STRUCTURE, VISCOSITY AND MIXING BETWEEN ALKALI AND ALKALINE-EARTH SILICATE MELTS.

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Introduction

The relationship between physical properties and structure of glass and melts in the system Na2O-CaO-SiO2 are of technical and geological importance, in particular for understanding the microscopic origin for the configurational thermodynamic properties. Geologically, this system contains two of the major alkali and alkaline-earths elements found in igneous rocks. The connection of these elements with the tetrahedral silicate network is fundamental to understand the physical properties of magmatic liquids. This sytem is technologically important since it represents nearly 80% of industrial glasses and in particular, soda-lime silica glasses are at the basis of conventional windows [Morey and Bowen, 1925] and container glasses, as well as bioactive glasses [Hench, 1991 and Kim et al. 1995, Clupper and Hench, 2003]. This system has been one of the most expensively studied during the last fifty years. The first works on this system were carried out by Morey and Bowen [1925] and Wyckoff and Morey [1925] who published melting relations together with X-ray diffraction pattern of crystalline phases. English [1923] published viscosity measurements between 970K and 1670K for glasses with high silica content belonging to this system. we are focused first on viscosity measurements on composition with lower amount of silica, 60 mole % for which a complete Ca-Na substitution is possible. With these new viscosity data and using the theory of relaxation processes of Adam and Gibbs [1965], the viscosity (h) can be linked to the configurational entropy of the liquid (Sconf) at temperature T, using this equation : log η = Ae + Be/TSconf(T).

Materials and experiments

Starting materials: The samples were obtained by melting mixtures of Na2CO3, CaCO3 and SiO2. About 100 g CaCO3-Na2CO3-SiO2 (Rectapur from Merck) was ground for 1 hour under alcohol in an agate mortar, heated slowly to decompose the carbonates, and then heated above the melting point [Morey and Bowen, 1925]. The chemical composition investigated have 60 mole % of SiO2, which is the SiO2 limit above which pure Ca-silicate glasses unmixed [Morey and Bowen, 1925]. At lower SiO2 content, Na-metasilicate crystallizes rapidly from glasses, making thus property measurements unfeasible. The six compositions investigated in this study are reported in Table 1, with the notation CN60.X, where X is the mole % of Na2O and 60 is the mole % of SiO2. The mol% of CaO corresponds to 100 - (60 + X).

High-viscosity measurements: Viscosity measurements on supercooled liquids were carried out in air condition, with the creep apparatus described by Neuville and Richet [1991]. We estimate the viscosity uncertainty to be less than 0.02 log units with this technique.

Low-viscosity measurements: The low-viscosity measurements were performed in a vertical tube furnace heated by Super Kanthal 33 elements in air [Neuville, 1992]. The precision of viscosity measurements was tested with NBS standard SRM 710, which shown that the uncertainty and the reproducibility are within 0.04 log Poise.

Raman spectroscopy: The measurements were made with a T64000 Jobin-Yvon confocal microRaman spectrometer equipped with a CCD detector. The 514.532 nm line of a Coherent 70-C5 Ar+ laser operating at 2.8 W at the sample was used for sample excitation. For the samples examined here, this excitation and CCD system result in signal-to-noise ratio between 30/1. The integration time was 60s. With our triple spectrometer, it is possible to take spectra at very low frequency (less than 10 cm-1). All reported spectra are unpolarized. A correction factor of the form proposed by Long [1977] and given correctly by Neuville and Mysen [1996] was used. The corrected Raman intensities were normalized to the data point of the greatest absolute intensity. The spectra were deconvoluted with the method of minimization of least squares described by Davidon [1966] (See also Seifert et al., 1982; Mysen et al., 1982; Mysen, 1990; and Mysen and Frantz, 1994 for detailed discussion).

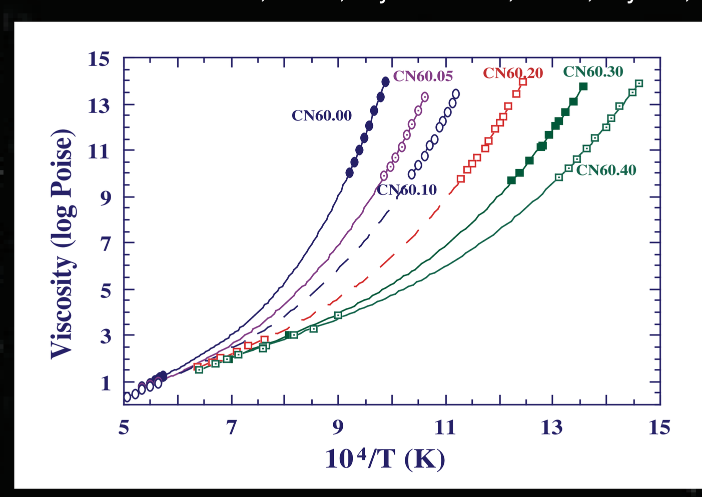

Figure 1 : Viscosity data of the soda-lime silicate glasses and melts as a function of reciprocal temperature

Rheologicals properties

The results of viscosity measurements on supercooled liquids are plotted in Figure 1, for each temperature, averaged over 15 or 20 measurements made at different stresses. In this system, no viscosity measurements between 10^3 and 10^{10} Poise are possible because of the very rapid rate of crystallization in the viscosity-temperature range [Meiling and Uhlmann, 1977 ; Mastelaro et al. 2000].

In Figure 1, we observe that the addition of 10 mole % Na2O to a lime-silicate melts modified more the viscosity than the addition of 10 mole % CaO to a soda-silicate melts. A striking difference exists in the behavior of the viscosity between pure Na-silicate liquid (CN60.40) and pure Ca-silicate liquid (CN60.00) (see Figure 2). Indeed, at constant viscosity and low temperature (Figure 1), the difference in temperature is greater than 300 K between pure soda and lime silicate glasses. This difference decreases with increasing temperature and becomes lower than 100 K at 1600 K. Moreover, at the same temperature near 1000K, we observed a difference in viscosity values of 10 orders of magnitude between pure soda and pure lime silicate compounds (Figure 2), while this difference is less than 1 order of magnitude a high temperature (1600K).

At high temperature (1600 K), the viscosity of silicate melts varies linearly upon Na2O/(Na2O+CaO), with a small decrease as the content of Na2O increases (Fig. 2). For temperatures near the glass transition (1000 K), the viscosity deviates negatively from a linear variation. The deviation from a linear variation is 4 orders of magnitude at 1000K and only 2.5 orders at 1050K and increases with decreasing temperature. Similar results were already observed by English [1923] in the same system with 75 mole % SiO2, 25 mole % of Na2O, and with a substitution up to 12 mole % CaO.

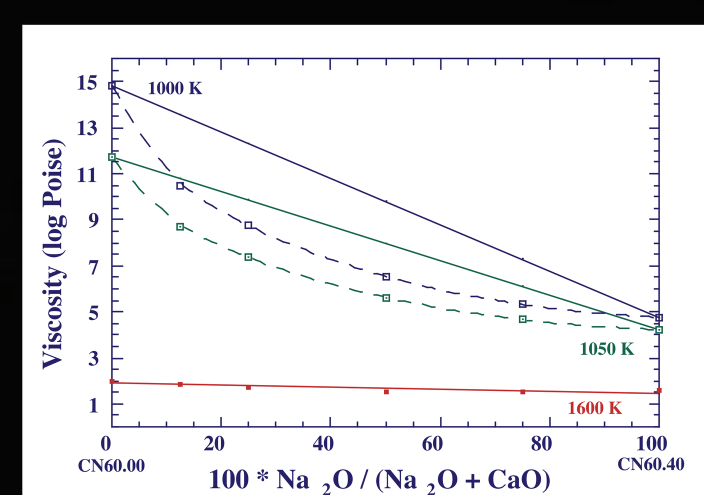

Figure 2 : Viscosity as a function chemical variation at constant temperature

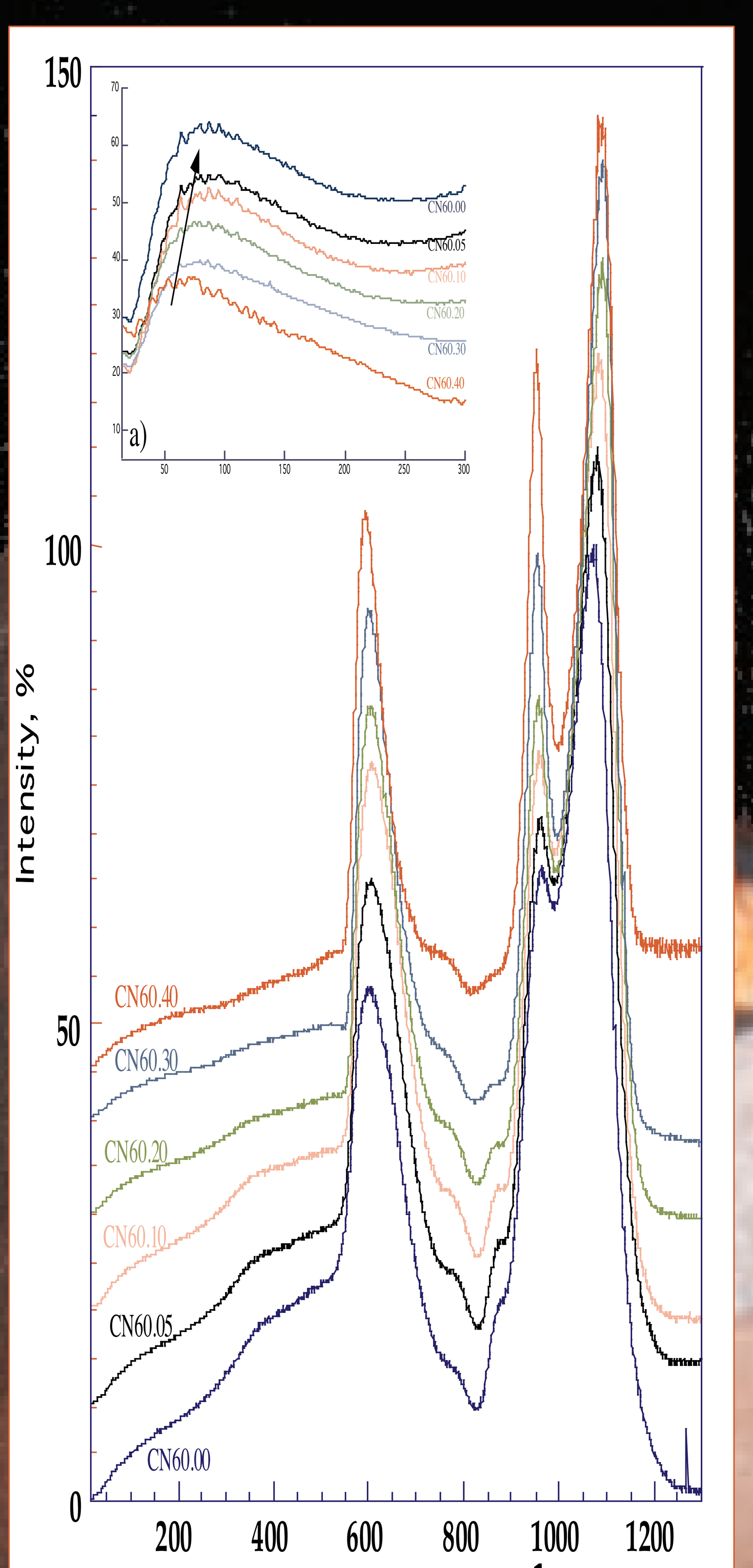

Figure 3 : Raman spectra of glasses at room temperature.

Raman spectroscopy

The effect of CaO on the Raman spectra of Na-silicate glass is shown in Figure 3. In this paper, we focus only on the Raman spectra of glasses at room temperature, which provide the most important configurational information on the structure of silicate. In fact, from the Raman spectra at high temperature, we can obtained some structural information on the liquid, but these informations cannot be compared with the configurational entropy obtained from the viscosity measurements [Neuville and Mysen, 1996]. The Raman spectroscopy at high temperature gives vibrational contribution and not configurational contribution which are more discernible at low temperature or at room temperature. The Raman spectra were recorded between 10 and 1300 cm^{-1}. The spectra can be divided into four regions: the boson region (10-250 cm^{-1}); the low frequency region (250-700 cm^{-1}); the medium frequency region (700-850 cm^{-1}); and the high frequency region (850-1300 cm-$^{-1}$). The boson region was study without normalization to opposite at the high frequency region (250-1300 cm^{-1}) where the intensity where corrected using the Long protocol (see the experimental part). The most important structural information is gained from the Si-O stretch frequencies with the Raman bands in the 850-1200 cm-1 region [see for example: Seifert et al., 1982; Mysen, 1988].

The boson region (10-250 cm^{-1}): Below 250 cm^{-1}, there is only a scattering continuum and the Raleigh tail of the exciting line, except at very low frequency where there is the so-called boson peak [i.e. Malinovsky and Sokolov, 1986 and Buchenau et al., 1986]. This peak correspond to a relative rotation of almost rigid tetrahedra [Buchenau et al., 1986 ; Helhen et al., 2002]. Helhen et al. consider that this peak observe on different SiO2 polymorphs, increase in intensity and shift to higher frequency with distorted the SiO4 polyhedra. In our case, an increase in intensity and a shift to high frequency were observed when CaO replaced Na2O in soda-silicate glasses.

The low frequency region (250-700 cm^{-1}): The Raman spectrum above 500 cm^{-1} is due primarily to the vibrations of the Si-O network with the modifiers essentially at rest. The Raman spectra are more sensitive to the network structure (the high frequency region) than to the details of the sites of the cation modifiers, but we can observe some small changes in ours Raman spectra in this low frequency region which are not yet understood. A shoulder at 390 cm^{-1} observed for lime silicate glasses disappears for more than 10 mole % of Na2O. The peaks at 580 and 600 cm^{-1} evolve in only one broad peak which becomes less asymmetric with the addition of CaO content. The peak at 580 cm^{-1} is assigned to Si-O0 rocking motions in fully polymerized SiO2 (Q4) units [after Bell and Dean, 1972; Phillips, 1984; Mysen and Frantz, 1994]. The maximum at 600 cm^{-1} is assigned to Si-O-Si bending motions in depolymerized structural units [after Lazarev, 1972; Furukawa et al., 1981 and Mysen and Frantz, 1994].

The intermediate frequency region (700-850 cm^{-1}): the broad peak at 755 cm^{-1} for the CN60.40 shifts to higher frequency with increasing CaO content (790 cm^{-1} for CN60.00). This observation is in good agreement with Frantz and Mysen [1995] who observed that this peak shifts to higher frequencies with increasing the size of the cation, in the order Ca<Sr<Ba.

The high frequency region (850-1200 cm^{-1}): The 950 and 1085 cm^{-1} peaks in the Raman spectra of CN60.40 evolve to one broad peak at 1050 cm^{-1} and a shoulder at 950 cm^{-1}, with increasing CaO content. From the derivation of the spectra, we observe that the frequency at 950 cm^{-1} increases. A similar increase in frequency is observed for the peaks at 800 and 600 cm^{-1} upon addition of CaO content whereas the peak at 1050 cm^{-1} decreases in frequency with higher CaO content. These findings are in good agreement with those reported by Mysen and Frantz [1992, 1994] on NS2 glass and by Frantz and Mysen [1995] on CS1.5 glass.

Spectra deconvolution

The high-frequency region (850-1200 cm-1) of the Raman spectra of the six glasses has been deconvoluted with a technique described by Mysen et al. [1982] and Mysen [1990] using four or five Gaussian bands at 870, 950, 1000, 1050 and 1150 cm^{-1}. In Figure 4 deconvolution were report for CN60.00, CN60.20 and CN60.40 glasses. The assignments of the 870, 950, 1100 and 1150 cm^{-1} bands correspond to Si-O stretch vibrations in specific structural units as already published. The small band at 870 cm^{-1} can be attributed to the Si-O- stretching in tetrahedral with three Non-Bridging Oxygen per Silicon (NBO/Si = 3; Q1). The band near 950 cm-1 is assigned to Si-O- stretching in structural units with two Non-Bridging Oxygen per Silicon (NBO/Si) (equal at Q2). The main band centered near 1050 cm^{-1} is due to the Si-O- stretching in units with one Non-Bridging Oxygen per Silicon (NBO/Si = 1; Q3). The high-frequency band at 1150 cm^{-1} result from the presence of fully polymerized units (Q4). The large band at slightly lower frequency, 1000 cm^{-1}, have been interpreted as a vibrational frequency assignable to a Si-O0 bridging oxygen stretching mode [Mysen and Frantz, 1994] or alternatively as a vibration in structural units associated with the metal cation [Fukumi et al., 1990]. The frequency of the bands assigned to Si-O stretching in Q4, Q2 units decreases in frequency with increasing the Na2O content whereas the three others bands, Q3, Q1 and 1000 cm^{-1} shift to higher frequency with increasing Na2O content (Figure 8). The increase in frequency of the 1000 cm^{-1} band is in good agreement with the idea developed by Fukumi et al. [1990] who attributed it to a vibration in structural units associated with the metal cation. Indeed, the NBO-Na bonding is lighter than the NBO-Ca bonding even if the frequency of this bonding can be higher than those of the Q-Ca vibrations.

The Q1 and Q4 species occur in a very small amount. This conclusion agrees with previous NMR results of Buckermann et al. (1992) ; and Raman spectra made by Mysen and Frantz, (1992; 1994) and Frantz and Mysen, (1995) that indicate the presence of the Q4, Q3, Q2 species in rich-SiO2 silicate glasses, like sodium disilicate NS2, and the presence of Q1 species only in the poor-SiO2 glasses, like CS1.5, (Frantz and Mysen, 1995; Buckermann et al., 1992; Brawer and White, 1977a,b).

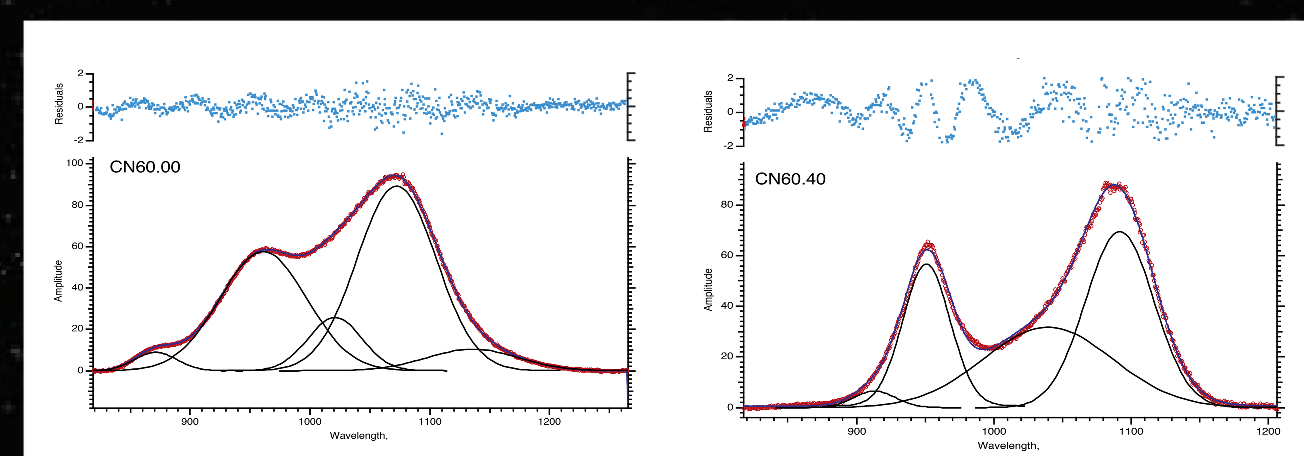

Figure 4 : Deconvolution of Raman spectra.

Discussion

Adam-Gibbs theory and configurational entropies : As previously shown [Neuville and Richet, 1990], it is necessary to use the Adam-Gibbs equation of viscosity to extrapolate the viscosity measurements. The Arrhenius or TVF equation can only be used to interpolate viscosity measurements. The configurational entropy can be determined for each chemical composition between lime (CN60.00) and soda (CN60.40) silicate glasses. The configurational heat capacity is the difference between the heat capacity of the liquid and that of the glass at the glass transition temperature (Tg). The calculation of these values was performed by using the model proposed by Richet [1987] for the heat capacity of glasses and by Richet and Bottinga [1985] for the heat capacity of the liquid. The configurational entropy at Tg, Sconf(Tg), and the other parameters of the Adam and Gibbs equation are plotted in Figure 5 as a function of Na2O content. The error bars of 5% for the values were obtained as described by Neuville and Richet [1991]. Between lime and soda silicate glasses, the Sconf(Tg) shows a non-linear variation. The configurational entropies increase near 30 % with addition of less than 5 mole % of Na2O to a lime-silicate glass, CN60.00. With increasing Na2O content, the configurational entropy remains nearly constant around 6.5 J/molK up to 6.9 J/molK for the pure soda-silicate glass (CN60.40). For alkali [Richet, 1984] and alkaline-earth elements [Neuville and Richet, 1991], the configurational entropy can be calculated using an ideal mixing term such as –RnXiLnXi with Xi=(Ca/Ca+Mg) or Na/(Na+K), R is the gas constant and n the number of atom exchange. In the present case, a good fit of the configurational entropy cannot be obtained using only a simple mixing term as proposed by Richet [1984]. This ideal mixing term can be interpreted by a random distribution of Ca and Mg or K and Na in the silicate or aluminosilicate network [Richet, 1984 and Neuville and Richet, 1991]. Instead, the fits of the configurational entropy presented in Figure 5 require the recourse to an excess term in the configurational entropy equation:

Sconf (Tg) = Smix + S xi Siconf (Tg) + Sexcess,

where Siconf, is the topological entropy of the end-members i that can be represented by the linear variation (dashed line in the figure 9), and Smix the mixing entropy [see Neuville and Richet, 1991]. The mixing term can be expressed using Richet [1984] by: Smix = - S R (xi) ln (xi),

where xi the molar fraction of Na2O in the Ca-silicate melts. This ideal mixing term is similar to that proposed by Richet [1984] and Neuville and Richet [1991]. In the present soda-lime silicate system, one calcium was replaced by two sodium. This substitution implies a significant change in the residual entropy and in the glass structure. To reproduce these entropy variation given in figure 5 an excess entropy term is needed. This term correspond to a mixing effect between the three binary interactions, Na2O-SiO2, CaO-SiO2 and Na2O-CaO and is not temperature dependent. Its exact expression can be obtained by fitting the experimental data:

Sexcess = -10.437 xNa2OxCaO + 53.801.10-3 xSiO2xCaO - 3.434.10-3 xSiO2xNa2O.

Using these equations, we can reproduce satisfactorily the entropy variations in Figure 5.

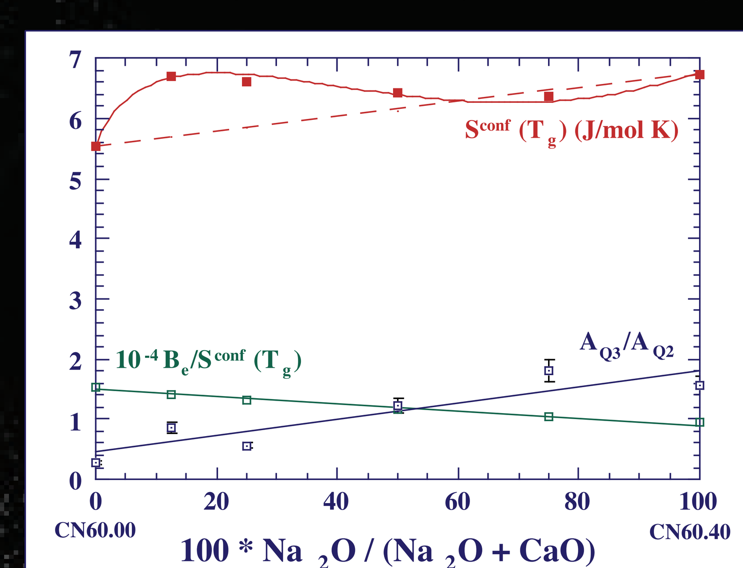

Figure 5 : Entropy and Q species as a function of chemical composition

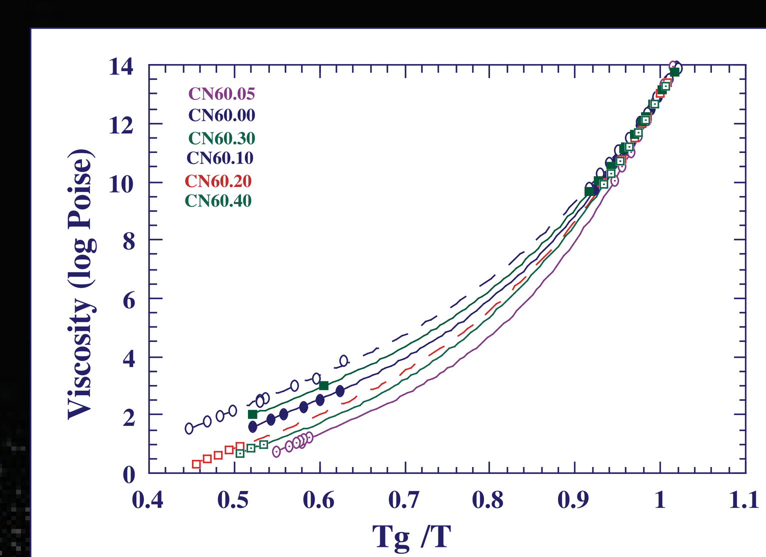

Figure 6 : Viscosity as a function of Tg/T.

Network polymerization : With adding up to 30 mol% Na2O in calcic silicate glass, we observed that the configurational entropy increases (Figure 5). This findings suggests an increase of the disorder in the glass and/or a change in the glass network polymerization. Structural changes that may account for the entropy evolution may be discerned in the Raman spectra of the glasses [Neuville and Mysen, 1996]. From the Raman spectroscopy, the polymerization network was evaluated in terms of Qn species. In Figure 5, the ratio AQ3/AQ2 is plotted as a function of a function of composition. There is a distinct increase of this ratio with adding Na2O in the lime silicate glass

Fragility

Angell [1991] proposed a classification of the liquids between strong and fragile. A strong liquid shows a linear variation of log h versus Tg/T, while this linear relation is not preserve in a fragile liquid. The configurational entropy also affects the fragility of silicate melts. The viscosities of the soda-lime silicate melts were plotted as a function of Tg/T in Figure 6. The strongest liquid is the pure soda silicate (CN60.40) while the most fragile liquid is the pure lime silicate (CN60.00). Other chemical compositions present an intermediate behavior between CN60.40 and CN60.00. These results for the heat capacity are in good agreement with those observed on the fragility.

Conclusions

We present some new viscosity measurements and Raman spectra on glasses in the SiO2-Na2O-CaO system. We can conclude that :
- The viscosity decreases rapidly with increasing Na2O in the Ca-silicate glasses.
- The configurational entropy along Na2O-MO silicate glasses with M=Ca, Sr shows a non-ideal mixing entropy.
- The fragility of the liquid decreases with adding Na2O in the Ca-silicate melts.
- The Q3/Q2 ratio increase with adding Na2O in the Ca-silicate melts.
- A non random distribution of Na and Ca were observed in a Ca-Na mixed silicate glasses.

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