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Optical properties and structure of R_2O–Ga_2O_3–SiO_2 and RO–Ga_2O_3–SiO_2 glasses

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Abstract Refractive index and molar refraction of Li_2O–, Na_2O–, CaO–, and BaO–Ga_2O_3–SiO_2 glasses have been used to test the validity of a structural model of silicate glasses containing Ga_2O_3 glasses. Ga_2O_3 enters these types of glass in a similar manner as Al_2O_3. It is assumed that, for $(SiO_2/Ga_2O_3) > 1$ and $(Ga_2O_3/R_2O) \leq 1$, Ga_2O_3 associates primarily with modifier oxides to form GaO_4 units. The rest of modifier oxide forms silicate units with non-bridging oxygen ions. Silicate structural units have the same factors as found for binary alkali- and alkaline earth silicate glasses. Differences between experimental and model values suggest another structure for $(Ga_2O_3/SiO_2) \geq 1$.

Introduction

There is a growing interest about the role of Ga_2O_3 in various types of glass. Glasses containing considerable amounts of Ga_2O_3 are characterized with high refractive index, density, infrared transmission, and nonlinear optical coefficients [1–6]. The role of Ga_2O_3 in the structure of oxide glasses is, to a great extent, similar to that of Al_2O_3 [7]. It is believed that Ga_2O_3 mostly forms GaO_4 tetrahedra that contribute to the structure as network former units [3–11]. Like AlO_4 units, the negative charge on the GaO_4 tetrahedron might be compensated by a positive charge. The latter may come through association of Ga_2O_3 with alkali- or alkaline earth oxide.

Further structural features were reported for Ga_2O_3 in oxide glasses. In addition to GaO_4 tetrahedra, minor concentration of GaO_6 octahedral units can form in glasses where modifier oxygen content is insufficient to convert Ga_2O_3 to GaO_4 tetrahedra. Examples for such glasses are $50PbO \cdot 50Ga_2O_3$ and $80Bi_2O_3 \cdot 20Ga_2O_3$ [9]. NMR investigations on Cs_2O–Ga_2O_3 glasses [10] indicated that only GaO_4 units are formed for $(Ga_2O_3/Cs_2O) < 3/7$. GaO_6 units were observed in the structure for higher Ga_2O_3 concentration. EXAFS analysis of $xPbO \cdot (1 - x)Ga_2O_3$ glasses ($x = 0.7$, 0.75, and 0.8) [12] indicated that most of Ga^{3+} ions form GaO_4 tetrahedra with less than 5% of GaO_6 octahedra. In analogy to Al_2O_3 that forms minor concentration of 5- and 6-coordinated aluminum ions in CaO–Al_2O_3–SiO_2 glasses [7] it is suggested that Ga^{3+} ions can form similar groups. Peng and Stebbins [7] came to a general conclusion that gallium ions occupy sites like those of aluminum ions and therefore, for the first approximation, they can be treated in a similar manner.

Furthermore, it has been reported that non-bridging oxygen ions (NBOs) can form at GaO_4 sites. Fukumi and Sakka [13] indicated that NBOs appear in alkali- and alkaline earth gallate glasses for modifier oxide content greater than about 43 mol%. The fraction of GaO_4 units containing NBOs increases with increasing the modifier oxide content. On the other hand, in a $66.7CaO \cdot 33.3Ga_2O_3$ glass there are only GaO_4 tetrahedra [14]. NBOs were observed at GaO_4 tetrahedra in BaO–SrO–Ga_2O_3 and MgO–SrO–Ga_2O_3 glasses. The fraction of NBOs decreases with substituting MgO for SrO [15]. A Raman band at about 650 cm^{-1} in the spectra of PbO–Bi_2O_3–Ga_2O_3 glasses is attributed to NBOs at the GaO_4 sites [16]. The increase in the content of PbO or Bi_2O_3 causes a decrease in the fraction of NBOs. Ruller and

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Jewell [17] used Raman and infrared spectroscopies to study the structure of the glasses $(80 - x)PbO \cdot (10 + x)$-$Ga_2O_3 \cdot 10SiO_2$ $(5 \leq x \leq 25$ mol%) and $(75 - x/2)PbO \cdot (25 - x/2)Ga_2O_3 \cdot xSiO_2$ $(0 \leq x \leq 20$ mol%). NBOs could be detected in all cases at the GaO_4 sites whereas there were no signs of NBOs at the silicate sites. Recently, $Li_2O \cdot Ga_2O_3$(or Al_2O_3) $\cdot 2SiO_2$, $Na_2O \cdot Ga_2O_3$ (or Al_2O_3) $\cdot 2SiO_2$, $CaO \cdot Ga_2O_3$(or Al_2O_3) $\cdot 2SiO_2$, and $Y_2O_3 \cdot Ga_2O_3$(or Al_2O_3) $\cdot 2SiO_2$ glasses were investigated using high resolution ^{27}Al MAS and two-dimensional triple-quantum MAS (3QMAS) NMR [7]. No NBOs were detected in the glasses containing Li_2O and Na_2O. A small fraction of NBOs was observed at the silicate sites in glasses containing CaO. Glasses containing Y_2O_3 have appreciable amount of NBOs at the silicate sites. In all cases the fraction of NBOs is relatively greater in glasses containing Ga_2O_3.

NBOs could also be detected at AlO_4 sites. A peak at 155 ppm in ^{17}O MAS NMR spectrum of the glass $61.5CaO \cdot 37.9Al_2O_3 \cdot 0.6SiO_2$ (mol%) is attributed to Al-NBOs. The fraction of Al-NBOs decreases with increasing the SiO_2 content. A minor fraction of Al-NBOs is found in the glass $52CaO \cdot 28Al_2O_3 \cdot 20SiO_2$ and it disappeared in the glass $50CaO \cdot 17Al_2O_3 \cdot 33SiO_2$ [18]. In $CaO–Al_2O_3–SiO_2$ with $CaO:Al_2O_3:SiO_2 = 3:1:2$, 3:1:3, and 2:2:3 (mole ratio) NBOs are detected only at the silicate sites, but not at AlO_4 tetrahedra [19]. In $xNa_2O \cdot (1 - x)Al_2O_3 \cdot SiO_2$ glasses ($x = 0.5$, 0.67, 0.83 and 1) NBOs were observed only at silicate sites for $x > 0.5$ [20].

The above information may lead to a conclusion that NBOs at GaO_4 units are formed under certain conditions. At first, they can form in glasses free of silica and having excess of modifier oxide, i.e. (modifier oxide/Ga_2O_3) >1. NBOs at GaO_4 sites can also form in glasses containing low concentration of SiO_2 and higher content of modifier oxide than that of Ga_2O_3. By low concentration of SiO_2 we mean, at the present time, that (SiO_2/Ga_2O_3) <1. The same can be said for NBOs at AlO_4 units. In all cases Ga_2O_3 has priority to associate itself with modifier oxides to form GaO_4 tetrahedra.

In a previous work [21] the density of Li_2O–, Na_2O–, CaO– and $BaO–Ga_2O_3–SiO_2$ glasses was analyzed by assuming priority of formation of NBOs at GaO_4 units. In the present work the distribution of structural units is revised and used to analyze the refractive index and molar refraction of those glasses.

Procedure

In the light of the above aspects, a simple structural model for $R_2O–Ga_2O_3–SiO_2$ and $RO–Ga_2O_3–SiO_2$ glasses, having (SiO_2/Ga_2O_3) >1, is suggested (R_2O and RO are alkali- and alkaline earth oxide, respectively). In this model the modifier oxide is distributed between Ga_2O_3 and SiO_2 as follows. In the first process the modifier oxide associates with Ga_2O_3 forming GaO_4 units. This process continues (at a rate of two GaO_4 units per Ga_2O_3 molecule) till the entire Ga_2O_3 content is converted. The rest of modifier oxide preferentially forms NBOs at the silicate sites. The type and fraction of silicate units depend on the quantity of modifier oxide available to associate with SiO_2. For ($R_2O–Ga_2O_3$)/SiO_2 $\leq$0.5 the matrix would contain Q_4 and Q_3 units (Q_4 is a SiO_4 tetrahedron without NBOs, Q_3 is a tetrahedra containing one NBO). In the region of $0.5 < (R_2O–Ga_2O_3)/SiO_2 \leq 1$ there should be Q_3 and Q_2 units, where the latter is a tetrahedron containing two NBOs [22].

The distribution of structural units in a glass having the molar formula $xR_2O \cdot yGa_2O_3 \cdot zSiO_2$ having (Ga_2O_3/R_2O) $\leq$1 and ($R_2O–Ga_2O_3$)/SiO_2 $\leq$0.5, can be expressed as

$$xR_2O + yGa_2O_3 + zSiO_2 \rightarrow 2yG_4 + 2(x - y)Q_3 + [z - 2(x - y)]Q_4. \quad (1)$$

Here G_4 is a GaO_4 tetrahedron containing four bridging oxygen ions. For such glasses the refractive index (μ) can be given as

$$\mu = \{2yf_{G4} + 2(x - y)f_{S3} + [z - 2(x - y)]f_{S4}\}N_A \quad (2)$$

where f_{G4} is the differential refraction [22] of the GaO_4 tetrahedron that has no NBOs, f_{S3} is the differential refraction of the Q_3 unit containing one NBO ion, f_{S4} is the factor for the Q_4 unit, and N_A is Avogadro's number. Equation 2 can also be used for $CaO–Ga_2O_3–SiO_2$ and $BaO–Ga_2O_3–SiO_2$ glasses. In these glasses each molecule of the modifier oxide converts a Ga_2O_3 molecule producing two G_4 units, depending on the composition. Here a G_4 unit would include a half Ca^{2+} or Ba^{2+} ion.

In $xR_2O \cdot yGa_2O_3 \cdot zSiO_2$ glasses having $x = y$ Eq. 2 would be

$$\mu = (2yf_{G4} + zf_{S4})N_A. \quad (2a)$$

In previous studies [22–24] it has been shown that in multi-component silicate glasses f_{S4} has mostly the same value found for vitreous SiO_2 (2.422×10^{-24}). This value can be used in Eq. 2a to calculate f_{G4}. The latter can also be obtained by solving Eq. 2a simultaneously for two μ values of such glasses. Another way to get f_{G4} is to use f_{S3} and f_{S4} of binary silicate glasses [22, 24] directly in Eq. 2. The values of f_{G4} given in Table 5 are obtained by applying these procedures. These values represent the average of the calculated values for each type of modifier oxide.

In $xR_2O \cdot yGa_2O_3 \cdot zSiO_2$ glasses having (Ga_2O_3/R_2O) $\leq$1 and $0.5 \leq (R_2O–Ga_2O_3)/SiO_2 \leq 1$ Q_4 units do not exist and Q_2 units are formed from Q_3 units. Q_2 unit is a tetrahedron containing two NBOs. In this case, formation of the structural units goes on as

$$xR_2O + yGa_2O_3 + zSiO_2 \rightarrow 2yG_4 + [2(x-y) - z]Q_2 + 2[z-(x-y)]Q_3. \quad (3)$$

Then the refractive index can be expressed as

$$\mu = \{2yf_{G4} + [2(x-y) - z]f_{S2} + 2[z-(x-y)]f_{S3}\}N_A \quad (4)$$

where f_{S2} is the differential refraction of the Q_2 unit that contains two NBO ions. Values of f_{G4} and f_{S3} can be used in Eq. 4 to obtain f_{S2}. It must be stated that the presented relations are approximated. Formation of GaO_5 and GaO_6, if there were, is not taken into consideration. In addition deviations from stoichiometry in the conversion process of silicate units are neglected. It has been indicated [25] that such deviations are so small to affect the proposed model. Similar relations were successfully applied for the refractive index of R_2O–Al_2O_3–SiO_2 and RO–Al_2O_3–SiO_2 glasses [23, 26].

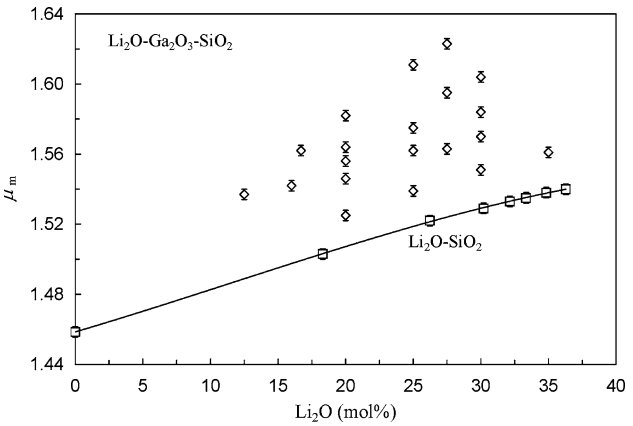

Fig. 1 Determined refractive index μ_m of Li_2O–Ga_2O_3–SiO_2 (◇) and Li_2O–SiO_2 (□) glasses as a function of the Li_2O content. The error limit is estimated as ±0.003. The data are taken from references [27–30]

Results and discussion

In Fig. 1 is given, as an example, the refractive index of Li_2O–Ga_2O_3–SiO_2 glasses as a function of the Li_2O content. The data are taken from various sources [27–30]. They are compared with the values for Li_2O–SiO_2 glasses [30]. At a specific concentration of Li_2O there are different values of μ. Similar behavior is also observed for Na_2O–Ga_2O_3–SiO_2 [30–34], CaO–Ga_2O_3–SiO_2 [30, 35, 36], and BaO–Ga_2O_3–SiO_2 [30, 37] glasses (Tables 1, 2, 3, and 4). The increase in μ is mainly related to an increase in the content of Ga_2O_3. This is because, for a constant Li_2O content, an increase in the concentration of Ga_2O_3 is accompanied with a decrease in the SiO_2 content.

Figure 2 shows the correlation between the determined (μ_m) and calculated (μ_c) values of refractive indices of the

Table 1 Compositions, determined refractive index μ_m [27–30], calculated refractive index μ_c, determined molar refraction R_m, and calculated molar refraction R_c for Li_2O–Ga_2O_3–SiO_2 glasses

Li_2O (mol%)	Ga_2O_3 (mol%)	SiO_2 (mol%)	μ_m	μ_c	R_m (cm^3)	R_c (cm^3)
0	0	100	1.458[a]	1.459	7.436	7.438
12.5	12.5	75	1.537	1.535	8.224	8.226
16.7	16.7	66.6	1.562	1.561	8.510	8.490
20	20	60	1.582	1.581	8.684	8.698
25	25	50	1.611	1.611	9.027	9.013
27.5	27.5	45	1.623	1.626	9.173	9.170
16	12	72	1.542	1.541	8.049	8.101
20	2.5	77.5	1.510	1.515	7.186	7.189
20	5	75	1.525	1.524	7.406	7.405
20	10	70	1.546	1.515	7.814	7.836
20	12.5	67.5	1.556	1.552	8.029	8.051
20	15	65	1.564	1.562	8.244	8.267
25	5	70	1.539	1.536	7.265	7.289
25	10.7	64.3	1.562	1.557	7.774	7.780
25	15	60	1.575	1.574	8.104	8.151
27.5	10.4	62.1	1.563	1.562	7.652	7.696
27.5	18.1	54.4	1.595	1.591	8.386	8.360
30	5	65	1.551	1.548	7.161	7.173
30	10	60	1.570	1.567	7.560	7.604
30	14	56	1.584	1.582	7.927	7.948
30	20	50	1.604	1.604	8.465	8.466
35	5	60	1.561	1.560	7.003	7.057

[a] Value of μ_m for vitreous silica is taken from [39]

Table 2 Compositions, determined refractive index μ_m [30–34], calculated refractive index μ_c, determined molar refraction R_m, and calculated molar refraction R_c for Na_2O–Ga_2O_3–SiO_2 glasses

Na_2O (mol%)	Ga_2O_3 (mol%)	SiO_2 (mol%)	μ_m	μ_c	R_m (cm^3)	R_c (cm^3)
12.5	12.5	75	1.519	1.517	8.517	8.478
15	15	70	1.527	1.529	–	–
16.66	16.66	66.68	1.537	1.537	8.790	8.825
20	20	60	1.556	1.553	9.090	9.102
25	25	50	1.574	1.576	9.519	9.518
15	5	80	1.503	1.497	–	–
15	10	75	1.515	1.513	–	–
16.66	8.33	75.01	1.514	1.510	7.971	8.079
16.66	12.5	70.84	1.530	1.524	8.408	8.452
18.3	11.7	70	1.524	1.524	8.262	8.370
20	10	70	1.527	1.521	8.201	8.207
21	9	70	1.529	1.519	7.973	8.111
21	11.3	67.7	1.531	1.526	8.297	8.317
24.2	10.8	65	1.531	1.530	8.183	8.252
25	15	60	1.545	1.544	8.558	8.623
28.6	14.3	57.1	1.545	1.547	8.530	8.537
30	5	65	1.519	1.520	7.653	7.695
30	10	60	1.533	1.536	8.129	8.143
30.3	9.1	60.6	1.535	1.533	8.106	8.061
31.7	4.8	63.5	1.520	1.522	7.681	7.667

Table 3 Compositions, determined refractive index μ_m [30, 35, 36], calculated refractive index μ_c, determined molar refraction R_m, and calculated molar refraction R_c for CaO–Ga_2O_3–SiO_2 glasses

CaO (mol%)	Ga_2O_3 (mol%)	SiO_2 (mol%)	μ_m	μ_c	R_m (cm^3)	R_c (cm^3)
15	15	70	1.570	1.570	8.638	8.627
20	20	60	1.610	1.607	9.008	9.023
25	25	50	1.645	1.645	9.393	9.419
30	30	40	1.684	1.682	9.887	9.815
40[a]	40	20	1.745	1.756	–	–
15	10	75	1.542	1.547	8.188	8.203
20	10	70	1.561	1.560	8.160	8.174
20	15	65	1.583	1.584	8.525	8.599
25	15	60	1.604	1.598	8.527	8.570
30	10	60	1.602	1.597	8.052	8.118
40	10	50	1.633	1.638	7.974	8.063
40	20	40	1.664	1.662	8.814	8.910
40[a]	30	30	1.708	1.709	9.854	9.759
50	10	40	1.664	1.668	7.931	8.011
50[a]	40	10	1.757	1.784	–	–

[a] Glasses having $y/z \geq 1$

glasses investigated. The μ_c values are obtained from Eqs. 2 and 4 and the f_u factors are given in Table 5. Figure 2 shows a reasonable agreement between μ_m and μ_c. However there are few deviated points. The small difference between μ_m and μ_c for these points implies that the cause might mostly be experimental. It is worthy to mention that μ_c values do not agree with μ_m for glasses with $Ga_2O_3/SiO_2 \geq 1$. This may suggest another distribution of the structural units in those glasses.

Considering that $z = (1 - 2y)$ in glasses having $x = y$, then Eq. 2a can be rewritten as

$$\mu = [2y(f_{G4} - f_{S4}) + f_{S4}]N_A. \quad (2b)$$

The slope of this straight-line is $2(f_{G4} - f_{S4})N_A$ and the intercept is $f_{S4}N_A$. The latter represents the refractive index of vitreous SiO_2. Figure 3 shows the dependence of μ on the modifier oxide content for glasses having $x = y$. Unfortunately the number of BaO–Ga_2O_3–SiO_2 glasses

Table 4 Compositions, determined refractive index μ_m [30, 37], calculated refractive index μ_c, determined molar refraction R_m, and calculated molar refraction R_c for BaO–Ga_2O_3–SiO_2 glasses

BaO (mol%)	Ga_2O_3 (mol%)	SiO_2 (mol%)	μ_m	μ_c	R_m (cm^3)	R_c (cm^3)
20	10	70	1.577	1.578	9.016	9.011
20	15	65	1.591	1.593	9.380	9.475
20	20	60	1.610	1.609	9.855	9.938
30	10	60	1.619	1.622	9.315	9.331
30	30	40	1.682	1.684	11.185	11.188
40	10	50	1.661	1.665	9.735	9.653
40	20	40	1.688	1.697	10.670	10.584
40[a]	30	30	1.710	1.728	–	–
40[a]	40	20	1.736	1.759	–	–

[a] Glasses having $y/z \geq 1$

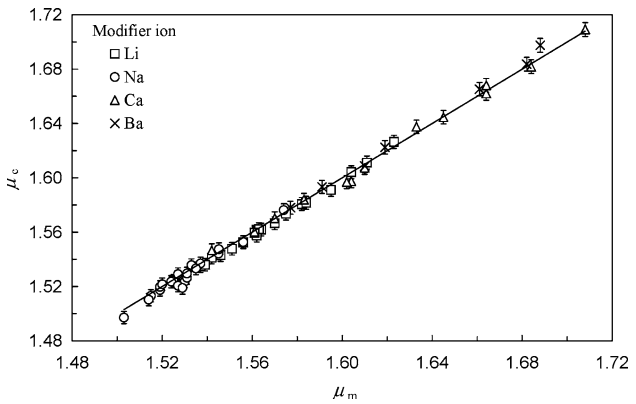

Fig. 2 Correlation between the calculated refractive index μ_c and the determined refractive index μ_m for Li_2O–Ga_2O_3–SiO_2 (□), Na_2O–Ga_2O_3–SiO_2 (○), CaO–Ga_2O_3–SiO_2 (Δ), and BaO–Ga_2O_3–SiO_2 (×) glasses. The μ_c values were obtained from Eqs. 2 and 4 and the factors given in Table 5. The μ_m data are taken from [27–37]. The solid line represents the fitting plot of the μ_m values

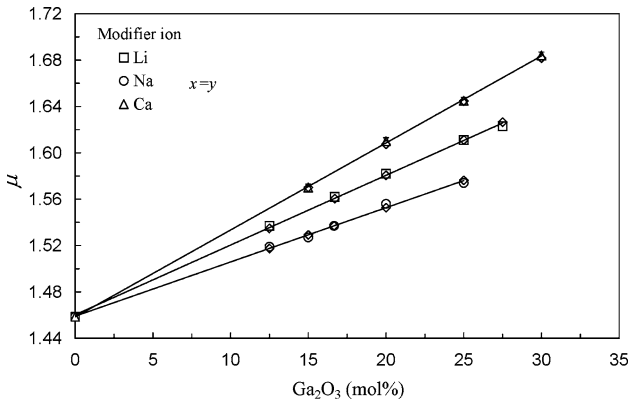

Fig. 3 Determined refractive index μ_m of Li_2O–Ga_2O_3–SiO_2 (□), Na_2O–Ga_2O_3–SiO_2 (○), and CaO–Ga_2O_3–SiO_2 (Δ) glasses in dependence of the modifier oxide content. The glasses presented have equal concentrations of Ga_2O_3 and the modifier oxide ($x/y = 1$). The data are taken from [27–36]. The calculated refractive indices (◇) are also presented. The solid lines are fitting plots of the μ_m values

Table 5 Differential refraction of the structural units in the investigated glasses and in the corresponding binary silicate glasses

Type of glass	f_{S4} (10^{-24})	f_{S3} (10^{-24})	f_{S2} (10^{-24})	f_{G4} (10^{-24})
Li_2O–Ga_2O_3–SiO_2	2.422	3.828	–	2.928
Na_2O–Ga_2O_3–SiO_2	2.422	3.758	–	2.813
CaO–Ga_2O_3–SiO_2	2.422	3.927	5.405	3.040
BaO–Ga_2O_3–SiO_2	2.422	4.002	5.555	3.045
Li_2O–SiO_2 [38]	2.422	3.832	–	–
Na_2O–SiO_2 [38]	2.422	3.758	–	–
CaO–SiO_2 [22]	2.422	3.927	5.405	–
BaO–SiO_2 [22]	2.422	4.002	5.555	–

with $x = y$ is insufficient to be presented. As shown both μ_m and μ_c verify Eq. 2b. The slopes of the lines are 0.0060, 0.0047, and 0.0075 mol^{-1} for Li_2O–Ga_2O_3–SiO_2, Na_2O–Ga_2O_3–SiO_2, and CaO–Ga_2O_3–SiO_2 glasses, respectively. Noting that the x-axis in Fig. 3 is given in mol%, whereas x, y, and z are mole fractions, thus when dealing with Eq. 2b the given slopes should be 0.60, 0.47, and 0.75. These slopes can be obtained when using the values of f_{G4} and f_{S4} given in Table 5. It is to notice that the slope in Eq. 2b depends only on the value of f_{G4}, i.e., on the type of the modifier ion, whereas the intercept is the same in all cases. Such features are verified in Fig. 3.

Similarly, by taking into consideration that $z = (1 - x - y)$, then for a constant value of x, the refractive index of glasses having $(R_2O$–$Ga_2O_3)/SiO_2 \leq 0.5$ would be

$$\mu = \{y(2f_{G4} - 2f_{S3} + f_{S4}) + [x(2f_{S3} - 3f_{S4}) + f_{S4}]\}N_A. \quad (5)$$

The slope of this straight-line equation is $(2f_{G4} - 2f_{S3} + f_{S4})N_A$ and its intercept is $[x(2f_{S3} - 3f_{S4}) + f_{S4}]N_A$. Figure 4 shows the dependence of μ on the Ga_2O_3 content in Li_2O–Ga_2O_3–SiO_2 glasses having constant Li_2O content. The data of all glasses having the same value of x are arranged on a straight-line. In Eq. 5 the slope does not depend on the value of x. On the other hand the latter determines the value of the intercept. The straight lines in Fig. 4 agree with these predictions.

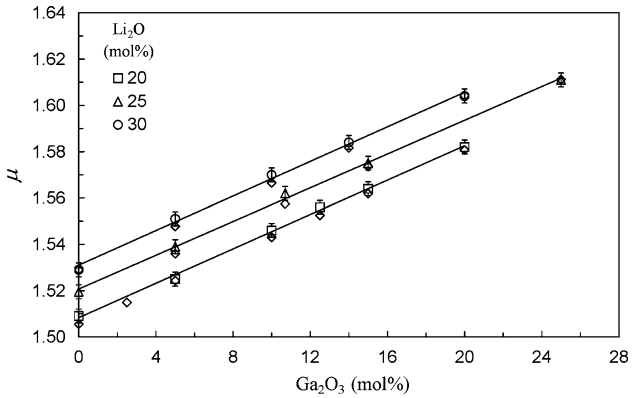

Fig. 4 Dependence of the determined refractive index μ_m (□, Δ, ○) on the Ga_2O_3 content for Li_2O–Ga_2O_3–SiO_2 glasses having constant concentrations of Li_2O. The data are taken from [27–30]. The calculated refractive indices (◇) are also presented. The solid lines are fitting plots of the μ_m values

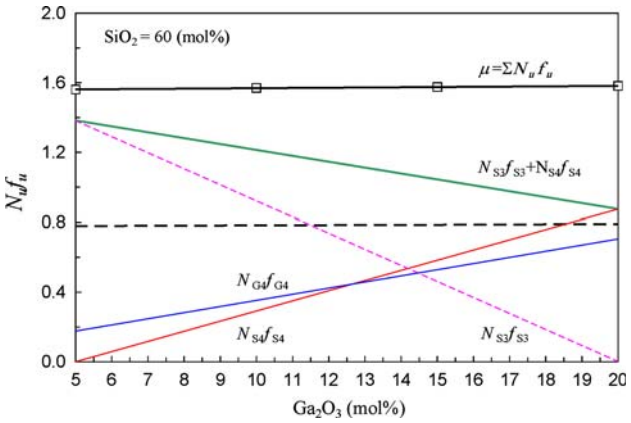

Fig. 5 Change with composition of $N_u f_u$ (the contribution to the refractive index of the structural units) in $(40 - X)Li_2O \cdot XGa_2O_3 \cdot 60SiO_2$ glasses. The heavy black solid line is the resultant contribution of all structural units in glass (μ_c). The □-symbol refers to μ_m values (Table 1)

For $(Ga_2O_3/R_2O) \leq 1$ and $(R_2O–Ga_2O_3)/SiO_2 \leq 0.5$, Eq. 2 can be reformed to

$$\mu = x[2(f_{S3} - f_{S4})N_A] + y[2(f_{G4} - f_{S3} + f_{S4})N_A] + z(f_{S4}N_A). \quad (6)$$

Likewise, for $0.5 \leq (R_2O–Ga_2O_3)/SiO_2 \leq 1$ Eq. 4 can be rewritten as

$$\mu = x[2(f_{S2} - f_{S3})N_A] + y[2(f_{G4} + f_{S3} - f_{S2})N_A] + z[(2f_{S3} - f_{S2})N_A]. \quad (7)$$

These relations can be used to calculate the refractive index in terms of factors for the individual oxides. For example, by using the factors given in Table 5 for Li_2O–Ga_2O_3–SiO_2 glasses, $(R_2O–Ga_2O_3)/SiO_2 \leq 0.5$, Eq. 6 becomes

$$\mu = 1.6934x + 1.8331y + 1.4585z. \quad (6a)$$

It appears that the empirically predicted factors used in technology for physical properties of various glasses might have structural bases.

From Eqs. 2 and 4 the concentration (N_u) of structural units in glass can be calculated. N_u is the number of structural unit per mole of glass. Thus the contribution ($N_u f_u$) of a structural unit to the refractive index can be obtained. Figure 5 shows the change, with composition, of the contribution of structural units in $(40 - X)Li_2O \cdot XGa_2O_3 \cdot 60SiO_2$ glasses ($5 \leq x \leq 20$ mol%). There is a linear change in the contribution of each type of structural units. As would be expected, from Eq. 2, $N_{G4}f_{G4}$ increases with increasing X. As the latter increases the quantity of Li_2O available to convert Q_4 units to Q_3 decreases and then $N_{G3}f_{G3}$ decreases. An increase in $N_{G4}f_{G4}$ follows the decrease in $N_{G3}f_{G3}$. The heavy black solid line in Fig. 5 represents the resultant contribution of all units in these glasses, i.e., the refractive index. As shown the heavy black solid line agrees well with the experimental data.

An interesting feature is observed in Fig. 5. The change in refractive index between 5 and 20 mol% Ga_2O_3 is relatively small (from 1.561 to 1.582) so that μ can be looked as unchanged with X and also with the Li_2O content. Figure 5 shows that there is a great decrease in $N_{S3}f_{S3}$ and a marked increase in $N_{S4}f_{S4}$ when X increases. Such changes might be embedded by some other effects. As shown in Fig. 5 the decrease in the resultant contribution of silicate units ($N_{S3}f_{S3} + N_{S4}f_{S4}$) is compensated with an increase in $N_{G4}f_{G4}$. The horizontal dashed line is the symmetry line between the plots of $N_{S3}f_{S3} + N_{S4}f_{S4}$ and $N_{G4}f_{G4}$. It can be said that in glasses having constant content of SiO_2 changes in the contribution of silicate units are compensated with changes in the gallate units. Similar features were reported for Na_2O–Al_2O_3–SiO_2 glasses [23]. For a constant SiO_2 content, the contribution from AlO_4 units compensates that of silicate units and the resultant μ does not change with changing the Al_2O_3 content.

The molar refraction is given by the Lorentz-Lorenz equation as:

$$R = \left(\frac{\mu^2 - 1}{\mu^2 + 2}\right) V_m, \quad (8)$$

where V_m is the molar volume and μ is the refractive index. Like μ, the molar refraction of $xR_2O \cdot yGa_2O_3 \cdot zSiO_2$ glasses having $(Ga_2O_3/R_2O) \leq 1$ and $(R_2O–Ga_2O_3)/SiO_2 \leq 0.5$, can be expressed as

$$R = \{2yR_{G4} + 2(x - y)R_{S3} + [z - 2(x - y)]R_{S4}\}N_A \quad (9)$$

where R_{G4} is the refraction [38] of the GaO_4 tetrahedron, R_{S3} is the refraction of Q_3, and R_{S4} is the factor for the Q_4 unit. Furthermore, for glasses having $(Ga_2O_3/R_2O) \leq 1$ and

Table 6 Refraction of the structural units in the investigated glasses and in the corresponding binary silicate glasses

Type of glass	R_{S4} (10^{-24} cm^3)	R_{S3} (10^{-24} cm^3)	R_{S2} (10^{-24} cm^3)	R_{G4} (10^{-24} cm^3)
Li_2O–Ga_2O_3–SiO_2	12.352	16.60	–	17.58
Na_2O–Ga_2O_3–SiO_2	12.352	18.00	–	19.26
CaO–Ga_2O_3–SiO_2	12.352	18.06	23.79	18.93
BaO–Ga_2O_3–SiO_2	12.352	21.21	30.00	22.73
Li_2O–SiO_2 [38]	12.352	16.60	–	–
Na_2O–SiO_2 [38]	12.352	18.12	–	–
CaO–SiO_2 [24]	12.400	18.11	23.79	–
BaO–SiO_2 [24]	12.400	21.21	30.00	–

$0.5 \leq (R_2O–Ga_2O_3)/SiO_2 \leq 1$ the refractive index can be expressed as

$$R = \{2yR_{G4} + [2(x-y) - z]R_{S2} + 2[z - (x-y)]R_{S3}\}N_A \quad (10)$$

where R_{S2} is the refraction of Q_2 unit. As indicated above for $x = y$ Eq. 9 would be

$$R = (2yR_{G4} + zR_{S4})N_A. \quad (11)$$

In this relation we can use the values of R_{S4} [24, 38] and R to get R_{G4}. The obtained values of R_{G4} for the glasses studied are given in Table 6. These values can be used in Eqs. 9 and 10 together with the previously obtained R_{S3} and R_{S4} [24, 38] to calculate R. Figure 6 shows a good agreement between the determined (R_m) and the calculated molar refraction (R_c).

By considering that $z = (1 - 2y)$ then Eq. 11 can be reformed to

$$R = [2y(R_{G4} - R_{S4}) + R_{S4}]N_A. \quad (11a)$$

This is a straight-line equation. Its slope is $2(R_{G4} - R_{S4})N_A$ and the intercept is $R_{S4}N_A$. The plots in Fig. 7 show that both R_m and R_c verify Eq. 11a. It is worthy to note here that the slopes of these lines can be used to calculate R_{G4}.

Like the case of μ, for glasses having $(Ga_2O_3/R_2O) \leq 1$ and $0.5 \leq (R_2O–Ga_2O_3)/SiO_2 \leq 1$, R can be given as

$$R = \{y(2R_{G4} - 2R_{S3} + R_{S4}) + [x(2R_{S3} - 3R_{S4}) + R_{S4}]\}N_A. \quad (12)$$

This is also a straight-line equation for either x or y being constant. Parameters of the lines in Figs. 8 and 9 agree well with these relations. The slope and intercept of lines as obtained from the fitting equations are in agreement with those calculated from Eq. 12.

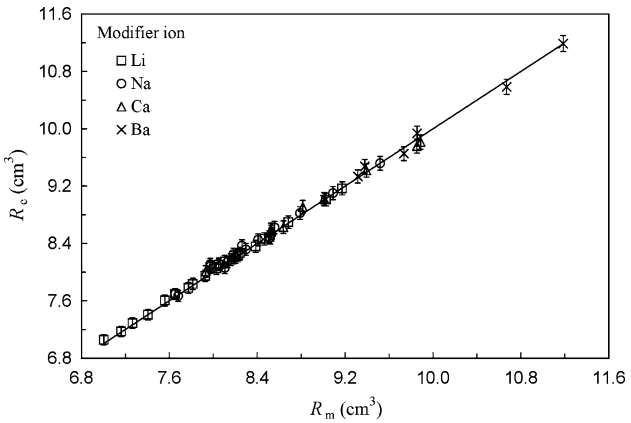

Fig. 6 Correlation between the calculated (R_c) and determined molar refraction (R_m) for Li_2O–Ga_2O_3–SiO_2 (□), Na_2O–Ga_2O_3–SiO_2 (○), CaO–Ga_2O_3–SiO_2 (Δ), and BaO–Ga_2O_3–SiO_2 (×) glasses. The R_c values were obtained from Eqs. 9 and 10 and the factors given in Table 6. The R_m data are obtained from Eq. 8 by using the μ_m values given in Tables 1, 2, 3, and 4 and the corresponding densities (collected in [21]). The error limit is estimated as ±1%. The solid line represents the fitting plot of the R_m values

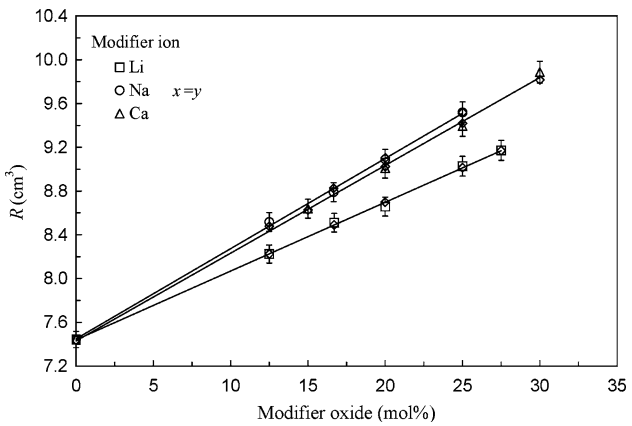

Fig. 7 Determined molar refraction R_m of Li_2O–Ga_2O_3–SiO_2 (□), Na_2O–Ga_2O_3–SiO_2 (○), and CaO–Ga_2O_3–SiO_2 (Δ) glasses in dependence of the modifier oxide content. The glasses presented have equal concentrations of Ga_2O_3 and the modifier oxide ($x/y = 1$). The R_m data are obtained from Eq. 8 by using the μ_m values given in Tables 1, 2, 3 and the corresponding densities (collected in [21]). The calculated molar refraction data R_c (◇) are also presented. The solid lines are the fitting plots of the R_m values

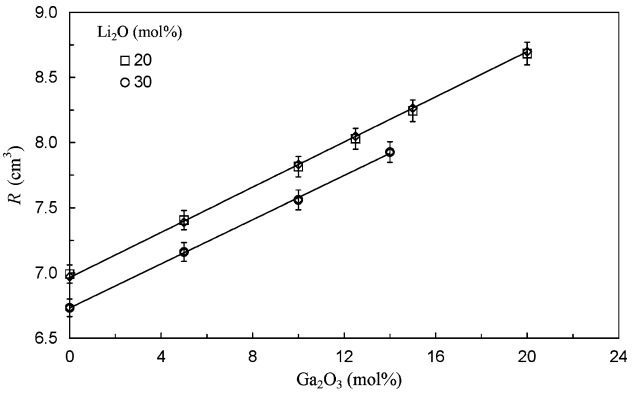

Fig. 8 Dependence of the determined molar refraction R_m (□, ○) on the Ga_2O_3 content for Li_2O–Ga_2O_3–SiO_2 glasses having constant concentration of Li_2O. The calculated molar refraction data R_c (◇) are also presented. The solid lines are fitting plots of the R_m values

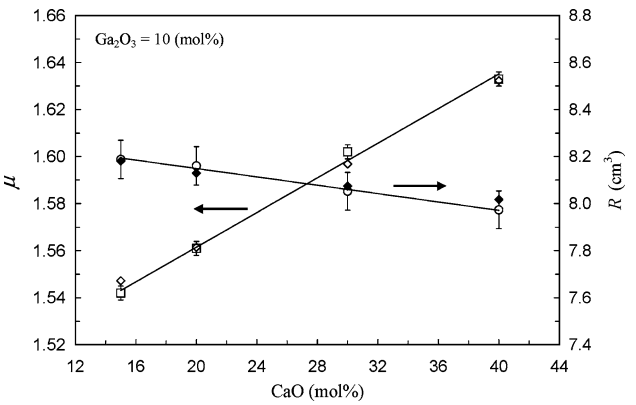

Fig. 9 Experimental (□, ○) and calculated data (◇, ◆) of refractive index and molar refraction of CaO–Ga_2O_3–SiO_2 glasses having constant concentration of Ga_2O_3 (10 mol%, Table 3). The data are presented as a function of the CaO content. The solid lines are fitting plots of the experimental data

Conclusion

The model presented can be used to follow the changes in μ and R for R_2O–Ga_2O_3–SiO_2 and RO–Ga_2O_3–SiO_2 glasses. The agreement in behavior and values between the calculated and experimental refractive index and molar refraction reveals that the presented model is adequate to describe the structure of these glasses. It is assumed that for $[Ga_2O_3/R_2O$ (or RO)$] \leq 1$ Ga_2O_3 has priority to consume an equivalent quantity of modifier oxide to form GaO_4 units. The rest of R_2O (or RO) associates with SiO_2 forming Q_3 or Q_2 units, depending on the composition.

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