Ion Refractivity of Oxygen in Binary Alkali Earth Silicate Glasses

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ABSTRACT

A mathematical model to predict the ion refractivity(R_o) of oxygen in binary alkaline silicate glasses from the chemical composition has been developed elsewhere as follows:

$$R_o = R_o^\circ + \Delta R_o \cdot 2x/(2 - x)$$

where R_o° and ΔR_o are the ion refractivity of oxygen in SiO_2 glass and the increase in the ion refractivity of oxygen due to the presence of non-bridging oxygen ions, respectively, and x is the mole fraction of alkaline metal oxides. In this paper, the ion refractivity of oxygen for binary alkali earth silicate glasses has been determined as a function of the chemical composition to confirm whether the mathematical model applies also in these glasses. Refractive indices and densities for SrO-SiO_2 glass were measured using an Abbé refractometer and by the Archimedean method, respectively, and published data of refractive indices and densities were reviewed for CaO-SiO_2 and BaO-SiO_2 glasses. Values of R_o calculated from refractive index and density data using the Lorentz-Lorenz equation have linear relations to the function of $2x/(2 - x)$, which indicates that the model is reasonable also in the alkali earth silicate glasses. It has been found that the value of ΔR_o represents the effective basicity for oxides doped in SiO_2 glass, and it has been determined that values of ΔR_o for CaO, SrO and BaO are 0.99, 1.24 and 1.58(in cm^3), respectively.

1. INTRODUCTION

Knowledge of the basicity of slags is very important to gain an understanding of the physicochemical properties of slag systems. Various indices of the basicity have been proposed, such as those represented by the ratios, $(\%CaO)/(\%SiO_2)$, $[(\%CaO)+(\%MgO)]/(\%SiO_2)$, $(\%CaO)/[(\%SiO_2)+(\%Al_2O_3)]$, $(\%CaO)/[(\%SiO_2)+(\%P_2O_5)]$ and so on,[1] and these have been frequently used owing to its usefulness in practice. However, these indices cannot express the basicity of the whole slag system.

Lewis has proposed a more generalised concept of the basicity, that is, an acid is a substance which acts as an electron pair acceptor and a base is a substance which acts as an electron pair donor.[2] According to Lewis acid-base theory, the basicity can be defined as the electron donor power of the base. In slags oxygen ions act as a base, and the basicity of a slag can be defined as the electron donor power of oxygen in the slag. One of the basicity indices proposed based upon this idea is the refraction basicity,[3] which is relevant to the refractive index of slags.

The refraction of light in a slag is caused by the interaction between light and constituent ions of the slag, ie, the electronic polarisation of ions due to an electric field of light. The electronic polarisability of an ion primarily indicates the ease with which the ion can be distorted by an electric field, which is closely related to the responsiveness of the ion to the presence of electric fields, particularly those arising from neighbouring ions. In slags the electron distribution of oxygen ions is affected most strongly by neighbouring cations, since only oxygen can become a negatively charged ion with excess electrons and these electrons are more weakly bound to a positively charged nucleus. Thus, the electronic polarisability(α_o) of oxygen can be a measure of the electron donor power of oxygen.

On the other hand, the ion refractivity(R_o) of oxygen is defined as $R_o = 4\pi\alpha_o N_A/3$, where N_A is Avogadro's number. This value can be considered as the electronic polarisability for 1 mol of oxygen ions, and can be derived from refractive index and density data of substances using the Lorentz-Lorenz equation. The refraction basicity is defined as the following ratio,[3]

$$R_o \text{ in a slag} / R_o \text{ in vitreous silica}(SiO_2 \text{ glass})$$

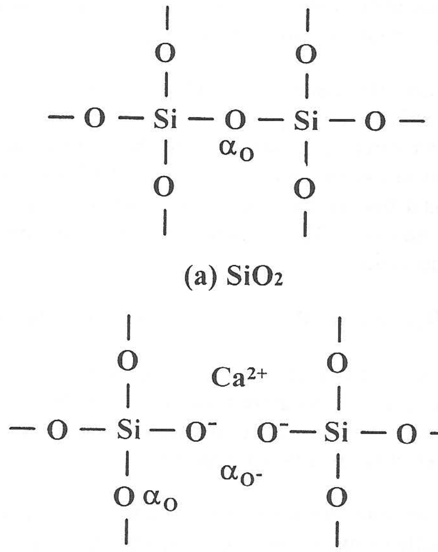
It can be considered that the refraction basicity could provide a useful, accurate measure of the basicity of the whole slag system, since refractive index and density measurements can give accurate data easily.

Furthermore, any mathematical model to predict the ion refractivity of oxygen in slags from the chemical composition would be very useful in practice. Because of this, a model for binary silicate glasses was developed earlier[4] based upon a structure model for the silicate glasses, and was verified using published data[3] for ion refractivities of oxygen. It has been shown that the model applies well in binary alkaline silicate glasses but does not apply very well in binary alkali earth silicate glasses. However, it has not been fully discussed whether the model is reasonable in binary alkali earth silicate glasses, owing to unreliability of the refractive index or density data for them.[3]

The aim of this study is to confirm the reasonability of the mathematical model in binary alkali earth silicate glasses by the determination of ion refractivities of oxygen in such glasses, for which refractive index and density data are required. Consequently, the refractive index and density for $SrO\text{-}SiO_2$ glass are measured, and those for $CaO\text{-}SiO_2$ and $BaO\text{-}SiO_2$ glasses are reviewed since there have been many extant data for these glasses.

2. MODELLING

The mathematical model to predict the ion refractivity of oxygen for binary silicate glasses has been described in detail elsewhere[4], the outline of which is summarised briefly below. Fig.1 shows structure models for SiO_2(a) and $CaO\text{-}SiO_2$(b) glasses. It is assumed that all oxygen ions in SiO_2 glass are bridging oxygen(BO) ions, which have an electronic polarisability of α_o. Accordingly, the ion refractivity ($R_o{}^\circ$) of oxygen in SiO_2 glass can be expressed as $R_o{}^\circ = 4\pi\alpha_o N_A/3$ (= 3.68 cm^3). On the other hand, it is assumed that $CaO\text{-}SiO_2$ glass contains only bridging(BO) and non-bridging oxygen (NBO) ions, which have electronic polarisabilities of α_o and α_{o^-} ($\alpha_{o^-} = \alpha_o + \Delta\alpha_o$), respectively. The presence of free oxygen ions(O^{2-}) has been neglected, since it has been reported by Sasaki et al that $CaO\text{-}SiO_2$, $SrO\text{-}SiO_2$ and $BaO\text{-}SiO_2$ glasses contain no O^{2-} ions in the range where the mole fraction of alkali earth metal oxides is less than 0.5, from the study using X-ray photoelectron spectroscopy.[5]



(a) SiO_2

(b) $CaO\text{-}SiO_2$

Fig.1 Structure models for SiO_2(a) and $CaO\text{-}SiO_2$ (b) glasses

Consider a silicate glass of $xAO\text{-}ySiO_2$, where A represents the alkali earth metal, x and y are the mole fractions of AO and SiO_2, respectively($x + y = 1$). As shown in Fig.1(b), doping of one CaO into SiO_2 produces two NBO ions. Thus, the number(N_{o^-}) of NBO ions in the silicate glass can be calculated as $2xN_A$, assuming that each AO produces two NBO ions. On the other hand, the total number(N_T) of oxygen ions in the silicate glass can be expressed as $(x + 2y)N_A$, which equals $(2 - x)N_A$ because of $x + y = 1$. Consequently, the difference between N_T and N_{o^-} equals the number(N_o) of BO ions, $(2 - 3x)N_A$.

Using these expressions, R_o for the silicate glass can be derived from the sum of ion refractivities of BO and NBO ions as follows:

$$R_o = (4\pi\alpha_o N_o/3 + 4\pi\alpha_{o^-}N_{o^-}/3)\cdot N_A/(N_o + N_{o^-}) \qquad (1)$$

where the term $N_A/(N_o + N_{o^-})$ is multiplied to obtain R_o for 1 mol of oxygen ions. Substitution of $\alpha_{o^-} = \alpha_o + \Delta\alpha_o$ into Eq.(1) gives Eq.(2).

$$R_o = 4\pi\alpha_o N_A/3 + 4\pi\Delta\alpha_o N_A/3\cdot N_{o^-}/(N_o + N_{o^-}) \qquad (2)$$

It can be seen from Eq.(2) that the value of R_o is linearly proportional to the fraction of NBO ions. Using the following relations $R_o{}^\circ = 4\pi\alpha_o N_A/3$, $N_o = (2 - 3x)N_A$ and $N_{o^-} = 2xN_A$, Eq.(2) can be simplified as Eq.(3).

$$R_o = R_o{}^\circ + \Delta R_o\cdot 2x/(2 - x) \qquad (3)$$

where the term ΔR_o is $4\pi\Delta\alpha_o N_A/3$ in Eq.(2). Eq.(3) indicates that there is a linear relation between R_o and $2x/(2 - x)$. The term ΔR_o means the increase in the ion refractivity of oxygen due to the presence of NBO ions, since the term $2x/(2 - x)$ represents the fraction of NBO ions. Furthermore, it can be considered that the magnitude of ΔR_o corresponds to the strength of bases of alkali earth metal oxides in SiO_2 glass, as discussed later.

3. EXPERIMENTAL

3.1 Samples

Samples of $SrO\text{-}SiO_2$ glass were prepared; the mole fraction of SrO ranged between 0.33 and 0.45. The samples were prepared from reagent grade SiO_2 and $SrCO_3$, the latter being decomposed to SrO by heating at 1350°C for 24 h. Weighed mixtures of the oxides were placed in platinum crucibles and heated in air at 1580°C for 3-10 h. Glassy samples were prepared by quenching the molten glasses onto a water-cooled copper plate.

Samples for refractive index measurements were prepared by machining and then polishing one face and a perpendicular face to the face of the quenched glasses. These faces were finally polished using abrasive of 0.3 μm in diameter.

3.2 Measurements

The refractive indices(n_D) for a wavelength of 589.3 nm were measured using an Abbé refractometer. Monobromonaphthalene was used as the contact liquid, since it has a refractive index of 1.64. The measurements were carried out at room temperature.

The measurements of density(ρ) were carried out at room temperature using the Archimedean method in which the apparent masses of samples were determined in air and when immersed in distilled water.

3.3 Review

Data of refractive indices and densities for CaO-SiO_2 and BaO-SiO_2 glasses have been collected in the handbook[6], from which data were employed for the refractive index measured for a wavelength of 589.3 nm at room temperature and the density measured at room temperature.

4.RESULTS

4.1 Refractive index

Fig.2 shows refractive indices for SrO-SiO_2 glass as a function of mole fractions of SrO. It can be seen that there is an increase of refractive index with the addition of SrO. It can also be noted that the results of the present investigation are in good agreement with those previously reported by Iwamoto and Makino[3], Eskola[7], and Yamane and Kojima.[8] Figs.3 and 4 show refractive indices for CaO-SiO_2[3,9-11] and BaO-SiO_2[3,7,12-14] glasses, respectively. Also in these glasses, additions of CaO and BaO result in increases of their refractive indices, and there is good agreement among the published data.

4.2 Density

The densities recorded in the present study for SrO-SiO_2 glass are compared with those reported by Iwamoto and Makino[3], Eskola[7] and Yamane and Kojima[8] in Fig.5. It can be seen that there is a linear increase of density with the addition of SrO. It should be noted that the data recorded by Iwamoto and Makino[3] are slightly larger than other data. Figs.6 and 7 show densities for CaO-SiO_2[3,9,10,15] and BaO-SiO_2[3,7,12,13,16] glasses, respectively. The densities for these glasses increase with increasing alkali earth metal oxide addition. Also in theses glasses, the values recorded by Iwamoto and Makino[3] exhibit the difference from other data.

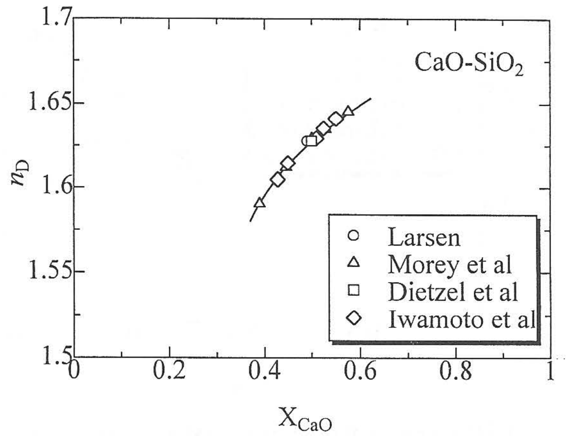


Fig.3 Refractive indices(n_D) for CaO-SiO_2 glass as a function of mole fractions(x) of CaO

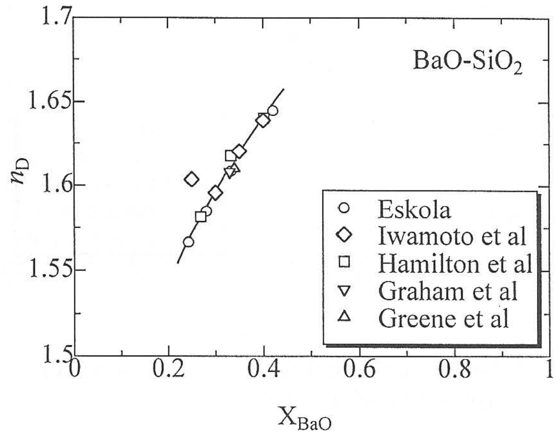


Fig.4 Refractive indices(n_D) for BaO-SiO_2 glass as a function of mole fractions(x) of BaO

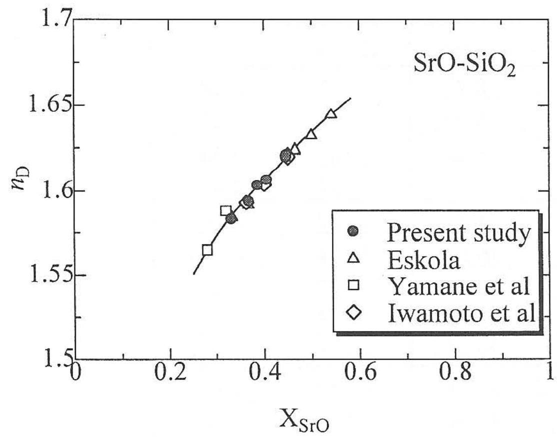


Fig.2 Refractive indices(n_D) for SrO-SiO_2 glass as a function of mole fractions(x) of SrO

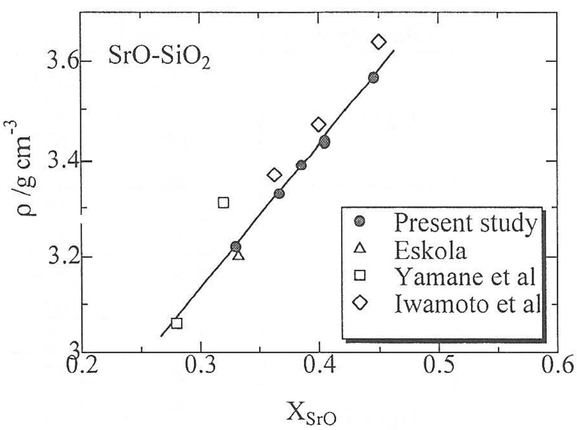


Fig.5 Densities(ρ) of SrO-SiO_2 glass as a function of mole fractions(x) of SrO

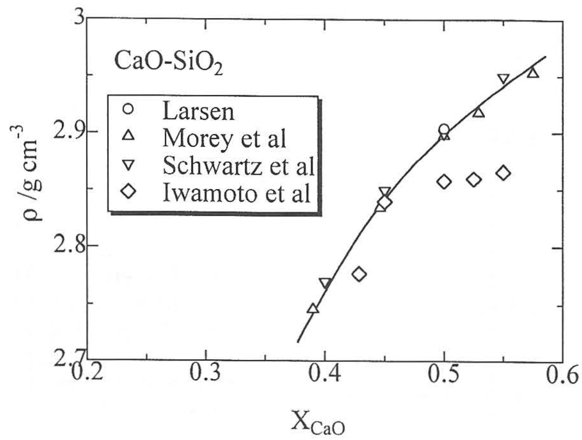


Fig.6 Densities(ρ) of CaO-SiO$_2$ glass as a function of mole fractions(x) of CaO

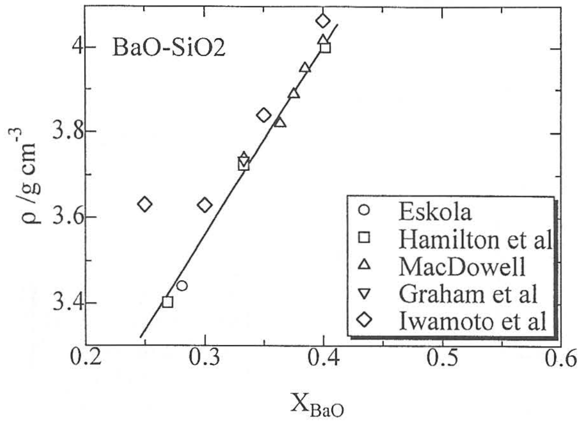


Fig.7 Densities(ρ) of BaO-SiO$_2$ glass as a function of mole fractions(x) of BaO

Table II Ion refractivities(R_o) of oxygen in CaO-SiO$_2$, SrO-SiO$_2$ and BaO-SiO$_2$ glasses, with other data used for the calculation

Glass system	MO /mol%	n_D	ρ /g·cm^{-3}	M /g·mol^{-1}	R /cm^3	R_O /cm^3
CaO-SiO$_2$	40.00	1.594	2.765	58.77	7.212	4.181
	45.00	1.612	2.845	58.60	7.161	4.247
	50.00	1.627	2.900	58.44	7.143	4.340
	55.00	1.639	2.945	58.28	7.121	4.437
SrO-SiO$_2$	33.05	1.583	3.221	74.47	7.727	4.165
	36.71	1.594	3.329	76.07	7.754	4.228
	38.56	1.604	3.391	76.87	7.797	4.279
	40.51	1.607	3.438	77.72	7.807	4.312
	44.55	1.621	3.568	79.48	7.835	4.388
BaO-SiO$_2$	25.00	1.577	3.330	83.39	8.299	4.132
	30.00	1.600	3.545	88.06	8.498	4.255
	35.00	1.622	3.785	92.72	8.627	4.343
	40.00	1.644	4.000	97.38	8.815	4.473

Accordingly, it is considered that values of R_o calculated using refractive index and density data measured by Iwamoto and Makino[3] have errors arising from inaccuracy in the density, leading to the failure of the mathematical model in alkali earth silicate glasses in the previous study.[4]

5.DISCUSSION

5.1 Determination of the ion refractivity of oxygen

The molar refractivity(R) of a silicate glass can be derived using refractive index(n) and density(ρ) data from the Lorentz-Lorenz equation, ie, Eq.(4),

$$R = \{(n^2 - 1)/(n^2 + 2)\}M/\rho \quad (4)$$

where M is the average molar mass of the glass. On the other hand, R can also be expressed as the sum of ion refractivities of oxygen and cations by Eq.(5).

$$R = N_o \cdot R_o + \sum N_i \cdot R_i \quad (5)$$

where N_o and N_i are the numbers of moles of oxygen and cations, respectively, in 1 mol of the glass: $N_o = x + 2y$, $N_A = x$ and $N_{Si} = y$ for the system xAO-ySiO$_2$ ($x + y = 1$), and R_i is the ion refractivity of cations, values of which are given in Table I.[17] Accordingly, R_o can be calculated from Eq.(5), assuming that values of R_i are not dependent upon the glass composition.

Table I Values for ion refractivities(Ri) of cations

Cation	Ca	Sr	Ba	Si
Ri / cm^3	1.182	2.17	4.02	0.084

Table II lists the ion refractivity of oxygen in $CaO-SiO_2$, $SrO-SiO_2$ and $BaO-SiO_2$ glasses along with other data used for the calculation. The calculation for $SrO-SiO_2$ glass has been carried out using values of the refractive index and density measured in the present study. Fig.8 shows the ion refractivity of oxygen for these glasses as a function of mole fractions of alkali earth metal oxides. It is noted that values of R_o are not linearly proportional to x.

Fig.9 shows the ion refractivity of oxygen for $CaO-SiO_2$, $SrO-SiO_2$ and $BaO-SiO_2$ glasses plotted as a function of 2x/(2 - x) based upon the mathematical model, Eq.(3). It can be seen that there are linear relations between R_o and 2x/(2 - x), and that the value of R_o at 2x/(2 - x) = 0, ie, x = 0 in each system equals 3.68 cm^3 which is a value for the ion refractivity of oxygen in SiO_2 glass. These indicate that the mathematical model is reasonable also in alkali earth silicate glasses.

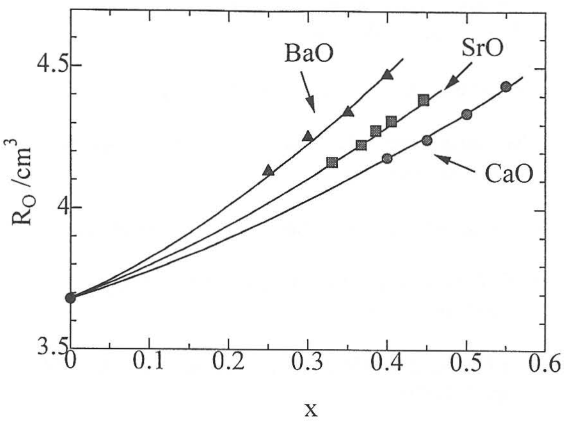


Fig.8 Ion refractivities(R_o) of oxygen in $CaO-SiO_2$, $SrO-SiO_2$ and $BaO-SiO_2$ glasses as a function of mole fractions(x) of alkali earth metal oxides.

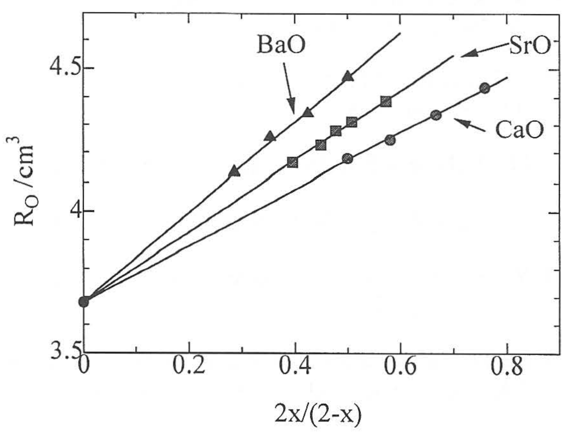


Fig.9 Ion refractivities(R_o) of oxygen in $CaO-SiO_2$, $SrO-SiO_2$ and $BaO-SiO_2$ glasses as a function of 2x/(2 - x), where x is the mole fraction of alkali earth metal oxides.

5.2 Effective basicity for oxides in SiO_2 glass

From the slope of the straight lines in Fig.9, values of ΔR_o are calculated as 0.99 for CaO, 1.24 for SrO and 1.58 for BaO. Values of ΔR_o for alkaline metal oxides have been determined in the previous report.[4] Table III summarises values of ΔR_o for both alkali earth metal oxides and alkaline metal oxides.

Table III Values of ΔR_o for alkali earth metal oxides and alkaline metal oxides

Oxide	CaO	SrO	BaO
ΔR_o / cm^3	0.99	1.24	1.58

Oxide	Li_2O	Na_2O	K_2O
ΔR_o / cm^3	0.69	1.19	1.63*

*The value of ΔR_o for K_2O was reported as 1.56 previously.[4] However, more reliable calculation has given a value of 1.63, using refractive indices recorded by Shmidt and Alekseeva[18] and densities recorded by Schroeder et al.[19]

The value of ΔR_o for these oxides means the increase of the ion refractivity of oxygen due to the presence of NBO ions, and furthermore, represents the degree of electronic polarisation of NBO ions bound to alkali earth or alkaline metal ions, as shown in Fig.1(b). Accordingly, NBO ions having larger values of ΔR_o have higher electron densities, resulting in larger electron donor power. Consequently, the value of ΔR_o means the effective basicity for oxides doped in SiO_2 glass, according to Lewis acid-base theory. It should be noted that the value of ΔR_o can be determined experimentally.

Furthermore, this consideration also agrees with the conventional concept of the basicity as follows: As the value of ΔR_o is larger, the bond between metal and NBO ions is more ionic, since the electron density is higher near NBO ions having larger values of ΔR_o. Thus, it can be considered that the value of ΔR_o is a measure of the bond ionicity, ie, the degree of ionic character in the bond between metal and NBO ions. On the other hand, it is generally said that oxides having higher bond ionicity are stronger bases. Consequently, the value of ΔR_o can be a measure of the effective basicity for oxides doped in SiO_2 glass.

It can be considered that the basicity measure using ΔR_o is more reliable, because values of ΔR_o have been determined experimentally, based upon Lewis acid-base theory which is a more generalised concept of the basicity. Using values of ΔR_o given in Table III, the strength of bases is in the hierarchy $K_2O > BaO > SrO > Na_2O > CaO > Li_2O$. Fig.10 compares the strength of bases determined from ΔR_o with that[1] from the optical basicity, for alkali earth and alkaline metal oxides.

Both basicity measures agree fairly well with each other, but the difference can be seen between Na_2O and SrO. It is noted that the basicity measure using ΔR_o can distinguish the differences in the basicity between Li_2O and CaO and between Na_2O and BaO. The determination of values of ΔR_o for various oxides would be very useful in science as well as in practice to gain a better understanding of the basicity for glasses and slags.

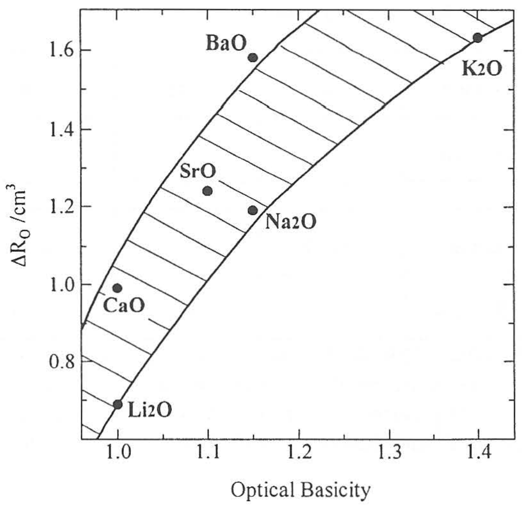


Fig.10 Comparison of the strength of bases using ΔR_o with that using the optical basicity.

6. CONCLUSIONS

The refractive indices and densities have been measured for $SrO-SiO_2$ glass and have been reviewed for $CaO-SiO_2$ and $BaO-SiO_2$ glasses. The ion refractivities(R_o) of oxygen in these glasses have been determined to discuss the reasonability of the mathematical model to predict values of R_o in binary alkali earth silicate glasses.

1. The ion refractivity of oxygen in binary alkali earth silicate glasses can be reasonably described by the mathematical model expressed by the following equation,

$$R_o = R_o^\circ + \Delta R_o \cdot 2x/(2 - x)$$

where R_o° and ΔR_o are the ion refractivity of oxygen in SiO_2 glass and the increase in the ion refractivity of oxygen due to the presence of non-bridging oxygen ions, respectively, and x is the mole fraction of alkali earth metal oxides.

2. The value of R_o expresses the basicity of the whole glass system. On the contrary, the value of ΔR_o means the effective basicity for oxides doped in SiO_2 glass, and those for alkali earth metal oxides have been determined as follows:

0.99(CaO), 1.24(SrO), 1.58(BaO) (in cm^3)

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