metal binding energy in the range 10–50 eV show O 1s binding energy in a very narrow range between 530.5 and 529.5 eV (see Table 3b). A few oxides, BaO, CdO, and SrO, with very low metal binding energy around 10–20 eV, have the lowest values of O 1s binding energy, below 529.5 eV (see Table 3c).

Briefly, in the case of simple oxides, in general high O 1s binding energy relates to high metal (or nonmetal) outermost cation binding energy and vice versa. The observed general correlation between O 1s binding energy and metal binding energy show that the origin of bulk basicity of an oxide closely relates to the interaction between a cation and an oxide ion to form an ionic–covalent bond.

*Interaction Parameter of the Oxides*

Fifty years ago, Yamashita and Kurosawa (52) proposed a general theory of the dielectric constant of simple ionic crystals based on a quantum-mechanical treatment of the electronic structure of constituent ions to take into account the effect of charge overlapping between neighboring ions. In that theory the perturbed wave function of 2p 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 the sum of three components,

$$\Delta E = \Delta E_0 + \Delta E_1 + \Delta E_2, \quad [14]$$

where  $\Delta E_0$  is the energy change of the positive and negative ions in the 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 the ionic pair in a high-frequency field can be regarded as the 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 with its nearest neighbors only. According to Yamashita and Kurosawa (52), 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 overlap between neighboring ions. Therefore, in the case of simple oxides it represents the interaction of the oxide ion with the neighboring cation. For a chosen cation–oxide ion pair, it represents the charge overlap of the oxide ion with its nearest positive neighbor and expresses the decrease in polarizability of the oxide ion placed in a crystal lattice with respect to the free-ion polarizability. From a chemical point of view such overlapping arises in chemical bonding. According to the fundamental theory (53), the formation of a chemical bond between two ions or atoms is the result of overlapping of their outermost electron clouds. In the case of simple oxides the bonding is realized due to the interaction between 2p electrons of the oxide ions and outermost valence electrons of the cation. The product of that interaction is an ionic–covalent chemical bond.

Dikshit and Kumar (54) found a simple approach to calculation of the interaction parameter  $A$  based on Yamashita and Kurosawa's theory and calculated  $A$  for a large number of halide crystals as well as for four alkaline-earth oxides, MgO, CaO, SrO, and BaO. Dimitrov and Komatsu (10) modified their equation using the approximation  $\alpha_c^+ \approx \alpha_f^+$  and for an average metal (nonmetal)–oxygen ionic pair the following equation was obtained,

$$A = [(\alpha_f^- - \alpha_{O2-})]/2(\alpha_f^+ + \alpha_f^-)(\alpha_f^+ + \alpha_{O2-}), \quad [15]$$

where  $\alpha_f^+$  and  $\alpha_c^+$  are the electronic polarizabilities of the positive ion in the free state and in the crystal, respectively.  $\alpha_f^-$  is the electronic polarizability of the free oxide ion and  $\alpha_{O2-}$  is its polarizability in the crystalline oxide under consideration. The authors have calculated the interaction parameter  $A$  for numerous simple oxides using Eq. [15] on the basis of the polarizability data of oxide ions and cations collected in Tables 1 and 3. Pauling's value of 3.921 Å<sup>3</sup> for the electronic polarizability of the free oxide ion is used. The results are given in Tables 4a–4c (column 2). As can be seen generally, semicovalent oxides such as BeO, B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, GeO<sub>2</sub>, and Ga<sub>2</sub>O<sub>3</sub> with O 1s binding energy in the range 530.5–533.0 eV, oxide ion polarizability between 1 and 2 Å<sup>3</sup>, and low optical basicity show the largest interaction parameter. The normal ionic oxides such as transition oxides and SnO<sub>2</sub>, CaO, TeO<sub>2</sub>, and In<sub>2</sub>O<sub>3</sub> with O 1s binding energy at 530 ± 0.5 eV, polarizability of the oxide ion between 2 and 3 Å<sup>3</sup>, and optical basicity close to that of CaO possess an intermediate interaction parameter. The very ionic oxides such as 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>, with O 1s binding energy in the

**TABLE 4**  
**Oxides, Interaction Parameter  $A$ , Average Oxide Ion Polarizability ( $\alpha_{O_2}^{av}$ ), and Optical Basicity ( $\Lambda$ )**

Oxides	$A$ ( $\text{\AA}^{-3}$ )	$(\alpha_{O_2}^{av})$ ( $\text{\AA}^3$ )	$\Lambda$
		(4a)	
BeO	0.258	1290	0.375
B <sub>2</sub> O <sub>3</sub>	0.244	1.345	0.425
P <sub>2</sub> O <sub>5</sub>	0.238	1.350	0.33 (0.40)
SiO <sub>2</sub>	0.216	1.427	0.50
Al <sub>2</sub> O <sub>3</sub>	0.204	1.460	0.60
MgO	0.156	1.687	0.68
GeO <sub>2</sub>	0.146	1.720	0.70
Ga <sub>2</sub> O <sub>3</sub>	0.126	1.822	0.755
		(4b)	
Li <sub>2</sub> O	0.110	2.090	0.87
CaO	0.059	2.420	1.00
Sc <sub>2</sub> O <sub>3</sub>	0.093	2.075	0.87
TiO <sub>2</sub>	0.081	2.278	0.97
V <sub>2</sub> O <sub>5</sub>	0.057	2.643	1.04
MnO	0.062	2.330	0.95
Fe <sub>2</sub> O <sub>3</sub>	0.052	2.557	1.02
CoO	0.059	2.405	0.98
NiO	0.083	2.210	0.915
CuO	0.035	2.900	1.10
ZnO	0.040	2.859	1.08
Y <sub>2</sub> O <sub>3</sub>	0.055	2.458	0.99
ZrO <sub>2</sub>	0.097	1.975	0.825
Nb <sub>2</sub> O <sub>5</sub>	0.051	2.679	1.05
MoO <sub>3</sub>	0.048	2.769	1.07
In <sub>2</sub> O <sub>3</sub>	0.037	2.762	1.07
SnO <sub>2</sub>	0.084	2.050	0.85
TeO <sub>2</sub>	0.034	2.401	0.93
CeO <sub>2</sub>	0.047	2.522	1.01
Ta <sub>2</sub> O <sub>5</sub>	0.080	2.291	0.94
WO <sub>3</sub>	0.055	2.670	1.045
		(4c)	
SrO	0.020	3.150	1.14
CdO	0.023	2.993	1.115
Sb <sub>2</sub> O <sub>3</sub>	0.011	3.429	1.18
BaO	0.003	3.741	1.22
PbO	0.005	3.381	1.18
Bi <sub>2</sub> O <sub>3</sub>	0.008	3.507	1.19

range 529.5–528.0 eV, polarizability of an oxide ion above  $3 \text{\AA}^3$ , and optical basicity higher than that of CaO present the lowest value of the interaction parameter. It has been proposed that the parameter  $A$  is closely related to the polarizability of the oxide ion as well as the optical basicity of the oxides. In this respect we plotted the data of optical basicity of the oxides as a function of the calculated data for the interaction parameter in Figs. 1–3. The obtained almost linear distribution in Figs. 1–3 of the basicity with respect to Yamashita and Kurosawa's parameter  $A$  could be used as

an optical basicity scale for simple oxides. The observed increase in polarizability of the oxide ion as well as optical basicity of simple oxides (Tables 4a–4c, Figs. 1–3) could be explained with decreased interaction inside the ionic pair, resulting in a smaller overlap between O  $2p$  and cation valence orbitals to form a chemical bond. As a result, the amount of the unshared  $2p$ -electron density available for donation of the average oxide ion increases. Therefore, it seems reasonable to assume an obvious correlation between parameter  $A$  and the relative amount of that density. Therefore, Yamashita and Kurosawa's interaction parameter  $A$  could be a representative quantity of oxide ion polarizability or optical basicity that is the origin of the chemical bond in simple oxides.

### CLASSIFICATION OF THE OXIDES

Analysis of the results recently obtained on average oxide ion polarizability, O  $1s$  binding energy, cation polarizability, metal (or nonmetal) binding energy, bulk basicity, and interaction parameter in simple oxides, as well as previously reported classifications, allows a more detailed classification of the oxides into three groups as shown in Table 5.

#### *Semicovalent Predominantly Acidic Oxides*

The first group includes oxides such as 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> with low oxide ion polarizability, high O  $1s$  binding energy, low cation polarizability, high metal (or nonmetal) outermost binding energy, comparatively low optical basicity, and strong interionic interaction.

#### *Ionic or Basic Oxides*

Some main group oxides such as CaO, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, and TeO<sub>2</sub> and most transition metal oxides show relatively high oxide ion polarizability, O  $1s$  binding energy in a very narrow medium range, high cation polarizability, and low metal (or nonmetal) binding energy. Their optical basicity varies in a narrow range and it is close to that of CaO assuming weaker interionic interaction.

#### *Very Ionic or Very Basic Oxides*

Few oxides, 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>, possess very high oxide ion polarizability, low O  $1s$  binding energy, very high cation polarizability, and very low metal (or nonmetal) binding energy. Their optical basicity is higher than that of CaO and the interionic interactions are very weak.



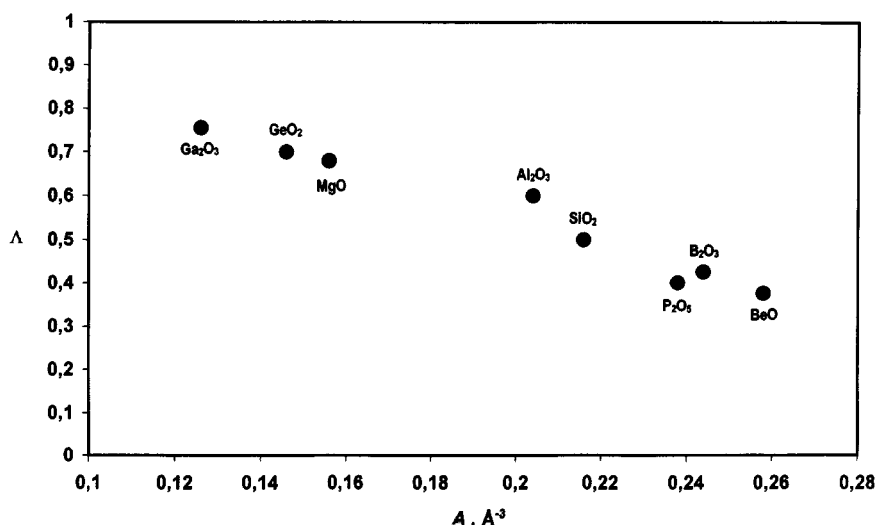


FIG. 1. Optical basicity  $\Lambda$  as a function of interaction parameter  $A$  of semicovalent predominantly acidic oxides.

### VALIDITY OF THE PROPOSED CLASSIFICATION OF SIMPLE OXIDES

#### Macroscopic Treatment

The main point of the classification proposed is the value of polarizability of the oxide ion in different oxides. As was discussed above, the oxide ion polarizabilities have been obtained by subtracting the cation polarizability from the experimental molar polarizability using the Lorentz-Lorenz equation. According to the present state of the polarizability approach, the cation polarizability is taken to be equal to the free-ion polarizability. But we assume that the subtraction is reasonable because the deformability of the electron cloud of the oxide ion is significantly larger

than that of the cations. Despite the large size, a cation is not likely to be particularly polarized because the cationic charge will tend to hold onto the cationic electrons (55).

Oxides of mainly  $p$ - and  $s$ -block elements belong in the first group of the classification proposed in Table 5. Their cations possess a low polarizability and most of them have a large positive charge. Their unit field strength is very large and they affect strongly the electron charge density of the oxide ion. As a result, the oxide ion polarizability is low. The second group consists of most transition metal oxides as well as oxides of some main group elements. The relatively high polarizability of the oxide ion in transition metal oxides of  $\text{Ti}^{4+}$ ,  $\text{V}^{5+}$ ,  $\text{Nb}^{5+}$ ,  $\text{Ta}^{5+}$ ,  $\text{W}^{6+}$ , and  $\text{Mo}^{6+}$  can be attributed to the empty  $d$  orbitals of the corresponding

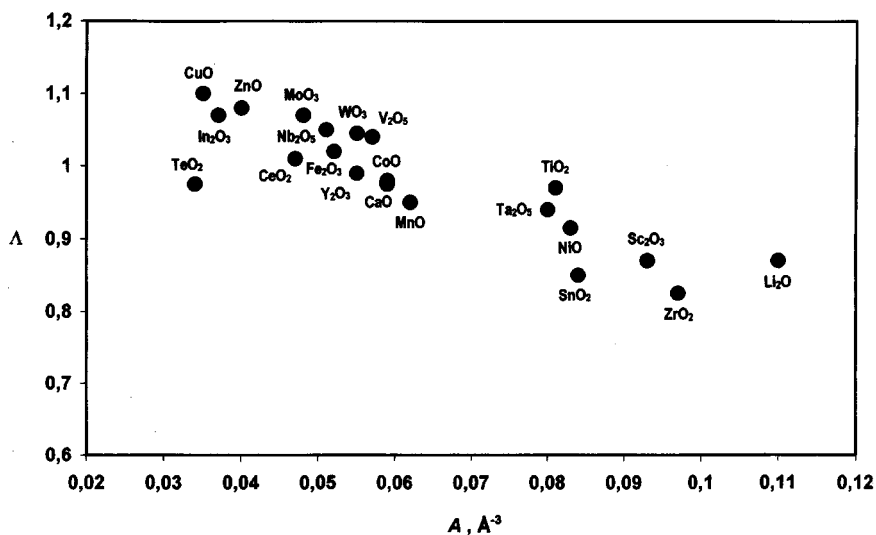


FIG. 2. Optical basicity  $\Lambda$  as a function of interaction parameter  $A$  of ionic or basic oxides.

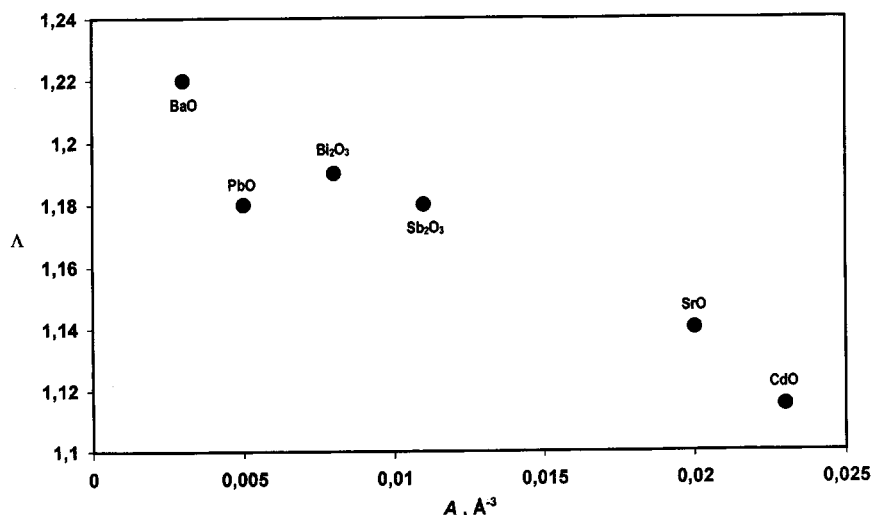


FIG. 3. Optical basicity  $\Lambda$  as a function of interaction parameter  $A$  of very ionic or very basic oxides.

cations, their high coordination number toward oxide ions, and relatively large cation polarizability. The third group oxides include mainly oxides of heavy  $s$ - and  $p$ -block elements. Their cations possess very high polarizability and some of them have a lone pair in the valence

shell, which is also strongly polarizable. These characteristics are responsible for the decreased polarizing effect of these cations on the electron charge cloud of the oxide ion. The electron polarizability of the oxide ion is very high.

TABLE 5

Classification of Simple Oxides (Group of Oxides, Oxide Ion Polarizability ( $\alpha_{O^{2-}}$ ), O 1s Binding Energy ( $E_b$ ), Cation Polarizability ( $\alpha_i$ ), Metal (or Nonmetal) Binding Energy ( $E_B$ ), Optical Basicity ( $\Lambda$ ), Interaction Parameter ( $A$ ), and Type of Bonding)

Oxides	$\alpha_{O^{2-}}$ ( $\text{\AA}^3$ )	$E_b$ (eV)	$\alpha_i$ ( $\text{\AA}^3$ )	$E_B$ (eV)	$\Lambda$	$A$ ( $\text{\AA}^{-3}$ )	Bonding
Semicovalent (predominantly acidic oxides)	$\approx 1-2$	$\approx 533.5-530.5$	$\approx 0.002-0.2$	$\approx 60-200$	$\approx 0.3-0.7$	$\approx 0.26-0.11$	Large overlap between O 2p and valence metal orbitals
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> , MgO, GeO <sub>2</sub> , Ga <sub>2</sub> O <sub>3</sub>	Low	High	Low	High	Acidic	Strong interionic interaction	Strong covalent bonds
Ionic (basic) Li <sub>2</sub> O, CaO, Sc <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub> , V <sub>2</sub> O <sub>5</sub> , MnO, Fe <sub>2</sub> O <sub>3</sub> , CoO, NiO, CuO, ZnO, Y <sub>2</sub> O <sub>3</sub> , ZrO <sub>2</sub> , Nb <sub>2</sub> O <sub>5</sub> , MoO <sub>3</sub> , In <sub>2</sub> O <sub>3</sub> , SnO <sub>2</sub> , TeO <sub>2</sub> , CeO <sub>2</sub> , Ta <sub>2</sub> O <sub>5</sub> , WO <sub>3</sub>	$\approx 2-3$	$\approx 530 \pm 0.4$	$\approx 0.2-0.8$	$\approx 15-60$	$\approx 0.8-1.1$	$\approx 0.11-0.03$	Smaller overlap between O 2p and metal valence orbitals
Very ionic (very basic) Na <sub>2</sub> O, SrO, CdO, Sb <sub>2</sub> O <sub>3</sub> , Cs <sub>2</sub> O, BaO, PbO, Bi <sub>2</sub> O <sub>3</sub>	High	Medium range	High	Low	Basic	Mainly weak interionic interaction	Bonds with increased ionicity
	$\approx > 3$	$\approx 529.5-528.0$	$\approx 0.8-3.7$	$\approx < 20$	$\approx > 1.1$	$\approx < 0.03$	Small overlap between O 2p and metal valence orbitals
	Very high	Low	Very high	Very low	Very basic	Very weak interionic interaction	Very ionic bonds

Note. The bonding assignment is made assuming an average metal (or nonmetal)-oxygen ionic pair.

The polarizability approach was successfully extended by Vithal *et al.* (56) and Dimitrov and Komatsu (5) to various binary oxide glasses. The oxide ion polarizability data obtained provide evidence for the additive nature of the oxide ion polarizabilities in glass systems. It was established that refractive-index-based oxide ion polarizability  $\alpha_{O_2-(n_0)}$  generally increases in the following sequence: phosphate, borate, silicate, germanate, tellurite, and titanate glasses. Similarly, Dimitrov and Komatsu (5) have proposed an optical basicity scale for the oxide glasses on the basis of good agreement observed between the calculated theoretical optical basicity  $\Lambda_{th}$  (Eq. [11]) and refractive-index-based optical basicity  $\Lambda(n_0)$  (Eqs. [7] and [10]). It is necessary to point out that  $\Lambda_{th}$  of the glasses was obtained on the basis of optical basicity data of simple oxides obtained by Duffy (16) and Dimitrov and Sakka (6) (see Tables 2a–2c). It should be emphasized that the observed trend in oxide ion polarizability and optical basicity in different oxide glasses is very close to that discussed here for simple oxides. This is significant proof about the validity of the classification proposed. For instance, the basicity of conventional phosphate, borate, and silicate glasses is low and it is below 0.75. They are more acidic glasses because the main component is a strong acidic oxide such as  $P_2O_5$  (0.33),  $B_2O_3$  (0.42), or  $SiO_2$  (0.48). The oxide ion polarizability  $\alpha_{O_2-(n_0)}$  and optical basicity  $\Lambda(n_0)$  of phosphate, borate, silicate, and germanate glasses increases significantly when the content of heavy metal oxides such as  $Sb_2O_3$  and  $Bi_2O_3$  is very large (5). The increase of the basicity correlates with the high optical basicity of  $Sb_2O_3$  and  $Bi_2O_3$ . According to Ref. (6), it is 1.14 and 1.19, respectively. The oxide ion polarizability and optical basicity of acidic glasses also increase when the content of transition metal oxides such as  $V_2O_5$  is large. For example, it has been found that in the  $V_2O_5-P_2O_5$  and  $V_2O_5-GeO_2$  systems with increasing  $V_2O_5$  content the refractive index  $n_0$  of the glasses increases rapidly, giving rise to an increase in the electronic oxide ion polarizability  $\alpha_{O_2-(n_0)}$  from 1.657 to 2.388  $\text{\AA}^3$  and optical basicity  $\Lambda(n_0)$  from 0.663 to 0.97 (5). This indicates that  $V_2O_5$  should possess high optical basicity much larger than 0.63, as proposed by Leboutellier and Courtine (34). According to Ref. (6), it is 1.04. Similarly, it was established that the optical basicity  $\Lambda(n_0)$  of titanate glasses is found in the range 0.8–1.11 (5). The values are in good correspondence with the optical basicity  $\Lambda(n_0)$  of  $TiO_2$  (0.96) (6) and are obviously larger than the value of 0.75 reported for  $TiO_2$  in Ref. (34).

The electronic oxide polarizability and basicity of tellurite glasses are also significant (5). The basicity is on the same order as that of  $CaO$  and it varies in a very narrow range (0.95–1.05).  $TeO_2$  as a conditional glass former is the main component of these glasses and obviously its acid–base properties have a significant effect. The optical basicity of  $TeO_2$  is 0.99, calculated on the basis of the refractive index

and 0.96 on the basis of the energy gap (6). From this point of view, the negligible change observed in oxide ion polarizability ( $\sim 2.3 \text{\AA}^3$ ) and optical basicity ( $\sim 0.95$ ) of a large number of binary tellurite glasses containing transition metal oxides such as  $TiO_2$ ,  $Nb_2O_5$ ,  $MoO_3$ , and  $WO_3$  with change in the composition shows that the oxide ion polarizability and optical basicity of these oxides are comparable with those of  $TeO_2$ . According to Ref. (6), their average values are 0.97, 1.05, 1.07, and 1.045, respectively, completely different from those reported by Leboutellier and Courtine (34) on the basis of metal electronegativity (see Table 2b). In our very recent paper, we applied the polarizability approach to a series of ternary tellurite glasses (14). It was found that even in the case of ternary glasses  $\alpha_{O_2-(n_0)}$  and  $\Lambda(n_0)$  hold well with the additivity rule and their values are close to that of  $TeO_2$ . A corrected value of 0.93 for  $TeO_2$  (see Table 2b) was assumed, which gives good agreement between  $\Lambda(n_0)$  and  $\Lambda_{th}$  in the case of tellurite glasses (14).

On the other hand, the next significant point proving the validity of the classification proposed is the established correlation between oxide ion polarizability as well as optical basicity, and O 1s binding energy in the case of simple oxides (see Tables 1a–1c and 2a–2c). A similar correlation has been shown by Miura and Nanba (36) in the case of a number of alkali phosphate, borate, silicate, germanate, tellurite, and bismuthate glasses. It was established that the optical basicity increases and the O 1s binding energy decreases in the same sequence of glasses pointed out above. Very recently, Honma *et al.* (13, 15) confirmed the correlation between oxide ion polarizability, that is, optical basicity, and O 1s binding energy peak position in  $Sb_2O_3-B_2O_3$  and  $Bi_2O_3-B_2O_3$  glasses. The oxide ion polarizability and optical basicity increase and the O 1s peak in the XPS spectra of the glasses shifts to lower binding energy with increasing  $Sb_2O_3$  or  $Bi_2O_3$  content.

In conclusion, the results discussed above unambiguously corroborate the reliability of the oxide ion polarizability and optical basicity data of simple oxides obtained on the basis of the refractive index and/or energy gap (6) used in the present oxide classification even in the case of transition metal oxides. Now, there is obvious evidence for the basic nature of these oxides. Therefore, it seems that oxide ion polarizability is a quantity more sensitive to the basicity of the medium than the element electronegativity. The electronegativity, even that used by Leboutellier and Courtine (34), does not take into account the real crystal structure of the oxide because the used Shannon radius represents an ideal average metal–oxide ion distance with respect to the valence and coordination state of the metal ion. It does not estimate the real distances of the chemical bonds in the structure under consideration. In contrast, oxide ion polarizability determined by Dimitrov and Sakka (6) is based on experimentally obtained materials constant such as

refractive index or energy gap, which is closely related to the real electronic structure of the oxides.

### Chemical Bonding Treatment

Since O 1s binding energy represents polarizability of the oxide ions and as was discussed above outermost metal (or nonmetal) binding energy represents cation polarizability, the close relationship established between O 1s binding energy and metal (or nonmetal) outermost binding energy in a series of simple oxides means that the polarizabilities of both species play an important role in the formation of the chemical bond. It is known that the valence band in the oxides is composed essentially from O 2p orbitals. According to Barr (17), a shift of the leading edge of an (O 2p)-dominated valence band in the XPS spectra of simple oxides toward the pseudo-Fermi level is a direct measurement of increased ionicity. This shift is accompanied by all other oxygen-dominated 2s and 1s levels moving down. Therefore, the discussed in the present paper, the O 1s chemical shift to lower binding energy in fact is a result of an O 2p chemical shift in the valence band of the oxide. From a polarizability point of view, this means increased polarizability of both oxide ions and cations, which is related to an increase in optical basicity. The reason for the low energy shift of the O 2p band is probably due to the interaction between the outermost filled cation orbital and the 2p electrons of the oxide ion (50). The interaction is more significant for the cation with low-lying outermost electrons. Very recently, experimentally it was proved that a possible reason for the O 1s chemical shift to lower binding energy in XPS spectra of  $\text{Sb}_2\text{O}_3\text{-B}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$  glasses is the repulsive interaction between the  $s^2$  outermost lone pair and oxygen 2p electrons (13, 15).

A larger shift of the O 2p band means increased electron density around the oxide ion. That relates to a larger contribution of O 2p orbitals in the valence band corresponding to increased electron donor ability, which leads to increased optical basicity of the oxides. In other words, the amount of the unshared electron density available for donation at an average oxide ion increases. As was shown, a quantity presenting the amount of unshared electron density at an average oxide ion could be the interaction parameter  $A$  introduced by Yamashita and Kurosawa (52). A small interaction parameter means a larger unshared electron density, which leads to increased ionicity of the chemical bond. From this point of view the obtained values on the parameter  $A$  for the simple oxides under consideration (see Tables 4a–4c, and Figs. 1–3) are a good proof of the validity of the simple oxide classification proposed here. Semi-covalent or predominantly acidic oxides possess a high interaction parameter, showing the formation of strong covalent bonds. In this connection, according to the valence band spectra of  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$ , O 2p lone pair electrons are

located at relatively high binding energy: 6.4–7.8 eV for  $\text{SiO}_2$  (57) and about 6 eV for  $\text{B}_2\text{O}_3$  (58). In contrast, the low values of the interaction parameter of the group of ionic or basic oxides indicate the formation of an average chemical bond with increased ionicity. For instance, the band mainly composed of O 2p orbitals in the valence band spectra of crystalline and vitreous  $\text{TeO}_2$  is located at about 3 eV (19, 51). The bond ionicity and the charge states of the Te and O atoms in  $\alpha\text{-TeO}_2$  are estimated as 0.75, +3, and –1.5, respectively (59). At the same time, the low values of the interaction parameter  $A$  in  $\text{V}_2\text{O}_5$  ( $0.055 \text{ \AA}^{-3}$ ),  $\text{MoO}_3$  ( $0.048 \text{ \AA}^{-3}$ ), and  $\text{WO}_3$  ( $0.055 \text{ \AA}^{-3}$ ) also show decreased interaction along an averaged cation–oxide ion pair. The results obtained in the present paper are probably unexpected from the point of view of the aqueous solution chemistry of cations with pronounced covalent character such as  $\text{V}^{5+}$ ,  $\text{Mo}^{6+}$ , and  $\text{W}^{6+}$ . But the results are in good agreement with the real crystal structures of the solids. According to Bachman *et al.* (60), the coordination polyhedron of  $\text{V}^{5+}$  in the crystal structure of  $\text{V}_2\text{O}_5$  is a highly deformed  $\text{VO}_6$  group containing V–O distances ranking from 1.585 to 2.787 Å. It is possible to calculate the ionicity of an individual V–O bond following the bond strength–bond length approach proposed by Brown and Shannon (61), obtaining 30% ionic character of the short bond and 87% ionic character of the longest bond. Similarly, according to Kihlberg (62), the crystal structure of  $\text{MoO}_3$  is built up of  $\text{MoO}_6$  octahedra which are rather distorted. The Mo–O distances vary from a very short 1.67 Å to a very long 2.33 Å. As in the case of  $\text{V}_2\text{O}_5$ , the different Mo–O distances obviously correlate with different ionicity of the chemical bonds. Recent studies concerning molecular orbital calculation for transition metal oxides also show that the bonding of Ti–O, V–O, and Cr–O bonds is ionic (63). The calculated interaction parameter in the case of third group oxides such as SrO, BaO,  $\text{Sb}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ , CdO, and PbO is very low, giving grounds to assume formation of very ionic bonds. This conclusion is in agreement with the results recently obtained about the ionicity of alkaline-earth oxides by means of low-energy  $\text{D}^+$  scattering (64). It has been found that the bond ionicity increases with an increase of cationic mass along the series MgO, CaO, SrO, and BaO. Also, recently, it was found that the interaction parameter  $A$  is closely related to the oxide ion polarizability and optical basicity, even in the case of binary oxide glasses in a manner similar to the case of simple oxides (12). It was established that experimental O 1s binding energy decreases with the decreasing refractive index based interaction parameter in the  $\text{Sb}_2\text{O}_3\text{-B}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$  glasses with an increasing heavy metal amount, which was attributed to the formation of chemical bonds with increased ionicity (13, 15). It is found that Bi–O bonds in  $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$  glasses are more ionic compared with Sb–O bonds in  $\text{Sb}_2\text{O}_3\text{-B}_2\text{O}_3$  glasses.

## CONCLUSIONS

The simple oxides have been separated into three groups based on their electronic ion polarizabilities, O 1s binding energy, metal (or nonmetal) binding energy, optical basicity, and interaction parameter. The reliability of the oxide ion polarizability and optical basicity of simple oxides obtained on the basis of refractive index and/or energy gap is proved using the close relationship between polarizability and binding energy. It is established that from a solid state chemistry point of view the oxide ion polarizability is a more sensitive quantity to the basicity of the medium than the element electronegativity. It is assumed that the optical basicity scale presented on the basis of the close relationship between the basicity and interaction parameter  $A$  probably is good proof of the validity of the simple oxide classification proposed.

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