The Canadian Mineralogist
Vol. 43, pp. 1643-1651 (2005)

THE STRUCTURE OF LITHIUM-CONTAINING SILICATE AND GERMANATE GLASSES

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ABSTRACT

The addition of alkali oxides to silicate glasses results in the disruption of the silicate network and the formation of non-bridging oxygen atoms and Q^n species. Lithium-containing silicate glasses behave differently than other alkali-containing silicate glasses. Addition of Li_2O to silicate and germanate glasses generates Q^2 species at low Li contents. Furthermore, the preference for Q^2 formation is enhanced in Li-germanate relative to Li-silicate glasses. The proposed mechanism for incorporation of the Li involves its bonding to pairs of non-bridging atoms of oxygen on adjacent Q^2 tetrahedra, resulting in a Li coordination of 4 in a square-planar configuration.

Keywords: glasses, structure, lithium, alkalis, germanates, melts, Q species, silicates.

SOMMAIRE

L'addition d'oxydes d'alcalins à la composition d'un verre silicaté cause la disruption de la trame siliceuse et la formation d'atomes d'oxygène non chevauchants, rattachés à seulement un atome de Si, et donc des espèces Q^n. Les compositions de verre siliceux lithinifères se comportent différemment des verres contenant un autre alcalin. L'addition de Li_2O aux compositions à base de silicate et de germanate génère des groupes Q^2 à faible teneur en Li. De plus, la formation préférentielle d'un tel groupe est encore plus marquée pour les compositions à base de germanate que pour celles à base de silicate. Nous préconisons un mécanisme impliquant la liaison du Li à une paire d'atomes d'oxygène non chevauchants, faisant donc partie de groupes adjacents de tétraèdres Q^2, assurant ainsi une coordinence quatre du Li, dans un agencement planaire carré.

(Traduit par la Rédaction)

Mots-clés: verres, structure, lithium, alcalins, germanates, bain fondu, espèces Q, silicates.

INTRODUCTION

Silicate glasses are used as models for the structure of silicate melts. The structure of a silicate glass at the glass-transition temperature (Tg) is considered to be representative of the melt structure. Also, being solid, glassy materials are easier to work with than melts (Wong & Angell 1976). Knowledge of the structure of silicate melts is important in order to understand the chemical and physical properties of magmas and melt systems, such as viscosity and density, which occur naturally within the earth and dominate geological processes (Mysen *et al.* 1982a, Mysen 1988).

Measurements of physical properties such as activation energy of viscous flow, molar volume and thermal expansion (*cf.* Stebbins 1995) indicate that the structures of alkali-containing glasses exhibit a dependence upon the type of alkali present in the glass (*cf.* Henderson 2005). Lithium in particular appears to behave differently to the other alkalis when incorporated into the glass network. The structures of lithium-containing silicate glasses were recently investigated by Soltay & Henderson (2005). In that study, series of lithium germanate and silicate glasses were investigated using Raman spectroscopy. Our results confirm that lithium-containing silicate glasses have a different distribution of Q^n species than the other alkali-containing silicate glasses. Furthermore, the distribution of Q^n species was found to be different in lithium-containing germanate glasses relative to lithium-containing silicate glasses. However, Soltay & Henderson (2005) merely reported their findings and did not elaborate upon possible structural mechanisms or reasons for the anomalous behavior of lithium in these glasses. Here, we review the current literature pertaining to lithium-containing silicate and germanate glasses and elaborate upon the possible

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[§] *E-mail address*: granth@geology.utoronto.ca structural mechanisms responsible for the anomalous behavior of lithium.

MODELS OF MELT STRUCTURE

A detailed review of silicate melt structure has been given by Henderson (2005), and only a brief synopsis of our understanding of oxide glass structure is given here. One of the most widely accepted models of oxide glass structure is the random network model of Zachariasen (1932). This model describes the structure of a pure oxide glass, such as vitreous SiO_2, as a continuous three-dimensional random network of silicon–oxygen tetrahedra. The random connectivity of the tetrahedra results in a structure that lacks periodicity, translational symmetry and long-range order. However, the bond lengths and bond angles within the SiO_4 tetrahedra are well defined, and the random nature of the glass structure arises from the variations in the distribution of both Si–O–Si and torsional angles between tetrahedra (Zachariasen 1932).

The structure of multicomponent glasses, such as alkali-containing silicate glasses, has been the focus of numerous studies, as they provide a more realistic, albeit simplified picture of naturally occurring silicate melts (*e.g.,* Furukawa & White 1980, Greaves *et al.* 1981, Mysen *et al.* 1982a, Matson *et al.* 1983, Dupree *et al.* 1986, Schneider *et al.* 1987, Stebbins 1987, Maekawa *et al.* 1991, Hannon *et al.* 1992, Smith *et al.* 1995, Vessal *et al.* 1996, Stebbins 1998, Uchino & Yoko 1999). Multicomponent glasses are composed of network formers and network modifiers. Network formers are elements such as silicon and germanium that form tetrahedra and make up the bulk of the structure through corner-sharing "bridging oxygen" atoms (BO). Network modifiers, such as alkali and alkaline earth metals, modify the continuous silicate network by breaking the Si–BO bonds to form negatively charged $Si–O^-$ "non-bridging oxygen" (NBO) atoms and Q^n species (where *n* is the number of bridging oxygen atoms per silicon–oxygen tetrahedra, *i.e.,* $0 < n < 4$). Of the alkali-containing silicate glass systems, sodium silicate glasses have been the most extensively studied. Warren & Biscoe (1938) conducted one of the earliest structural studies of sodium silicate glasses and observed that these do not contain simple discrete SiO_2, Na_2O, $Na_2Si_2O_5$ or Na_2SiO_3 molecules. Instead, the structure was interpreted to consist of silicon atoms surrounded by four oxygen atoms forming SiO_4 tetrahedra. A Si–O bond distance of 1.62 Å was determined and was attributed to a proportion of oxygen atoms bonded to two silicon atoms (BO), with the remaining bonded to one silicon atom (NBO). Sodium ions were observed to be randomly distributed in holes throughout the silicate network and surrounded by six oxygen atoms with a bond distance of 2.35 Å. Warren & Biscoe (1938) also noted that with an increase in the content of sodium, the proportion of NBO atoms increases. They concluded that even though the structure is quite definite, it does not repeat periodically and therefore is noncrystalline.

There have been many structural studies and models of alkali silicate glasses following that of Warren & Biscoe (1938). The currently accepted model was developed by Greaves *et al.* (1981) and Greaves (1985), who performed Na and Si *K*-edge extended X-ray fine-structure spectroscopy (EXAFS) on a series of sodium silicate glasses. Silicon EXAFS data revealed that the structures of sodium silicate glasses, with varying sodium contents, are similar and have distinct similarities to vitreous SiO_2 owing to the presence of common rigid SiO_4 tetrahedra within the glass networks. Minor differences in the EXAFS data were attributed to the addition of the network modifier and changes to the distribution of Q^n species. The Na EXAFS spectra show a higher frequency of oscillations than the Si EXAFS spectra, indicating that the Na–O bond is longer than the Si–O bond, and that different bonding interactions are taking place. Their data indicated that the local short-range structure around the alkali cations is well defined, but varies with composition. They proposed the modified random network (MRN) model to explain their results. This model takes into account both the covalent bonding nature of the silicon atoms and the ionic interaction of the alkali cations. It describes the structure of sodium silicate glass as an interpenetration of two sublattices, a random continuous covalent SiO_2 network intercalated by an ionic fraction of the modifying cation component (Na_2O). The NBO atoms provide the structural link between the two sublattices, by coordinating with the modifying cations. This results in local structural ordering, with the sodium cations arranged around the non-bridging oxygen atoms, and the formation of percolation channels. This model has been supported by ionic and channel-diffusion measurements (Ingram 1987, Sunyer *et al.* 2002) as well as molecular dynamics (MD) simulations (*cf.* Vessal *et al.* 1996, Smith *et al.* 1995).

THE STRUCTURE OF LITHIUM SILICATE GLASSES

As noted above, the presence of different alkali cations in a silicate glass has been shown to have a number of effects on the physical properties of the glass (*e.g.,* Furukawa & White 1980, Greaves *et al.* 1981, Mysen *et al.* 1982a, Matson *et al.* 1983, Dupree *et al.* 1986, Maekawa *et al.* 1991, Hannon *et al.* 1992, Schneider *et al.* 1987, Stebbins 1987, 1988, Smith *et al.* 1995, Vessal *et al.* 1996, Uchino & Yoko 1999). Studies using magic-angle spinning nuclear magnetic resonance spectroscopy (MAS–NMR) (*e.g.,* Murdoch *et al.* 1985, Schneider *et al.* 1987, Stebbins 1987, 1988, Dupree *et al.* 1990, Emerson & Bray 1994, Mortuza *et al.* 2001, Sen & Youngman 2003), infrared and Raman spectroscopy (Matson *et al.* 1983, Furukawa & White 1980, You *et al.* 2001), neutron scattering (Misawa *et al*. 1980, Hannon *et al*. 1992, Uhlig *et al*. 1996, Zhao *et al*. 1998) and molecular dynamics simulations (Vedishcheva *et al*. 1995, Huang *et al*. 1996, Uchino & Yoko 1999), have revealed cation-dependent structural changes of alkali silicate glasses and have shown that lithium silicate glasses behave significantly differently from other alkali-containing silicate glasses.

Hannon *et al*. (1992) studied the short-range order of lithium and potassium silicate glasses by neutron diffraction. For lithium silicate glasses, they determined a ratio of interatomic distances ($r_{O–O}/r_{Si–O}$) and a coordination number of Si that is close to the expected value for SiO_4 tetrahedra, indicating that lithium silicate glasses exist as a network of silicon–oxygen tetrahedra. Hannon *et al*. (1992) also calculated that the Li–O bond distance is 1.97 Å, consistent with the average Li–O distance, 1.94 Å, for crystalline lithium silicates. However, unlike crystalline lithium silicates, where lithium has a coordination of four, they observed a coordination of ~2 for lithium. Conversely, Hannon *et al*. (1992) observed a coordination of four for potassium in potassium silicate glasses of similar composition. The coordination of two for Li is also substantially lower than the coordination number for sodium, observed to be five in sodium silicate glasses by Greaves *et al*. (1981) and Greaves (1985). Hannon *et al*. (1992) interpreted these results to imply that lithium occupies a distinctly different position in alkali silicate glasses, compared to other alkalis, and exists in pairs between two non-bridging oxygen atoms (Fig. 1a).

Using ^{29}Si MAS–NMR, Schramm *et al*. (1984) studied lithium silicate glasses containing 15–40 mol.% Li_2O. By calculating the relative areas of the NMR peaks using a curve-fitting procedure, they estimated the concentration of Q^n species. They observed a statistical distribution of Q^2, Q^3 and Q^4 species (Q^n species are present in ratios determined by stoichiometry) within the 15–40 mol.% Li_2O interval of concentration. With the addition of lithium, the Q^4 species decreased linearly, and the Q^3 species exhibited a linear increase, reaching a maximum at 30 mol.% Li_2O, beyond which it decreased. However, the distribution of Q^2 species was observed to behave quite differently, remaining approximately constant below 30 mol.% Li_2O, but then sharply increasing above this lithium concentration. On the other hand, in a ^{29}Si NMR study of lithium silicate glasses, Grimmer *et al*. (1984) reported that lithium silicates follow a binary distribution, where only Q^n and $Q^{n–1}$ species are present at each composition.

Later, Dupree *et al*. (1986) performed a ^{29}Si and ^{133}Cs MAS–NMR of rubidium and cesium alkali silicate glasses and compared their results with sodium- and lithium-containing silicate glasses from earlier studies (De Jong *et al*. 1981, Matson *et al*. 1983, Schramm *et al*. 1984). In comparison to the earlier studies, Dupree *et al*. (1986) observed that for low concentrations of rubidium and cesium, there is little change in the glass structure, and a uniform distribution of Q^3 species and associated cations exists. However, they also observed that at high concentrations of alkali (>40 mol.%) where there is more than one NBO and one cation associated with each silicate tetrahedron, then the Q^n species becomes more variable, resulting in the formation of Q^1, Q^2 and Q^3 species.

In a similar study to those of Schramm *et al*. (1984) and Grimmer *et al*. (1984), Emerson *et al*. (1989) investigated the Q^n species of lithium silicate glasses.

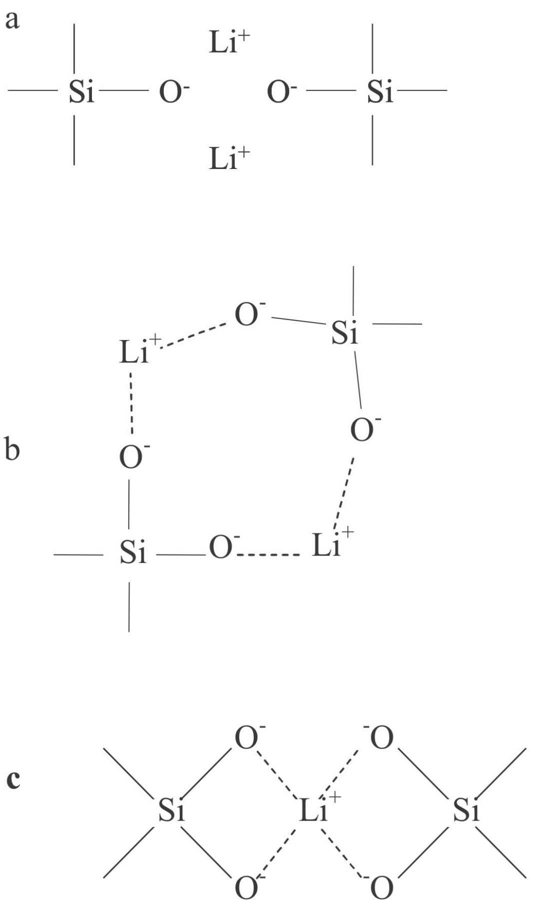

FIG. 1. a) Pairing arrangement of lithium cations between NBO atoms, as described by Hannon *et al*. (1992). This arrangement requires that the Li cations be in pairs in order to be consistent with a coordination number of 2. However, it also assumes that Li bonds exclusively with Q^3 species. b) This alternative arrangement is consistent with Q^2 formation if the coordination number of Li is 2. This configuration would not require Li cations to be in pairs, although they would need to be near the Q^2 tetrahedra. c) A possible configuration consistent with Q^2 formation and Li coordination of 4. Again Li pairing would not be required.

They confirmed the presence of Q^2, Q^3 and Q^4 species in lithium silicate glasses with $Li_2O–nSiO_2$ ($n = 2, 4$) compositions and Q^1, Q^2 and Q^3 species in glasses of $Li_2O–SiO_2$ composition. By comparing their results with equivalent Na, K and Rb silicate glasses, they concluded that lithium silicate glasses contain significantly more Q^2 and Q^4 species relative to other alkali silicate glasses, the latter having more Q^3 species.

Dupree *et al.* (1990) performed another ^{29}Si MAS–NMR study of lithium silicate glasses containing 25–39 mol.% Li_2O. They focused upon this compositional region as they were interested in observing the Q^n distribution around 33 mol.% Li_2O, since it is at this concentration that all Q^4 species should have transformed to Q^3 species for a binary distribution model. Dupree *et al.* (1990) observed that within this compositional range, lithium silicate glasses contain a distribution of Q^2, Q^3 and Q^4 species. However, they reported that the amount of Q^4 species observed for lithium silicate glasses is greater than that observed by Stebbins (1987) for sodium silicate glasses of equivalent alkali concentrations. As the number of NBO atoms is controlled by the lithium concentration, Dupree *et al.* (1990) suggested that a stoichiometric relation must exist between the Q^2, Q^3 and Q^4 species. Therefore, any excess of Q^4 must be accommodated by the presence of an equivalent amount of Q^2 species, in accordance with the disproportionation reaction: $2Q^3 \Leftrightarrow Q^4 + Q^2$.

Lithium, sodium and potassium silicate glasses containing 20–56 mol.% alkali oxide were investigated by ^{29}Si MAS–NMR by Maekawa *et al.* (1991). Mixed Q^n distributions were observed, with lithium silicate glasses showing an increased preference for the formation of Q^2 and Q^4 species compared to potassium and sodium silicate glasses. From the calculated Q^n distributions, Maekawa *et al.* (1991) determined the equilibrium constants for the disproportionation reactions $2Q^n \Leftrightarrow Q^{n-1} + Q^{n+1}$ (n = 3, 2, 1). They observed the effect of different network-modifying cations as a shift in the equilibrium reaction to the right, with increasing cationic potential (Z/r) of the alkali, in the order $Li^+ > Na^+ > K^+$.

Raman spectroscopy has also been used to quantify the Q^n species distribution of alkali silicate glasses (*e.g.*, Furukawa & White 1980, De Jong *et al.* 1981, Mysen *et al.* 1982a, b, Matson *et al.* 1983, McMillan 1984, Phillips 1985). Matson *et al.* (1983) compared the Raman spectra of alkali (Li, Na, K, Rb, Cs) silicate glasses. Upon comparing the intensity of the 950 and 1100 cm^{-1} frequency bands (relating to Q^2 and Q^3 species, respectively) of different alkali silicate glasses, they observed that lithium exhibits a greater preference for forming Q^2 species at low alkali concentrations, and that this Q^2-forming tendency decreases with increasing cation size. Xu *et al.* (1989) also performed a Raman study of lithium silicate glasses (24–33.3 mol.% Li_2O) and observed the presence of Q^4 Q^3 and Q^2 species. However, as the concentration of Li_2O is less than 33.3 mol.%, Xu *et al.* (1989) attributed the presence of significant Q^2 species to indicate that the distribution of NBO atoms is not random and that Li^+ and NBO atoms have a tendency to arrange into regions of high-Li content, forming both Li-rich and Si-rich regions within the glass network.

An in-depth Raman study of lithium silicate glasses containing high mol.% Li_2O was performed by Umesaki *et al.* (1993). Their results showed that lithium silicate glasses with high concentrations of Li contain SiO_4 units with Q^4 to Q^1 species. The Q^n distribution observed by Umesaki *et al.* (1993) is in agreement with the distribution observed in an MAS–NMR study performed by Dupree *et al.* (1990). Umesaki *et al.* (1993) also performed an X-ray structural analysis on high-Li silicate glasses and, in accordance with Hannon *et al.* (1992), reported lithium atoms to be coordinated by 2~3 atoms of oxygen.

Most recently, Soltay & Henderson (2005) performed a Raman study of lithium silicate glasses (5–20 mol.% Li_2O). They assigned Raman bands at 1065 and 1200 cm^{-1} to the transverse optical (TO) and longitudinal optical (LO) split components of the asymmetric stretching of Q^4 bands. Raman bands at 1100 and 950 cm^{-1} were observed to correspond to the symmetric stretching motions of $Si–O^-$ bonds in Q^3 and Q^2 species, respectively. By curve-fitting the high-frequency spectral envelope, the relative distribution of Q^n species was determined. The intensity of the Q^4 bands decreased, whereas the Q^2 and Q^3 bands increased with the addition of lithium oxide, owing to the disruption of the polymerized silicate network and the formation of Q^2 and Q^3 species. This was in contrast to other alkali silicate glasses, where Q^2 species are not observed at low concentrations of alkali (*cf.* Dupree *et al.* 1986).

A MD simulation of sodium silicate and potassium silicate glass by Huang & Cormack (1991) showed the alkali cations to be positioned around NBO atoms, forming regions rich in Q^3 species and creating extended silica-rich regions with alkali-rich channels contained within them. These observed structures are consistent with the MRN model (Greaves *et al.* 1981, Greaves 1985). Even though the clustering behavior of alkali ions was observed for both sodium and potassium silicate glasses, Huang & Cormack (1991) proposed that the percentage of silicon atoms with more than one NBO (Q^2, Q^1 and Q^0 species) is reflected in the distribution of the alkali and NBO clusters, with Q^3 species dominating at the disilicate composition. However, the simulations performed by Huang & Cormack (1991) indicate that the distribution of the alkali and NBO is more uniform for potassium silicate glasses than sodium silicate glasses, thus suggesting that different alkali cations behave differently in modifying the structure of alkali silicate glasses. Further analysis revealed that the distribution of NBO per silicon decreases in the order of Li > Na > K.

Molecular dynamics simulations of sodium silicate glasses by Smith *et al*. (1995) supported the formation of Q^3 and silica-rich regions as observed by Huang & Cormack (1990, 1991). Smith *et al*. (1995) observed the structure of sodium silicate glass to be inhomogeneous on the nanometer scale, with a non-uniform distribution of sodium ions and clustering of sodium around the NBO atoms. They reported that with increasing amounts of sodium, the sodium-rich and silicate-rich regions were observed to extend three-dimensionally.

Lithium was also observed to behave differently in an *ab initio* molecular orbital study of sodium and lithium silicate glasses by Uchino & Yoko (1999). Using a cluster model calculation approach, they found the coordination number of sodium to be larger than that of lithium in silicate glasses. This change in coordination number was interpreted to be a result of the atomic radius of lithium being smaller than that of sodium. However, upon examining the charge distributions of the sodium and lithium clusters by Mulliken population analysis, Uchino & Yoko (1999) reported that the coordination environments are influenced by the electronegativities of the alkalis. The Li–O bond overlap is considerably larger than that for the Na–O bond, and the Li–NBO bonds have strong covalent interactions. Lithium thus is more likely to interact with NBO atoms, whereas the lower covalency of sodium would result in its more likely interaction with both BO and NBO atoms, thus resulting in a higher coordination-number. These results contradict the MRN model, in which the alkali cations interact with NBO atoms only.

The Structure of Lithium Germanate Glasses

Germanate glasses have been considered to be analogous to silicate glasses, as germanium is isochemical with silicon. Like silicate glasses, germanate glasses contain a tetrahedral arrangement with a germanium atom bonded to four oxygen atoms. The addition of network modifiers similarly results in the disruption of the GeO_2 continuous network and the formation of NBO atoms. Therefore, the structure of alkali germanates also can be described by a distribution of Q^n species. However, there have been relatively few structural studies that have provided insights into the Q^n distribution of these glasses (Hass 1970, Verweij & Buster 1979, Sakka & Kamiya 1982, Di Martino *et al*. 2001, Henderson & Wang 2002). Verweij & Buster (1979) examined lithium, sodium and potassium germanate glasses by Raman spectroscopy. Their Raman spectra revealed the formation of NBO atoms and Q^3 species in the high-frequency region, and they reported that the structure of lithium germanate glasses are distinct from sodium- and potassium-containing glasses in having greater NBO bandwidths than sodium and potassium germanate glasses.

Huang *et al*. (1994, 1996) used K and Ge *K*-edge EXAFS to examine potassium and rubidium germanate glasses containing 2–25 mol.% potassium and rubidium. Their data indicate a high degree of disorder around the potassium and rubidium in the respective glasses. In another study, Lu *et al*. (1996) investigated the structure of potassium and rubidium germanate glasses using high-resolution X-ray photoelectron spectroscopy (XPS). In contrast to the other studies (*cf*. Verweij & Buster 1979), they observed the formation of NBO atoms at low alkali contents, ~2 mol.% for K and ~5 mol.% for Rb. In addition, Lu *et al*. (1996) observed more NBO atoms to be formed in potassium germanate glasses than rubidium germanate glasses. However, it should be kept in mind that XPS is a surface technique, and they may have been observing only the NBO atoms at the surface.

A study by Di Martino *et al*. (2001) focused on the structure of sodium- and cesium-containing germanate glasses using Raman spectroscopy, with compositions of 0–35 mol.% sodium and 0–25 mol.% cesium. Di Martino *et al*. (2001) reported the appearance of significant concentrations of Q^3 species above 18 mol.% Na_2O and 15 mol.% Cs_2O, with little evidence for the formation of NBO atoms at lower alkali content.

Alkali germanate glasses (Li, Na, K, Rb, Cs) have also been investigated by Henderson & Wang (2002), who reported a change in structure with increasing alkali content. Their Raman spectra indicated an increase formation of Q^3 and Q^2 species with increasing alkali content. In general, Q^3 species were observed only at greater than 10 mol.% alkali content, and Q^2 species, only at very high alkali content. However, the actual alkali composition at which the Q^2 and Q^3 species were observed in the Raman spectra was found to depend on the alkali type. Even though Henderson & Wang (2002) did not comment on the specific distribution of Q^n species, their Raman spectra indicate the presence of Q^2 and Q^3 species appearing at lower lithium concentrations than for sodium and potassium germanate glasses. Furthermore, Henderson & Wang (2002) reported that the relative difference between the Q^2 and Q^3 concentrations increases in the order $Li < Na < K < Rb = Cs$, *i.e*., the Q^2/Q^3 decreased in the order $Li < Na < K < Rb = Cs$. Despite the absence of Q^3 and Q^2 intensities in the Raman spectra below ~10 mol.% alkali oxides, Henderson & Wang (2002) suggested that NBO atoms are probably being formed but are either not sufficient in number to be observed, or their vibrational characteristics have been changed, with subsequent suppression of Raman intensities, as suggested by Henderson & Fleet (1991).

Most studies of alkali germanate glasses have focused on sodium and potassium as the network-modifying cations and have not provided much insight into their respective Q^n distributions. Unlike the previous investigators, who observed few NBO atoms and Q^3 species at alkali concentrations below 10 mol.% (Verweij & Buster 1979, Di Martino *et al*. 2001, Henderson & Wang 2002), Soltay & Henderson (2005) observed significant amounts of Q^2 and Q^3 species at relatively low Li_2O contents. Curve fits of the high-frequency region of lithium germanate glasses (Fig. 2) show the presence of Q^2, Q^3 and Q^4 species. The data also indicate that the concentration of Q^3 species increases linearly, whereas the Q^2 concentration increases nonlinearly with the addition of lithium. The Q^2 species undergoes a rapid increase at low concentrations of lithium, reaching a maximum of 20% of the total Q^n species concentration at approximately 10 mol.% Li_2O. The Q^2 concentration then decreases to ~12% of the total concentration of Q^n species at 20 mol.% Li_2O, after which it remains relatively constant. According to Soltay & Henderson (2005), this distinct Q^2 behavior suggests that the formation of Q^2 species is favored in lithium germanate glasses at low concentrations of lithium.

COMPARISON OF LITHIUM GERMANATE AND SILICATE GLASSES

The addition of lithium to germanate and silicate glasses clearly results in the formation of NBO atoms and Q^n species. However, the distributions of Q^n species are distinctly different for lithium silicate glasses and lithium germanate glasses. Lithium silicate glasses have been observed to contain varying amounts of Q^2, Q^3 and Q^4 species at low alkali concentrations (Schramm *et al.* 1984, Emerson *et al.* 1989, Xu *et al.* 1989, Maekawa *et*

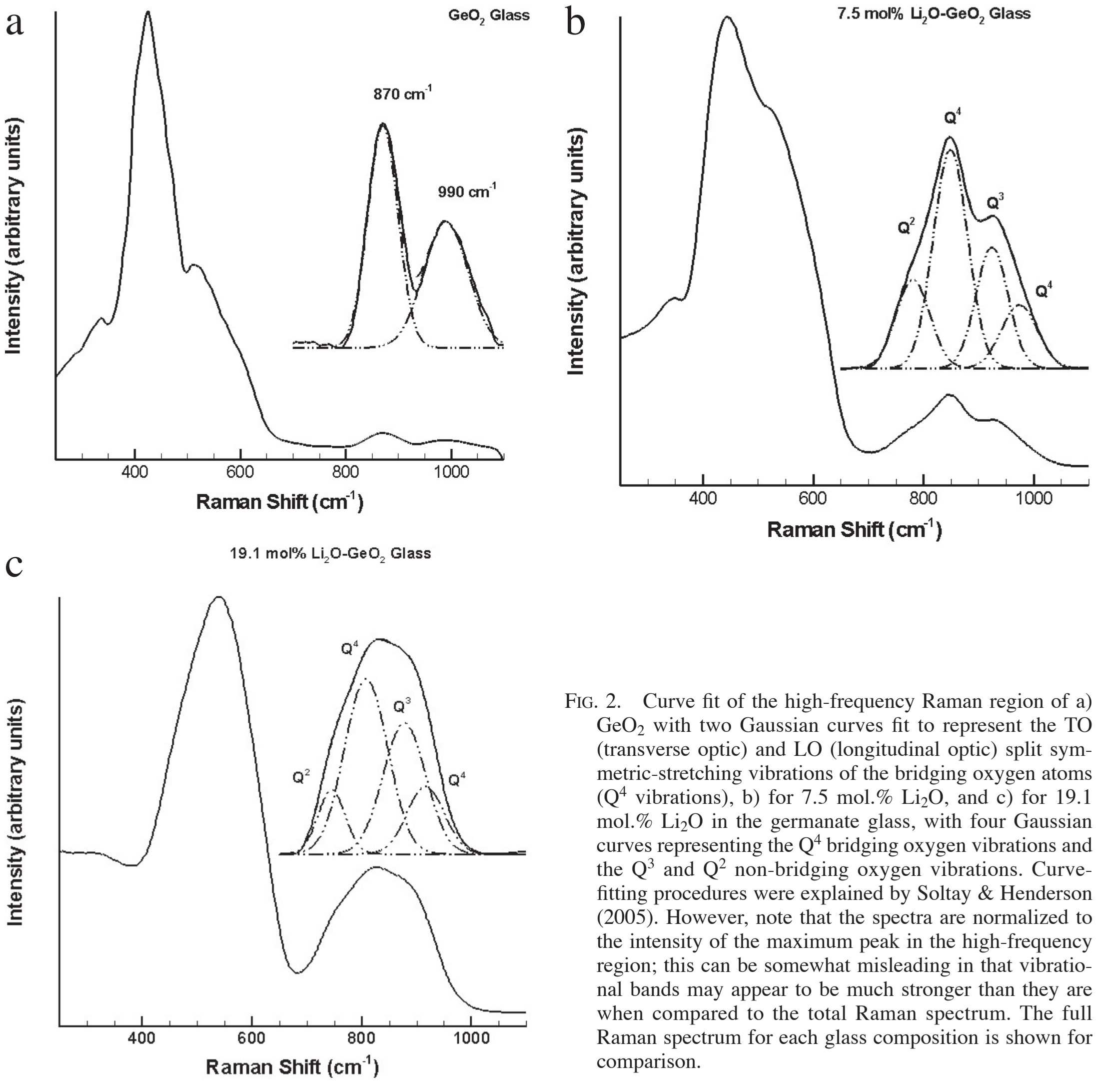

FIG. 2. Curve fit of the high-frequency Raman region of a) GeO_2 with two Gaussian curves fit to represent the TO (transverse optic) and LO (longitudinal optic) split symmetric-stretching vibrations of the bridging oxygen atoms (Q^4 vibrations), b) for 7.5 mol.% Li_2O, and c) for 19.1 mol.% Li_2O in the germanate glass, with four Gaussian curves representing the Q^4 bridging oxygen vibrations and the Q^3 and Q^2 non-bridging oxygen vibrations. Curve-fitting procedures were explained by Soltay & Henderson (2005). However, note that the spectra are normalized to the intensity of the maximum peak in the high-frequency region; this can be somewhat misleading in that vibrational bands may appear to be much stronger than they are when compared to the total Raman spectrum. The full Raman spectrum for each glass composition is shown for comparison.

al. 1991, Umesaki *et al*. 1993, Uchino & Yoko 1999, Henderson & Wang 2002, Soltay & Henderson 2005). It is the presence of significant numbers of Q^2 species at low lithium concentrations that sets lithium silicate glasses apart from other alkali silicate glasses (*cf*. Emerson *et al*. 1989). This Q^2 population implies that there is an increased tendency to form silicon atoms with two NBO atoms; the arrangement of lithium is non-random, and Li has some structural control on the silicate network.

In a MAS–NMR study of rubidium and cesium alkali silicate glasses, Dupree *et al*. (1986) have shown that for low concentrations of Rb and Cs, there is little change in the silicate structure, and a more uniform distribution of Q^3 species exists. However, at high Rb and Cs concentrations (>40 mol.% alkali oxide), the Q^n species become more variable, resulting in the formation of Q^3, Q^2 and Q^1 species. This difference in Q^n distribution for rubidium and cesium silicate glasses compared to lithium and sodium silicate glasses was attributed to the large size of the Rb and Cs as modifying cations. As large cations, Rb and Cs have greater steric and electrostatic interactions than the smaller alkali cations. These interactions are minimized by evenly distributing the cations throughout the silicate network. Once each silicate tetrahedron has accommodated a single cation, it will then start to accept additional cations to form Q^2 and Q^1 species. Thus Q^2 and Q^1 species are observed only at high concentrations of alkali.

As noted previously, lithium has a smaller coordination-number than sodium and potassium in alkali-containing silicate and germanate glasses (Hannon *et al*. 1992, Umesaki *et al*. 1993, Uchino & Yoko 1999). This lower coordination-number has been attributed to the increased covalency of the Li–O bond and the tendency for lithium to prefer bonding with NBO atoms. Figure 1a shows the bonding arrangement suggested by Hannon *et al*. (1992). The lithium cation is coordinated to a single oxygen atom on a Q^3 tetrahedron, and the Li cations must be in pairs to satisfy the experimentally determined coordination number of two. However, Uhlig *et al*. (1996) and Zhao *et al*. (1998) found that Li is coordinated to four atoms of oxygen. For this coordination, Li would not be required to form Li pairs. The pronounced Q^2 formation observed by Soltay & Henderson (2005) suggests that the lithium atoms may be bound in two possible configurations (Fig. 1) where Q^2 tetrahedra form. Which configuration is preferred would, however, depend upon whether or not the coordination number of Li is two or four. The first configuration (b of Fig. 1) occurs if each Li atom bonds to a NBO atom on two adjacent Q^2 tetrahedra. The Li atoms have a coordination number of two, and although they need not be paired, the configuration does require that the Li atoms be positioned near two Q^2 tetrahedra. This configuration is also compatible with an interpretation requiring only the formation of Q^3 tetrahedra. Each Li atom would then need to bond to a single NBO atom on adjacent Q^3 tetrahedra, and there would be no need for pairing of the Li cations. A second configuration (c, Fig. 1) also is possible. Here, the Li bonds to two NBO atoms on two adjacent Q^2 tetrahedra with a coordination number of four, and there is no clustering of the Li atoms. Configuration (c) is consistent with the results of Uhlig *et al*. (1996) who found, using reverse Monte Carlo calculations, that Li occupies a square-planar configuration with an O–Li–O angle of 90°. Furthermore, the Si–O–Li angle for this configuration is approximately 84° (assuming an O–Si–O angle of 109°), which is also consistent with the Si–O–Li angle found in crystalline $Li_2Si_2O_5$ (Liebau 1961).

Clearly, it is not possible to distinguish between the two mechanisms, although a detailed analysis of the behavior of the Q^2 vibrational bands with the addition of Li (beyond the scope of this paper) may provide some insight. However, Soltay & Henderson (2005) tentatively attributed the preferred formation of Q^2 species in lithium germanate glasses, compared to lithium silicate glasses, to the difference in the size of germanium and silicon atoms. The larger germanium atoms and longer Ge–O bonds would favor mechanism c, as the lengthened Ge–O bonds should reduce steric strain by opening both the Si–O–Li and O–Li–O angles.

CONCLUSIONS

Spectroscopic studies, neutron diffraction and molecular dynamic simulations have indicated that the structure of alkali silicate glasses and the distributions of their Q^n species are dependent upon the type of alkali cation present. The structure of lithium silicate glasses differs from that of other alkali-containing silicate glasses in exhibiting a preference for the formation of Q^2 and Q^3 tetrahedra. Furthermore, the behavior of the Q species with addition of Li_2O is different for Li-containing germanate relative to silicate glasses. In Li-silicate glasses, there is a linear trend in Q^2/Q^3 values with increasing Li content, whereas for germanates, the trend is nonlinear. The latter indicates that Li has a greater preference for forming Q^2 species in germanate glasses. Two mechanisms for incorporation of Li into both silicate and germanate glasses are proposed. Only one of these mechanisms requires the presence of Q^2 tetrahedra and is consistent with recent theoretical and experimental results suggesting the presence of Li in a square-planar configuration with a coordination number of four.

ACKNOWLEDGEMENTS

We dedicate this paper to Mike Fleet upon his retirement from the Earth Sciences faculty at the University of Western Ontario.This work was funded by NSERC of Canada in the form of a discovery grant to GSH. Two anonymous referees are thanked for their constructive comments.

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Received October 14, 2004, revised manuscript accepted October 13, 2005.