

# New Estimation of Oxide Basicity Based on Bond Character

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## Abstract

A new measure called “non-covalent basicity” was proposed for estimating oxide basicity on the basis of the power function formula,  $d^n$  of interatomic distance ( $d$ ). From a good linearity between the value of  $d^n$  and the polarizability of oxygen in oxide, the study results indicated that non-covalent basicity corresponds well to refraction basicity. For some sp-bonded oxides with a peculiar coordination and transition metal oxides, large discrepancies existed between theoretical optical basicity values and non-covalent basicity values. Furthermore, the results indicated that these highly polarized oxygen states can be estimated using both non-covalent and refraction basicity, but not by the theoretical optical basicity.

(Keywords) Covalency, interatomic distance, Non-covalent basicity, Refraction basicity, Optical basicity, Oxide slag,

## 1. Introduction

Many measures for basicity have been proposed for understanding the characteristics of metallurgical slags[1,2]. In the simple approaches, basicities have been defined by the ratio of the total content of basic oxides to that of acidic oxides, dividing the constituent oxides into basic and acidic oxides[3]. Using this definition, many problems arise, such as the treatment of amphoteric oxides and judging the degree of basicity for respective oxides. Among the various types of basicity proposed up to now, it seems that optical basicity is the one most widely used for defining the characteristics of glasses and metallurgical slags[4,5]. In practice, several successful results have been obtained for determining the sulfide and phosphide capacities of slags through correlation to optical basicity [6,7]. However, there are indications that the dependency of these capacities on optical basicity cannot be expressed as a linear relationship. That is, the relationships between these capacities and the optical basicity are influenced by the slag constituents. For example, different linear relationships between sulfide capacity and optical basicity have been reported for  $\text{Na}_2\text{O-SiO}_2$  slags[8], and CaO-based slags. Furthermore, the effects of fluoride additions on sulfide capacity are not completely understood[9]. Therefore, other means of defining basicity have been investigated, for example, basicity based on redox equilibrium[10], solubility of metallic indicators[11], and so on.

The author has proposed the use of refraction basicity, which is based on the ionic refraction of oxygen in several amorphous silicates[12] and suggested that there is some discrepancy between the refraction basicity and optical basicity, especially for binary amorphous silicates containing titanium and lead oxides[13]. The suggestion has partly been accepted[14,15], though substantial problems regarding the discrepancies between the two different basicities remain unclear. Recently, the basicity of oxide slags based on the refractivity has been considered from a new standpoint[16,17]. Thus, the basicity concept based on polarization is expecting to be available for explaining the chemical character of oxide slags. However, in order to understand the basicity of oxides as well as of other compounds such as fluorides, sulfides and phosphides, which are of great interest in steel refining and welding, it is necessary to be able to elucidate the chemical characteristics of cation-anion bonding in any compound. In the study reported on here, a definition of oxide basicity was tried on the basis of covalent band gap concept for the purpose of reconsidering the physical meaning of basicity. A comparison of optical basicity with a newly proposed basicity (later defined as non-covalent basicity) and refraction basicity was performed.

## 2. Calculation of Covalency

In previous papers by Van Vechten and Phillips [18,19], two types of band gaps for diatomic compounds can be defined from their bond length and dielectric constant. According to the one gap model, the ionicity  $f_i$  of AB-type compounds can be defined by the formula:  $f_i = C^2 / (C^2 + E_h^2)$ , where  $E_h$  and  $C$  are the covalent and ionic band gaps, respectively. Assuming that the character of an A-B bond can be expressed by the ionic-covalent concept, the covalency ( $1 - f_i$ ) of the A-B bond can be calculated by:

$$1 - f_i = E_h^2 / (C^2 + E_h^2). \quad (1)$$

The covalent band gap ( $E_h$ ) for AB-type compounds with  $sp^3$ -character can be calculated by the formula:  $E_h = Id^{2.5}$ , where  $d$  and  $I$  are the interatomic distance and a constant, respectively. Thus, the covalent character of the A-B bond based on s and p electrons can be estimated from the interatomic distance. However, the relationship between covalent band gap and interatomic distance can clearly not be applied in the case of the  $sp$ -bonded compound without  $sp^3$ -character and to transition metal and lanthanide compounds with d and f electrons.

For  $sp^3$ -bonded AB compounds[20], the bulk modulus can be expressed by the power function formula:  $B = kd^{3.5}$ , where  $k$  is a constant, assuming that the strength of the A-B bond and its electron density are proportional to  $E_h$  and  $1/d$ , respectively. Though the power function formula could well estimate the bulk moduli of  $sp^3$ -bonded B4-type compounds, some deviation has been noted when compounds contain post-transition metals such as Zn and Cd[20]. Furthermore, the bulk moduli of transition metals can not be estimated by the  $B = kd^{3.5}$  formula. This limitation probably arises from the effect of d electrons (in some cases,

f electrons) in their inner cores, which can not be expressed by a formula with the power value of  $-3.5$ . In the recent paper[21], power function formulas with different power values have been proposed for reproducing the bulk moduli of transition metals and lanthanides. Moreover, it is indicated that these power function formulas enable estimation of the bulk moduli of various compounds with several simple crystal structures.

In this study, the power function formula based on interatomic distance was used as a measure of estimating covalency for the respective oxides, assuming that the electron densities for M-O bonds (M refers to *metallic ion*) in these compounds are still proportional to  $1/d$ . That is, the form of  $d^n$  was taken as the relative scale for estimating the covalency of the respective compound. The  $n$  value for the respective bond mode was determined by subtracting one from the power,  $m$ , in the respective relationship between  $B$  and  $d$  for the elemental substances with respective bond mode. These values for respective bonding mode are listed in **Table 1** together with the values of the power determined by the relationship between  $B$  and  $d$ [21]. When a compound consists of elements belonging to different bond modes, the  $n$  value for an  $A_aB_b$  compound is calculated by the following equation considering the atomic ratio:

$$n = \sqrt[a+b]{n_A^a n_B^b} \quad (2)$$

where  $n_B=3.25$  because atom B is oxygen in this case. By using equation (2), the polarizability of 26 oxides, which are listed in **Table 2**, was estimated because these values are available in the literature[22]. This table also specifies the interatomic distance of these oxides[23]. The basicity of each of these oxides, defined later as the “*non-covalent basicity*”, was estimated using CaO as the standard oxide to facilitate comparison with optical basicity.

### 3. Results and Discussion

Firstly, the dependence of oxygen polarizability on the value of  $d^{2.5}$  was examined for 26 diatomic oxides in order to examine the relationship between oxygen polarizability and the inverse of covalency for  $sp^3$ -bonds. As illustrated in **Fig.1**, a relationship with good linearity was obtained for the seven standard compounds, which are  $B_2O_3$ ,  $Al_2O_3$ ,  $SiO_2$  and four alkaline-earth oxides (MgO, CaO, SrO and BaO). The data plotted for several  $sp$ -bonded compounds also lie close to the line defining the linear relationship for the seven standard compounds though some deviation can be observed. However, most of the transition metal oxides and some non-transition metal oxides such as  $Sb_2O_3$ , show significant deviation. This deviation most likely arises from characteristic effects of peculiar  $sp$ -bonding and d electrons, unlike so-called “ $sp^3$ -bonding”. Therefore, the inverse of their covalencies for these oxides should be estimated by  $d^n$ , instead of  $d^{2.5}$ , as the covalency of the compound including d electron effects should be generally considered by the power formula of  $d^n$ . Selecting  $d^n$  as the abscissa in plotting the values, the polarizability values of 26 oxides are proportional to the values of  $d^n$ , as shown in **Fig.2**. The scatter of the plotted values may arise from erroneous

estimation of the effect of d electrons on the oxygen polarizability. The scatter is attributed to the geometrically averaged interatomic distances for several compounds with complex structures, in which several different interatomic distances are observed. However, a clear linear relationship with a small intercept was obtained (**Fig.3**), when non-covalent basicity and refraction basicity are compared by defining the non-covalent basicity as the ratio of the  $d^n$  value for the respective oxide to the value for CaO. Thus, it is concluded that the non-covalent basicity corresponds well to the refraction basicity, in which the effect of d electrons can be considered.

Based on the power function formula, the non-covalent basicity values of twelve oxides were compared with those of recommended optical basicities[5, 22]. The results are shown in **Fig.4**. Except for  $\text{Li}_2\text{O}$  and  $\text{BaO}$ , the non-covalent basicity values of the oxides consisting of sp-elements show good agreement with these optical basicities. Comparing the optical basicity and non-covalent basicity values of  $\text{TiO}_2$  and  $\text{ZrO}_2$ [24], the optical basicity for  $\text{ZrO}_2$  is higher than its non-covalent basicity counterpart based on the sp-bonding, while the optical basicity value for  $\text{TiO}_2$  agrees with that of the non-covalent basicity considering peculiar effects due to d electrons. Furthermore, the optical basicity for  $\text{PbO}$  is quite close to the corresponding non-covalent basicity excluding the peculiar effect due to pyramidal coordination [25]. This suggests that the Pb-O bond in silicate slags is not in a highly polarized state. However, with an increase in the content of  $\text{PbO}$  in amorphous lead silicate slag, its refraction index, that is, its polarization, increases[13]. It is therefore suggested that, in increasing the  $\text{PbO}$  content, the highly polarized effect due to pyramidal coordination should be considered for the optical basicity.

Subsequently, non-covalent basicity, with and without the consideration of d electron effects, were studied for MO-type transition metal oxides. The results are given in **Fig.5**. In this figure, the basicities for alkaline-earth oxides and  $\text{PbO}$  are also plotted for comparison. Unfortunately, the optical basicity values of all MO-type transition metal oxides have not been determined experimentally, so their two sorts of non-covalent basicities were compared with corresponding refraction basicities in **Fig.5**. As can be seen for the transition metal mono-oxides, except  $\text{MnO}$  and  $\text{CdO}$ , there is good agreement between non-covalent basicity (with d electron effect) values and refraction basicity values. For  $\text{MnO}$  and  $\text{CdO}$ , results indicated a medium contribution of d electrons to their polarization. The medium contribution is easily supported by previous results in which sd hybridization ratios were estimated to be 58% for Mn and 46% for Cd from the relationship between effective pseudopotential radius and interatomic distance of elemental substances[23]. However, the strong contribution of d electrons in  $\text{CuO}$  and  $\text{ZnO}$  is not well expressed by the ratio of sd hybridization because these ratios are 57% for Cu and 33% for Zn[23]. Conclusively, a highly polarized state of oxygen in transition metal oxides can be described by non-covalent basicity with the effect of d electrons. Furthermore, the good agreement between refraction basicity and non-covalent

basicity considering d electron effects indicates that the effect of d electrons is reflected in the refraction basicity.

Lastly, a comparison of theoretical optical basicity,  $\Lambda(\text{th})$ , with both refraction basicity and non-covalent basicity was made (**Fig.6**). In this figure, the data for the  $\Lambda(\text{th})$  were plotted as four different groups, that is, two sorts of non-transition metal oxides (non-TM1 and non-TM2) and two sorts of transition metal oxides (TM1 and TM2). The data for oxides denoted by non-TM1 and TM1 lie close to the line defining the relationship between the non-covalent and refraction basicities. However, the plotted values for the non-TM2 and TM2 oxides are located around 0.5 irrespective of the increase in refraction basicity. These results suggest that  $\Lambda(\text{th})$  can not be used to estimate highly polarized states of oxygen in these oxides. Taking PbO as an example, its theoretical optical basicity is about half that of its experimental optical basicity,  $\Lambda(\text{exp})$  (see Fig.6). The discrepancy is attributed to the fact that the contribution of the pyramidal coordination in PbO to oxygen polarizability can not be estimated by  $\Lambda(\text{th})$  but fairly well detected by  $\Lambda(\text{exp})$ . Thus, it is indicated that  $\Lambda(\text{th})$  can not be used to estimate a highly polarized state of oxygen due to d electrons effect and peculiar sp-bonding such as in Pb-O and Sb-O bonds. One of the reasons for this may arise from the simple usage of Pauling electronegativity to estimate basicity. Moreover, the effect of d electrons and other peculiar bonding may not be detected well in the measurement of basicity using s-p transition of indicator atoms.

#### 4.Summary

With the purpose of defining a new oxide basicity based on polarization, the relationship of polarization to interatomic distance( $d$ ) was examined for twenty-six simple oxides. It was found that the polarization of oxygen in these oxides could be linearly correlated with the values given by the power function formulas of interatomic distance,  $d^n$ , where the value of  $n$  of the respective oxide is determined on the basis of the empirical relationship between the bulk modulus and interatomic distance and expression of the covalent band gap( $E_h$ ) by the one gap model. From the one gap model, the form of  $d^n$  may be interpreted to be an extended concept of the covalent band gap. Accordingly, the polarization of oxygen in oxides can be expressed by the inverse of the covalent band gap and non-covalent basicity can be defined by the ratio of polarization of the respective oxide to that of CaO. In other words, the non-covalent basicity is thought of as a sort of “theoretical refraction basicity”. In comparing with theoretical optical basicity, highly polarized states of oxygen due to peculiar coordination and d electron effects can be reflected in the non-covalent basicity, while these highly polarized states can not be estimated by the theoretical optical basicity. In comparison with the experimental optical basicity, this discrepancy is also observed, though to a somewhat lesser degree.

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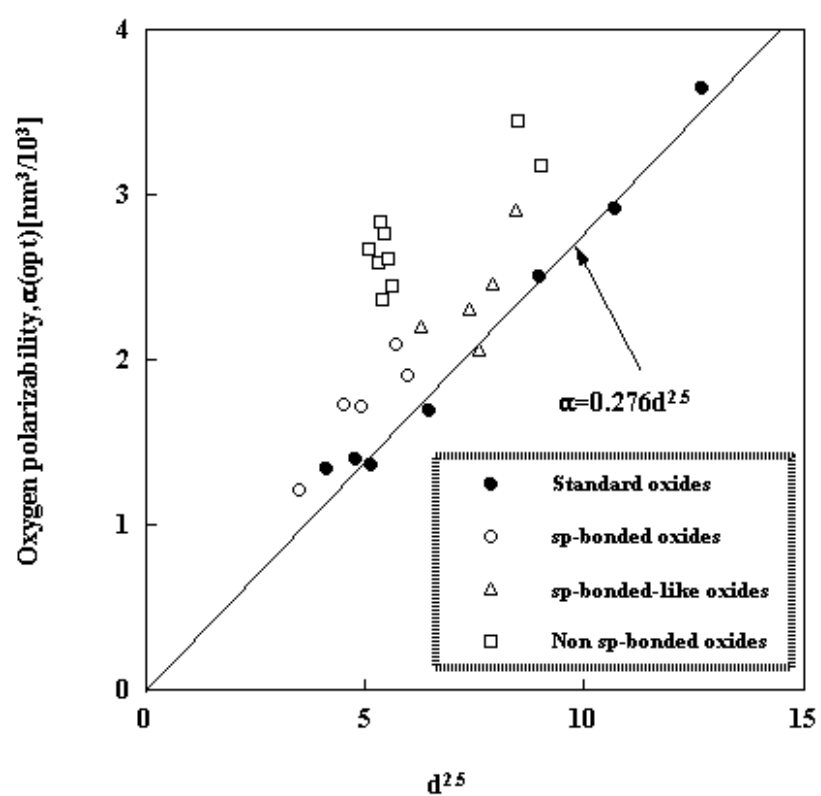


Fig.1 Relation between oxygen polarizability and the value of  $d^{2.5}$

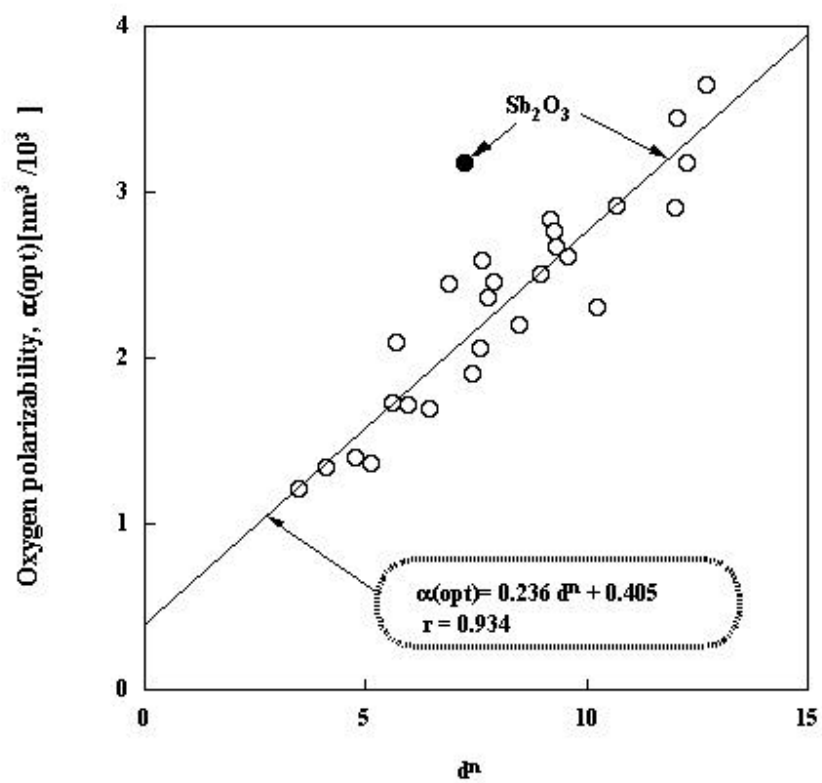


Fig.2 Relation between oxygen polarizability and the value of  $d^n$



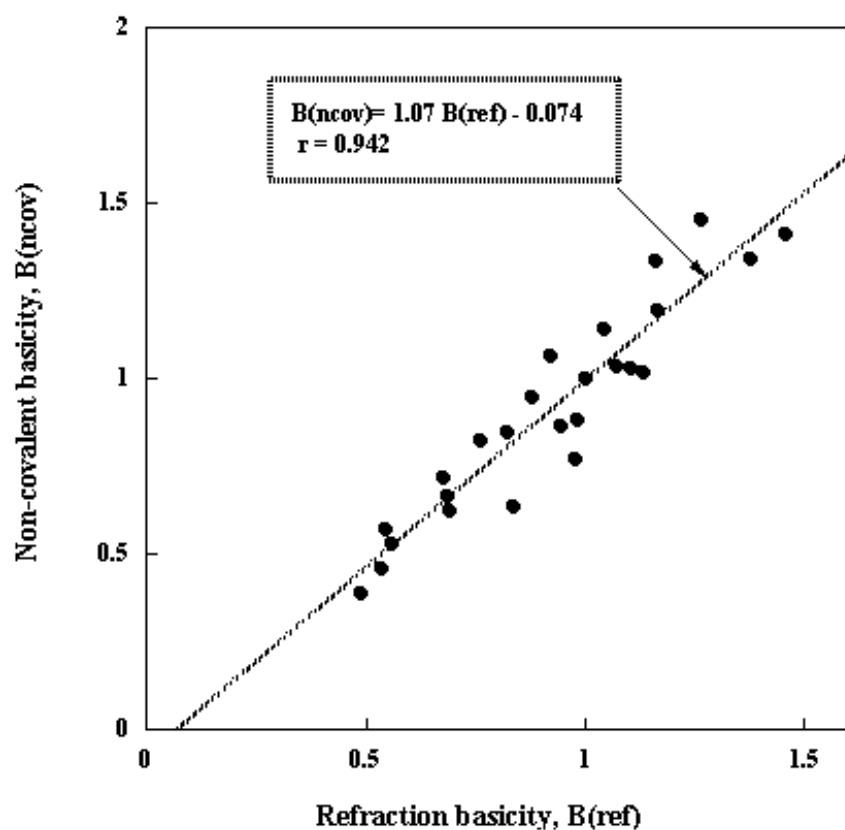


Fig.3 Relation between non-covalent basicity and refraction basicity

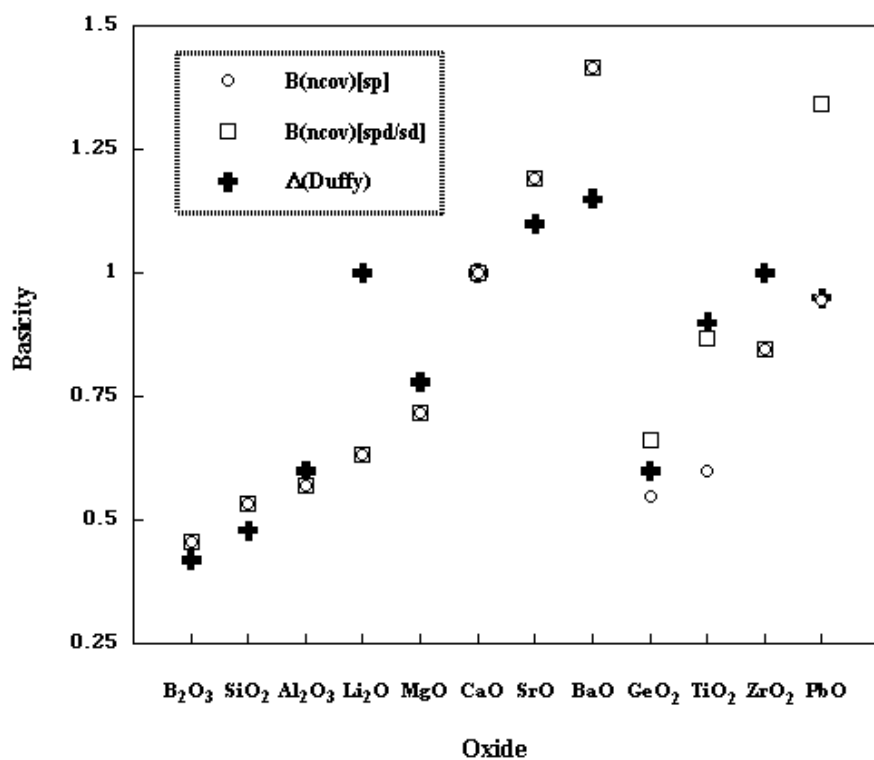


Fig.4 Comparison between non-covalent basicities and optical basicity in simple oxides

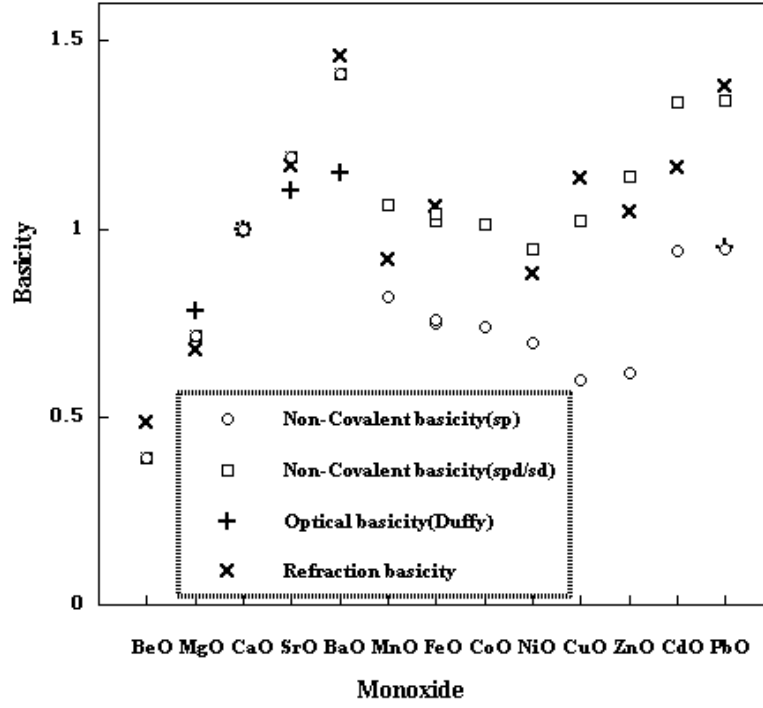


Fig.5 Comparison between non-covalent basicities, optical basicity and refraction basicity

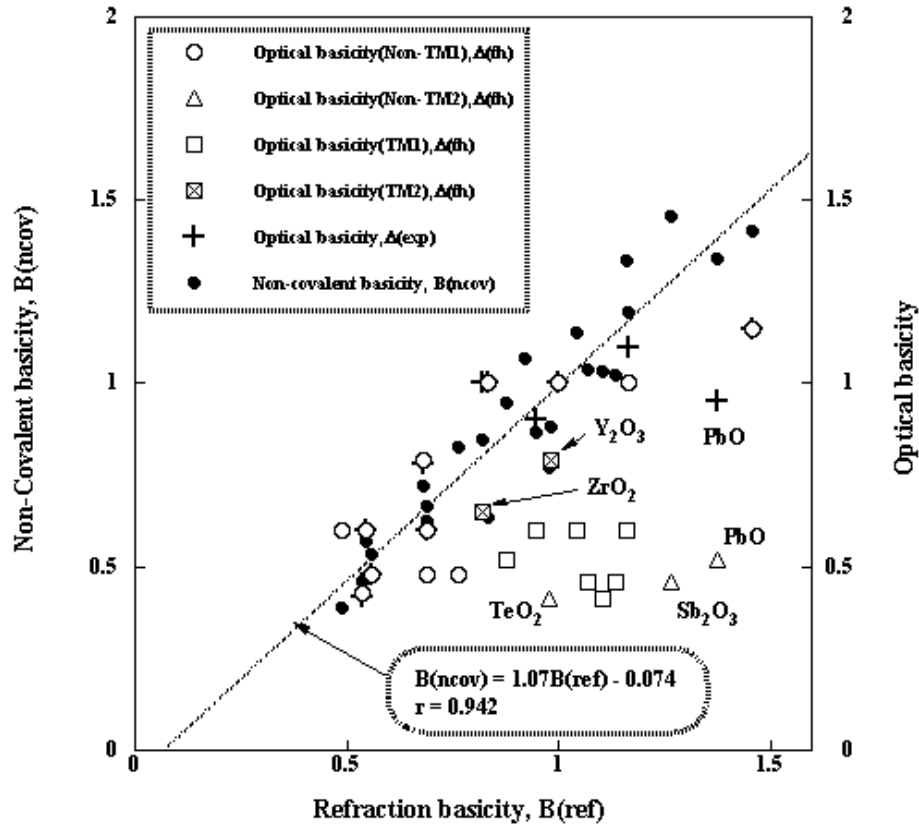


Fig. 6 Comparison between non-covalent basicity, theoretical and experimental optical basicities by taking refraction basicity as abscissa

**Table 1** The numerical values of the power  $n$  in the power function formulas,  $d^n$ , and the power,  $m$ , in the empirical power function formulas between bulk modulus and interatomic distance.

Bonding mode	Power $n$	Power $m$	Element
$sp^3$	-2.60	-3.60	C(d), Si, Ge, Sn(w)
spd	-3.25	-4.25	Li, Be, B, N, O, F, Na, Mg, Al, P, S, Cl, K, Ga, Mn, Zn, Cd, Hg, Rb, Cs
3d	-4.14	-5.14	Ca, In, Sc, Ti, V, Cr, Fe, Co, Ni, Cu
4d	-6.27	-7.27	Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Sb
5d/4f	-7.24	-8.24	Ba, Tl, Bi, Po, Hf, Ta, W, Re, Os, Ir, Pt, Au, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

**Table 2** Polarizability of oxygen in various compounds, estimated by the respective interatomic distance and power function formula.

Compound	Polarizability of oxygen	Interatomic distance	Compound	Polarizability of oxygen	Interatomic distance
BeO	$1.218 \square^3$	$1.649 \square$	$Sb_2O_3^*$	$3.172 \square^3$	$2.00*\square$
MgO	1.699	2.106	$Sb_2O_3$	3.172	2.408
CaO	2.505	2.405	ZnO	2.612	1.982
SrO	2.918	2.58	CdO	2.909	2.348
BaO	3.652	2.762	MnO	2.303	2.223
$Li_2O$	2.090	2.004	NiO	2.202	2.084
$B_2O_3$	1.345	1.766	CuO	2.828	1.956
$Al_2O_3$	1.365	1.92	$Y_2O_3$	2.458	2.286
$Ga_2O_3$	1.732	1.83	$TiO_2(a)$	2.584	1.946
$SiO_2$	1.401	1.87	$TiO_2(r)$	2.368	1.959
$GeO_2$	1.720	1.89	$ZrO_2$	2.054	2.251
$SnO_2$	1.908	2.045	$MoO_3$	2.769	1.966
$TeO_2$	2.444	1.993	$WO_3$	2.677	1.916
PbO	3.450	2.351			

$\square$  The longest interatomic distance is neglected in the interatomic distance of  $Sb_2O_3$ .