JOURNAL OF MATERIALS SCIENCE 37 (2002) 4703–4709

Density-structure predictions of silicate glasses containing Ga_2O_3

H. DOWEIDAR, G. EL-DAMRAWI, S. ABD EL-MAKSOUD
Glass Research Group, Physics Department, Faculty of Science, Mansoura University, Mansoura 35516, POB 83, Egypt
E-mail: sinfac@mum.mans.eun.eg

The density data of Li_2O-, Na_2O-, CaO- and BaO-Ga_2O_3-SiO_2 glasses have been analyzed. The analysis is based on a structural model predicted from the results of the current spectroscopic investigations. It is assumed that for (R_2O or RO)/$Ga_2O_3 = 1$ the modifier oxide is used only by the gallate network to form GaO_4 tetrahedra without non-bridging oxygen ions. For $1 <$ (R_2O or RO)/$Ga_2O_3 \leq 2$ the excess of modifier form non-bridging oxygen ions in the gallate network. There is a remarkable difference between the determined and the calculated density for $Ga_2O_3/SiO_2 > 0.75$. This is suggestive for a different distribution of the modifier oxide between the two networks. Empirical relations have been obtained to calculate the density as a function of the composition.

1. Introduction

Glasses containing pronounced contents of Ga_2O_3 are of special importance owing to their high refractive index and density [1, 2]. Some of these glasses are characterized with high infrared transmission and nonlinear optical coefficients [3–6]. It is believed that Ga_2O_3 enters the glass structure mostly in the form of GaO_4 tetrahedra as a network former [2, 3–9]. In this case the excess negative charge of GaO_4 tetrahedra must be compensated by a positive charge. Lapp and Shelby [10] indicated that in $20R_2O$-$20Ga_2O_3$-$60SiO_2$ glasses (R_2O refers to alkali oxides) the charge compensation takes place through association of R_2O with Ga_2O_3 to form GaO_4 units. Therefore non-bridging oxygen ions could not form in the silica sites. On the other hand Miyaji *et al.* [8] assumed that in $50PbO \cdot 50GaO_{1.5}$ and $80BiO_{1.5} \cdot 20GaO_{1.5}$ glasses there is a fraction of about 10% of six-coordinated Ga^{3+} ions. The latter can form in the case of a shortage in oxygen to maintain charge compensation. These trends are consistent with those observed from NMR studies on Cs_2O-Ga_2O_3 glasses [9]. In these glasses almost all the gallium atoms form GaO_4 tetrahedra when the Ga_2O_3/Cs_2O ratio is less than 3/7. Upon increasing this ratio, the excess of Ga_2O_3 enters the structure as GaO_6 units.

In previous studies [11–15] the densities of different glass systems were analyzed to get the volumes of the structural units present in the glass. The analysis is based on the available structural information for each glass system. The present work is an investigation of the density-structure relations in Li_2O-Ga_2O_3-SiO_2, Na_2O-Ga_2O_3-SiO_2, CaO-Ga_2O_3-SiO_2 and BaO-Ga_2O_3-SiO_2 glasses.

2. Procedure

The structural role of Ga_2O_3 in oxide glasses is, to a great extent, similar to that of Al_2O_3. Both of these oxides have insufficient oxygen to form a tetrahedral network. Ga^{3+} and Al^{3+} cations become four-coordinated with oxygen if there were sufficient oxygen ions from the modifier oxides in the glass. In alkali alumino-silicate glasses Al_2O_3 associates itself with an equivalent quantity of alkali oxide R_2O (in mol%) to form AlO_4 tetrahedra [15, 16]. The transformation takes place at a rate of two AlO_4 units for each molecule of R_2O. A similar behavior can be assumed for Ga_2O_3 in silicate glasses. Besides, it is believed that the Ga atoms are more likely than Al atoms in forming fourfold coordination rather than sixfold coordination [17]. There is, however, a basic difference between the AlO_4 and GaO_4 tetrahedra. The former can be incorporated into the structure only through bridging oxygen ions, whereas the latter can form NBOs [2, 8, 17–19] in the presence of sufficient modifier oxide concentration.

It has been indicated that NBOs appear in alkali and alkaline earth gallate glasses when the modifier oxide content exceeds about 43 mol% [17]. The fraction of GaO_4 tetrahedra containing NBOs increases when increasing the modifier oxide. Furthermore, Fukumi and Sakka [20] reported that in a $30Cs_2O \cdot 70Ga_2O_3$ glass the Ga^{3+} ions mainly form GaO_4 tetrahedra and there is about 15% of GaO_6 octahedra. This agrees with the assumption that GaO_6 units are formed when there is a deficiency of oxygen in the gallate matrix. In such a case there are some three-coordinated oxygens (shared by three GaO_4 tetrahedra). On the other hand, in a $66.7CaO \cdot 33.3Ga_2O_3$ glass the gallate network

contains only GaO_4 tetrahedra and there are neither GaO_6 units nor three-coordinated oxygens [20].

Ruller and Jewell [19] employed Raman and infrared spectroscopies to investigate the structure of the glasses $(80-x)$PbO-$(10+x)$ Ga_2O_3-$10SiO_2$ $(5 \leq x \leq 25$ mol%) and $(75-x/2)$ PbO-$(25-x/2)Ga_2O_3-xSiO_2$ $(0 \leq x \leq 20$ mol%). In all these glasses NBOs could be detected in the gallium tetrahedra whereas there were no signs for the presence of NBOs in the silica sites. This may indicate that the GaO_4 tetrahedra have priority to form NBOs when they are found with SiO_4 tetrahedra in the structure.

On the basis of the above-mentioned assumptions the structure of a glass having the molar formula $xR_2O \cdot yGa_2O_3 \cdot zSiO_2$ would depend on the values of x, y and z. For $(y \leq x \leq 2y)$ Ga_2O_3 is incorporated in the structure, at first, as GaO_4 units by consuming an equivalent R_2O or RO quantity. In this case each Ga_2O_3 molecule would produce two GaO_4 tetrahedra without NBOs. In addition, the remaining modifier oxide would be consumed in the formation of NBOs in the gallate network with a rate of one NBO ion per GaO_4 unit. In such glasses the SiO_2 content would be in the form of SiO_4 tetrahedra without NBOs (Q_4 units).

In the light of the above mentioned assumptions, the structural units in a $xR_2O \cdot yGa_2O_3 \cdot zSiO_2$ glass having $y \leq x \leq 2y$ form as

$$xR_2O + yGa_2O_3 + zSiO_2 \rightarrow [2y - 2(x-y)] \times G_4 + 2(x-y)G_3 + zQ_4 \quad (1)$$

where G_4 and G_3 are GaO_4 tetrahedra containing four and three bridging oxygen ions, respectively. The density D of the glass can be given as

$$D = \{[2y - 2(x-y)]M_{G4} + 2(x-y)M_{G3} + zM_{S4}\} / \{[2y - 2(x-y)]V_{G4} + 2(x-y)V_{G3} + zV_{S4}\} \quad (2)$$

where M_{G4} is the mass of the GaO_4 tetrahedron without NBOs (the mass of $Ga^{3+} + 2O^{2-} + R^+$), M_{G3} is the mass of the G_3 unit containing one NBO ion (the mass of $Ga^{3+} + 2.5O^{2-} + 2R^+$) and M_{S4} is the mass of the Q_4 unit (the mass of $Si^{4+} + 2O^{2-}$). V_{G4}, V_{G3}, and V_{S4} are the volumes of the G_4, G_3 and Q_4 units respectively. The volume of a structural unit is the volume of the constituting ions besides its portion of the free volume in glass.

CaO and BaO are assumed to enter the glass network as modifier oxides [21]. In a CaO-Ga_2O_3-SiO_2 glass it can be assumed that each CaO molecule converts a Ga_2O_3 molecule producing two GaO_4 units. The same is to be considered for BaO in BaO-Ga_2O_3-SiO_2 glasses. In these cases a GaO_4 tetrahedron would include a half Ca^{2+} or Ba^{2+} ion whereas the G_3 unit includes one of these ions.

3. Results

Fig. 1 shows the dependence of the determined density (D_m) on the composition for Na_2O-Ga_2O_3-SiO_2 glasses (as an example of the studied glasses). This presentation enables to understand how the composition varies the density of glass. As an example in Fig. 1 it is shown that, at $Na_2O = 13$ mol%, the density increases greatly with increasing the Ga_2O_3 content (compare with Table I). This reflects a strong influence of the Ga_2O_3 concentration on the density of such glasses. In Fig. 2 is shown that the ratio Ga_2O_3/SiO_2 predominates the change in density. The behaviour observed in Figs 1 and 2 is also found for Li_2O-Ga_2O_3-SiO_2, CaO-Ga_2O_3-SiO_2 and BaO-Ga_2O_3-SiO_2 glasses. The

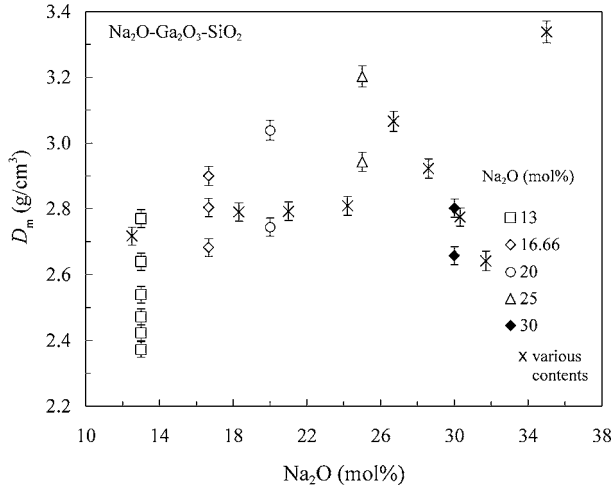

Figure 1 Dependence of the determined density D_m of Na_2O-Ga_2O_3-SiO_2 glasses on the Na_2O content. At a specific content of Na_2O D_m increases due to the increase in the concentration of Ga_2O_3 at the expense of SiO_2 (compare with Table I). The error limit is estimated as $\pm 1\%$. The data are taken from references [24–28, 33].

TABLE I Compositions, determined densities D_m [24–28, 33] and calculated densities D_c for Na_2O-Ga_2O_3-SiO_2 glasses

Na_2O (mol%)	Ga_2O_3 (mol%)	SiO_2 (mol%)	D_m (g/cm^3)	D_c (g/cm^3)
13	1.5	85.5	2.372	2.384
13	3	84	2.423	2.437
13	4.5	82.5	2.472	2.489
13	6	81	2.539	2.540
13	9	78	2.64	2.635
13	13	74	2.77	2.755
16.66	8.33	75.01	2.682	2.648
16.66	12.5	70.84	2.804	2.775
16.66	16.66	66.68	2.9	2.896
20	10	70	2.744	2.732
20	20	60	3.039	3.022
25	15	60	2.943	2.932
25	25	50	3.203	3.207
30	5	65	2.658	2.651
30	10	60	2.802	2.822
12.5	12.5	75	2.717	2.736
18.3	11.7	70	2.79	2.767
21	11.3	67.7	2.792	2.782
24.2	10.8	65	2.809	2.796
26.7	20	53.3	3.066	3.091
28.6	14.3	57.1	2.923	2.949
30.3	9.1	60.6	2.775	2.795
31.7	4.8	63.5	2.644	2.660
35*	30	35	3.338	3.442

*Glasses having $(Ga_2O_3/SiO_2) > 0.75$, also in Tables III and IV.

TABLE II Compositions, determined densities D_m [22, 23, 33] and calculated densities D_c for Li_2O-Ga_2O_3-SiO_2 glasses

Li_2O (mol%)	Ga_2O_3 (mol%)	SiO_2 (mol%)	D_m (g/cm^3)	D_c (g/cm^3)
12.5	12.5	75	2.743	2.750
16.7	16.7	66.6	2.918	2.916
20	20	60	3.065	3.047
25	25	50	3.245	3.248
27.5	27.5	45	3.337	3.349
16	12	72	2.758	2.752
20	12.5	67.5	2.801	2.792
20	15	65	2.886	2.879
25	15	60	2.921	2.912
27.5	18.1	54.4	3.032	3.038
30	20	50	3.108	3.124
20	10	70	2.706	2.702
27.5	10.4	62.1	2.76	2.757
30	14	56	2.907	2.909
25	10.5	64.5	2.76	2.747
30	10	60	2.767	2.756
20	5	75	2.5	2.512
25	5	70	2.54	2.533
30	5	65	2.557	2.555
35	5	60	2.584	2.579
20	2.5	77.5	2.392	2.414

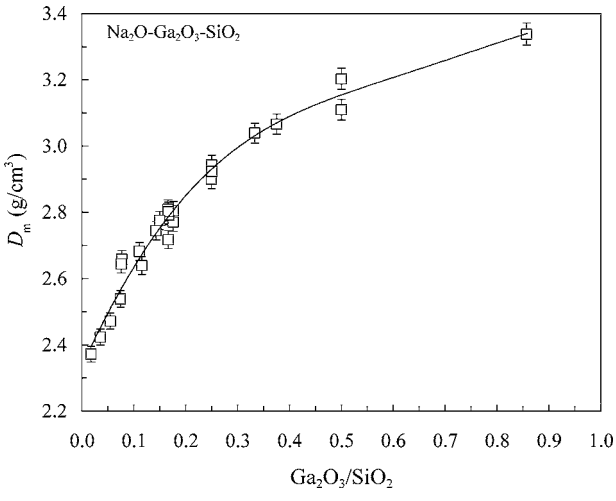

Figure 2 Dependence of the determined density D_m on the ratio Ga_2O_3/SiO_2 for Na_2O-Ga_2O_3-SiO_2 glasses. The error limit is estimated as ±1%. The data are taken from references [24–28, 33]. The solid line is a guide for the eye.

density data are taken from different sources [22–33]. The data are given in Tables I–IV.

4. Discussion

Equation 2 can be used to calculate the volumes of the structural units in $xR_2O \cdot yGa_2O_3 \cdot zSiO_2$ glasses. For $x = y$ Equation 2 can be rewritten as

$$D = (2yM_{G4} + zM_{S4})/(2yV_{G4} + zV_{S4}). \quad (2\text{-a})$$

In Tables I–IV there are some glasses in each system verifying the condition $x = y$. For example, Fig. 3 shows the dependence of D_m on the SiO_2 content for Li_2O-Ga_2O_3-SiO_2 glasses having $Li_2O/Ga_2O_3 = 1$. There is a linear decrease in D_m as the SiO_2 content

TABLE III Compositions, determined densities D_m [29–31, 33] and calculated densities D_c for CaO-Ga_2O_3-SiO_2 glasses

CaO (mol%)	Ga_2O_3 (mol%)	SiO_2 (mol%)	D_m (g/cm^3)	D_c (g/cm^3)
12.5	12.5	75	2.846	2.867
15	10	75	2.776	2.802
15	15	70	2.985	2.992
19	19	62	3.202	3.193
20	10	70	2.858	2.864
20	15	65	3.073	3.057
20	20	60	3.262	3.244
25	15	60	3.154	3.126
25	25	50	3.509	3.498
30	30	40	3.728	3.755
35*	35	30	3.912	4.015
38*	38	24	3.998	4.172
40*	30	30	3.826	3.930
40*	40	20	4.079	4.277

TABLE IV Compositions, determined densities D_m [32, 33] and calculated densities D_c for BaO-Ga_2O_3-SiO_2 glasses

BaO (mol%)	Ga_2O_3 (mol%)	SiO_2 (mol%)	D_m (g/cm^3)	D_c (g/cm^3)
20	20	60	3.666	3.661
30	30	40	4.276	4.293
20	15	65	3.525	3.515
20	10	70	3.362	3.361
40	20	40	4.391	4.408
30	10	60	3.796	3.774
40	10	50	4.181	4.203
40*	30	30	4.571	4.659
40*	40	20	4.742	4.885

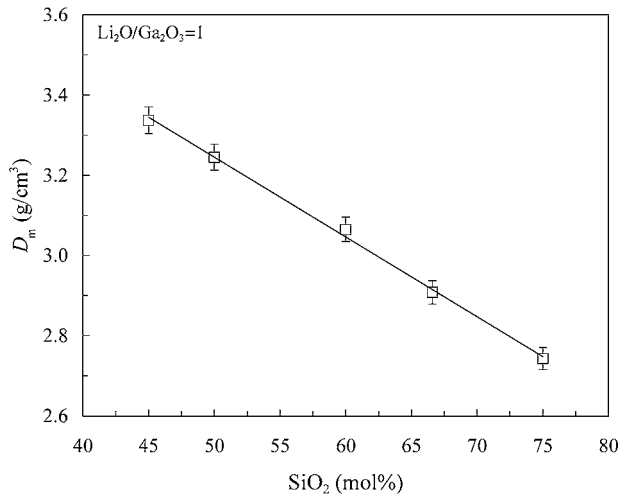

Figure 3 Dependence of the determined density D_m on the SiO_2 content for $Li_2O \cdot Ga_2O_3 \cdot SiO_2$ glasses having $Li_2O/Ga_2O_3 = 1$. The data are taken from reference [33]. The solid line represents the fitting plot of the data.

increases. The straight-line in Fig. 3 can be represented by the relation:

$$D = -0.0199C + 4.240, \quad (3)$$

where C is the content of SiO_2 in (mol%). The density values obtained from Equation 3 can be used in Equation 2a to calculate V_{G4} and V_{S4}. This can be done

by taking the density of two compositions having y values close to each other. At the first approximation one may assume that V_{G4} and V_{S4} in both compositions are constants. As an example $D = 3.0460$ g/cm^3 for $x = 20$ mol% and 3.0261 g/cm^3 for $x = 19.5$ mol%. By solving Equation 2a simultaneously for these values one obtains $V_{G4} = 42.24 \times 10^{-24}$ cm^3 and $V_{S4} = 44.09 \times 10^{-24}$ cm^3. These volumes would be considered for a glass having $x = y = 19.75$ mol% (the mean x value of the taken compositions). The obtained volumes are nearly constant (the change is less than 1% over the SiO_2 content investigated). The average values of the volumes are $V_{G4} = (42.20 \pm 0.13) \times 10^{-24}$ cm^3 and $V_{S4} = (44.08 \pm 0.08) \times 10^{-24}$ cm^3. This value of V_{S4} is about 3% lower than that found for the vitreous SiO_2, alkali and/or alkaline-earth silicate glasses (45.25×10^{-24} cm^3) [13, 15]. Similar reduction was observed in V_{S4} for Na_2O-Al_2O_3-SiO_2 [14] and Na_2O-B_2O_3-SiO_2 [34] glasses, i.e., in glasses containing different network forming units. It is assumed that this reduction is due to competition between the different network forming units to occupy space in the structure. The volumes obtained for V_{G4} and V_{S4} can be used in Equation 2 to calculate V_{G3} for glasses having ($y < x \leq 2y$). The average value obtained for V_{G3} is $(50.93 \pm 0.68) \times 10^{-24}$ cm^3.

The volumes obtained for V_{G4}, V_{G3} and V_{S4} can in turn be used in Equation 2 to get the calculated density (D_c). Fig. 4 shows the correlation between D_c and D_m for Li_2O-Ga_2O_3-SiO_2 glasses (◇-symbol). The agreement is quite good between the D_c and D_m values. Similar plots could be obtained for Na_2O-Ga_2O_3-SiO_2, CaO-Ga_2O_3-SiO_2 and BaO-Ga_2O_3-SiO_2 glasses (Figs 5–7, respectively). The data for D_c are given in Tables (I–IV). The D_c values were calculated following similar procedure to that used for Li_2O-Ga_2O_3-SiO_2 glasses. The volumes used for the G_3 units are given in Table V. The maximum difference between the D_c and D_m values for the investigated glasses is about ±1%. Fukumi and Sakka [20] reported that the gallate

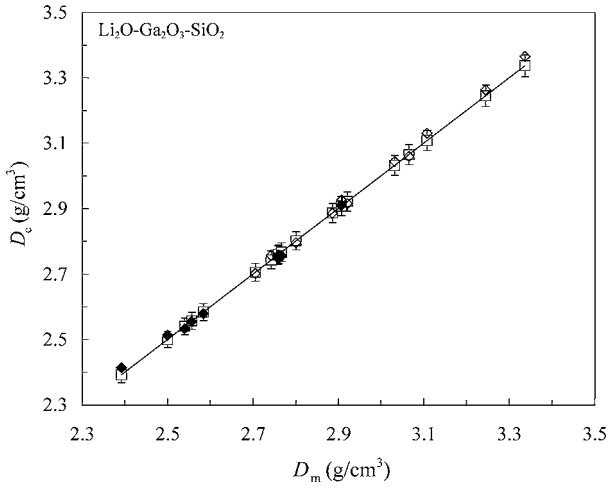

Figure 4 The calculated density D_c in dependence of the determined density D_m (□) for Li_2O-Ga_2O_3-SiO_2 glasses. The D_c values were obtained from Equations 2 (◇) and 5 (⧫) and the volumes given in Table V. The D_m data are taken from reference [22, 23, 33]. The solid line represents the fitting plot of the D_m values.

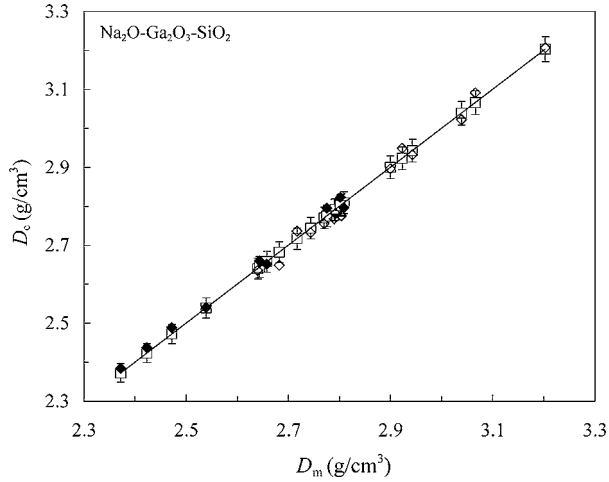

Figure 5 The calculated density D_c in dependence of the determined density D_m (□) for Na_2O-Ga_2O_3-SiO_2 glasses. The D_c values were obtained from Equations 2 (◇) and 5 (⧫) and the volumes given in Table V. The D_m data are taken from reference [24–28, 33]. The solid line represents the fitting plot of the D_m values.

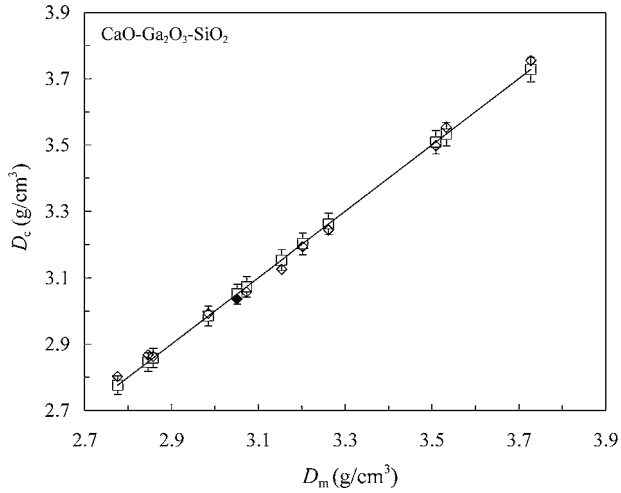

Figure 6 The calculated density D_c in dependence of the determined density D_m (□) for CaO-Ga_2O_3-SiO_2 glasses. The D_c values were obtained from Equations 2 (◇) and 5 (⧫) and the volumes given in Table V. The D_m data are taken from reference [29–31, 33]. The solid line represents the fitting plot of the D_m values.

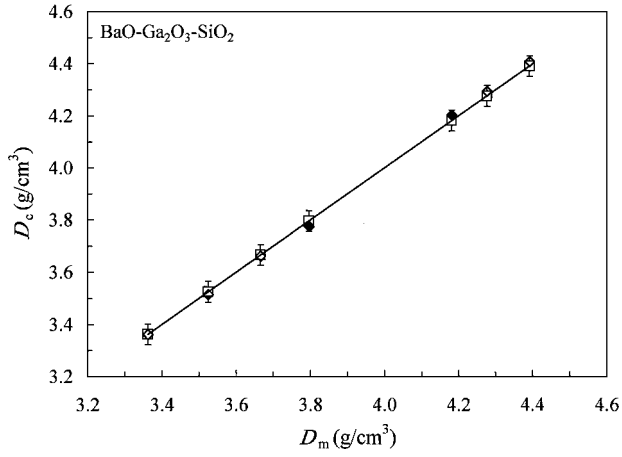

Figure 7 The calculated density D_c in dependence of the determined density D_m (□) for BaO-Ga_2O_3-SiO_2 glasses. The D_c values were obtained from Equations 2 (◇) and 5 (⧫) and the volumes given in Table V. The D_m data are taken from reference [32, 33]. The solid line represents the fitting plot of the D_m values.

TABLE V Volumes of the structural units in the glasses investigated

Glass type	V_{G4} (10^{-24} cm^3)	V_{G3} (10^{-24} cm^3)	V_{S4} (10^{-24} cm^3)	V_{S3} (10^{-24} cm^3)
Li_2O-Ga_2O_3-SiO_2	42.18	50.93	44.08 (45.25)[a]	52.97 (52.97)[a]
Na_2O-Ga_2O_3-SiO_2	51	66	44.7 (45.25)[a]	60.5 (60.5)[a]
CaO-Ga_2O_3-SiO_2	42.03	53.8	44.29 (45.25)[a]	53.5 (54.5)[a]
BaO-Ga_2O_3-SiO_2	51.95	71.5	44.1 (45.25)[a]	61.95 (60.95)[a]

[a]Values for the corresponding binary alkali- or alkaline earth silicate glasses [12, 13, 15].

network in a $66.7CaO \cdot 33.3Ga_2O_3$ glass consists of GaO_4 tetrahedra only. They gave the density of that glass as 4.62 g/cm^3. By using Equation 2 and the volumes given in Table V for CaO-Ga_2O_3-SiO_2 one obtains a D_c value of 4.624 g/cm^3.

In Na_2O-Al_2O_3-SiO_2 glasses [14] Al_2O_3 has priority to associate itself with an equimolar quantity of Na_2O to form AlO_4 tetrahedra. The excess of Na_2O incorporates into the silicate network producing NBOs. Moreover, in R_2O-B_2O_3-SiO_2 glasses NBOs can form in both the borate and the silicate networks after reaching the maximum concentration of BO_4 units [34, 35]. These effects may indicate that NBOs start to form in the SiO_4 sites when the prior processes become saturated. In analogy it can be assumed that in R_2O-Ga_2O_3-SiO_2 glasses the excess of modifier oxide, that remains after complete conversion of G_4 units into G_3 ones, would associate with the SiO_2 content to produce SiO_4 units with NBOs. At the first step, Q_3 units would be produced. These are SiO_4 tetrahedra containing one NBO ion per tetrahedron. The Q_3 units can form in glasses having $x > 2y$ and $(x - y)/z \leq 0.5$. In Table I the glasses having $2y < x$ fulfill the last condition.

By taking these assumptions in consideration, the distribution of the structural units in xR_2O-yGa_2O_3-$zSiO_2$ glasses having $x > 2y$ and $(x - y)/z \leq 0.5$ would be

$$xR_2O + yGa_2O_3 + zSiO_2 \rightarrow 2yG_3 + 2(x - 2y)Q_3 + [z - 2(x - 2y)]Q_4. \quad (4)$$

The density of such glasses is then

$$D = \{2yM_{G3} + 2(x - 2y)M_{S3} + [z - 2(x - 2y)]M_{S4}\} / \{2yV_{G3} + 2(x - 2y)V_{S3} + [z - 2(x - 2y)]V_{S4}\}. \quad (5)$$

Here M_{S3} is the mass of the Q_3 unit (the mass of $Si^{4+} + 2.5O^{2-} + R^+$) and V_{S3} is its volume.

The densities of different silicate glasses [12–15, 36, 37] were used to calculate the volumes of structural units. It was found that the volumes of the units present in the binary silicate glasses are the same in more complicated ones. For example, the volume of the silicate units in Na_2O-SiO_2 glasses [13] are the same in Na_2O-Rb_2O-SiO_2 glasses [36] and Na_2O-CaO-SiO_2 [37]. This means that the volumes of the silicate units are independent of the glass matrix. Therefore, the volumes of the Q_3 units determined for R_2O-SiO_2 and RO-SiO_2 glasses (Table V) can be used in Equation 5 to calculate the density of xR_2O-yGa_2O_3-$zSiO_2$ glasses having $x > 2y$ and $(x - y)/z \leq 0.5$. The agreement between the D_c and D_m values in the systems investigated, Figs 4–7 (♦-symbol) and Tables (I–IV), is indicative for the validity of the presented structural model.

TABLE VI Densities of the structural units in the glasses investigated

Glass type	D_{G4} (g/cm^3)	D_{G3} (g/cm^3)	D_{S4} (g/cm^3)	D_{S3} (g/cm^3)
Li_2O-Ga_2O_3-SiO_2	4.295	4.030	2.263	2.364
Na_2O-Ga_2O_3-SiO_2	4.061	3.917	2.232	2.500
CaO-Ga_2O_3-SiO_2	4.811	4.624	2.253	2.736
BaO-Ga_2O_3-SiO_2	5.441	5.730	2.263	23.666

The densities of the structural units in the studied glasses are given in Tables VI. The density of a structural unit is obtained as (its mass/its volume). It can be noticed that the density of units in the gallate matrix is much higher than the density of the units in the silicate matrix. This explains the great difference in the density between the R_2O (or RO)-Ga_2O_3-SiO_2 and the corresponding Ga_2O_3-free glasses (Fig. 1, as example).

It is noticed that the D_c values obtained from Equations 2 and 5 for the glasses having $Ga_2O_3/SiO_2 > 0.75$ are markedly different from the experimental values (Table I–IV). This result reveals that there might be another distribution of the modifier oxide between the gallate and the silicate networks. Similar processes were reported for Na_2O-B_2O_3-SiO_2 glasses, where the ratio SiO_2/B_2O_3 plays the dominant role in the distribution of Na_2O between SiO_2 and B_2O_3. It is assumed that for $SiO_2/B_2O_3 = 1$ the alkali oxide associates with B_2O_3 only, till NBOs start forming in the borate matrix [35]. On the other hand the distribution of Na_2O is greatly different in glasses having $SiO_2/B_2O_3 \leq 0.5$ [38, 39]. The glasses treated in the present study have $(x - 2y)/z \leq 0.5$. In such glasses Q_4 units convert into Q_3 ones. It would be of interest to know how the alkali oxide would be distributed for $(x - 2y)/z > 0.5$, where Q_2 units (SiO_4 tetrahedra with two NBOs) can form from Q_3 units. Similarly, how would be the distribution of alkali oxide in glasses having $Ga_2O_3/SiO_2 > 0.75$? Certainly more spectroscopic investigations are needed to explore the structure of those glasses.

The molar volume $V_{m(D)}$ of a glass can be determined from the relation:

$$V_{m(D)} = M/D \quad (6)$$

where M is the molecular weight of the glass. On the other hand, the molar volume can be calculated from the volumes of the structural units. For xR_2O-yGa_2O_3-$zSiO_2$ glasses with $y \leq x \leq 2y$ the calculated molar

volume $V_{m(C)}$ can be obtained (according to Equation 2) as:

$$V_{m(C)} = \{[2y - 2(x - y)]V_{G4} + 2(x - y)V_{G3} + zV_{S4}\}N_A. \quad (7)$$

Where N_A is Avogadro's number. Similarly for $x > 2y$ and $(x - y)/z \leq 0.5$ $V_{m(C)}$ would be:

$$V_{m(C)} = \{2yV_{G3} + 2(x - 2y)V_{S3} + [z - 2(x - 2y)]V_{S4}\}N_A. \quad (8)$$

Fig. 8 shows a good agreement between $V_{m(C)}$ and $V_{m(D)}$ for the studied Li_2O-Ga_2O_3-SiO_2 glasses.

At a constant content of Li_2O Equation 7 can be rewritten in another form. As an example, for $0.2R_2O$-yGa_2O_3-$(0.8 - y)SiO_2$ Equation 7 leads to:

$$V_{m(C)} = y(4V_{G4} - 2V_{G3} - V_{S4})N_A + (0.4V_{G3} - 0.4V_{G4} + 0.8V_{S4})N_A. \quad (9)$$

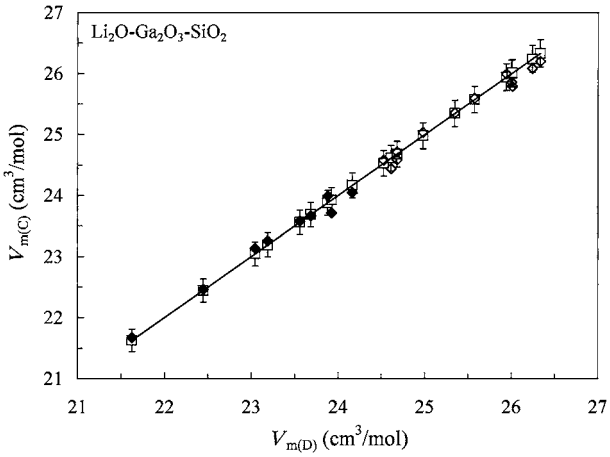

Figure 8 The calculated molar volume $V_{m(C)}$ in dependence of the determined molar volume $V_{m(D)}$ (□) (Equation 6) for Li_2O-Ga_2O_3-SiO_2 glasses. The $V_{m(C)}$ values were obtained from Equations 7 (◇) and 8 (⧫) and the volumes given in Table V. The solid line represents the fitting plot of the $V_{m(D)}$ values.

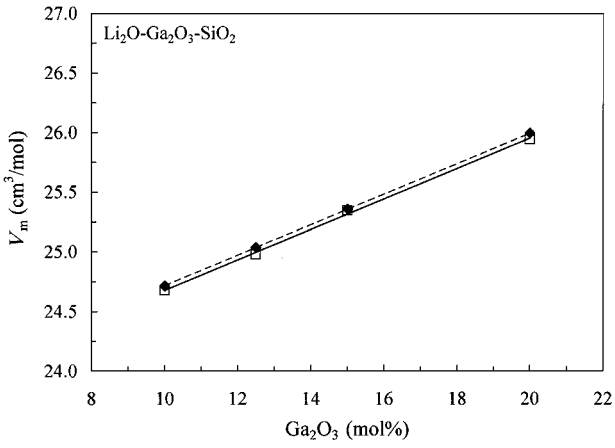

Figure 9 Molar volume as a function of the Ga_2O_3 content in Li_2O-Ga_2O_3-SiO_2 glasses with constant Li_2O concentration (20 mol%). The symbol (□) represents determined molar volume (Equation 6) and (⧫) calculated molar volume (Equation 9). The lines represent the fitting plots of the data.

This is a straight-line relation having a slope that is $(4V_{G4}\text{-}2V_{G3} - V_{S4})N_A$. Fig. 9 represents the change of $V_{m(D)}$ with Ga_2O_3 content (mol%) for $0.2R_2O$-yGa_2O_3-$(0.8 - y)SiO_2$ glasses. It is shown that $V_{m(D)}$ increases linearly with increasing the content of Ga_2O_3. This is consistent with Equation 9. A quite good agreement is also shown in Fig. 9 between $V_{m(D)}$ and $V_{m(C)}$. The agreement obtained reveals that the presented model is adequate to describe the structure of studied glasses.

5. Conclusion

The analysis in this study suggests a structural model for R_2O or (RO)-Ga_2O_3-SiO_2 glasses. For (R_2O or RO)/$Ga_2O_3 \leq 1$ the modifier oxide is incorporated into the gallate matrix forming GaO_4 units without NBOs. In glasses having $1 <$ (R_2O or RO)/$Ga_2O_3 \leq 2$ NBOs can be created in the gallate matrix. This proposition is based on the information available from the spectroscopic studies on Ga_2O_3-containing glasses. The agreement between the D_m and D_c values for (R_2O or RO)/$Ga_2O_3 > 2$ suggests that the excess modifier oxide would associate with SiO_2 forming NBOs. The density of the glasses investigated is mainly determined by the densities of the structural units in the gallate matrix. Significant differences between the D_m and the D_c values for the glasses having $Ga_2O_3/SiO_2 > 0.75$ suggest another distribution of the modifier oxide.

References

1. J. E. SHELBY, *J. Amer. Ceram. Soc.* **71** (1988), c254.
2. M. M. WIERZBICKI and J. E. SHELBY, *Phys. Chem. Glasses* **36** (1995) 150.
3. W. H. DUMBAUGH, *ibid.* **27** (1986) 119.
4. D. W. HALL, M. A. NEWHOUSE, N. F. BORRELLI, W. H. DUMBAUGH and D. L. WEIDEMAN, *Appl. Phys. Lett.* **54** (1989) 1293.
5. W. H. DUMBAUGH and J. C. LAPP, *J. Amer. Ceram. Soc.* **75** (1992) 2315.
6. J. C. LAPP, *Am. Ceram. Soc. Bull.* **71** (1992) 1543.
7. F. MIYAJI, K. TADANAGA, T. YOKO and S. SAKKA, *J. Non-Cryst. Solids* **139** (1992) 268.
8. F. MIYAJI, T. YOKO, J. JIN, S. SAKKA, T. FUKUNAGA and M. MISAWA, *ibid.* **175** (1994) 211.
9. J. ZHONG and P. J. BRAY, *ibid.* **94** (1987) 122.
10. J. C. LAPP and J. E. SHELBY, *ibid.* **86** (1986) 350.
11. H. DOWEIDAR, *Phys. Chem. Glasses* **38** (1997) 69.
12. *Idem.*, *ibid.* **39** (1998) 286.
13. H. DOWEIDAR, S. FELLER, M. AFFATIGATO, B. TISHENDORF, C. MA and E. HAMMARSTEN, *ibid.* **40**(6) (1999) 339.
14. H. DOWEIDAR, *J. Non-Cryst. Solids* **240** (1998) 55.
15. *Idem.*, *ibid.* **249** (1999) 194.
16. G. EL-DAMRAWI, W. MÜLLER-WARMUTH, H. DOWEIDAR and I. A. GOHAR, *Phys. Chem. Glasses* **34** (1993) 52.
17. K. FUKUMI and S. SAKKA, *ibid.* **29** (1988) 1.
18. F. MIYAJI and S. SAKKA, *J. Non-Cryst. Solids* **137** (1991) 77.
19. J. A. RULLER and J. M. JEWELL, *ibid.* **175** (1994) 91.
20. K. FUKUMI and S. SAKKA, *ibid.* **95/96** (1987) 193.
21. H. SCHOLZE, "Glass: Nature, Structure and Properties" (Springer Verlag, New York, 1990).
22. S. K. DUBROVO, M. V. ZASOLOTSKAYA and T. S. TSEKHOMSKAYA, *J. Appl. Chem. USSR (Engl. Transl.)* **42** (1969) 2295 (cited in reference 33).
23. T. S. TSEKHOMSKAYA and S. K. DUBROVO, *ibid.* **41** (1968) 468 (cited in reference 33).

24. S. K. DUBROVO, N. P. DANILOVA and T. S. TSEKHOMSKAYA, *Issled. Obl. Khim. Silik. Okislov* (1965) 11 (cited in reference 33).
25. E. I. GALANT, *Dokl. Akad. Nauk SSSR* **141** (1961) 417 (cited in reference 33).
26. A. O. IVANOV and E. I. GALANT, *Opt.-Mekh. Prom.* (1963) (3) 43 (cited in reference 33).
27. K. TAKAHASHI, N. MOCHIDA and G. HATTA, *Yogyo Kyokaishi* **83** (1975) 103 (cited in reference 33).
28. T. HANADA, S. GOTO, R. OTA and N. SOGA, *Nippon Kagaku Kaishi* **13** (1981) 1577 (cited in reference 33).
29. N. P. DANILOVA, *Steklo* (1) (1967) 89 (cited in reference 33).
30. N. P. DANILOVA and S. K. DUBROVO, *J. Appl. Chem. USSR (Engl. Transl.)* **40** (1967) 959 (cited in reference 33).
31. A. A. LISENENKOV and A. I. VASILEV, *Sov. J. Glass Phys. Chem. (Engl. Transl.)* **5** (1979) 485 (cited in reference 33).
32. N. P. DANILOVA and S. K. DUBROVO, "Glass Formation of Silicates of Barium," 1971, 3509-71, Dep. VINITI (cited in reference 33).
33. N. B. BANSAL and R. H. DOREMUS, "Handbook of Glass Properties" (Academic Press, Orlando, Fl, 1990).
34. H. DOWEIDAR, *Phys. Chem. Solids* **53** (1992) 807.
35. W. J. DELL, P. J. BRAY and S. Z. XIAO, *J. Non-Cryst. Solids* **58** (1983) 1.
36. H. DOWEIDAR, *J. Non-Cryst. Solids* **194** (1996) 155.
37. *Idem.*, *Phys. Chem. Glasses* **40** (1999) 85.
38. G. EL-DAMRAWI, W. MÜLLER-WARMUTH, H. DOWEIDAR and I. A. GOHAR, *J. Non-Cryst. Solids* **146** (1992) 137.
39. H. DOWEIDAR, M. S. MEIKHAIL and D. HOLLAND, *ibid.* **101** (1988) 280.

Received 30 December 1999
and accepted 18 December 2000