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Refractive index and density of Li-, Na- and K-germanosilicate glasses

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Refractive index and density measurements in the ternary systems $Li_2O–SiO_2–GeO_2$, $Na_2O–SiO_2–GeO_2$ and $K_2O–SiO_2–GeO_2$ are given. Molar refraction data are correlated to the structure of these glasses. In the $Li_2O–SiO_2–GeO_2$ system, phase separation occurs which can be suppressed by rapid cooling. In the systems $Na_2O–SiO_2–GeO_2$ and $K_2O–SiO_2–GeO_2$ no such phase separation is observed; in these systems the molar refraction data indicate that, contrary to the $Li_2O–SiO_2–GeO_2$ system, the four-six co-ordination change of Ge^{4+} is not affected by the presence of SiO_2 as second network former.

1. Introduction

Glasses in the binary systems $Li_2O–GeO_2$, $Na_2O–GeO_2$ and $K_2O–GeO_2$ show optical properties which deviate markedly from those of the binary alkali silicate glasses [1]. The silicate glasses have a refractive index which is a monotonically increasing function of alkali content, whereas in the germanate glasses the refractive index shows a maximum as a function of the alkali content. This maximum has been explained in terms of a change in the co-ordination number of germanium by oxygen [2, 3]. There is also a considerable difference in refractive index of Li-, Na- and K-germanate glasses, which have the same molar alkali content. This difference is also observed in the more stable ternary alkali oxide–germania–silica glasses. The application of these glasses for fibres for optical communication is studied [4]. In the fibres the fibre core is based on a sodium germanosilicate glass which has a higher refractive index than the fibre cladding which is based on a potassium germanosilicate glass. In the fibres, an optimum refractive index profile can be obtained by allowing the Na^+ and the K^+ ions to exchange partly during the fibre-drawing process.

2. Experimental

2.1. Sample preparation

The glasses were prepared from:

Li_2CO_3 † (>99.0%)

Na_2CO_3 † (reagent grade dried for 20 h at 300° C)

K_2CO_3 † (reagent grade dried for 20 h at 300° C)

SiO_2 ‡ (α-quartz)

GeO_2 § (extra pure).

The compositions are: $x\ A_2O\ (1-x)\ \{(1-y)\ SiO_2, yGeO_2\}$ in which $x = 0.111, 0.2, 0.333$, and 0.5 corresponding to $A_2O/(Si, Ge)O_2 = 1/8, 1/4, 1/2, 1$ and $y = 0.0, 0.2, 0.4, 0.6, 0.8, 1$. A = Li, Na or K. Li glasses with $x = 0.5$ and the Na glass with $x = 0.5$ and $y = 1$ could not be prepared because of crystallization. The glasses were prepared by mixing the components followed by

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TABLE I Conditions of preparation for alkali germanosilicate glasses: $x\mathrm{A_2O}(1-x)\{(1-y)\,\mathrm{SiO_2}, y\mathrm{GeO_2}\}$

A	x	y	Melting temperature (°C)	Quench* conditions	Crucible material
Li	0.111	0–0.4	1600	w	Pt/10Rh
Li	0.111	0.6–0.8	1400	c	Pt/10Rh
Li	0.111	1.0	1400	p, a	Pt/10Rh
Li	0.2	0.0–0.4	1400	w	Pt/10Rh
Li	0.2	0.6–0.8	1400	c	Pt/10Rh
Li	0.2	1.0	1400	p, a	Pt/10Rh
Na, K	0.111	0–0.4	1600	a	Pt/10Rh
Na, K	0.111	0.6–1.0	1400	a	Pt/10Rh
Na, K	0.2	0–0.4	1500	a	Pt/10Rh
Na, K	0.2	0.6–1.0	1400	a	Pt/10Rh
Na	0.333	0–1.0	1400	p, a	$\mathrm{Al_2O_3}$
K	0.333	0–1.0	1400	c	$\mathrm{Al_2O_3}$
Na, K	0.5	0–1.0	1200	c	$\mathrm{Al_2O_3}$

*a = air-quenched, c = quenched between copper plates, w = water quenched, p, a = poured into graphite mould followed by cooling in air.

melting in an electrically heated furnace. Oxygen was bubbled through for ½ h in order to homogenize the melt. After bubbling, the melt was allowed to become bubble-free.

All lithium-containing glasses and the sodium- and potassium-containing glasses with $x = 0.111$ and 0.2, were melted in 250 ml Pt/10Rh crucibles. Because of their reactivity towards Pt/10Rh, the sodium- and potassium- containing glasses with $x = 0.333$ and 0.50 were melted in 100 ml $\mathrm{Al_2O_3}$ containers*.

On normal cooling, the lithium-containing melts with $x = 0.111$ and 0.2 and $y = 0.0$ to 0.8 turned to completely white, non-transparent glasses (opaque glasses). This phenomenon is apparently caused by liquid–liquid phase separation. Transparent fragments of these glasses were obtained by water-quenching small portions (in the case of high-viscosity glasses) or by pressing between two cold copper plates. The lithium glasses with $x = 0.333$ and $y = 0.6$ to 1.0 were also pressed between cold copper plates in order to suppress crystallization. The other lithium-containing glasses were obtained by air-quenching.

The sodium-containing glasses with $x = 0.111$, 0.2 and 0.333 were obtained by air-quenching, as were the potassium-containing glasses with $x = 0.111$ and 0.2. The sodium-containing glasses with $x = 0.333$ were slightly hygroscopic but the glasses with $x = 0.5$ were very hygroscopic; the glass with $x = 0.5$ and $y = 1.0$ could not be obtained because of crystallization. The potassium-containing glasses with $x = 0.333$ and 0.5 were very hygroscopic.

The hygroscopic sodium- and potassium-containing glasses could be obtained by air-quenching. In order to obtain them in a shape suitable for refractive index measurement by an IML method (see below), they were remelted and pressed to 2 mm thick between copper plates. The pieces obtained in this way were immediately transferred into nitrogen-filled air-tight bottles, and further sample handling at room temperature took place inside nitrogen filled "glove bags"†. The conditions of preparation are summarized in Table I.

2.2. Refractive index measurements

The non-hygroscopic or slightly hygroscopic glasses that were air-quenched were cut, ground and polished to dimensions 5 x 10 x 20 mm^3 after which the refractive index, n_D, was measured on an Abbe refractometer‡ (precision 10^{-4}). The refractive index of the other glasses was measured by an immersion method (precision 10^{-3}) [5]. The results are given in Tables II to IV for Li-, Na and K-containing glasses.

2.3. Density measurements

The density measurements on the air-quenched samples were performed by weighing in $\mathrm{C_6H_5Br}$ and in air at 25° C (precision 10^{-4}). The densities

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TABLE II Refractive index (n_D), density (D_4^{25}), and molecular refraction (R) of Li germanosilicate glasses. $x\mathrm{Li_2O}(1-x)\{(1-y)\mathrm{SiO_2}, y\mathrm{GeO_2}\}$

Composition		n_D	D_4^{25} (cm^3 g^{-1})	R (cm^3)	$\pm\Delta R$ (cm^3)
x	y				
0.111	0.0	1.4790 (a*)	2.236 (w*)	7.19	0.04
0.111	0.2	1.501 (i)	2.52 (p*)	7.64	0.09
0.111	0.4	1.525 (i)	2.81 (p)	7.96	0.09
0.111	0.6	1.554 (i)	3.105 (w)	8.29	0.06
0.111	0.8	1.623 (i)	3.583 (w)	8.70	0.06
0.111	1.0	1.705 (a)	4.117 (w)	9.99	0.04
0.2	0.0	1.497 (i)	2.278 (w)	6.94	0.06
0.2	0.2	1.523 (i)	2.53 (p)	7.38	0.09
0.2	0.4	1.550 (i)	2.77 (p)	7.85	0.09
0.2	0.6	1.602 (i)	3.17 (p)	8.15	0.09
0.2	0.8	1.658 (i)	3.66 (w)	8.30	0.06
0.2	1.0	1.7242 (a)	4.12 (w)	8.63	0.04
0.333	0.0	1.5369 (a)	2.345 (w)	6.66	0.04
0.333	0.2	1.5644 (a)	2.614 (w)	6.96	0.04
0.333	0.4	1.5977 (a)	2.911 (w)	7.25	0.04
0.333	0.6	1.624 (i)	3.180 (w)	7.53	0.06
0.333	0.8	1.656 (i)	3.487 (w)	7.77	0.06
0.333	1.0	1.686 (i)	3.744 (w)	8.10	0.06

*a : measured with Abbe refractometer $\pm\ \Delta n = 0.0003$.
i : measured with immersion method $\pm\ \Delta n = 0.003$.
w : measured by weighing in $\mathrm{C_6H_5Br}$. $\pm\ \Delta D = 0.001$ g cm^{-3}.
p : measured in a 5 ml pyknometer $\pm\ \Delta D = 0.01$ g cm^{-3}.

TABLE III Refractive index (n_D), density (D_4^{25}), and molar refraction (R) of Na germanosilicate glasses: $x\mathrm{Na_2O}$ $(1-x)\{(1-y)\mathrm{SiO_2}, y\mathrm{GeO_2}\}$

Composition		n_D	D_4^{25} (cm^3 g^{-1})	R (cm^3)	$\pm\Delta R$ (cm^3)
x	y				
0.111	0.0	1.4744 (a*)	2.297 (w*)	7.38	0.04
0.111	0.2	1.5150 (a)	2.647 (w)	7.77	0.04
0.111	0.4	1.5578 (a)	3.007 (w)	8.16	0.04
0.111	0.6	1.6063 (a)	3.418 (w)	8.48	0.04
0.111	0.8	1.6457 (a)	3.755 (w)	8.88	0.03
0.111	1.0	1.6810 (a)	4.044 (w)	9.34	0.03
0.2	0.0	1.4901 (a)	2.384 (w)	7.33	0.04
0.2	0.2	1.5314 (a)	2.733 (w)	7.66	0.04
0.2	0.4	1.5672 (a)	3.047 (w)	8.01	0.04
0.2	0.6	1.6068 (a)	3.368 (w)	8.39	0.04
0.2	0.8	1.6432 (a)	3.683 (w)	8.74	0.03
0.2	1.0	1.6787 (a)	3.968 (w)	9.14	0.03
0.333	0.0	1.5061 (a)	2.488 (w)	7.25	0.04
0.333	0.2	1.5272 (a)	2.701 (w)	7.59	0.04
0.333	0.4	1.5497 (a)	2.918 (w)	7.92	0.04
0.333	0.6	1.5793 (a)	3.148 (w)	8.29	0.04
0.333	0.8	1.6002 (a)	3.349 (w)	8.63	0.04
0.333	1.0	1.6263 (a)	3.562 (w)	8.99	0.03
0.5	0.0	1.517 (i*)	2.54 (p*)	7.27	0.09
0.5	0.2	1.530 (i)	2.65 (p)	7.64	0.09
0.5	0.4	1.540 (i)	2.82 (p)	7.79	0.09
0.5	0.6	1.554 (i)	2.89 (p)	8.24	0.09
0.5	0.8	1.570 (i)	3.06 (p)	8.77	0.08

*See Table II.

TABLE IV Refractive index (n_D), density (D_4^{25}), and molar refraction (R) for K germanosilicate glasses: $x\mathrm{K_2O}$ $(1-x)\{(1-y)\mathrm{SiO_2}\ y\mathrm{GeO_2}\}$

Composition		n_D	D_4^{25} (cm^3 g^{-1})	R (cm^3)	$\pm\Delta R$ (cm^3)
x	y				
0.111	0.0	1.4799 (a*)	2.306 (w*)	7.87	0.04
0.111	0.2	1.5239 (a)	2.672 (w)	8.22	0.04
0.111	0.4	1.5628 (a)	3.024 (w)	9.56	0.04
0.111	0.6	1.5951 (a)	3.306 (w)	9.01	0.04
0.111	0.8	1.6292 (a)	3.606 (w)	9.42	0.03
0.111	1.0	1.6631 (a)	3.922 (w)	9.77	0.03
0.2	0.0	1.4910 (a)	2.369 (w)	8.18	0.04
0.2	0.2	1.5275 (a)	2.689 (w)	8.47	0.04
0.2	0.4	1.5548 (a)	2.943 (w)	8.85	0.04
0.2	0.6	1.5831 (a)	3.194 (w)	9.24	0.04
0.2	0.8	1.6080 (a)	3.419 (w)	9.65	0.04
0.2	1.0	1.6420 (a)	3.696 (w)	10.02	0.03
0.333	0.0	1.510 (i*)	2.48 (p*)	8.62	0.10
0.333	0.2	1.520 (i)	2.63 (p)	8.84	0.10
0.333	0.4	1.533 (i)	2.73 (p)	9.46	0.10
0.333	0.6	1.557 (i)	2.93 (p)	9.80	0.10
0.333	0.8	1.571 (i)	3.15 (p)	9.93	0.10
0.333	1.0	1.589 (i)	3.24 (p)	10.51	0.10

*See Table II.

of the other glasses were measured with a pyknometer, also using $\mathrm{C_6H_5Br}$ (precision 10^{-3}). The results are given in Tables II to IV.

3. Results and discussion

3.1. The binary system $\mathrm{SiO_2}$–$\mathrm{GeO_2}$

Recently, Huang *et al.* [6] gave a study of density, index of refraction and molar refraction of glasses in the $\mathrm{SiO_2}$–$\mathrm{GeO_2}$ binary, prepared by a flame deposition technique. They found a linear relationship between index of refraction and composition, and density and composition. They concluded from their results an interconnected structure of $\mathrm{SiO_4}$ and $\mathrm{GeO_4}$ tetrahedral units, as occurs in vitreous $\mathrm{SiO_2}$ and $\mathrm{GeO_2}$. The molar refraction data are used in the present study on alkali-germanosilicate glasses.

3.2. The binary systems $\mathrm{Li_2O}$–$\mathrm{SiO_2}$, $\mathrm{Na_2O}$–$\mathrm{SiO_2}$ and $\mathrm{K_2O}$–$\mathrm{SiO_2}$

Studies of refractive index and density on the binary silicate systems have been reported [7–11]. In Fig. 1 a plot of the molar refraction of these

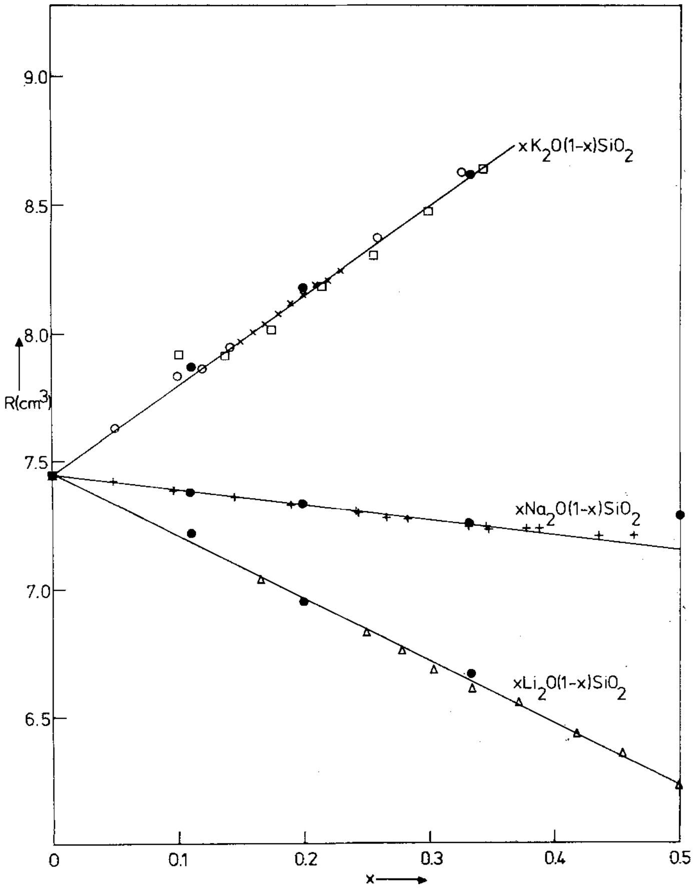


Figure 1 Molar refraction of binary silicate glasses as a function of composition ■ [6], ● present authors, △ [7], + [8], ×□○ [9–11].

glasses as a function of composition is given. The molar refraction is given as:

$$R = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{\bar{M}}{D}, \tag{1}$$

where n_D is the index of refraction at 5893 Å; $\bar{M}$ is the average molecular weight, defined as $xM(A_2O) + (1-x)\{(1-y)M(SiO_2) + yM(GeO_2)\}$; D is the density in g cm^{-3}. For a survey of the molar refraction of glasses, see [1]. It can be observed from Fig. 1 that R is a linear function of the molar alkali content. Least-square fits give for Li_2O: $R(x) = -2.489x + 7.465$; Na_2O: $R(x) = -0.614x + 7.452$; K_2O: $R(x) = 3.495x + 7.444$.

The introduction of A_2O into silica leads to the break up of the tetrahedral network, with each molecule of R_2O giving rise to two non-bridging oxygens (NBOs) in place of one bridging oxygen (BO). The linear dependence of R on the alkali oxide content x, can be expected when R is thought to be build up additively from $R_{Si^{4+}}$; R_{Li^+,Na^+,K^+}, R_{BO} and R_{NBO} [1]:

$$\begin{aligned} R(x) &= 2xR_{Li^+,Na^+,K^+} + (1-x)R_{Si^{4+}} \\ &\quad + 2xR_{NBO} + (2-3x)R_{BO} \\ &= x(2R_{Li^+,Na^+,K^+} - R_{Si^{4+}} + \\ &\quad + 2R_{NBO} - 3R_{BO}) + R_{SiO_2}. \end{aligned} \tag{2}$$

For glasses with composition of about 50 K_2O–50 SiO_2, a large scatter in molar refraction data is observed; this is probably caused by the presence of large quantities of CO_3^{2-} which remain dissolved in the melt [12].

When we use the following molar refraction data from [13]:

$$R_{Li^+} = 0.07; R_{Na^+} = 0.72; R_{K^+} = 2.90$$

$$R_{Si^{4+}} = 0.04\,\text{cm}^3$$

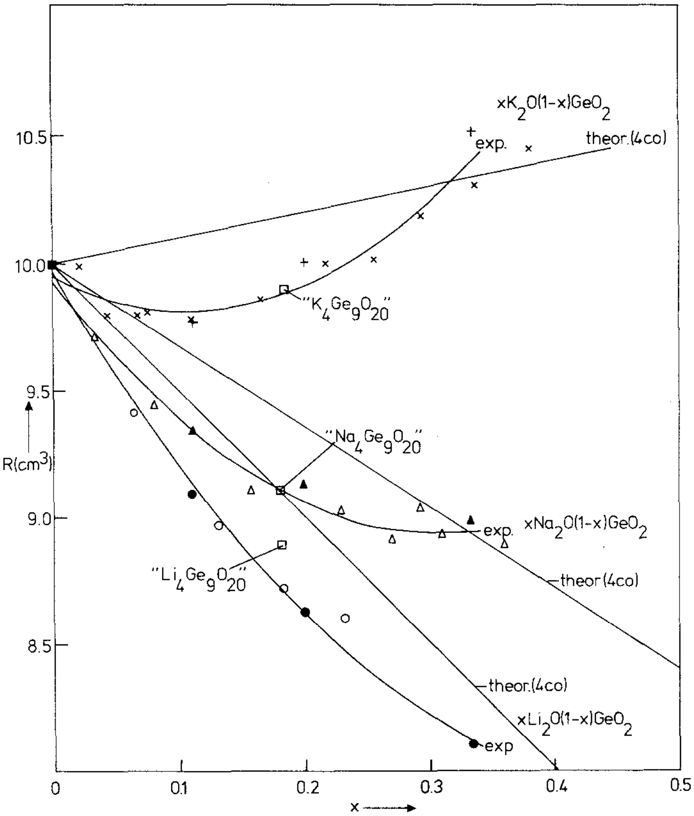
we calculate:

I $R_{BO} = \frac{1}{2}(R_{SiO_2} - R_{Si^{4+}}) = 3.70\,\text{cm}^3$

II (a) for lithium-containing glasses:
$R_{NBO} = 4.26\,\text{cm}^3$

(b) for sodium-containing glasses:
$R_{NBO} = 4.55\,\text{cm}^3$

Figure 2 Molar refraction of binary germanate glasses as a function of composition ■ [6], +▲● present authors, ○△x [3, 14].



(c) for potassium-containing glasses:

$R_{\mathrm{NBO}} = 4.43\,\mathrm{cm}^3$

The R_{NBO}s are most severely influenced by the alkali ions because they are directly bound to the NBOs so they are calculated for every alkali ion separately.

In the silicate glasses the differences in n_{D} between Li, Na and K glasses of the same molar composition are very small since the increase of R is just compensated by a decrease in molar density $D/\bar{M}$ on replacement of Li$^+$ by Na$^+$, etc.

3.3. The binary systems Li_2O-GeO_2, Na_2O-GeO_2 and K_2O-GeO_2

Refractive index and density studies of the binary germanate systems have been reported previously [3, 14, 15]. Efimov and Mazurina [14] calculated a "network atomic refraction" for glasses in the binary A_2O-GeO_2 system with A = Li, Na and K in the composition range of about 0 to 30 mol% A_2O. Large differences were found between the network refractions of Li, Na and K germanate glasses. These differences were thought to be entirely due to differences in the atomic refraction of the Ge^{4+} ions. Furthermore, Efimov and Mazurina [14] assumed that structures of the "$A_2O \cdot 4GeO_2$ type" occur in the germanate glasses; this conclusion agrees qualitatively with the conclusion given below. In Fig. 2 the molar refraction of these glasses is plotted as a function of composition. It can be observed from Fig. 2 that the behaviour of the molar refraction as a function of composition differs significantly from that of the molar refraction of the binary silicate glasses.

We calculated the molar refraction of the binary germanate glasses as a function of composition for the hypothetical case that the germanate glasses are structurally equivalent to the silicate glasses; in other words, the case that germanium is only four-co-ordinated by oxygen. In that case we find analogous to Equation 2:

$$\begin{aligned} R(x) &= 2xR_{\mathrm{Li^+,Na^+,K^+}} + (1-x)R_{\mathrm{Ge^{4+}}} \\ &\quad + 2xR_{\mathrm{NBO}} + (2-3x)R_{\mathrm{BO}} \\ &= x\,(2R_{\mathrm{Li^+,Na^+,K^+}} - R_{\mathrm{Ge^{4+}}} \\ &\quad + 2R_{\mathrm{NBO}} - 3R_{\mathrm{BO}}) + R_{\mathrm{GeO_2}} \end{aligned} \tag{3}$$

$R(x) = -5.04x + 10.00\,\mathrm{cm}^3$
for lithium germanate glasses

$$R(x) = -3.16x + 10.00\,\text{cm}^3 \quad \text{for sodium germanate glasses}$$

$$R(x) = 0.96x + 10.00\,\text{cm}^3 \quad \text{for potassium germanate glasses.} \tag{4}$$

For the calculations, we used the data for the molar oxygen refractions from Section 3.2 and calculated $R_{\text{Ge}^{4+}}$ as:

$$R_{\text{Ge}^{4+}} = R_{\text{GeO}_2} - 2R_{\text{BO}} = 2.60\,\text{cm}^3.$$

The hypothetical x-dependences of Equation 4 have been plotted in Fig. 2 and we observe that the real molar refraction deviates negatively.

Raman spectroscopic investigations indicate [16] that $x\text{A}_2\text{O}(1-x)\text{GeO}_2$ glasses with $0.33 < x < 0.50$ consist of digermanate and metagermanate networks which contain only 4-co-ordinated Ge^{4+}. From Fig. 2 we indeed observe that the measured R curves intersect the straight lines at about $x = 0.33$. Furthermore, the Raman spectroscopic investigations indicate that for $0 < x < 0.33$, network structures occur like those which are present in the crystalline compounds $2\text{Li}_2\text{O}\cdot 9\text{GeO}_2$ [17], $2\text{Na}_2\text{O}\cdot 9\text{GeO}_2$ [18] and $2\text{K}_2\text{O}\cdot 9\text{GeO}_2$ [19]. In these compounds, chains of GeO_4 tetrahedra (4-co-ordination) are present which are interconnected by GeO_6 octahedra (6-co-ordination); the oxygens of the GeO_4 tetrahedra which are not used for the connection of two GeO_4 tetrahedra are all used for the formation of GeO_6 octahedra, so the polarizability of these oxygens will tend towards the polarizability of BOs. This conclusion is consistent with the fact that the measured R-value is significantly lower in the region of $0 < x < 0.33$ than the R value calculated, which assumes that only 4-co-ordination is present.

The molar refraction of the $(\text{Li}, \text{Na}, \text{K})_4\text{Ge}_9\text{O}_{20}$ networks can be estimated from the molar refraction data used in Equation 3:

$$R[(\text{Li}, \text{Na}, \text{K})_4\text{Ge}_9\text{O}_{20}] = 4R_{\text{Li}^+,\,\text{Na}^+,\,\text{K}^+} + 9R_{\text{Ge}^{4+}} + 20R_{\text{BO}}.$$

It is assumed that $R_{\text{Ge}^{4+}}$ is independent of the co-ordination state and that R_{BO} is the same for oxygen bonded to Si^{4+} or Ge^{4+} in the 4- or 6-co-ordinated state. We obtain for:

$$(\text{Li}_4\text{Ge}_9\text{O}_{20})/11 \;:\; R = 8.88\,\text{cm}^3$$

$$(\text{Na}_4\text{Ge}_9\text{O}_{20})/11 \;:\; R = 9.12\,\text{cm}^3$$

$$(\text{K}_4\text{Ge}_9\text{O}_{20})/11 \;:\; R = 9.91\,\text{cm}^3.$$

These results are plotted in Fig. 2, and it can be observed that for Na and K glasses the agreement is excellent. For Li glasses the model fails partly; this may be explained by the less ionic character of the Li ions, so that the assumption of additivity of the molar refractions is not correct.

In contrast to the results for silicate glasses, in the alkali germanate glasses the differences in n_D between Li, Na and K glasses are considerable. In this case, the increase of R is overcompensated by a decrease in the molar density $D/\bar{M}$ on replacement of Li^+ by Na^+, etc.

3.4. The ternary system $\text{Li}_2\text{O}-\text{SiO}_2-\text{GeO}_2$

The ternary diagrams for the system $\text{Li}_2\text{O}-\text{SiO}_2-\text{GeO}_2$ with lines of constant n_D and density are given in Fig. 3a and b. The anomalies in refractive index and density which show a maximum with increasing alkali content as observed in the binary alkali-germanate glasses instead of the normal steady increase as observed in the binary silicates, are present in the ternary Li_2O glasses only at low SiO_2 concentration. Following lines of increasing alkali-oxide concentration at constant y, it can be observed that the anomalies have disappeared when y is about 0.5. This indicates that in the ternary $\text{Li}_2\text{O}-\text{SiO}_2-\text{GeO}_2$ system Ge^{4+} prefers to be completely 4-co-ordinated, in which case there is no anomaly. This is also related to the strong tendency towards phase separation, as will be shown below.

The molar refraction of the glasses with $x = 0.111$, 0.2 and 0.333 is plotted as a function of y in Fig. 4. Here it can be observed that within the error of determination, the curves for $x = 0.111$ and $x = 0.333$ depend linearly on y and that the curve for $x = 0.2$ shows a non-linear dependence.

When the lithium ions have no special preference for silicate or germanate groups (in other words, the lithium ions are divided among the silicate and the germanate part of the network according to the $\text{SiO}_2/\text{GeO}_2$ ratio) and the 4/6 co-ordination ratio of Ge^{4+} is not affected by the presence of silicate in the network, the molar refraction of $x\text{Li}_2\text{O}(1-x)\{(1-y)\text{SiO}_2, y\text{GeO}_2\}$ glasses can be calculated as:

$$R(y) = (1-y)R_{\text{silicate}} + yR_{\text{germanate}}$$

in which R_{silicate} is the molar refraction of $x\text{Li}_2\text{O}(1-x)\text{SiO}_2$ glass and $R_{\text{germanate}}$ is the

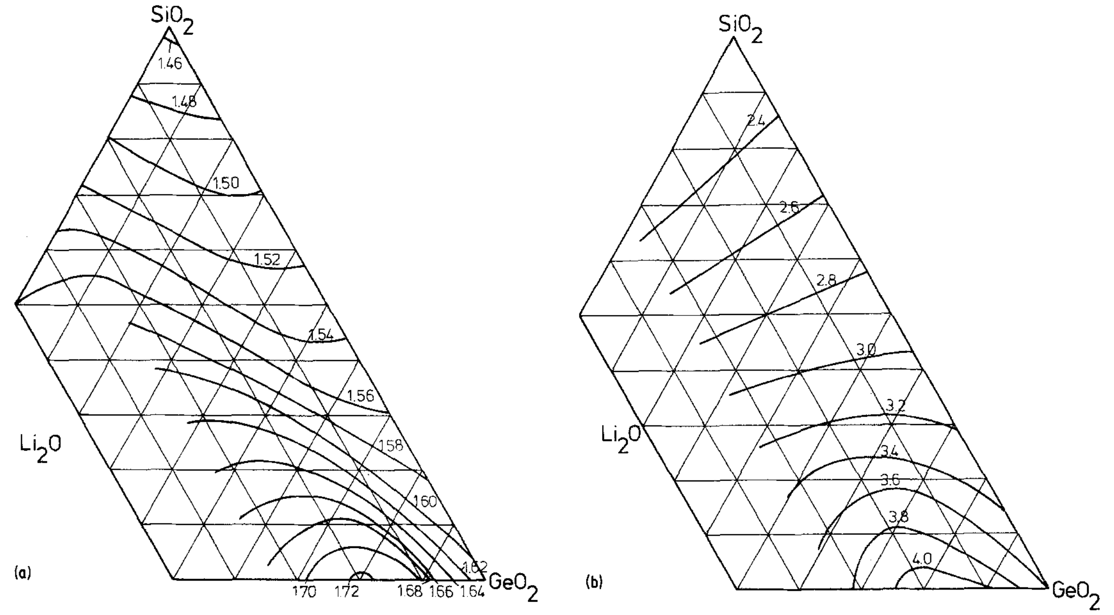


Figure 3 Lines of equal n_D (a) and density (b) in the ternary system $Li_2O-SiO_2-GeO_2$; data from [3, 6, 7, 15] (binaries) and present authors (ternary).

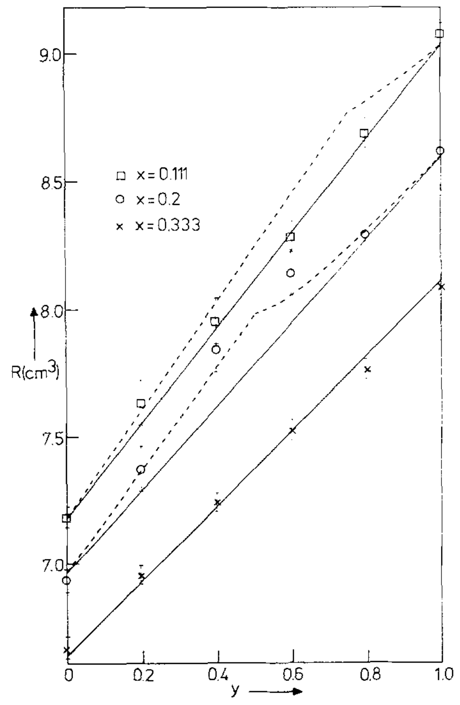


Figure 4 Molar refraction of $xLi_2O(1-x)[(1-y)SiO_2yGeO_2]$ glasses with $x = 0.111$, 0.2, and 0.333 as a function of y.

molar refraction of $xLi_2O(1-x)GeO_2$ glass. In this case R is a linear function of y and R_{silicate} and $R_{\text{germanate}}$ are independent of y.

When the lithiums have a preference for the germanate or the silicate part of the network or the ratio of 4-co-ordinated and 6-co-ordinated Ge^{4+} is affected by the presence of silicate in the network, in general, a non-linear dependence of $R(y)$ on y may be expected which is, in fact, observed for $x = 0.2$. By trial and error it was found that the non-linear behaviour of the molar refraction of $0.2\,Li_2O-0.8\{(1-y)SiO_2, yGeO_2\}$ glass as a function of y can be explained best if one assumes that the Li ions have a preference for a disilicate-type network. We found the best agreement with the experiments when calculating R as a function of y for the extreme case that all Li^+ goes into the silicate part of the network until the silicate reaches a "saturation" composition of $0.333\,Li_2O-0.667\,SiO_2$ (disilicate network):

$$\begin{aligned} R &= R[0.20Li_2O-0.80\{(1-y)SiO_2, yGeO_2\}] \\ &= 0.80yR_{GeO_2} + (1.0-0.80y) \\ &\quad \times R\left[\frac{0.20}{(1-0.80y)}Li_2O\frac{0.80(1-y)}{(1-0.80y)}SiO_2\right] \\ &\quad (0<y<0.5). \qquad (6a) \end{aligned}$$

At $y = 0.5$, having reached the composition $0.333\,Li_2O-0.667\,SiO_2$, the silicate network is saturated with Li^+ and part of the Li^+ goes into the germanate network, then:

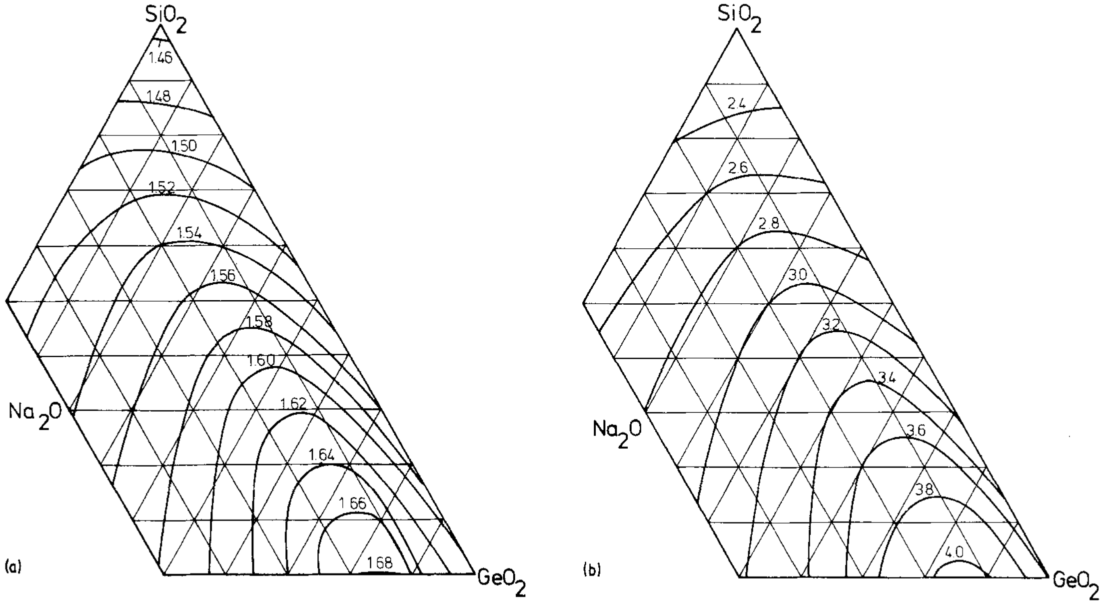


Figure 5 Lines of equal n_D (a) and density (b) in the ternary system Na_2O–SiO_2–GeO_2; data from [3, 6, 8, 15] (binaries) and present authors (ternary).

$$R = 1.20 + (1-y) \times R[0.333\,Li_2O\text{–}0.667\,SiO_2] + (1.20y-0.20) \times R\left[\frac{(0.40y-0.20)}{(1.20y-0.20)}Li_2O\,\frac{(0.80y)}{(1.20y-0.20)}GeO_2\right] \quad (0.5<y<1). \qquad (6b)$$

The same calculation can be performed for the Li glasses with $x = 0.111$. For the glasses with $x = 0.333$ the saturation composition for the silicate network has been attained for all values of y. In Fig. 4 the calculated molar refractions are plotted as solid lines for the case of no preference of the Li^+ ions for some network, and as broken lines for the case of preference of the Li^+ ions for a disilicate-type network (until saturation at 0.333 Li_2O–0.667 SiO_2). For $x = 0.333$ both cases coincide.

For $x = 0.111$ the accuracy of measurement does not permit a conclusion on the preference of lithium for a disilicate-type network. The calculation above does not give a unique structural interpretation as an isostructural exchange of Si^{4+} in the disilicate and 4-co-ordinated Ge^{4+} does not affect the results. The conclusion that can be made is that Ge^{4+} is present in a completely 4-co-ordinated network when $y < 0.5$.

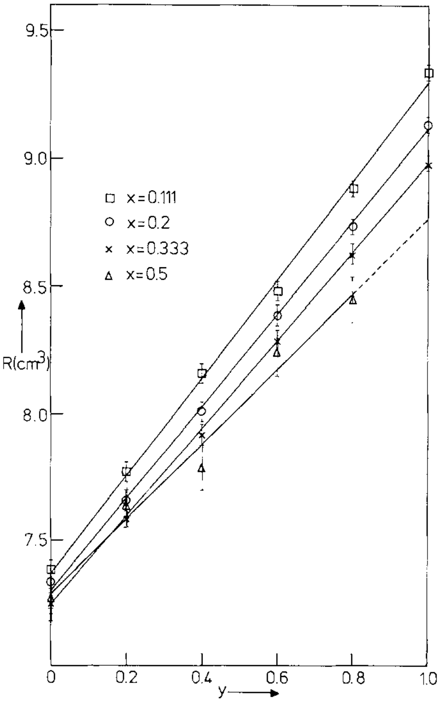


Figure 6 Molar refraction of $x Na_2O(1-x)[(1-y)SiO_2 y GeO_2]$ glasses with $x = 0.111$, 0.2 and 0.333 as a function of y.

3.5. The ternary system Na_2O–SiO_2–GeO_2

Ternary diagrams for the Na_2O–SiO_2–GeO_2 system with lines of constant n_D and density are given in Fig. 5a and b. It can be observed in Fig. 5a

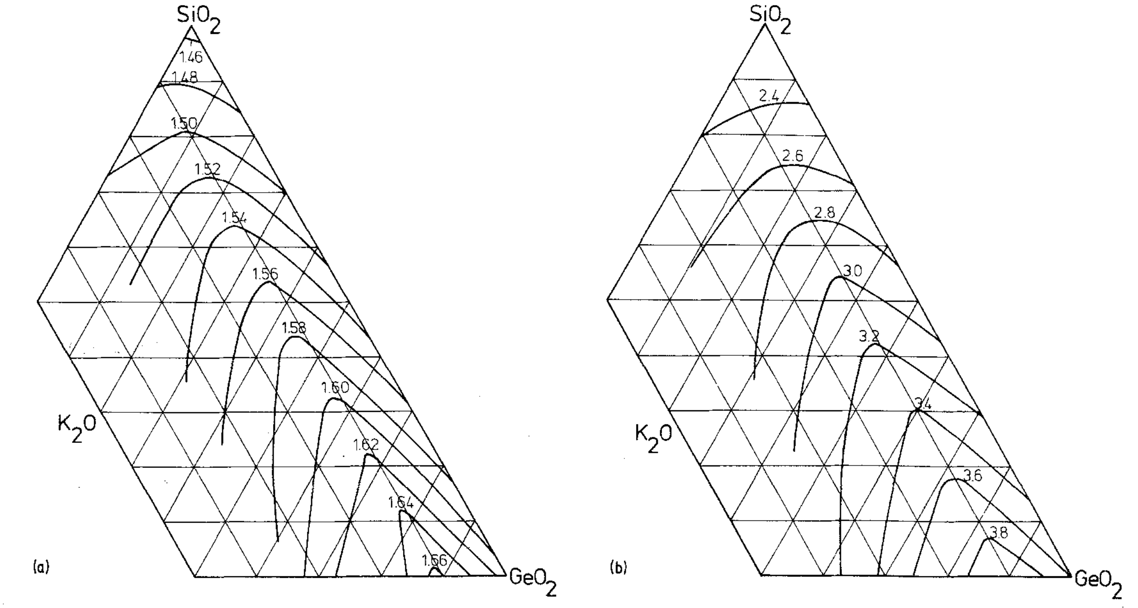


Figure 7 Lines of equal n_D (a) and density (b) in the ternary system $K_2(O-SiO_2-GeO_2$; data from [3, 6, 9–11, 15] (binaries) and present authors (ternary).

and b that the refractive index and density anomaly of the binary Na_2O-GeO_2 glasses is present throughout the whole system. The SiO_2 has only a diluting effect. In Fig. 6 the molar refraction of $xNa_2O(1-x)\{(1-y)SiO_2, yGeO_2\}$ glasses (with $x = 0.111$, 0.2, 0.333 and 0.5) as a function of y is plotted. From Fig. 6 it can be seen that within the error of determination, all curves show a linear dependence of R on y. As indicated in Section 3.4, the linear dependence of R on y shows that the sodium ions have no influence on the 4/6 co-ordination ratio of Ge^{4+}. In Fig. 6, calculated molar refractions are plotted as solid lines.

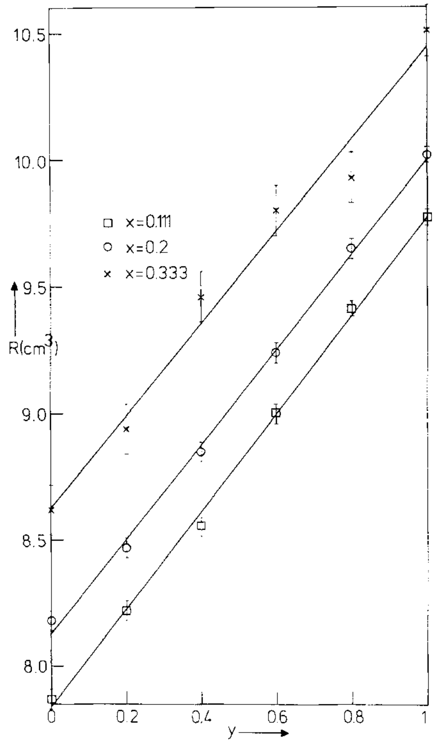


Figure 8 Molar refraction of $xK_2O(1-x)[(1-y)SiO_2 yGeO_2]$ glasses with $x = 0.111$, 0.2 and 0.333 as a function of y.

3.6. The ternary system $K_2O-SiO_2-GeO_2$

The ternary diagrams for the $K_2O-SiO_2-GeO_2$ system with lines of constant n_D and density are given in Fig. 7a and b. It can be seen that the $K_2O-SiO_2-GeO_2$ and the $Na_2O-GeO_2-SiO_2$ systems behave qualitatively the same for n_D and density. In the $K_2O-SiO_2-GeO_2$ system, the refractive index and density anomaly is conserved too, almost throughout the whole glass-forming region. The data for glasses with (oxide) composition 0.5 K_2O–0.5 $\{(1-y)SiO_2, yGeO_2\}$ were badly reproducible, especially for n_D. This can be ascribed to the presence of large uncontrollable quantities of CO_3^{2-} ions (about 10% K_2CO_3 is not converted, see also [12]), which have a high molar refraction. We omitted the data for these glasses here. In Fig. 8 the molar refraction of $xK_2O(1-x)\{(1-y)SiO_2, yGeO_2\}$ glasses (with $x = 0.111$, 0.2, 0.333 and 0.5) as a function of y

is plotted. From the figure it can be observed that within the error of determination all curves show a linear dependence of R on y which indicates that the potassium ions have no influence on the 4/6 co-ordination ratio of Ge^{4+}. In Fig. 8 calculated molar refractions are plotted as solid lines.

4. Conclusions

In the binary alkali germanate glasses, the dependence of R on x deviates from the expected behaviour, assuming that only 4-co-ordinated Ge^{4+} is present. The deviation can be explained by assuming a network similar to that of the crystalline compounds $Li_4Ge_9O_{20}$ and $Na_4Ge_9O_{20}$ with only "bridging type" oxygen atoms.

The molar refraction data for $Li_2O-SiO_2-GeO_2$ glasses show a tendency for Ge^{4+} to go into a 4-co-ordinated Ge network. Because of this, the index of refraction and density anomaly in the ternary system $Li_2O-SiO_2-GeO_2$ decreases rather quickly on increase of the SiO_2 content in the system.

In the systems $Na_2O-SiO_2-GeO_2$ and $K_2O-SiO_2-GeO_2$, the molar refraction data do not show any preference for the alkalies to go into the silicate or the germanate part of the network.

The index of refraction and density anomalies in the sodium and potassium germanosilicate glasses decrease almost linearly with SiO_2 content.

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