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PROPERTIES AND STRUCTURE OF GERMANATE GLASSES

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ABSTRACT

The presence of extrema in the composition dependence of physical properties of modified germanate glasses is known as the “germanate anomaly” effect. The explanation of this phenomenon is still a matter of controversy. In this study, a quantitative description of the germanate network structure is employed to simulate the density of potassium germanate glasses with K₂O contents up to 40 mol%. The results show that the knowledge of the short range order structure, i.e. the nature and population of the network building units, is not sufficient to reproduce the maximum in density. Instead, the introduction into the simulation procedure of changes (in the medium range order structure) results in an excellent agreement between experimental and simulated density values. Therefore, the combined consideration of short and medium range order structural change as metal oxide is added to GeO₂ seems to offer an adequate explanation of the “germanate anomaly” effect.

1. INTRODUCTION

Alkali germanate glasses, $xM_2O \cdot (1-x)GeO_2$ (M=alkali metal), are characterised by the presence of extrema in their property-composition relations, a phenomenon known as the “germanate anomaly” effect. In particular, the density of alkali germanate glasses exhibits maximum value at *ca.* 15 mol% M₂O [1-3].

Early investigations attributed the “germanate anomaly” effect to the formation of octahedral germanate units GeO_6^{2-} (\emptyset =bridging oxygen atom) as M₂O is added to GeO₂ in the composition range $0 < x \leq 0.20$, and the subsequent formation of non-bridging oxygen (NBO) atoms in germanate tetrahedra Q^i , with 4-i NBO's per tetrahedron, at higher metal oxide contents [3-6]. In a different approach, it was proposed that formation of germanium-oxygen tetrahedral units with NBO's is the only structural modification mechanism of the glass network. According to this model, the maximum in density is associated with the formation of 3-membered rings of germanium-oxygen tetrahedral species [7].

Recent spectroscopic studies of germanate glasses suggested that both modification mechanisms, i.e. creation of GeO_6^{2-} octahedra and Q^i tetrahedra with NBO's, co-exist throughout a wide composition range [8-12]. Weber applied the method of bond volumes and concluded that the redistribution of free volume is the leading mechanism responsible for the “germanate anomaly” effect [13].

We have investigated Rb- and K-germanate glasses by Raman and infrared spectroscopy and derived a quantitative description of the short range order (SRO) structure in terms of the fractions of local germanate polyhedra [9-11]. This knowledge of SRO structure is employed in this work in an attempt to simulate the density of potassium germanate glasses.

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2. STRUCTURE AND DENSITY OF POTASSIUM GERMANATE GLASSES

The mol fractions of the local germanate polyhedra in $x\text{K}_2\text{O}\cdot(1-x)\text{GeO}_2$ glasses were obtained in our previous studies and are shown in Fig. 1. These include the fractions X_i of tetrahedral germanate units, Q^i , and the fraction N_6 of octahedral units, GeO_6^{2-} . Details concerning spectral analysis and calculations can be found elsewhere [9-11].

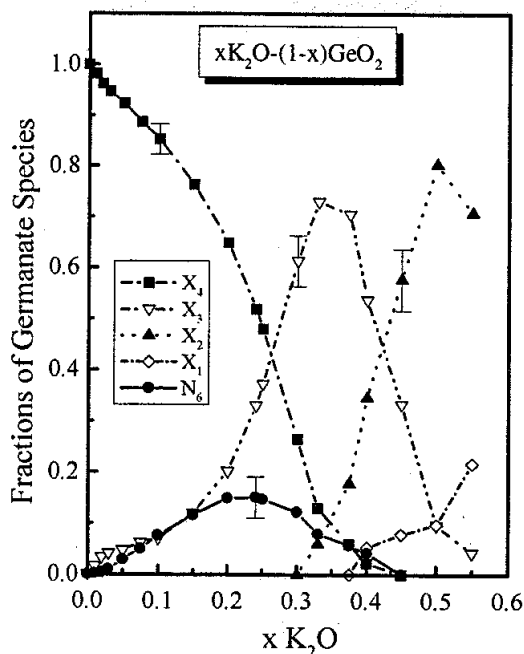


Fig. 1 Mole fractions of octahedral GeO_6^{2-} units, N_6 , and of tetrahedral Q^i species, X_i , in $x\text{K}_2\text{O}\cdot(1-x)\text{GeO}_2$ glasses [9-11]. Lines are drawn as guides to the eye.

As shown in Fig. 1, alkali oxide addition up to *ca.* 25 mol% K_2O results in the formation of GeO_6^{2-} octahedral and GeO_3O^- tetrahedral (Q^3) units. For higher alkali oxide contents up to *ca.* 40 mol% K_2O the conversion of GeO_6^{2-} into mainly Q^3 species prevails, while for $x > 0.4$ the creation of Q^2 and Q^1 units is the dominating structural modification mechanism. This quantitative presentation of the SRO structure will be employed to simulate the density of K-germanate glasses.

Densities of K-germanate glasses are depicted in Fig. 2 for compositions in the range $0 \leq x \leq 0.40$ [1-3]. The "germanate anomaly" is manifested by the density maximum at *ca.* 10 mol% K_2O and can be attributed to the formation of GeO_6^{2-} octahedral species [14-16], or alternatively to the creation of small 3-membered rings of Q^4 tetrahedra [7, 13]. The gradual decrease in density, for K_2O contents above *ca.* 15 mol%, results from the progressive depolymerization of the glass network due to creation of NBO-containing tetrahedral units.

3. DENSITY SIMULATION FOR POTASSIUM GERMANATE GLASSES

The composition dependence of density can be written in the form:

$$d(x) = \frac{\sum_i M_i X_i(x)}{\sum_i V_i X_i(x)} \quad (1)$$

where M_i , X_i and V_i are the molar mass, mol fraction and molar volume of the i^{th} local structural unit [17]. Molar masses for structural units in K-germanate glasses are given in

Table 1 where Q^i ($i=4, 3, 2$) denotes germanate tetrahedral units charge-compensated by 4- i K^+ ions, and Q^6 indicates the GeO_6^{2-} octahedral species charge-balanced by two K^+ ions. It is noted that Q^2 and Q^6 species are isomeric and thus have the same molar mass.

Table 1. Short range order structural units, molar masses, M_i , effective molar volumes, V_i , and effective densities, d_i , in K-germanate glasses. Q^4_L and Q^4_S indicate Q^4 tetrahedral units in large (L) and small (S) ring arrangements, respectively

Structural Unit	M_i (g/mol)	V_i (cm ³ /mol)	d_i (g/cm ³)
Q^4 GeO ₂	104.6	28 ± 2	3.7 ± 0.2
Q^3 KGeO _{2.5}	151.7	45.6 ± 0.2	3.33 ± 0.01
Q^2 K ₂ GeO ₃	198.8	66.3 ± 0.1	3.00 ± 0.01
Q^6 K ₂ GeO ₃	198.8	70 ± 3	2.8 ± 0.1
Q^4_L GeO ₂	104.6	28 ± 2	3.7 ± 0.2
Q^4_S GeO ₂	104.6	19.4 ± 0.4	5.4 ± 0.1

In a first attempt, the experimental density data were fitted using the reported values for X_i and M_i (Fig. 1 and Table 1), and composition independent molar volumes, V_i , as the fitting parameters. The results of this non-linear least square fit are shown in Fig. 2a and are similar to those reproduced in a very recent study of alkali-germanate glasses [16]. For $x > 0.15$ the simulated curve compares quite well with the experimental data, whereas in the range $0 < x < 0.15$ the agreement is poor. This finding suggests that the knowledge of the SRO structure alone is not sufficient to describe the initial increase in density.

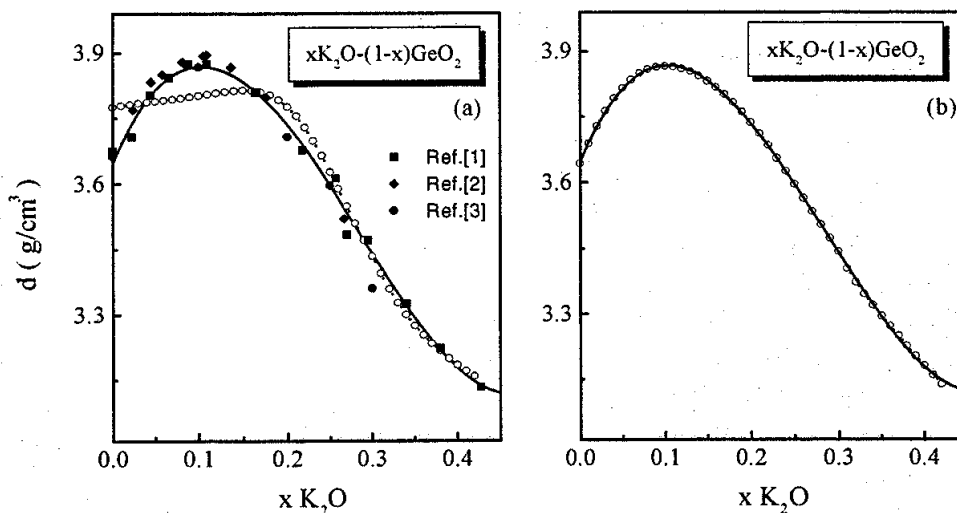


Fig. 2 Simulations (o) of experimental density data [1-3] in $xK_2O \cdot (1-x)GeO_2$ glasses. (a) Composition independent molar volumes, (b) Composition dependent molar volume of Q^4 species. The solid line is a polynomial fit of experimental data.

We note from Fig. 1 that in the composition range $0 < x < 0.15$ where the simulation fails the predominant structural unit is the Q^4 species, and that previous studies suggested a redistribution of Q^4 species in rings smaller than those encountered in glassy GeO₂ [7,9,10]. Therefore, we proceed by assuming now as fitting parameters a composition dependent molar

volume of Q^4 species, $V_4=V_4(x)$, and composition independent volumes V_3 , V_2 and V_6 . With these assumptions, it was found that the following function:

$$V_4(x) = A_1 + A_2 \exp(-x/A_3) \quad (2)$$

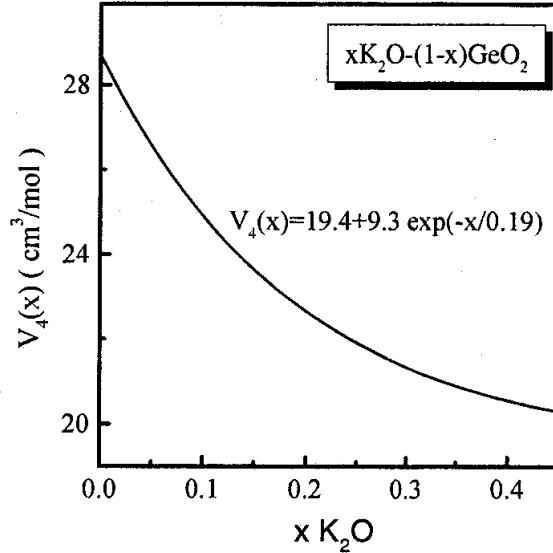


Fig. 3 Composition dependence of the molar volume $V_4(x)$ of Q^4 units in $xK_2O \cdot (1-x)GeO_2$ glasses

with $A_1=19.4$ cm³/mol, $A_2=9.3$ cm³/mol and $A_3=0.19$, can successfully simulate the experimental density data (Fig. 2b). The calculated effective molar volumes of the SRO structural units are given in Table 1, where the value for the Q^4 unit corresponds to that in glassy GeO_2 . The obtained volume $V_4(x)$ from the density fit is shown in Fig. 3, and exhibits an exponential decrease from its maximum value in GeO_2 glass ($V_{4,max} = A_1+A_2$) towards the asymptotic minimum ($V_{4,min} = A_1$) for glasses with large K_2O contents.

4. DISCUSSION

The results of density simulations indicate that a detailed description of the SRO structure alone cannot provide the explanation of the “germanate anomaly” effect. Instead, introduction of changes in the medium range order (MRO) structure of the glass, induced by alkali addition to GeO_2 , may play a decisive role. Such MRO changes could involve topological rearrangements of large (i.e. 6-membered) rings formed by Q^4 species in GeO_2 glass towards smaller (i.e. 3-membered) rings as alkali oxide is added to vitreous germania [7,9,10,13]. In order to investigate the MRO structure of K-germanate glasses we exploit further the composition dependence of volume $V_4(x)$ of Q^4 species.

It is assumed that a fraction $X_4^L(x)$ of Q^4 species is forming large (L) rings, and a corresponding fraction $X_4^S(x)$ is in small (S) ring arrangements, with the effective molar volumes of Q^4 species being $V_4^L=V_{4,max}=A_1+A_2$ and $V_4^S=V_{4,min}=A_1$, respectively. With these notations we can write:

$$X_4(x) = X_4^L(x) + X_4^S(x) \quad \text{and} \quad X_4(x) V_4(x) = X_4^L(x) V_4^L + X_4^S(x) V_4^S \quad (3)$$

and derive the fractions $X_4^L(x)$ and $X_4^S(x)$ as follows:

$$X_4^L(x) = X_4(x) \left\{ \frac{(V_4(x) - V_4^S)}{(V_4^L - V_4^S)} \right\} \quad (4)$$

$$X_4^S(x) = X_4(x) \left\{ \frac{(V_4^L - V_4(x))}{(V_4^L - V_4^S)} \right\} \quad (5)$$

The fractions $X_4^L(x)$ and $X_4^S(x)$ of Q^4 species are shown in Fig. 4, in comparison with total fraction $X_4(x)$ reported in Fig. 1. It is evident that $X_4^L(x)$ decreases with K_2O content, while $X_4^S(x)$ increases and reaches its maximum value at ~ 17 mol% K_2O . Regarding this trend of $X_4^L(x)$ we note that the density maximum appears at *ca.* 10 mol% K_2O and the fraction of GeO_6^{2-} octahedral units, N_6 , shows its maximum above 20 mol% K_2O (see Fig. 1).

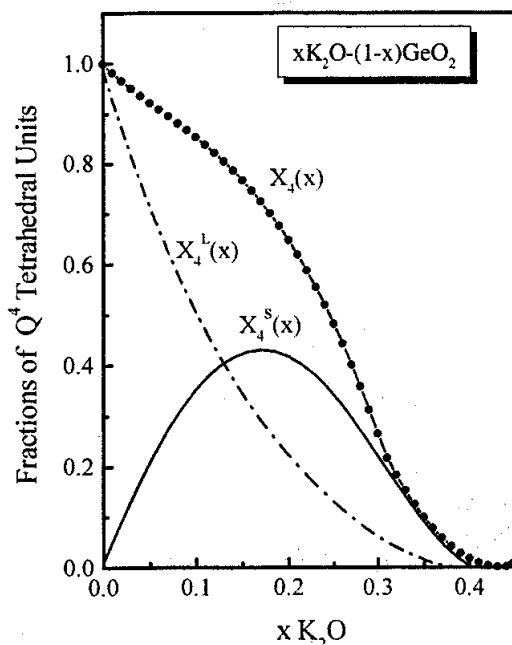


Fig. 4 Fractions of Q^4 species in large, X_4^L , and small, X_4^S , rings in $xK_2O \cdot (1-x)GeO_2$ glasses. X_4 is the total fraction of Q^4 units as determined from the analysis of the vibrational spectra (see Fig. 1).

To examine further which structural modification mechanism is mainly responsible for the appearance of the density maximum, we calculate the effective densities, d_i , of the various network building SRO units and of Q^4 species in large and small rings (Table 1). Inspection of Table 1 shows that the creation of Q^3 , Q^2 and Q^6 units would result in a net decrease of the glass density since their effective density values are lower than that of Q^4 units in GeO_2 glass. Instead, it seems that the formation of the particularly dense small rings of Q^4 units, $d(Q_4^S) = 5.4 \text{ g/cm}^3$, may account for the initial increase of density up to *ca.* 10 mol% K_2O . This finding demonstrates clearly the importance of MRO structural changes towards a better understanding of the composition dependence of density, and lends support to previous reports on change in ring statistics in alkali germanate glasses [7-10,13].

5. CONCLUSIONS

The relationship between density and structural characteristics of K-germanate glasses, $xK_2O \cdot (1-x)GeO_2$, was investigated in the composition range $0 \leq x \leq 0.40$ in order to shed light on the "germanate anomaly" effect. Simulations of experimental density data in terms of the short range order (SRO) structural picture, obtained from the analysis of the vibrational spectra, showed that the formation of GeO_6^{2-} octahedral units and non-bridging oxygen containing tetrahedral species is not sufficient to account for the "germanate anomaly" effect in density.

The introduction in the simulation procedure of a composition dependent molar volume of Q^4 tetrahedral species, resulting from a change of ring statistics towards smaller rings, gave an excellent agreement between experimental and simulated density. This work shows clearly that a combined consideration of the composition dependence of short and medium range order structures sets the basis for a better understanding of the "germanate anomaly" effect.

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