

# Optical Basicity and Refractivity of Germanate Glasses

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The acid–base properties of germanate glasses cannot presently be compared quantitatively with those of silicate, borate, and several other glasses because the optical basicity of the parent oxide,  $\Lambda(\text{GeO}_2)$ , has not yet been unequivocally established. The usual method of measuring optical basicity, relying on probe ions such as  $\text{Ti}^{4+}$  or  $\text{Pb}^{2+}$ , is prevented by the restricted ultraviolet transparency range of germanate glasses. An alternative method is used, based on refractivity data and the correlation between oxide polarizability and theoretical optical basicity known to operate in other glass systems. Data for alkali metal germanate systems (up to approximately 0.4 mole fraction alkali metal oxide) yield the value  $\Lambda(\text{GeO}_2) = 0.61$  and basicity moderating parameter for  $\text{Ge}^{4+}$ ,  $\gamma$ , of 1.64. These values are supported by calculations based on the far-infrared “rattling” frequencies,  $\nu_{\text{eff}}$ , of alkali metal ions in germanate glasses  $x\text{M}_2\text{O}-(1-x)\text{GeO}_2$ ,  $\text{M} = \text{K}, \text{Rb}$ . The latter approach has led to the establishment of a new optical basicity scale for the germanate glasses,  $\Lambda = (\nu_{\text{eff}}/\nu_0 + 1.94)/4.64$ ,  $\nu_0 = \nu_{\text{eff}}(x \rightarrow 0)$ . This new “far-infrared” basicity scale gives  $\Lambda(\text{GeO}_2) = 0.63$ .  $\text{GeO}_2$  therefore has a basicity which is close to that of  $\text{Al}_2\text{O}_3$  ( $\Lambda = 0.60$ ) but greater than of  $\text{SiO}_2$  (0.48). The previously established data concerning the ratio of 6-fold coordinated germanium in the  $\text{K}_2\text{O}-\text{GeO}_2$  system allows calculation of  $\gamma = 2.5 (\pm 0.5)$  for 6-fold coordinated  $\text{Ge}^{4+}$ .

## 1. Introduction

Germanate glasses have attracted much interest in recent years especially because of their technological applications, for example, in optical fibers and nonlinear optical devices. Of particular importance is the property that germanate–silicate glasses have in undergoing permanent changes in refractive index when exposed to intense ultraviolet radiation, and this has been used to create Bragg gratings within optical fibers and waveguides.<sup>1–4</sup> Effects of this type are obviously related to changes in refractivity of the glass, and therefore demand investigation into such factors as polarization and polarizability that are associated with  $\text{GeO}_2$ -based glasses.

In any oxide glass, oxygen is present in the oxidation state of  $-2$ . The oxide ion,  $\text{O}^{2-}$ , is fundamentally unstable, and it is impossible to attribute a single value for its electronic polarizability,  $\alpha_{\text{O}^{2-}}$ . This is unlike the situation for stable anions, such as  $\text{Cl}^-$  or  $\text{Br}^-$ , where their polarizability values show good consistency when considering the refractivity data for metal chlorides, bromides, etc. The charge on oxygen varies according to the bonding, and it decreases on proceeding from what might be described as an “ionic” situation, e.g., in  $\text{CaO}$ , to a more covalent one such as the bonding in  $\text{SiO}_2$ . It appears that this decrease in charge is accompanied by a decrease in  $\alpha_{\text{O}^{2-}}$ , complying with Weyl and Marboe’s description of a “tightening” of the electronic charge cloud.<sup>5</sup> The extent of negative charge borne by oxide(–II) can be expressed by using the optical basicity model,<sup>6–8</sup> which allows for a simple quantitative relationship between the optical basicity value  $\Lambda$  of an oxidic

medium and the oxide(–II) polarizability.<sup>9–11</sup> The optical basicity has been proved also to be a useful parameter for correlating and predicting properties of oxidic systems covering a broad range of applications, e.g., from the performance of metallurgical slags in blast furnaces<sup>12,13</sup> to the control of redox reactions in melts, such as the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  equilibrium.<sup>14–16</sup>

The original method for measuring the optical basicity of oxidic systems was based on the use of  $d^{10}s^2$  ions, such as  $\text{Ti}^{4+}$  and  $\text{Pb}^{2+}$ , dissolved in the glass.<sup>6</sup> These ions are sensitive to the charge on the oxygen atoms and respond to any variation of this, effected by, e.g., a compositional change, through frequency shifts of their characteristic  $^1\text{S}_0 \rightarrow ^3\text{P}_1$  ultraviolet absorption band. Unfortunately, many oxidic systems, including the technologically important germanate glasses, have insufficient transparency in the ultraviolet (UV) region and, therefore, such optical transmission measurements cannot be made. To overcome the difficulty of poor UV transparency, alternative methods have been developed for the measurement of optical basicity. The present situation regarding the optical basicity of germanium oxide,  $\Lambda(\text{GeO}_2)$ , can be summarized as follows.

Nakamura et al.<sup>17</sup> employed the photoacoustic spectroscopic technique to measure the ultraviolet response of highly UV absorbing oxidic systems doped with  $\text{Pb}^{2+}$  probe ions and obtained a value of 0.57 for  $\Lambda(\text{GeO}_2)$ . Todoroki et al.<sup>18</sup> discussed the local structure around  $\text{Eu}^{3+}$  ions in several oxide glasses in terms of the electron donor power of nonbridging oxygen atoms. This was correlated with the microscopic changes in optical basicity occurring with increasing alkali metal oxide content, and a value of 0.42 was obtained for the optical basicity of the unmodified  $\text{GeO}_2$  glass. Dimitrov and Sakka<sup>19</sup> and subsequently

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Dimitrov and Komatsu<sup>20</sup> have established correlations between the electronic polarizability of oxide ion,  $\alpha_{O^{2-}}$ , and the linear refractive index,  $n$ , as well as the energy gap,  $E_g$ , in numerous single and binary oxide systems. These correlations were employed to calculate optical basicity values  $\Lambda(n)$  and  $\Lambda(E_g)$ , respectively, for other oxide systems, and while for most oxides the optical basicity values derived by such correlations are in close agreement, a quite large deviation was found for  $\text{GeO}_2$  with  $\Lambda(n) = 0.70$  and  $\Lambda(E_g) = 0.94$ .<sup>19</sup> Miura and Nanba<sup>21</sup> employed the O 1s chemical shift in the X-ray photoelectron spectra (XPS) of binary alkali metal silicate, borate, germanate, phosphate, tellurite, and bismuthate glasses to propose a new basicity scale of oxide glasses. From their data, the values  $\Lambda(\text{GeO}_2) = 0.45$  and  $0.51$  can be obtained depending on whether the electronegativity of germanium atom is optimized for the charge on the oxygen or for the glass basicity.<sup>21</sup> Leboutellier and Courtine<sup>22</sup> reported correlations between the optical basicity of simple oxides and the corresponding ionic-covalent parameter (ICP) used to quantify the metal-oxygen bonding in oxides exhibiting mixed ionic-covalent character. It is of interest to note that different ICP values were reported for  $\text{Ge}^{4+}$  in 4- and 6-fold coordination with oxygen atoms, giving  $\Lambda(\text{GeO}_2) = 0.60$  for tetrahedral coordination and  $0.82$  for the octahedral coordination.<sup>22</sup> Recently, Reddy and co-workers<sup>23</sup> extended the approach of Dimitrov et al.<sup>19,20</sup> by introducing an average electronegativity of the oxidic system,  $\chi_{av}$ , and showed that correlations based on  $\chi_{av}$  and  $E_g$  lead to similar optical basicity values for germanium oxide:  $\Lambda(\chi_{av}) = 0.90$  and  $\Lambda(E_g) = 0.96$ .

The reported data for germanium oxide were obtained using different methods and demonstrate an excessively broad range of basicity values. The lower value of basicity ( $0.42$ ) suggests that  $\text{GeO}_2$  is equally acidic with the typical glass former  $\text{B}_2\text{O}_3$ , while the highest value reported ( $0.96$ ) reflects a strongly basic oxide, slightly less basic than the typical glass modifier  $\text{CaO}$  with  $\Lambda(\text{CaO}) = 1$ .<sup>6-8</sup> Since the known chemistry of germanium oxide does not reflect such a wide a range of acid-base properties, it is evident that a careful reassessment of its optical basicity is required. In addressing this problem, the present work employs alternative methods using refractivity, spectroscopic, and structural data for various alkali metal germanate glasses.

## 2. Optical Basicity of Germanium Oxide

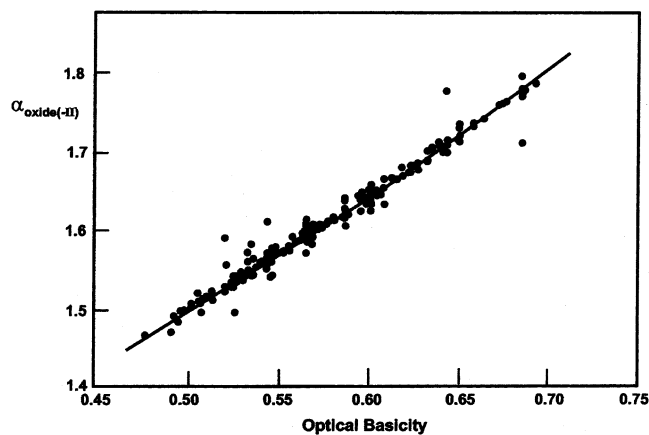
**2.1. Oxide Refractivity and Basicity.** The molar electronic polarizability of a compound,  $\alpha_m$ , can be calculated from experimental refractivity measurements using the Lorentz-Lorentz relationship<sup>9-11,19,20</sup>

$$\alpha_m = \frac{3V_m n^2 - 1}{4\pi N n^2 + 2} \quad (1)$$

where  $n$  is the linear refractive index,  $V_m$  is the molar volume (molecular weight divided by density), and  $N$  is Avogadro's number. As shown in previous studies,<sup>9-11</sup> there is an intimate relationship between the average (or theoretical) optical basicity,  $\Lambda$ , and the average oxygen polarizability,  $\alpha_{O^{2-}}$ , in single and binary oxide systems. This relationship has been refined recently in order to extend it to oxidic glass systems.<sup>24</sup> For the optical basicity range of approximately  $0.35$ – $0.75$  (which includes the oxides  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$ ),  $\Lambda$  for a glass or an oxide is given by

$$\Lambda = \frac{(3.133\alpha_{O^{2-}} - 2.868)^{1/2}}{1.567} - 0.362 \quad (2)$$

where  $\alpha_{O^{2-}}$  is calculated from the molar electronic polarizability



**Figure 1.** Plot of oxide polarizability,  $\alpha_{O^{2-}}$  (in  $\text{\AA}^3$ ), versus optical basicity for silicate glasses in the systems  $\text{Li}_2\text{O-SiO}_2$ ,  $\text{Na}_2\text{O-SiO}_2$ ,  $\text{K}_2\text{O-SiO}_2$ ,  $\text{CaO-SiO}_2$ , and  $\text{Na}_2\text{O-CaO-SiO}_2$ , showing proximity of data points to eq 2.

(calculated from eq 1) by subtracting the total cation polarizability. Figure 1 shows that eq 2, established originally for glasses in the binary system  $\text{CaO-SiO}_2$ ,<sup>24</sup> describes well the relationship between  $\alpha_{O^{2-}}$  and  $\Lambda$  for silicate glasses in the systems  $\text{Li}_2\text{O-SiO}_2$ ,  $\text{Na}_2\text{O-SiO}_2$ ,  $\text{K}_2\text{O-SiO}_2$ ,  $\text{CaO-SiO}_2$ , and  $\text{Na}_2\text{O-CaO-SiO}_2$ .

Table 1 compares refractivity data for  $\text{GeO}_2$  in the glassy<sup>25-28</sup> and crystalline forms, i.e., quartz<sup>25,29</sup> and rutile.<sup>30</sup> The molar polarizability of the three  $\text{GeO}_2$  polymorphs is calculated through eq 1 and is used to obtain  $\alpha_{O^{2-}}$  by subtracting the germanium polarizability,  $\alpha_{\text{Ge}^{4+}} = 0.60 \text{ \AA}^3$  (see Appendix). These values of  $\alpha_{O^{2-}}$  are substituted in eq 2, yielding  $\Lambda(\text{GeO}_2)$  values of  $0.61$  for the glassy state and  $0.54$  (average) for the quartz crystal structure. For the rutile structure,  $\Lambda(\text{GeO}_2)$  has the much lower value of  $0.42$ , suggesting that structural and bonding details affect the basicity of germanium oxide. Table 1 also includes values obtained for the basicity moderating parameter of the  $\text{Ge}^{4+}$  ion,  $\gamma_{\text{Ge}}$  (see below).

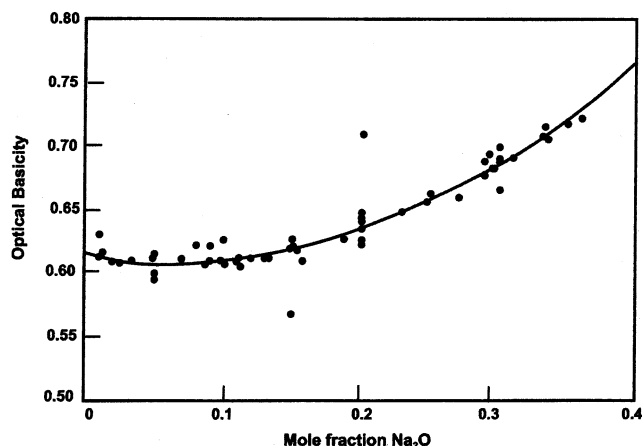
**2.2. Alkali Metal Germanate Glasses.** With the indication that  $\Lambda(\text{GeO}_2)$  lies between  $0.54$  and  $0.61$ , we next examine refractivity data for alkali metal germanate glass. SciGlass software<sup>31</sup> provides data for the following systems  $\text{Li}_2\text{O-GeO}_2$  (15 points),  $\text{Na}_2\text{O-GeO}_2$  (64 points), and  $\text{K}_2\text{O-GeO}_2$  (47 points). A smaller number of data were available for the systems  $\text{Rb}_2\text{O-GeO}_2$  (12 points) and  $\text{Cs}_2\text{O-GeO}_2$  (8 points). The molar polarizability of each glass was calculated through eq 1 and was used to obtain  $\alpha_{O^{2-}}$  by subtracting the polarizability of germanium ( $\alpha_{\text{Ge}^{4+}} = 0.60 \text{ \AA}^3$ ) and the alkali metal ( $\alpha_{\text{Li}^+} = 0.029 \text{ \AA}^3$ ,  $\alpha_{\text{Na}^+} = 0.179 \text{ \AA}^3$ ,  $\alpha_{\text{K}^+} = 0.83 \text{ \AA}^3$ ,  $\alpha_{\text{Rb}^+} = 1.40 \text{ \AA}^3$ ,  $\alpha_{\text{Cs}^+} = 2.42 \text{ \AA}^3$ ). These values of  $\alpha_{O^{2-}}$  then provided, by eq 2, the optical basicity value,  $\Lambda$ , for each glass. Plotted versus molar fraction of alkali metal oxide, nearly all the data points, for each of the five systems, fitted closely to a quadratic equation:  $\Lambda = ax^2 + bx + c$ . For example, the  $\text{Na}_2\text{O-GeO}_2$  system had  $a = 1.32$ ,  $b = -0.146$ , and the intercept on the ordinate  $c = 0.611$  (see Figure 2).

Since the intercept corresponds to zero alkali metal oxide content, it represents the optical basicity value for  $\text{GeO}_2$ . For the  $\text{Li}_2\text{O-GeO}_2$  system  $c = 0.611$  and for  $\text{K}_2\text{O-GeO}_2$   $c = 0.605$ , and with  $c = 0.611$  for the sodium system,  $\Lambda(\text{GeO}_2)$  can be taken as  $0.61$ . This is in excellent agreement with that found for glassy  $\text{GeO}_2$  in the previous section (Table 1). (For the rubidium and cesium systems, values of  $0.59$  and  $0.62$ , respectively, were obtained, but in view of the restricted data these are less precise.) It should be noted that this value places

**TABLE 1: Refractive Index ( $n$ ), Density ( $d$ ), Molar Polarizability ( $\alpha_m$ ), Oxygen Polarizability ( $\alpha_{O^{2-}}$ ), and Optical Basicity ( $\Lambda$ ) for GeO<sub>2</sub> Polymorphs and Basicity Moderating Parameter for Ge<sup>4+</sup>,  $\gamma_{Ge}$** 

structure	ref	$n$	$d$ (g/cm <sup>3</sup> )	$\alpha_m$ (Å <sup>3</sup> )	$\alpha_{O^{2-}}$ (Å <sup>3</sup> )	$\Lambda$	$\gamma_{Ge}$
glass	25	1.608	3.665	3.914	1.657	0.61	1.64
	26, 27	1.607	3.656	3.918	1.659	0.61	1.64
	28	1.607	3.680	3.892	1.646	0.60	1.66
quartz	25	1.713	4.225	3.849	1.624	0.59	1.70
	29	1.650	4.228	3.578	1.489	0.49	2.03
rutile	30	2.04	6.26	3.40	1.40	0.42	2.37

<sup>a</sup> Based on  $\alpha_{Ge^{4+}} = 0.60$  Å<sup>3</sup> (see Appendix).

**Figure 2.** Plot of optical basicity,  $\Lambda$  (obtained from refractivity data), versus mole fraction,  $x$ , of Na<sub>2</sub>O for the Na<sub>2</sub>O–GeO<sub>2</sub> glass system.

the basicity of GeO<sub>2</sub> at a higher value than that of silica ( $\Lambda(\text{SiO}_2) = 0.48$ ) and almost equal to that of Al<sub>2</sub>O<sub>3</sub> (0.60).

**2.3. Far-infrared Spectra and Optical Basicity.** The above treatment, whereby optical basicity is obtained from refractivity data, is compared now with an alternative method based on far-infrared spectroscopy. This measures the “rattling” frequency of the constituent metal ions in their oxidic sites, which has previously been found to vary linearly with optical basicity.<sup>32,33</sup> The relationship is not straightforward, however, because the “microscopic” optical basicity of the site occupied by a metal ion might differ from the overall or average optical basicity of the glass. In the alkali metal borate glasses, for example, there are two distinctly different sites for the alkali metal ions, one of higher optical basicity and one of lower,<sup>32,33</sup> compared with the average (theoretical) optical basicity,  $\Lambda$ , calculated from composition (see below). For these glass systems it is necessary to obtain an “effective” far-infrared frequency,  $\nu_{\text{eff}}$ , corresponding to an average metal ion site, which takes into account the distribution of the alkali metal ions in the two sites. This is done by using weighting factors,  $f_H$  for metal ions in the sites of higher frequency and  $f_L$  for those in the sites of lower frequency, and the two infrared frequencies, ( $\nu_H$ ,  $\nu_L$ ) associated with these sites.<sup>32,33</sup> The  $\nu_{\text{eff}}$  frequency is given by

$$\nu_{\text{eff}} = (f_H \nu_H^2 + f_L \nu_L^2)^{1/2} \quad (3)$$

where  $f_H$  and  $f_L$  are calculated from the expression  $f_{H(L)} = A_{H(L)} / (A_H + A_L)$ , with  $A_H$  and  $A_L$  being the integrated intensities of the two far-infrared component bands.

By plotting frequency  $\nu_{\text{eff}}$  against alkali metal oxide content for each of the five alkali metal glasses (from Li to Cs), it is possible to obtain, by extrapolation to zero alkali metal content, the characteristic frequency of cation site vibration at infinite dilution of the metal ions in the borate glass matrix,  $\nu_0$ . The numerical value of  $\nu_0$  can be used for dividing  $\nu_{\text{eff}}$  so as to obtain a reduced frequency,  $\nu_{\text{red}}$ , which has general applicability to all

five alkali metal borate glass systems irrespective of which alkali metal ion is present ( $\nu_{\text{eff}}/\nu_0 = \nu_{\text{red}}$ ). The plot of this reduced frequency,  $\nu_{\text{red}}$ , against the average basicity,  $\Lambda$ , for the alkali metal borate glass systems has been shown<sup>33</sup> to correspond to the linear relationship

$$\nu_{\text{red}} = -0.52 + 3.47\Lambda \quad (4)$$

It is emphasized that this relationship holds for all five alkali metal borate systems, regardless of the different size or polarizing power of the metal ion. Relationships similar to eq 4 have also been found to operate for silver and barium borate<sup>34,35</sup> glass systems.

If it is assumed that the linearity of eq 4 extends over the whole compositional range, then it is possible to obtain values of  $\nu_{\text{red}}$  and hence  $\nu_{\text{eff}}$  since  $\nu_{\text{eff}} = \nu_{\text{red}}\nu_0$ , which correspond to hypothetical glasses composed entirely of the alkali metal oxide, simply by substituting the optical basicity value of the alkali metal oxide into eq 4. For example, with  $\Lambda(\text{K}_2\text{O}) = 1.4$  and  $\nu_0 = 103$  cm<sup>−1</sup> (obtained by extrapolating data in ref 33 to zero K<sub>2</sub>O, see above), “glassy” potassium oxide has  $\nu_{\text{eff}} = 447$  cm<sup>−1</sup>. Similarly, for Rb<sub>2</sub>O,  $\Lambda = 1.55$  and  $\nu_0$  is found to be 80 cm<sup>−1</sup>, yielding a value of  $\nu_{\text{eff}} = 389$  cm<sup>−1</sup> for “glassy” rubidium oxide.

Such data for “glassy” alkali metal oxides, based on the systematic study of borate glasses, can be transferred to other alkali metal glass systems, here the potassium and rubidium germanate systems for which far-infrared spectra have previously been measured and analyzed.<sup>36,37</sup> For these glasses, the effective metal ion site vibration frequencies,  $\nu_{\text{eff}}$ , were obtained and are found to vary linearly with metal oxide content (see Figure 3), giving  $\nu_0 = 98$  cm<sup>−1</sup> for potassium and  $\nu_0 = 74$  cm<sup>−1</sup> for rubidium ions in the germanate matrix. If it is assumed for the alkali metal germanate glasses that a relationship similar to eq 4 applies, then

$$\nu_{\text{red}} = (\nu_{\text{eff}}/\nu_0) = A + B\Lambda \quad (5)$$

Applying eq 5 to the extreme situation of “glassy” K<sub>2</sub>O and “glassy” Rb<sub>2</sub>O yields

$$447/98 = A + 1.4B \quad (6a)$$

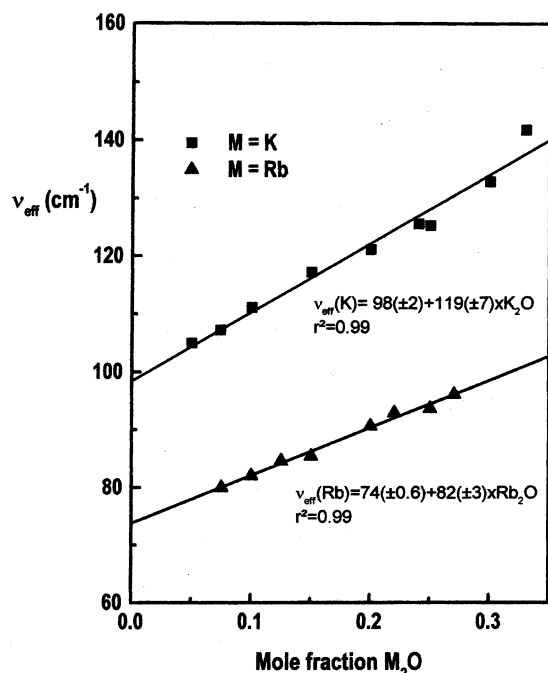
$$389/74 = A + 1.55B \quad (6b)$$

from which  $A = -1.94$  and  $B = 4.64$ . Thus, for alkali metal germanate glasses we derive the following equation relating the far-infrared response of metal ions with the basicity of the hosting glass:

$$\nu_{\text{red}} = \nu_{\text{eff}}/\nu_0 = -1.94 + 4.64\Lambda \quad (7)$$

At the infinite dilution of metal ions in the germanate glass matrix, i.e., for GeO<sub>2</sub> glass, it holds by definition that  $\nu_{\text{eff}} = \nu_0$ , and thus, it follows directly from eq 7 that  $\Lambda(\text{GeO}_2) = 0.63$ . This is acceptably close to the value of 0.61 obtained in the previous section from the refractivity of GeO<sub>2</sub> glass. Therefore,





**Figure 3.** Relationship between the effective metal ion site vibration frequency,  $\nu_{\text{eff}}$ , and the alkali metal oxide content,  $x\text{M}_2\text{O}$ , in K and Rb germanate glasses  $x\text{M}_2\text{O}-(1-x)\text{GeO}_2$  ( $\text{M} = \text{K}, \text{Rb}$ ). Data for  $\nu_{\text{eff}}$  are obtained from far-infrared spectra measured and analyzed in previous works.<sup>36,37</sup> Lines are least-squares fits to the data.

two independent methods give practically the same optical basicity value for glassy  $\text{GeO}_2$ . Equation 7 can be rearranged to give

$$\Lambda = \frac{1}{4.64} \left( \frac{\nu_{\text{eff}}}{\nu_0} + 1.94 \right) \quad (8)$$

thereby indicating the facility for obtaining the optical basicity of germanate glasses from infrared spectroscopy.

It is worth pointing out, in general, that a significant difference between this infrared method and the UV method using  $\text{Ti}^{4+}$ ,  $\text{Pb}^{2+}$  probe ions<sup>6–8</sup> is that, by making measurements of the metal ion site vibration, there is no possibility of the oxidic medium undergoing a structural modification as a result of probe ion inclusion. The two methods are complimentary: the infrared method yielding the basicity of the sites of constituent metal ions and the UV method indicating the basicity the oxidic medium offers when hosting solute metal ions. It has been observed that usually the results from the two methods are similar.<sup>32–34</sup>

**2.4. Coordination Number of Germanium.** In the alkali metal germanate glasses considered above,  $\text{Ge}^{4+}$  is almost entirely 4-fold coordinated for low alkali metal contents. The extrapolation to zero alkali metal content, yielding  $\Lambda(\text{GeO}_2) = 0.61$ , is therefore for the condition that germanium exercises a coordination number of 4. However, it is known that the coordination number can change to 6 depending on the content of modifier oxide.<sup>26–28</sup> The question arises of whether this stereochemical change is accompanied by a change in the effective value of  $\Lambda(\text{GeO}_2)$ . The trend in  $\Lambda$  for the  $\text{Na}_2\text{O}-\text{GeO}_2$  glasses in Figure 2 would indicate that this is so because there is almost no increase in  $\Lambda$  with initial concentrations of  $\text{Na}_2\text{O}$  (up to approximately 15%  $\text{Na}_2\text{O}$ ). This suggests that on changing from 4-fold to 6-fold coordination a smaller value for the effective optical basicity of  $\text{GeO}_2$  results.

This problem is simplified by considering, first of all, not the optical basicity of  $\text{GeO}_2$  but rather the basicity moderating

parameter,  $\gamma$ , of the  $\text{Ge}^{4+}$  ion. It has been described several times how the optical basicity of a glass can be calculated from composition using the formula<sup>8,11,24</sup>

$$\Lambda = \frac{X(\text{AO}_{a/2})}{\gamma_A} + \frac{X(\text{BO}_{b/2})}{\gamma_B} + \dots \quad (9)$$

where  $X(\text{AO}_{a/2})$ ,  $X(\text{BO}_{b/2})$ , ... are the proportions of oxygen contributed by each of the oxides  $\text{AO}_{a/2}$ ,  $\text{BO}_{b/2}$ , ..., that is, their equivalent fractions. It follows from eq 9 that for a single oxide,  $\text{AO}_{a/2}$ , its optical basicity,  $\Lambda(\text{AO}_{a/2})$ , is simply  $1/\gamma_A$ , and that eq 9 can be expressed as

$$\Lambda = X(\text{AO}_{a/2}) \Lambda(\text{AO}_{a/2}) + X(\text{BO}_{b/2}) \Lambda(\text{BO}_{b/2}) + \dots \quad (10)$$

With  $\Lambda(\text{GeO}_2) = 0.61$ , it is apparent that the basicity moderating parameter of 4-fold coordinated  $\text{Ge}^{4+}$ ,  $\gamma_{\text{Ge}(4)}$ , can be taken as 1.64.

We now use the trends in optical basicity, e.g., as in Figure 2, to track changes in  $\gamma_{\text{Ge}}$  as a function of alkali metal oxide content. This is done by adapting eq 9 for binary alkali metal germanate glasses,  $x\text{M}_2\text{O}-(1-x)\text{GeO}_2$ . In going from equivalent fractions to mole fractions ( $X(\text{M}_2\text{O}) = x/(2-x)$  and  $X(\text{GeO}_2) = 2(1-x)/(2-x)$ ), eq 9 can be arranged to give

$$\gamma_{\text{Ge}} = \frac{2(1-x)}{\Lambda(2-x) - x/\gamma_M} \quad (11)$$

Calculations were made for lithium, sodium, and potassium germanate systems (the  $\gamma_M$  values used were those appropriate for optical basicity work relevant to refractivity data, namely,  $\gamma_{\text{Li}} = 1.23$ ,  $\gamma_{\text{Na}} = 0.905$ , and  $\gamma_{\text{K}} = 0.76$ ; the slight difference from original values has previously been discussed in ref 24). The values of  $\gamma_{\text{Ge}}$  so obtained were plotted against mole fraction of alkali metal oxide, as shown in Figure 4a for the  $\text{K}_2\text{O}-\text{GeO}_2$  system.

For the three systems it was apparent that for zero alkali metal oxide content  $\gamma_{\text{Ge}}$  was equal to 1.64, agreeing with the value of 0.61 found above for  $\Lambda(\text{GeO}_2)$ . (The  $\text{K}_2\text{O}-\text{GeO}_2$  system differs very slightly, see above.) With increasing alkali metal oxide content the trend in (effective)  $\gamma_{\text{Ge}}$  suggests that 6-fold coordinated germanium has a basicity moderating parameter that is significantly greater than that for 4-fold. This is strongly supported by the observation that the maximum in  $\gamma_{\text{Ge}}$  (Figure 4a) occurs at the same alkali metal oxide content as previously found for the maximum for 6-fold coordinated germanium, Figure 4b.<sup>38</sup>

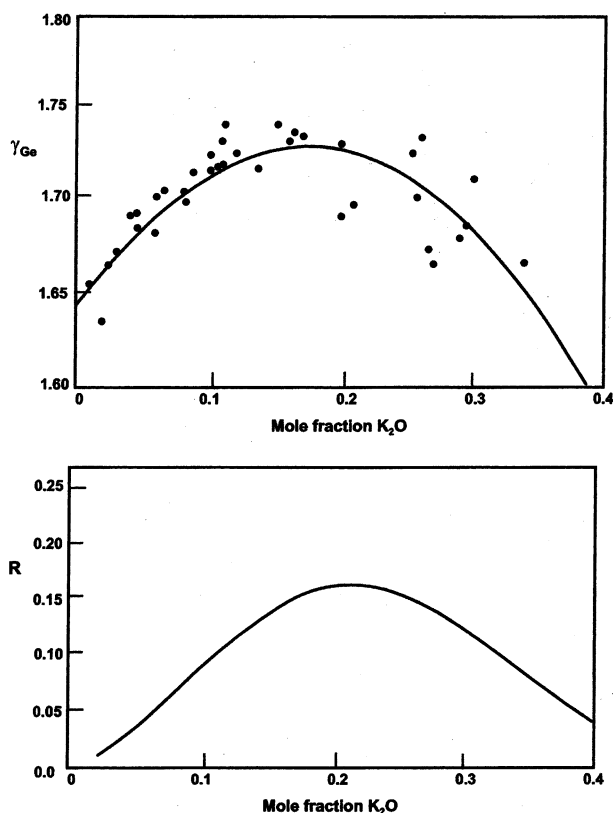
It is possible to use the data contained in Figure 4 to obtain  $\gamma_{\text{Ge}}$  for 6-fold coordinated germanium. If the basicity moderating parameters for the two coordinations are denoted as  $\gamma_{\text{Ge}(4)}$  and  $\gamma_{\text{Ge}(6)}$ , then eq 11 can be expressed as

$$\Lambda = \frac{x}{(2-x)\gamma_K} + \frac{2(1-x)}{(2-x)\gamma_{\text{Ge}(4)}}(1-R) + \frac{2(1-x)}{(2-x)\gamma_{\text{Ge}(6)}}R \quad (12)$$

where  $R$  is the fraction of 6-fold germanium in the glass; that is,  $R = (\text{6-fold Ge})/(\text{total Ge})$ . On rearrangement, this gives

$$\gamma_{\text{Ge}(6)} = \frac{2(1-x)R}{\Lambda(2-x) - (x/\gamma_K) - [2(1-x)(1-R)/\gamma_{\text{Ge}(4)}]} \quad (13)$$

Here,  $\Lambda$  has already been obtained for each potassium germanate glass (by eq 2),  $\gamma_{\text{Ge}(4)}$  has been determined as 1.64 (see above),



**Figure 4.** (a, top) Plot of effective  $\gamma_{\text{Ge}}$  (from substitution in eq 11) versus mole fraction,  $x$ , of  $\text{K}_2\text{O}$  for the  $\text{K}_2\text{O}$ – $\text{GeO}_2$  glass system and (b, bottom) trend in the fraction of 6-fold coordinated germanium,  $R$ , with  $\text{K}_2\text{O}$  content for the same glass system.

and  $R$  is known from previous work<sup>38</sup> for values of  $x$  up to approximately 0.4. Using eq 13, values of  $\gamma_{\text{Ge}(6)}$  were calculated for glasses containing 20% and more  $\text{K}_2\text{O}$ . Glasses containing less than 20%  $\text{K}_2\text{O}$  were excluded owing to error magnification which could result from very small denominators in eq 13. The results, Table 2, are plotted in Figure 5, and it is clear that, apart from two disparate points, a value for  $\gamma_{\text{Ge}(6)}$  of  $2.5 (\pm 0.5)$  is indicated, which is in good agreement with the  $\gamma$  value found for germanium in the rutile form of  $\text{GeO}_2$  (Table 1). The lack of precision partly arises, probably, owing to the relatively small presence of 6-fold coordinated germanium in the glasses ( $R$  is never greater than 0.16). Nevertheless, the results do indicate that there is a very significant increase in the polarizing power of germanium when it changes from 4-fold to 6-fold coordination. A similar effect has been found for boron when its coordination number changes from 3 to 4.<sup>24</sup>

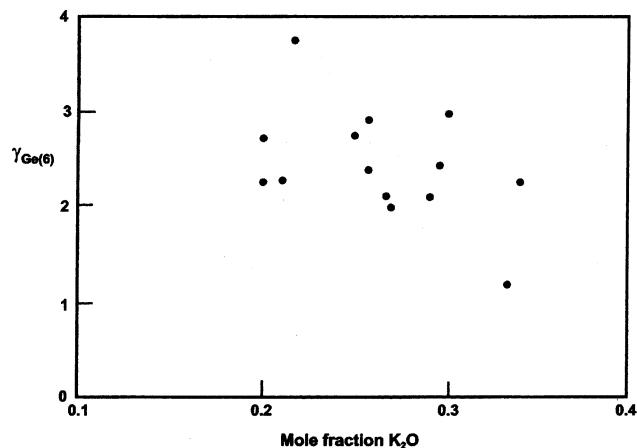
### 3. Concluding Remarks

We have presented here alternative methods for obtaining the optical basicity of germanium oxide,  $\Lambda(\text{GeO}_2)$ , for which the values reported cover a broad range of basicity extending from the very acidic to the quite basic part of the scale. These methods have been applied to alkali metal germanate glasses for which refractivity, density, spectroscopic, and structural data are available. The first method exploits refractivity data and the previously established correlation between oxide polarizability and optical basicity in oxidic systems,<sup>24</sup> and yields an optical basicity value of 0.61 for  $\text{GeO}_2$ , and a basicity moderating parameter of 1.64, operational for 4-fold coordinated germanium in germanate glass systems. These values are compared in Table 1 with those obtained for crystalline  $\text{GeO}_2$  in the quartz and rutile structures.

**TABLE 2: Basicity Moderating Parameter,  $\gamma_{\text{Ge}(6)}$ , of 6-fold Coordinated Germanium in  $x\text{K}_2\text{O}-(1-x)\text{GeO}_2$  Glasses**

$x\text{K}_2\text{O}$	$R^a$	$\gamma_{\text{Ge}}(\text{effective})$	$\gamma_{\text{Ge}(6)}$
0.20	0.16	1.73	2.7
0.20	0.16	1.69	2.3
0.21	0.16	1.70	2.3
0.25	0.15	1.73	2.7
0.257	0.15	1.70	2.4
0.267	0.15	1.67	2.1
0.27	0.15	1.67	2.0
0.295	0.12	1.68	2.1
0.30	0.12	1.71	2.9
0.34	0.10	1.67	2.3

<sup>a</sup> Fraction of Ge with 6-fold coordination.



**Figure 5.** Values of basicity moderating parameter for 6-fold coordinated germanium,  $\gamma_{\text{Ge}(6)}$ , for different compositions in the  $\text{K}_2\text{O}$ – $\text{GeO}_2$  glass system.

The second method relies on experimental measurements of the far-infrared “rattling” frequencies of alkali metal ions in the glasses and leads to a new optical basicity scale for the UV-opaque germanate glasses, eq 8. This scale gives for the basicity of  $\text{GeO}_2$  glass the value  $\Lambda(\text{GeO}_2) = 0.63$ , in good agreement with the results of the first method.

Trends for the alkali metal germanate glasses, obtained from refractivity data, show a much smaller increase in optical basicity than expected for the above value for  $\Lambda(\text{GeO}_2)$ . Examination of the  $\text{K}_2\text{O}$ – $\text{GeO}_2$  system, together with quantitative data for the fraction of Ge in 6-fold coordination, indicates that the trend in  $\Lambda$  is owing to the larger basicity moderating parameter of  $2.5 (\pm 0.5)$  for 6-fold coordinated Ge. This agrees well with the value obtained for the rutile form of  $\text{GeO}_2$  in which all the germanium has 6-fold coordination (Table 1).

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### Appendix

Although for most purposes, Pauling polarizability values are satisfactory, they are somewhat unreliable for certain covalent compounds such as the halides of cations in oxidation states +4 or higher. For these compounds, polarizability additivity operates better using values by Tessman et al.<sup>39</sup> Refractivity data for  $\text{GeCl}_4$  and  $\text{GeBr}_4$  ( $d = 1.8443 \text{ g/cm}^3$ ,  $n = 1.464$ ;  $d = 3.132 \text{ g/cm}^3$ ,  $n = 1.6269$ , respectively, ref 29), and Tessman polarizabilities of 2.96 and  $4.16 \text{ \AA}^3$  for chloride and bromide yield Tessman-type values for  $\alpha_{\text{Ge}^{4+}}$  of 0.86 and  $0.94 \text{ \AA}^3$ , respectively. Because correlations developed in previous studies

have been based on Pauling polarizabilities, for reasons described elsewhere<sup>9–13,24</sup> it is necessary to convert these polarizabilities (or rather, the average  $0.90 \text{ \AA}^3$ ) into a Pauling-type value. This was achieved using the conversion factor in the relationship  $\alpha_{\text{(Pauling)}} = 0.67\alpha_{\text{(Tessman)}}$ , which is obtained by making the plot (not shown here) of Pauling's polarizability,  $\alpha_{\text{(Pauling)}}$  against Tessman's,  $\alpha_{\text{(Tessman)}}$ , for those ions for which both values have been assigned.<sup>39</sup> This process yields  $0.60 \text{ \AA}^3$  for  $\alpha_{\text{Ge}^{4+}}$ .

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