JOURNAL OF MATERIALS SCIENCE 16 (1981) 1059–1062

# Refractive index and density of alkali lime borogermanosilicate glasses

G. A. C. M. SPIERINGS, G. P. MELIS
*Philips Research Laboratories, Eindhoven, The Netherlands*

Refractive index and density data of glasses having molar compositions 15% $A_2O$–10% CaO–45% $SiO_2$–(30 – $x$)% $GeO_2$–$x$% $B_2O_3$ with $A$ = Na or K are reported. From these data the molar refraction and the contribution of oxygen to the molar refraction are calculated. The co-ordination of germanium and boron in these glasses is discussed. At $x = 0$, $GeO_6$ octahedra are observed which are gradually transformed into $GeO_4$ tetrahedra as the $GeO_2$ is replaced by $B_2O_3$. In $B_2O_3$-rich glasses no $GeO_6$ octahedra are present and the structure of the $B_2O_3$-rich glasses is found to be the same as that of comparable alkali borosilicate glasses.

## 1. Introduction

The structure of borate or germanate groups formed on the incorporation of $B_2O_3$ or $GeO_2$ in alkali silicate glasses has been found to depend on the total bulk composition [1–4]. In alkali borosilicate glasses the presence of a variety of units containing $BO_3$ triangles and $BO_4$ tetrahedra has been postulated [1, 2, 5, 6]. In alkali germanosilicate glasses the occurrence of both $GeO_4$ tetrahedra and $GeO_6$ octahedra has been observed [7]. The mutual influence between the co-ordination types of Ge and B in alkali borogermanate glasses has been reported by Riebling, Blaszyk and Smith [8] and Krupkin and Evetrop'ev [9]. In both papers it is concluded that with increasing $B_2O_3$ content, the $GeO_6$ octahedra are gradually transformed into $GeO_4$ tetrahedra. At the ratio $B_2O_3/GeO_2 = 1$, no remaining $GeO_6$ octahedra are observed [9]. A study of the density and refractive index of alkali lime borogermanosilicate glasses is reported here. Using the molar refractivity data, B and Ge co-ordination is investigated.

The alkali lime borogermanosilicate glasses may be of interest in the production of optical fibres [10]. Alkali lime germanosilicate glasses are used for preparing graded index optical fibres, making use of the refractive index difference between the $Na_2O$ and $K_2O$ glasses. The incorporation of some $B_2O_3$ significantly lowers the melting and fibre drawing temperature while the refractive index differences between the $Na_2O$ and $K_2O$ glass is maintained.

## 2. Experimental procedure

The glasses were prepared from $Na_2CO_3$*, $K_2CO_3$*, $CaCO_3$*, $B_2O_3$*, $SiO_2$† and $GeO_2$‡ in batches of 400 g. The glass compositions were 15 mol % $A_2O$–30 mol % CaO–45 mol % $SiO_2$–(30 – $x$) mol % $GeO_2$–$x$ mol % $B_2O_3$ with $A$ = Na or K. The glasses were prepared by manually mixing the components, followed by melting in Pt–10% Rh crucibles in an electrically heated furnace. The melting temperatures ranged from 1350° C for glasses with $x = 0$ to 1100° C for $x = 30$. Dry oxygen was bubbled through the melt for 1 h to achieve homogenization. After bubbling, the temperature was decreased by 100° C for fining and subsequently the melt was poured into graphite moulds and annealed.

The refractive index $n_D$ was measured on an Abbe refractometer§ with an accuracy of $2 \times 10^{-4}$. The density $D$ was determined by measuring the weight of the samples, both in air and in water at 25° C (precision $5 \times 10^{-3}$ g cm$^{-3}$).

---

*Reagent grade, Merck, Darmstadt, W. Germany.
†α-quartz, Hereaus, Hanau, W. Germany.
‡Extra-pure, Hoboken, Belgium.
§Zeiss, Oberkochen, W. Germany.

0022–2461/81/041059–04$02.40/0

TABLE I Refractive index ($n_D$), density ($D$), molar refraction ($R$) and contribution of oxygen to the molar refraction $R(O^{2-})$ for glasses with a molar composition 15% $Na_2O$–10% CaO–45% $SiO_2$–$(30-x)$% $GeO_2$–$x$% $B_2O_3$

| Composition $x$ (wt %) | $n_D$ | $D$ (g $cm^{-3}$) | $R$ ($cm^3$) | $R(O^{2-})$ ($cm^3$) |
|---|---|---|---|---|
| 0 | 1.5799 | 3.059 | 7.97 | 3.90 |
| 3.8 | 1.5760 | 3.009 | 7.92 | 3.84 |
| 7.5 | 1.5723 | 2.945 | 7.90 | 3.80 |
| 11.3 | 1.5683 | 2.898 | 7.83 | 3.74 |
| 15.0 | 1.5632 | 2.834 | 7.80 | 3.70 |
| 18.8 | 1.5585 | 2.760 | 7.80 | 3.67 |
| 22.5 | 1.5542 | 2.694 | 7.79 | 3.64 |
| 26.3 | 1.5488 | 2.620 | 7.78 | 3.61 |
| 30.0 | 1.5415 | 2.551 | 7.75 | 3.57 |

## 3. Results

Tables I and II give the refractive indices $n_D$ and densities $D$ of the glasses as function of $x$. From these data the molar refraction $R$ of the glasses can be calculated using the Lorentz–Lorenz equation

$$R = \frac{(n_D^2 - 1)\bar{M}}{(n_D^2 + 2)D}, \qquad (1)$$

where $\bar{M}$ is the average molar weight, $\bar{M} = 0.15\, M(A_2O) + 0.10 M(CaO) + 0.45 M(SiO_2) + (0.30 - 0.01x) M(GeO_2) + 0.01x\, M(B_2O_3)$, where $M$ is the molecular weight. The molar refraction $R$, also given in Tables I and II is usually thought of as being additively composed of the contributions of each ion in the glass [7, 11, 12]. Therefore, for the glasses discussed here $R$ can be calculated according to

$$\begin{aligned} R = {} & 0.3 R(A^+) + 0.1 R(Ca^{2+}) + 0.45 R(Si^{4+}) \\ & + (0.30 - 0.01x) R(Ge^{4+}) \\ & + 0.02x\, R(B^{3+}) + (1.75 + 0.01x) R(O^{2-}). \end{aligned} \qquad (2)$$

TABLE II Refractive index ($n_D$), density ($D$), molar refraction ($R$) and contribution of oxygen to the molar refraction $R(O^{2-})$ for glasses with a molar composition 15% $K_2O$–10% CaO–45% $SiO_2$–$(30-x)$% $GeO_2$–$x$% $B_2O_3$

| Composition $x$ (wt %) | $n_D$ | $D$ (g $cm^{-3}$) | $R$ ($cm^3$) | $R(O^{2-})$ ($cm^3$) |
|---|---|---|---|---|
| 0 | 1.5616 | 2.931 | 8.64 | 3.91 |
| 3.8 | 1.5598 | 2.891 | 8.59 | 3.85 |
| 7.5 | 1.5579 | 2.854 | 8.53 | 3.79 |
| 11.3 | 1.5545 | 2.804 | 8.49 | 3.74 |
| 15.0 | 1.5503 | 2.747 | 8.47 | 3.70 |
| 18.8 | 1.5463 | 2.685 | 8.45 | 3.67 |
| 22.5 | 1.5411 | 2.619 | 8.44 | 3.65 |
| 25.0 | 1.5394 | 2.580 | 8.43 | 3.60 |
| 30.0 | 1.5311 | 2.491 | 8.41 | 3.57 |

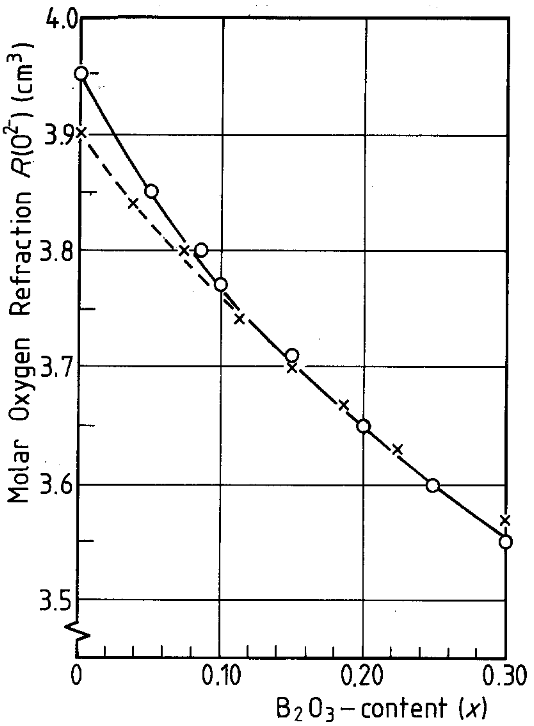

*Figure 1* $R(O^{2-})$ for glasses with molar compositions 25% $Na_2O$–$(75-x)$% $SiO_2$–$x$% $B_2O_3$ (○) and 15% $Na_2O$–10% CaO–45% $SiO_2$–$(30-x)$% $GeO_2$–$x$% $B_2O_3$ (×).

All ion refractions except $R(O^{2-})$ are generally considered to be independent of the glass composition and can be obtained from Verwey *et al.* [7] and Scholze [12]. $R(Na^+) = 0.72\,cm^3$; $R(K^+) = 2.90\,cm^3$; $R(Si^{4+}) = 0.04\,cm^3$; $R(Ge^{4+}) = 2.60\,cm^3$ [7]; $R(Ca^{2+}) = 1.33\,cm^3$ and $R(B^{3+}) = 0.1\,cm^3$ [12]. Insertion of the known ion refractions into Equation 2 gives $R(O^{2-})$, which is given in Tables I and II.

For comparison, $R(O^{2-})$ for 25 mol% $Na_2O$–$(75-x)$ mol% $SiO_2$–$x$ mol% $B_2O_3$ glasses was calculated from the refractive index and density data given by Akimov [13]. The values of $R(O^{2-})$ obtained are also shown in Fig. 1. In these glasses $SiO_2$ instead of $GeO_2$ is replaced by $B_2O_3$. Because 15 mol% $Na_2O$–10 mol% CaO–borogermanosilicate glasses are compared with 25 mol% $Na_2O$–borosilicate glasses, the influence of the replacement of some $Na_2O$ by CaO on $R(O^{2-})$ was determined in glasses with composition $(25-x)$ mol% $Na_2O$–$x$ mol% CaO–45 mol% $SiO_2$–30 mol% $B_2O_3$. Table III gives $n_D$, $D$, $R$ and $R(O^{2-})$ for these glasses.

## 4. Discussion

The oxygen refraction $R(O^{2-})$ is strongly depen-

TABLE III Refractive index ($n_D$), density ($D$), molar refraction ($R$) and contribution of oxygen to the molar refraction $R(O^{2-})$ for glasses with a molar composition $(25-x)\% A_2O$–$x\%$ CaO–45% $SiO_2$–30% $B_2O_3$

| Composition<br>$x$ (wt %) | $n_D$ | $D$<br>(g cm$^{-3}$) | $R$<br>(cm$^3$) | $R(O^{2-})$<br>(cm$^3$) |
|---|---|---|---|---|
| $A = K$ | | | | |
| 0 | 1.5228 | 2.476 | 8.82 | 3.55 |
| 10 | 1.5321 | 2.495 | 8.51 | 3.57 |
| 15 | 1.5418 | 2.520 | 8.21 | 3.58 |
| $A = Na$ | | | | |
| 0 | 1.5271 | 2.526 | 7.72 | 3.55 |
| 5 | 1.5353 | 2.543 | 7.74 | 3.56 |
| 10 | 1.5424 | 2.546 | 7.78 | 3.58 |
| 15 | 1.5506 | 2.560 | 7.78 | 3.59 |

dent on the way the oxygen ions are present in the glass. This has been shown, for instance, by Verwey, Buster and Remmers [7] for alkali germanosilicate glasses. The molar refraction $R$ for these glasses could be explained by assigning $R(O^{2-}) = 3.70\,cm^3$ to the bridging oxygens (BO) and $R(O^{2-}) = 4.55$ or $4.43\,cm^3$ to non-bridging oxygens (NBO) in $Na_2O$ and $K_2O$ glasses, respectively. On calculating $R(O^{2-})$ for glasses containing $B_2O_3$ it was found that both for BO's and NBO's the value of $R(O^{2-})$ was glass composition dependent. Consequently the experimental $R(O^{2-})$ values for alkali lime borogermanosilicate glasses can only be discussed qualitatively, comparing them with $R(O^{2-})$ values obtained for comparable alkali borosilicate glasses. Such a comparison is possible because the substitution of CaO for $Na_2O$ or $K_2O$ does not alter $R(O^{2-})$ significantly, as shown in Table III. In the $GeO_2$-rich glasses a lower value of $R(O^{2-})$ in the borogermanosilicate glass is observed. For $x = 0$, alkali silicate and germanosilicate glasses are considered for which $R(O^{2-})$ can be calculated if the numbers of BO's and NBO's are known using the $R(O^{2-})$ values given above [7]. 1 mole of a glass with molar composition 25% $Na_2O$–75% $SiO_2$ contains 1.25 mole BO and 0.50 mole NBO, resulting in a $R(O^{2-})$ value of $3.95\,cm^3$. For alkali lime germanosilicate glass the structure is more complicated because both 4 and 6 co-ordinated germanium ions are present, of which the latter are surrounded by BO's only. Because $SiO_2$ is found to dilute the germanate network, leaving the ratio between 4 and 6 co-ordinated Ge unchanged [7], the number of BO's and NBO's can be obtained from the results of Verwey and Buster [14]: 1 mole of a glass with molar composition 15% $Na_2O$–10% CaO–30% $GeO_2$–45% $SiO_2$ contains 1.34 mole BO and 0.41 mole NBO, yielding $R(O^{2-}) = 3.90\,cm^3$. Both theoretical values of $R(O^{2-})$ agree very well with the experimental ones in Fig. 1. Therefore, it is reasonable to assume that the lower $R(O^{2-})$ value in the borogermanosilicate glass is caused by the presence of 6 co-ordinated germanium. As $x$ increases, $R(O^{2-})$ values for the two glasses both decrease and the difference in $R(O^{2-})$ becomes smaller. It appears that for $x$ larger than about 10%, the difference in $R(O^{2-})$ values becomes very small, within experimental accuracy, indicating that no more 6 co-ordinated germanium is present in the $B_2O_3$-rich glass. The same finding has also been reported for alkali borogermanate glasses which indicates that $SiO_2$ only dilutes the borogermanate network. This has also been observed upon the introduction of $SiO_2$ into the separate borate and germanate glasses [6, 7].

It is not clear in what manner $B_2O_3$ is present at small $B_2O_3$ contents. According to Yun and Bray [5], who conducted an investigation using nuclear magnetic resonance (NMR) techniques $B_2O_3$ is taken up in $BSi_4O_{10}$ units, as observed in Reedmergnite. In these units boron is co-ordinated by four BO's. Konijnendijk [6], using laser Raman spectroscopy, observed only 3 co-ordinated boron with one NBO (metaborate groups). The relatively large decrease in $R(O^{2-})$ values as $x$ increases (Fig. 1) indicates that BO's are formed at the expense of BNO's, supporting the interpretation of Yun and Bray [5].

No difference in $R(O^{2-})$ for both glasses is observed in the $B_2O_3$-rich region. It appears that the structure of both glasses is equivalent and germanium is present in 4 co-ordination only. The structure of these types of alkali borosilicate glasses has been extensively studied by e.g. Bray and co-workers [1, 5] and Konijnendijk [6]. No detailed additional information about the structure of these glasses can be obtained from the $R(O^{2-})$ value, due to glass content dependency of $R(O^{2-})$ for oxygens bound to boron.

## 5. Conclusions

In $GeO_2$-rich alkali lime germanosilicate glasses part of the germanium is in sites that are 6 co-ordinated by oxygen ions. As $B_2O_3$ is substituted for $GeO_2$, the $GeO_6$ octahedra are gradually transformed into 4 co-ordinated germanium. In the $B_2O_3$-rich glasses the structure of the alkali lime borogermanosilicate glasses is comparable with that of alkali borosilicate glasses.

## References

1. P. J. BRAY and J. G. O'KEEFE, *Phys. Chem. Glasses* **4** (1963) 37.
2. M. E. MILBERG, J. G. O'KEEFE, R. A. VERHELST and H. O. HOPPER, *ibid.* **13** (1972) 79.
3. K. S. EVSTROP'EV and A. O. IVANOV, "Advances in Glass Technology", Vol. 2 (Plenum Press, New York, 1963) pp. 79–85.
4. M. KRISHNA MURTHY and J. IP, *Nature* **201** (1964) 283.
5. Y. H. YUN and P. J. BRAY, *J. Non-Cryst. Sol.* **27** (1978) 363.
6. W. L. KONIJNENDIJK, Ph.D. thesis, Philips Research Report, Supplement No. 1 (1975).
7. H. VERWEY, J. H. J. M. BUSTER and G. F. REMMERS, *J. Mater. Sci.* **14** (1979) 931.
8. E. F. RIEBLING, P. E. BLASZYK and D. W. SMITH, *J. Amer. Ceram. Soc.* **50** (1967) 641.
9. Yu. S. KRUPKIN and K. S. EVSTROP'EV, *Neorg. Mater.* **7** (1971) 1591.
10. G. A. C M. SPIERINGS, C. M. G. JOCHEM, T. P. M. MEEUWSEN, F. MEYER and P. J. W. SEVERIN, *Phys. Chem. Glasses* **21** (1980) 31.
11. K. J. FAJANS and N. J. KREIDL, *J. Amer. Ceram. Soc.* **31** (1948) 105.
12. H. SCHOLZE, "Glas" (Vieweg Verlag, Braunschweig, 1965) p. 130.
13. V. V. AKIMOV, *Zh. Prikl. Khim.* **33** (1960) 2404.
14. H. VERWEY and J. H. J. M. BUSTER, *J. Non. Cryst. Sol.* **34** (1979) 81.

Received 21 August and accepted 10 October 1980.