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Refractive index and density of Na-, Rb- and mixed Na, Rb-aluminogermanate glasses

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Refractive index and density measurements are given for the ternary systems $X\ M_2O:Y\ Al_2O_3:(1-X-Y)GeO_2$ where M = sodium and rubidium for Na/(Na + Rb) = 0, 0.3, 0.5, 0.7 and 1.0; $(1-X-Y) = 0.7$, 0.8 and 0.9 and $Y/X = 0$, 0.3 and 1.0. The values of the molar refractivity, R, are related to the structure of the glass. At low alkali concentrations, the decrease in R with increasing X is related to the closer packing of the network. At high alkali concentrations the changes in R appear to be controlled by the introduction of non-bridging oxygens into the network. Alumina additions to the germania network strongly increase R and this appears to be related to change in the network packing brought about by the conversion of Ge^{4+} from octahedral to tetrahedral coordination.

1. Introduction

The early studies on alkali germanate glasses [1, 2] showed that the density and refractive index of the glasses as a function of alkali oxide concentration, $D(X)$ and $n_D(X)$, contrasted strongly with that found for alkali silicate glasses (X is the mole fraction of alkali oxide). Although $D(X)$ and $n_D(X)$ increase monotonically with X for the silicates glasses [3], both $D(X)$ and $n_D(X)$ for the germanate glasses increase up to a certain X and then decrease. More detailed work was reported by Murthy and Ip [2] for lithium- [4], sodium- [5] and potassium- [6] germanate glasses and extended to the lithium-, sodium- and potassium-aluminogermanate glasses [7]. The considerable difference in the refractive index of different alkali germanate glasses with the same X is of interest in the production of optical fibres and prompted the $n_D(X)$ measurements of Verweij *et al.* [8], who investigated the lithium-, sodium- and potassium-germanosilicate glasses.

As noted by Verweij *et al.* [8] the anomalous changes in $D(X)$ and $n_D(X)$ are related to the change of germanium from four (tetrahedral) to six (octahedral) coordination upon addition of alkali. This interpretation followed from the earlier studies [1, 2] and from their own studies [9] of lithium-, sodium- and potassium-germanate glasses by Raman spectroscopy. Verweij and Buster [9] suggested that for the sodium-germanate glasses with $X < 0.18$ the glass network resembled the crystal structure $Na_4Ge_9O_{20}$ [10] and that the concentration of germanium in octahedral coordination, $N_6 = 2X/(1-X)$, i.e. one molecule of Na_2O provides two octahedral structural units. In recent years there has been a number of studies of the structure of alkali germanate glasses including Raman [11], neutron [12] and X-ray [13] scattering together with EXAFS [13–16] and XPS [17] measurements. Although all measurements confirmed the proposed germanium coordination change, the more recent studies [12, 13] suggested that for the sodium germanate glasses with $X < 0.18$, a network structure similar to $Na_2Ge_4O_9$ [18] and $N_6 = X/(1-X)$. Yin *et al.* [19] have measured chemical shifts of sodium germanate glasses using a fluorescence X-ray spectrometer and analysed their data with a combination of both N_6 concentration dependencies. It appears to be clear [9, 11–15, 17] that for sodium germanate glasses with $X \gtrsim 0.18$ non-bridging oxygens are formed and N_6 decreases so that for $X \gtrsim 0.33$ all germanium atoms are in tetrahedral coordination [9, 12, 17, 19] and the sodium is compensated by non-bridging oxygens in all analogous way to that found for sodium silicate glasses with $X \geqslant 0$ [3, 11].

The influence of the kind of alkali ion on alkali germanate glasses becomes more evident when the molar volume (molecular weight/density) is considered. In Fig. 1 the molar volumes of lithium-, sodium-, potassium- and rubidium-germanate glasses are plotted as a function of alkali molar fraction, X. (The experimental points are omitted as they are within ±1% of the line for all glasses and considerably better for the lithium- and sodium-germanate glass data.) The minima in molar volumes as a function of X, occurs at lower X in the sequence sodium ($X \sim 0.18$),

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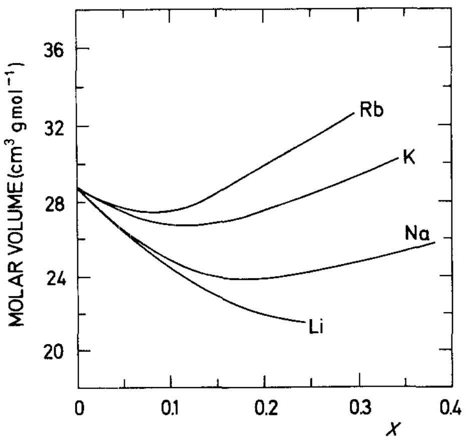

Figure 1 The molar volume of $X\,M_2O$: $(1 - X)GeO_2$ as a function of X for M = lithium, sodium, potassium, rubidium. Data for lithium [2, 14, 13], sodium [2, 5, 13, 20, 30, present work], potassium [2, 6, 13, 20] and rubidium [2, 21, present work].

potassium ($X \sim 0.12$) and rubidium ($X \sim 0.09$). It is interesting to note that approximately at the minimum in the molar volume a crystalline compound has been found for sodium germanates ($2Na_2O : 9GeO_2$ [10]) and potassium germanates ($K_2O : 8GeO_2$ [9]). The molar volume of the lithium germanate glasses appear to approach a minimum value for $X \gtrsim 0.25$ and a crystalline lithium germanate, $3Li_2O : 8GeO_2$ has been found [4, 9]. Most of the structural studies [9–19] discussed above have been for sodium germanate glasses where it was found that at the same molar fraction at which the molar volume is a minimum ($X \sim 0.18$), the concentration of octahedrally coordinated germanium is a maximum, and for higher X, non-bridging oxygens are formed. The molar volume data suggest the same structural characteristics apply to the other alkali germanates and that the value of X for minimum molar volume and maximum N_6 occurs at successively lower X as the size of the alkali ion is increased. At present no structural studies have been made to support this conjecture, and ionic conductivity studies in potassium- [22] and rubidium- [22, 23] germanate glasses suggest that not all alkali germanate glasses follow the same structural changes as sodium germanate glass.

The work of Verweij *et al.* [8] showed that adding silica to alkali germanate glasses decreased both $D(X)$ and $n_D(X)$ such that the molar refraction (R) of alkali germanosilicate glass with a particular value of X was linearly dependent on the Ge/Si ratio. (Deviations from linearity were seen for lithium germanosilicate glass with $X = 0.2$.) Their data indicated that the alkali ions have no preference for the silicate or germanate part of the network and the addition of silica to the network has no influence on the 4/6 coordination ratio of Ge^{4+}. However, Riebling's work [24–26] on molten sodium alumino-germanates with $0 \leqslant Al/Na \leqslant 1$ showed that in those sodium germanates ($X < 0.33$) where germanium occurs in octahedral coordination, the introduction of AlO_4 tetrahedra to the germania network creates an unstable environment for GeO_6 and leads to their elimination. Raman spectroscopic studies of sodium aluminogermanate glasses [27] with $Al/Na = 1$ and over a wide range of X showed that there was no evidence for germanium in octahedral coordination.

Additions of alumina to alkali germanate glasses clearly perturb the glass network in contrast to the effect of silica additions and the present work studies the effect of alumina additions to sodium- and rubidium- and mixed (Na/Rb)-germanate glasses on both $D(X)$ and $n_D(X)$. The study is part of a programme which is examining the effect of aluminium additions on the ionic conductivity of sodium- and rubidium-germanate glasses [23, 28].

2. Experimental techniques

2.1. Glass preparation

The glasses were prepared by melting batches (10 to 30 g) of appropriate mixtures of sodium nitrate, aluminium oxide (J. T. Baker Chemical Co., reagent grade) rubidium carbonate (Atomergic Chemetals Corp., reagent grade) and germanium dioxide (Atomergic Chemetals Corp., 99.999% pure). All raw materials were dried at 120° C for 6 h. The mixtures were prereacted in a platinum crucible at 1000 to 1200° C. Only small quantities of the mixed powders were used to avoid spillage due to frothing during the reaction at high temperatures. When a batch powder became a sintered oxide glass at 1000 to 1200° C the platinum crucible was transferred to a melting furnace at 1230 to 1550° C. Dry oxygen (< 1 p.p.m. (vol.) H_2O) was bubbled through the melt for 1 to 3 h to remove moisture and aid the removal of gas bubbles. The oxygen was dried by a molecular sieve and the moisture content monitored by a Panametrics Model 2000 Hygrometer. Any remaining bubbles were removed by stirring to obtain a clear, homogeneous melt. Each melt was cast into a preheated stainless steel mould and transferred immediately to an annealing furnace. In order to provide all the glass samples with a uniform thermal history, each glass was annealed for ~3 h at a temperature within 10° C of its glass transformation temperature, T_g, and then furnace cooled. The glass transformation temperatures for sodium-, rubidium-, and mixed (Na, Rb)-germanates were interpolated values from Shelby's work [29]. Our own thermal measurements of a sodium germanate glass with $X = 0.289$ gave $T_g = 459°$ C in good agreement with an interpolation of the previous measurements. Thermal expansion measurements of T_g were also made of three soda aluminogermanate glasses (Samples 10C, 20C and 30C). The values of T_g for all of the other aluminogermanate glasses were estimated. The appearance of the glass samples under polarized light indicated that the annealing procedure, as indicated by the absence of interference fringes, was satisfactory.

The samples were prepared first for ionic conductivity measurements. The conductivity samples were prepared by cutting rectangular parallelepipeds approximately 1.0 cm × 1.0 cm × 0.5 cm from the centre of each glass casting. The sides of the parallelepiped were ground true with a parallel grinder. Material from the volume immediately adjacent to the sample was analysed by atomic absorption spectroscopy. The chemical analyses are given in Table I and

TABLE I Composition, refractive index (n_D), and Abbe number (ν_D) of sodium/rubidium aluminogermanate glasses

Sample no.	Composition (mol %)				n_D	$n_F - n_C$	Abbe number, ν_D
	Na_2O	Rb_2O	Al_2O_3	GeO_2			
1A0	1.2	0	0	98.8	1.621 59	0.015 02	41.38
1A10	0.16	1.24	0	98.6	1.621 57	0.014 84	41.88
5A0	4.9	0	0	95.1	1.648 83	–	–
5A10	0.19	4.9	0	94.92	1.643 22	0.015 47	41.57
10A0	9.84	0.13	0	90.03	1.675 9	0.016 93	39.92
10A3	6.67	2.71	0	90.62	1.669 98	0.016 47	40.67
10A5	4.92	4.6	0	90.48	1.665 61	0.016 33	40.75
10A7	3.11	6.19	0	90.7	1.661 75	0.016 01	41.33
10A10	0	8.83	0	91.17	1.656 96	0.016 01	41.03
10B0	7.58	0	2.27	90.15	1.643 11	0.015 41	41.73
10B3	(5.25)	(2.25)	(2.5)	(90.0)	1.641 04	0.015 93	40.24
10B5	3.7	3.33	2.19	90.78	1.637 89	0.015 32	41.63
10B7	(2.25)	(5.25)	(2.5)	(90.0)	1.635 61	0.015 56	40.84
10B10	0.38	6.55	2.44	90.63	1.631 98	0.015 43	40.95
10C0	5.51	0	4.88	89.61	1.611 42	0.014 68	41.64
10C3	3.67	1.56	4.73	90.04	1.605 97	0.014 92	40.61
10C5	2.56	2.31	4.57	90.56	1.604 59	0.014 58	41.46
10C7	1.55	3.43	4.45	90.57	1.604 93	0.014 4	42.0
10C10	0	4.68	4.68	90.65	1.598 51	0.014 18	42.2
15A0	14.95	0	0	85.05	1.686 55	0.017 43	39.38
15A3	(10.5)	(4.5)	(0)	(85.0)	1.675 93	0.016 68	40.52
15A5	7.55	7.05	0	85.4	1.669 8	0.016 42	40.79
15A7	(4.5)	(10.5)	(0)	(85.0)	1.664 91	0.016 18	41.09
15A10	0	15.1	0	84.9	1.654 15	–	–
20A0	18.68	0	0.3	81.01	1.681 39	0.016 7	40.8
20A3	13.86	5.38	0	80.76	1.669 73	0.016 77	39.93
20A5	10.07	9.2	0	80.73	1.661 37	0.016 4	40.32
20A7	5.98	12.86	0	81.16	1.652 84	0.016 1	40.54
20A10	0	21.9	0	78.1	1.634 29	0.015 6	40.65
20B0	14.65	0	5.11	80.23	1.651 87	0.015 9	40.99
20B3	(10.5)	(4.5)	(5)	(80.0)	1.643 5	0.015 91	40.44
20B5	7.43	7.09	4.77	80.71	1.638 09	0.015 17	42.06
20B7	(4.5)	(10.5)	(5)	(80.0)	1.633 85	0.015 46	40.99
20B10	0.25	14.14	4.49	81.11	1.626 68	0.014 86	42.17
20D0	15.86	0	3.24	80.9	1 665 17	0.016 28	40.85
20E0	12.6	0	7.08	80.31	1.630 19	0.015 03	41.92
20C0	9.97	0	10.85	79.18	1.598 3	0.013 78	43.41
20C3	(7.0)	(3.0)	(10.0)	(80.0)	1.593 86	0.013 68	43.41
20C5	4.96	4.55	9.43	81.07	1.592 3	–	–
20C7	(3.0)	(7.0)	(10.0)	(80.0)	1.590 07	0.014 13	41.76
20C10	0.24	9.27	9.25	81.24	1.584 25	0.013 25	44.09
30A0	28.94	0	0	71.06	1.647 5	0.017 04	37.99
30A3	20.21	7.6	0	72.19	1.640 37	0.016 5	38.81
30A5	15.2	12.82	0	71.99	1.634 4	0.016 52	38.4
30A7	9.62	15.98	0	74.4	1.634 5	0.016 32	38.87
30A10	0	29.1	0	70.9	–	–	–
30B0	21.41	0	7.17	71.42	1.633 66	0.015 35	41.28
30B3	(15.75)	(6.75)	(7.5)	(70.0)	1.622 67	0.015 73	39.58
30B5	11.24	10.03	6.8	71.93	1.616 97	0.015 56	39.65
30B7	(6.75)	(15.75)	(7.5)	(70.0)	1.610 79	0.014 81	41.24
30B10	1.04	18.76	7.46	72.74	1.604 39	–	–
30C0	15.74	0	14.1	70.17	1.590 72	0.013 28	44.48
30C3	(10.5)	(4.5)	(15)	(70.0)	1.585 27	0.013 3	44.0
30C5	7.50	6.58	14.01	71.91	1.581 62	0.013 23	43.96
30C7	(4.5)	(10.5)	(15)	(70.0)	1.576 58	0.013 51	42.67
30C10	0.25	14.09	13.81	71.85	1.573 09	–	–
40C0	20.53	0	18.77	60.7	1.579 29	0.013 05	44.39

are expected to be accurate to ± 2% of the amount of element present. The $X(Na_2O, Rb_2O):Y\ Al_2O_3:(1 - X - Y)GeO_2$ glass compositions were chosen to look at (a) the effect of varying X (nominally 0.01, 0.05, 0.10, 0.15, 0.20, and 0.30), (b) the effect of replacing alkali with alumina at $(1 - X) \sim 0.9$, 0.8, and 0.7, and (c) the effect of replacing sodium by rubidium such that for ten glass series with fixed Al/Ge ratios glasses were made with the ratio $Na/(Na + Rb) \sim 0$, 0.3, 0.5, 0.7 and 1.0. A total of 57 glasses were made and in Table I sample numbers are used to help group the glass in the various series. The measured compositions reflect soda and rubidia losses during the melt.

2.2. Density measurements

The density, D, of each sample is given in Table II and was obtained directly from the sample weight

TABLE II Refractive index (n_D), molar refractivity (R), molecular weight (M), and density (D) of sodium/rubidium aluminogermanate glasses

Sample no.	D ($\mathrm{g\,cm^{-3}}$)	M (g)	n_D	R ($\mathrm{cm^3}$)
1A0	3.718	104.07	1.621 59	9.85
1A10	3.733	105.54	1.621 57	9.95
5A0	3.867	102.5	1.648 83	9.65
5A10	3.904	108.55	1.643 22	10.05
10A0	4.004	100.5	1.675 9	9.44
10A3	4.031	103.97	1.669 98	9.63
10A5	4.040	106.28	1.665 61	9.73
10A7	4.057	108.36	1.661 75	9.92
10A10	4.069	111.86	1.656 96	10.11
10B0	3.763	101.3	1.643 11	9.73
10B3	3.871	104.14	1.641 04	9.7
10B5	3.839	105.69	1.637 89	9.89
10B7	3.848	107.88	1.635 61	10.04
10B10	3.860	109.75	1.631 98	10.14
10C0	3.561	102.11	1.611 42	9.96
10C3	3.596	104.18	1.605 97	9.99
10C5	3.603	105.28	1.604 59	10.05
10C7	3.618	106.63	1.604 93	10.14
10C10	3.605	108.33	1.598 51	10.25
15A0	4.054	98.21	1.686 55	9.22
15A3	4.078	103.82	1.675 93	9.57
15A5	4.093	107.17	1.669 8	9.77
15A7	4.108	111.31	1.664 91	10.06
15A10	4.081	117.02	1.654 15	10.51
20A0	4.000	96.61	1.681 39	9.14
20A3	4.043	103.11	1.669 73	9.52
20A5	4.064	107.87	1.661 37	9.81
20A7	4.093	112.63	1.652 84	10.07
20A10	4.062	122.62	1.634 29	10.79
20B0	3.789	98.2	1.651 87	9.47
20B3	3.840	103.69	1.643 5	9.77
20B5	3.854	107.13	1.638 09	9.99
20B7	3.879	111.18	1.633 85	10.24
20B10	3.853	115.99	1.626 68	10.66
20D0	3.896	97.74	1.665 17	9.31
20E0	3.667	99.02	1.630 19	9.6
20C0	3.426	100.05	1.598 3	9.96
20C3	3.499	103.81	1.593 86	10.06
20C5	3.504	105.98	1.592 3	10.23
20C7	3.545	108.81	1.590 07	10.35
20C10	3.541	111.87	1.584 25	10.57
30A0	3.719	92.25	1.647 5	9.01
30A3	3.867	102.23	1.640 37	9.52
30A5	3.921	108.68	1.634 4	9.91
30A7	3.990	113.65	1.634 5	10.19
30A10	3.969	128.55	–	–
30B0	3.595	95.27	1.633 66	9.47
30B3	3.687	103.24	1.622 67	9.86
30B5	3.726	107.88	1.616 97	10.13
30B7	3.742	114.48	1.610 79	10.61
30B10	3.743	119.39	1.604 39	10.97
30C0	3.337	97.52	1.590 72	9.87
30C3	3.426	103.42	1.585 27	10.12
30C5	3.440	106.44	1.581 62	10.32
30C7	3.412	110.92	1.576 58	10.76
30C10	3.488	115.72	1.573 09	10.93
40C0	3.232	95.34	1.579 29	9.8

and dimensions. The values of D for sodium and rubidium germanates were in such good agreement with earlier measurements (sodium [5, 13, 20, 30], rubidium [2, 21]) that pycnometric methods were not used. The densities and the molecular weights (determined from the chemical analyses) are given for each sample in Table II. Cost precluded the analysis of 12 glasses and for each of these glasses the nominal composition is listed in Table I in brackets.

2.3. Refractive index measurements

The conductivity samples were polished with 60 grade SiC paper and their refractive index measured on a V-prism refractometer (precision 3×10^{-5}). Measurements were made using the D, F, C, e and g lines for all but four of the glass samples. The refractive indices n_D, dispersion $(n_F - n_C)$ and Abbe number $\{\nu_D = (n_D - 1)/(n_F - n_c)\}$ are listed in Table I (the refractive indices at other wavelengths are available on request).

3. Results and discussion

3.1. Single alkali germanate glasses

3.1.1. Sodium germanate

As already noted, the $D(X)$ data are in good agreement with earlier work [5, 13, 20, 30]. The values of $n_D(X)$ are in excellent agreement with the work of Verweij *et al.* [8]. The $n_D(X)$ values of Murthy and Aguayo [5] are 0.2 to 0.4% lower than the present work for $X > 0.15$.

3.1.2. Rubidium germanate

The $D(X)$ values agree well with previous work [2, 21]. The $n_D(X)$ values agree with those of Murthy and Ip (taken from their figure [2]) for high X but appear to be as much as 0.6% high at $X = 0.06$.

3.1.3. Comparison with other alkali germanate glasses

Measurements of $D(X)$ and $n_D(X)$ have been made for lithium [4, 8] and for potassium–germanate glass [6, 8] and the data from different workers are in good agreement with each other. Together with the data for sodium- and rubidium-germanate glasses it is clear that for each alkali germanate glass $n_D(X)$ and $D(X)$ increase from the value for germania glass up to a maximum value and then decrease. This maximum value in $n_D(X)$ and minimum value in the molar volume occur at progressively smaller values of X for lithium ($X \sim 0.23$), sodium ($X \sim 0.15$), potassium ($X \sim 0.12$) and rubidium ($X \sim 0.09$).

The refractive index for waves of infinite wavelength, n, is connected to the polarizability, α, of the atoms by the Lorentz–Lorenz equation which for an elementary monatomic gas is given by

$$\alpha = \frac{3\varepsilon_0}{N}\left[\frac{n^2 - 1}{n^2 + 2}\right]\frac{M}{D} = \frac{3\varepsilon_0}{N} R_\infty$$

where $\varepsilon_0 = 8.854 \times 10^{-12}\,\mathrm{F\,m^{-1}}$ is the dielectric constant *in vacuo*, N is Avogadro's number and R_∞ is the molar refractivity. Molar refractivities, R, in the present work are determined with $n = n_D$ and given in Table II. Values of R for the sodium- and rubidium-germanate glasses are plotted as a function of X in Fig. 2. The lines fitted to the data are reproduced in Fig. 3, where they are compared to the earlier data [4, 6, 8] for lithium- and potassium-germanate glasses. The Lorentz–Lorenz equation shows that the molar refractivity is directly proportional to the polarizability of the atoms, i.e. increasing the negative charge or increasing the ion size will increase α and therefore R. However, in a glass, R is the sum of the refractivities of each separate ion. Some of the trends in

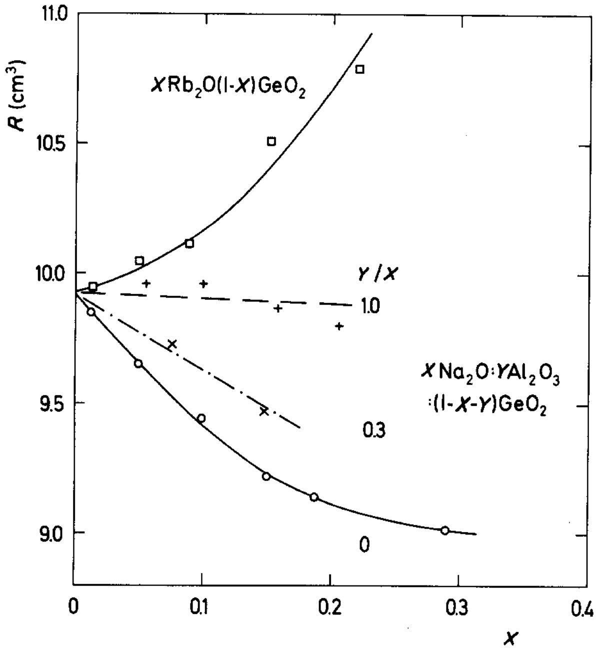

Figure 2 The molar refractivity, R, as a function of X for $X\mathrm{Na_2O}:Y$ $\mathrm{Al_2O_3}:(1 - X - Y)\mathrm{GeO_2}$ for $Y/X = 0$, 0.3 and 1.0 and for X $\mathrm{Rb_2O}:(1 - X)\mathrm{GeO_2}$.

Fig. 4 are to be expected; the larger the alkali ion and the larger the number of orbital electrons, the larger α and therefore R. The dominant influence on R with increasing X appears to be the decreasing molar volume (see Fig. 1) at least for X smaller than that for the minimum in the molar volume $(X)_{\mathrm{min}}$. The present values of n_{D} for rubidium-germanate glass lead to $R(X)$ always increasing with X: however, the lower values of $n_{\mathrm{D}}(X \leqslant 0.06)$ measured by Murthy and Ip [2] suggest a minimum in $R(X)$ at $X \sim 0.03$. For $X \geqslant (X)_{\mathrm{min}}$ the slopes of $R(X)$ for each alkali germanate glass approach a slope similar to that found for the analogous alkali silicate glass (see Fig. 1 of [8]). For $X > 0.33$ in sodium germanate glass, all germania is in tetrahedral coordination and each additional $\mathrm{Na_2O}$ molecule gives rise to two non-bridging oxygens (NBO). The similarity of the slopes suggest that in the region where the addition of alkali is compensated by the formation of NBO, changes in the polarizability with X are similar in both germanates and silicates. The dependence of $R(X)$ on molar volume, changes to a dependence on the formation of NBO at a lower X as the size of the alkali ion increases. It would appear that the same changes in the network structure which result in the changes of molar volume with X(Fig. 1) also result in parallel changes in α and therefore R.

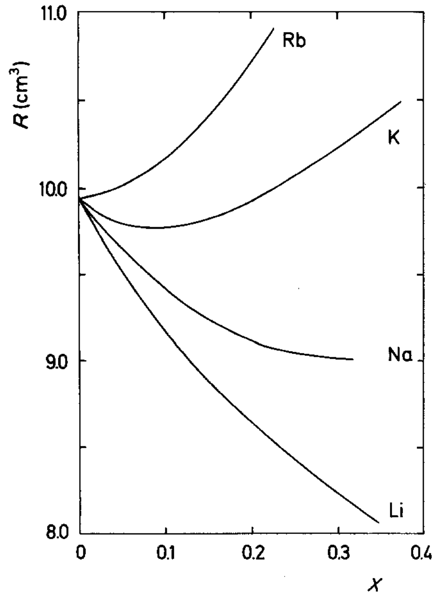

Figure 3 The molar refractivity, R, as a function of X for lithium-, sodium-, potassium- and rubidium-germanate glasses. Curves for sodium- and rubidium-germanates from Fig. 2. Curves for lithium- and potassium-germanates from [4, 6, 8].

3.2. Alkali aluminogermanate glasses

3.2.1. Sodium aluminogermanate glasses

The molar volumes (molecular weight/density) are plotted as a function of X in Fig. 4 where they are compared to the data of Murthy and Scroggie [7] (full lines). The present data agree with $\pm 1\%$ with the interpolated values of the earlier work with the exception of samples 20C and 30C which were 2 to 3% higher. The dashed line in Fig. 4 connects glasses with Al/Na ~ 1.0 and shows that for these glasses the dependence of molar volume on alkali content appears to be linear and weak. The $n_{\mathrm{D}}(X)$ data are also in good agreement ($\pm 0.1\%$) with the earlier work [7] with the exception of samples 20B, 20D and 30B which were within $\pm 0.2\%$.

Additions of alumina to the germania network decrease both $D(X)$ and $n_{\mathrm{D}}(X)$ and also greatly diminish the magnitude of the anomalous maximum in these properties. Silica additions to sodium germanate glasses [8] have a similar effect but require much larger proportions of silica to achieve the same effect. The work of Verweij *et al.* [8] covered glasses from pure germanates to pure silicates. This range is not available for the aluminogermanate glasses because for Al/Na > 1 the glasses crystallize (present work and [7]). To quantify the effect on molar refractivity, R, of aluminia additions compared to silica additions to sodium germanate glass we consider the glasses 5A, 10C; 10A, 20C; 15A, 20B, 30C; 20A, 30B, 40C (glasses in each group have the same alkali content and only the ratio of alumina to soda is changed). We find that alumina additions increase R whereas silica additions decrease R [8]. The effect is not linear and is weaker with increasing alkali content. However, at $X \sim 0.2$

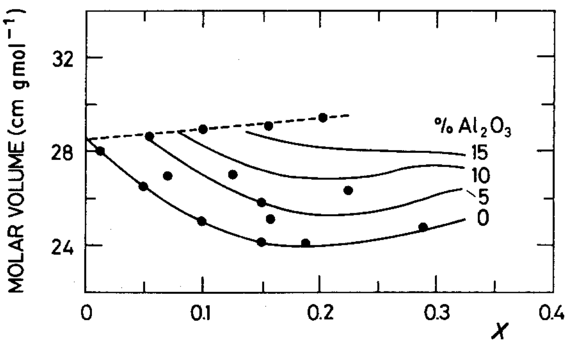

Figure 4 The molar volumes of $X\mathrm{Na_2O}:Y\mathrm{Al_2O_3}:(1 - X - Y)\mathrm{GeO_2}$ as a function of X and Y. Full lines from the data of Murthy and Scroggie [7]. The points are present work. The dashed line connects the values for glasses for which Al/Na ~ 1.0.

(5 mol % AlO_3 increases $R(0.2)$ ~ 2%) it is still much stronger than the effect of silica additions (5 mol % SiO_2 decreases $R(0.2)$ ~ 0.9%). The large decrease in $D(X)$ upon addition of alumina is a major factor in the increase of $R(X)$. It is known from earlier work [24–27] that alumina additions to sodium germanate glasses with $X < 0.33$ convert germania existing in octahedral coordination back to germania in tetrahedral coordination. Such a change would be expected to be non-linear and also to have a greater effect than silica additions which do not affect the coordination ratio of Ge^{4+} [8]. The effects of alumina additions to $R(X)$ are shown in Fig. 2 for glasses with Al/Na ~ 0.3 (dash-dot line) and for Al/Na ~ 1.0 (dashed line). The same trends can be seen in the work of Murthy and Scroggie [7]. The molar refractivity for sodium aluminogermanate glasses with Al/Na ~ 1.0 show little change with X, possibly because the packing of the network changes little with X (Fig. 4) but also because there are no changes in the concentration of charge compensating centres such as germanium in octahedral coordination or NBO.

3.2.2. *Rubidium aluminogermanate glasses*

There are no prior data with which to compare the present results but the effect of alumina additions to rubidium germanate glasses are closely similar to the result for sodium aluminogermanate glasses. Additions of Al_2O_3 decrease $D(X)$ and $n_D(X)$ but it is clear, even within the scatter of the data, that the effect of Al_2O_3 is less strong for the rubidium germanate glasses. The strong changes in R with increasing X presumably result from the strong polarizability of the rubidium ion and the effect of alumina additions is a weaker effect than for the sodium aluminogermanate glasses.

3.2.3. *Mixed sodium rubidium aluminogermanate glasses*

Values of $D(X)$ and $n_D(X)$ have been measured for ten mixed sodium rubidium aluminogermanate glass series (10A, 10B, 10C, 15A, 20A, 20B, 20C, 30A, 30B and 30C) where the total fraction of alkali is kept constant and the Al/Ge ratio fixed for each glass series. As $D(X)$ and $n_D(X)$ are not physical properties that involve ion transport, a mixed alkali effect [31] was not expected or indeed found. In all ten of the glass series $D(X)$ and $n_D(X)$ increase as rubidium replaces sodium as is to be expected for a heavier and more polarizable ion. In six of the glass series $D(X)$ decreases slightly (~ 1/2%) from glasses with Na/(Na + Rb) ~ 0.3 to pure rubidium glasses (compared to an overall increase of 2 to 3% from pure sodium to pure rubidium glasses). The refractive index shows not even this small anomaly and decreases steadily as rubidium is substituted for sodium (a total decrease of ~ 1%). The combined effect of these changes results in the molar refractivity increasing linearly with rubidium replacement of sodium (see Fig. 5; 10A, 15A, 20A). The effect is stronger for series with greater total alkali content; $\Delta R(0.1)$ ~ 7%, $\Delta R(0.15)$ ~ 14%, $\Delta R(0.2)$ ~ 18% and although $n_D(0.3)$ for rubidium germanate glass could not be measured, the other glasses in the series suggest $\Delta R(0.3)$ ~ 23%. A larger effect is to be expected for glasses with a greater proportion of total alkali because of the greater proportional change in the number of more polarizable rubidium ions. The distinct dependence on total alkali content is also seen when glass series with the same alkali content (10A, 20C; 15A, 20B, 30C; 20A, 30B) are compared (Fig. 5). The changes in R are approximately the same for the same alkali content whatever the Al/Ge ratio. Changing the ratio of aluminium/(total alkali) from 0 to 1 increases the molar refractivity ~ 5% in all the glasses. The molar refractivity of these glasses appears to be clearly the sum of the refractivities of the separate ions.

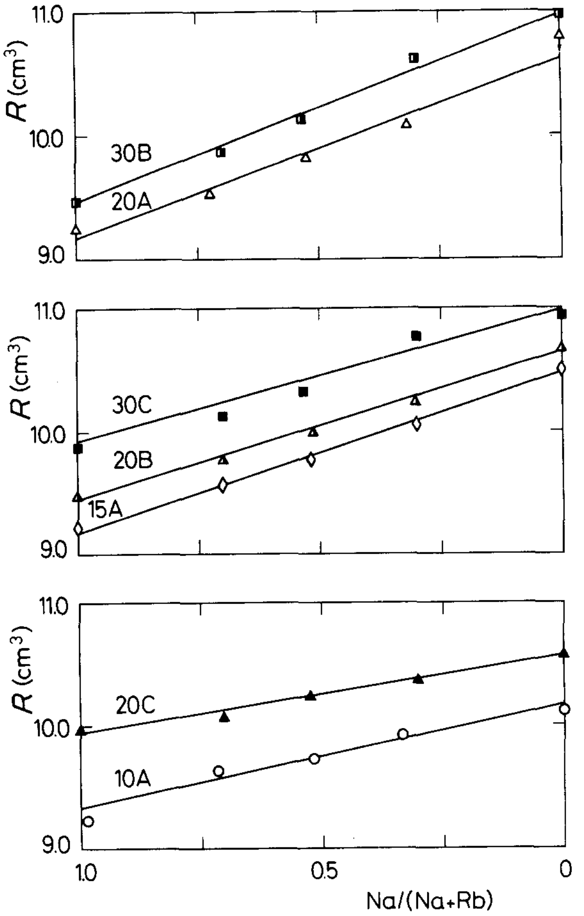

Figure 5 The molar refractivity R of $XM_2O:YAl_2O_3:(1 - X - Y)GeO_2$ as a function of Na/(Na + Rb) for (a) $(1 - X - Y) = 0.9$, $Y/X = 0$ and 1.0; (b) $(1 - X - Y) = 0.85$; $Y/X = 0$, 0.3 and 1.0; (c) $(1 - X - Y) = 0.8$, $Y/X = 0$ and 0.3.

4. Conclusions

The dependence of R on X for the sodium germanate glasses is in good agreement with earlier work [5, 8]. The present measurements of $R(X)$ on sodium- and rubidium-germanate glasses together with the earlier work on lithium-, sodium- and potassium-germanate glasses [8] suggest a common pattern of behaviour for all these alkali germanate glasses. At low X the dominant effect on R of increasing X is to increase the packing of the network and to lower R. At higher X the changes in R are dominated by the introduction of non-bridging oxygens. The changeover between these two regions occurs at lower X for increasingly alkali ions.

Additions of alumina strongly increase the molar refractivity of sodium- and rubidium-germanate glasses and it is suggested this results from the conversion of germanium from octahedral coordination to tetrahedral coordination.

The molar refractivity in all of the mixed alkali germanate and aluminogermanate glass series increased linearly with the replacement of sodium by rubidium and indicates that for these glasses R is the sum of the refractivities of the separate ions.

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