Structure of Na_2O-CaO-Al_2O_3-SiO_2 glasses using Raman spectroscopy

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Raman spectra were recorded on glasses in the SiO_2-CaO-Na_2O-Al_2O_3 system. We examine the influence of the Si/Al substitution on the structure at middle range. We observe a strong decrease in frequencies with increasing Al_2O_3 in the Na-Ca silicate glasses, which indicates that Al enters preferentially in Q^4 species.

Introduction

The SiO_2-CaO-Na_2O-Al_2O_3 system is one of the most important in glass making industry and for understanding mass transfer in the Earth. Nevertheless, there have been few structural studies on glasses in this system, especially by Raman spectroscopy. Raman spectra give structural information on the middle range order of the aluminosilicate network, such as the basic Q^n units (*n* is the number of bridging oxygens per tetrahedron) or the connected rings. The presence and the nature of non network former cations, such as Ca and Na, may affect the aluminosilicate network. Indeed, calcium and sodium can play a different structural role: either as a modifier that participates to the network depolymerisation or as a charge compensator at the proximity of $(AlO_4)^-$ tetrahedra.

In this study, we present a Raman investigation on soda lime aluminosilicate glasses with a constant Na/Ca ratio. Replacing Al by Si at constant Na_2O/CaO ratio, we observe a rapid decrease of the high frequency region (1100 cm^{-1}). This decrease can be attributed to the substitution of Si by Al. The basic structural units of the aluminosilicate network are Q^4, Q^3 and Q^2. Tetrahedrally coordinated Al^{3+} is probably partitioned between these units. The abundance of units and Al^{3+} partitioning are functions of chemical composition **and temperature**. These structural variations are related to the changes in the configurational entropy.

Experimental Method

Sample preparation

The mixtures used were all made by melting the calculated quantities of Na_2CO_3, $CaCO_3$, Al_2O_3 and SiO_2. About 100 g $CaCO_3$-Na_2CO_3-Al_2O_3-SiO_2 (Rectapur from Merck) was ground for 1 hour under alcohol in an agate mortar, then heated slowly to decompose the carbonates, and then heated above the melting point. The compositions investigated (60-30 mol% SiO_2) are plotted in Fig. 1. We use the notation NCAx.y.z, where x, y and z refer to the molar percent of SiO_2, Al_2O_3 and Na_2O respectively, and 1-x-y-z is the CaO molar content. These glasses were melted in covered Pt crucibles, for a few hours at high temperature (1 800K) in air condition and stirred to obtain the bubble-free products required for the viscosity measurements. The samples were quenched by immersion of the bottom of the Pt crucible into pure water. The heating was repeated until no crystallization could be detected by optical microscope and X-ray diffraction. Chemical composition was obtained by electron microprobe analyses (made in Paris with a Camebax SX50).

Raman Spectroscopy

The Raman spectra were obtained with a Dilor XY confocal microRaman spectrometer equipped with a CCD detector. The 488 nm line of a SpectraPhyscics model 2025 Ar^+ laser operating at 0.8 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 20/1 for room-temperature measurements. The integration time was 60 s. All reported spectra are unpolarized. The spectra were corrected for temperature- and frequency-dependent scattering intensity before statistical analysis. A correction factor of the form proposed by Long[1] and gave by Neuville and Mysen[2] 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],[3] (See also Seifert *et al.*,[4] Mysen *et al.*,[5] Mysen[6] and Mysen and Frantz,[7] for detailed discussion). In the curve-fitting procedure, all parameters (wavenumbers, widths and intensities) are independent and not constrained.

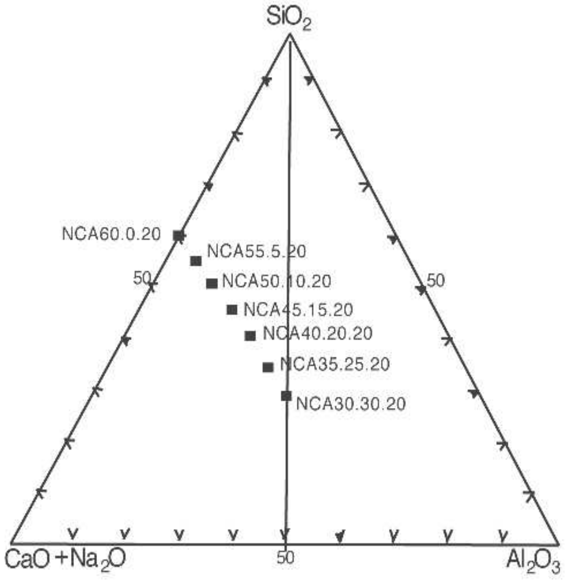

Figure 1 : Ternary system SiO2-Al2O3-(Na2O-CaO).

Results and discussion

In figure 2, we show the Raman spectra of the Ca-Na silicate glasses with increasing Al_2O_3 content. We focus only on the Raman spectra of glass at room temperature, which provide the most important configurational information on the structure of silicate glasses. From the Raman spectra at high temperature, we can obtained some structural information on the liquid, but this information is not comparable with the configurational entropy obtained from the viscosity measurements.[2] Indeed, Raman spectroscopy at high temperature gives vibrational contribution and not configurational contribution, which are more discernible at low temperature or room temperature.

The Raman spectra were recorded between 10 and 1300 cm^{-1}. The spectra can be divided into two regions: the low frequency region (10-800 cm^{-1}) and the high frequency region (800-1300 cm^{-1}). The most important structural information is obtained from the *Si-O* stretching frequencies with the Raman bands in the 800-1300 cm^{-1} region.[4,8] In figure 2, for NCA60.00.20, the Al_2O_3-free glass, we observe four peaks at 600, 780, 950 and 1100 cm^{-1} (extracted from derivative spectra). These peaks evolve in intensities as a function of Al_2O_3 content, to give finally for the NCA30.30.20 sample a large peak at 550 and an other peak at 950 cm^{-1}.

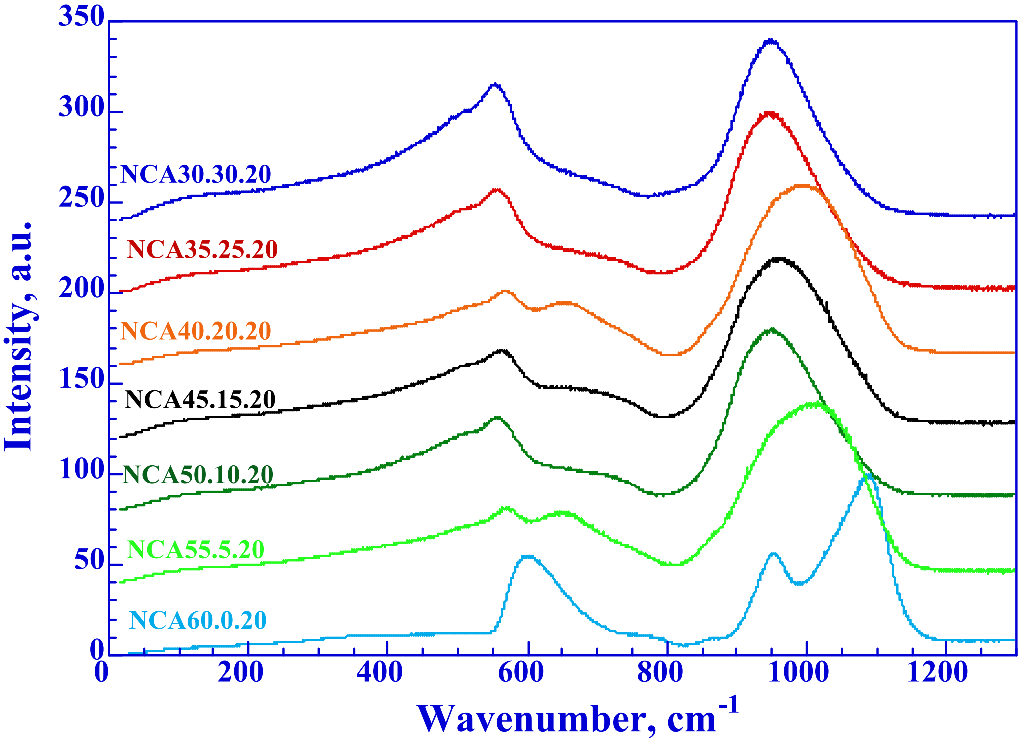

Figure 2 : Raman spectra of the NCA glasses.

The low frequency region (10-800 cm-1)

Below 500 cm^{-1}, there is only a scattering continuum and the Raleigh tail of the exciting line, except at very low frequency where there is a bump, the so-called boson peak.[9,10] The Raman spectra above 500 cm^{-1} is due mainly to the vibrations of the *Si-O* network. 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. However, we can observe some small change in ours Raman spectra in the low frequency region, which are likely due to cations modifier but the origin of these bands remains unclear.

The peak at 600 cm^{-1} evolve in two peaks localized at 580 and 650 cm^{-1} with the addition of 5 mol% Al_2O_3. This maximum is assigned to *Si-O-Si* bending motions in depolymerised structural units (Q^2 and Q^3).[7,11,12] The peak at 580 cm^{-1} is assigned to *Si-O*^{0} rocking motions in fully polymerised SiO_2 (Q^4) units[7,13] and the peaks at 650 cm^{-1} can be attributed to *Si-O-Si* bending motions in depolymerised structural units (Q^1). With increasing the Al_2O_3 content, we observe a shift of the band at 580 cm^{-1} towards 550 cm^{-1}, with a shoulder at 500 cm^{-1}. This variation can be attributed to Al in more depolymerised structural units (Q^2 and Q^3).

The high frequency region (800-1300 cm-1)

The 950 and 1085 cm^{-1} peaks in the Raman spectra of NCA60.0.20 evolve to one broad peak at 1000 cm^{-1} with increasing Al_2O_3 content. Addition of Al_2O_3 to the silicate network (NCA55.05.20 sample) yield to a breaking of the network, which is initially composes mainly of Si in Q^3 and Q^2 species and replaces by Al and Si in Q^4, Q^3 and Q^2 species. At higher Al_2O_3 content, a large band centred at 970 cm^{-1} is present and a deconvolution of this band is required for its understanding.

Spectra deconvolution

The high-frequency region of the Raman spectra (850-1200 cm^{-1}) for the six glasses has been deconvoluted with a technique proposed by Mysen *et al.*[5] using five Gaussian bands at 870, 950, 1000, 1050 and 1150 cm^{-1}. The assignment of the 870, 950, 1100 and 1150 cm^{-1} bands correspond to *Si-O* stretching vibrations in specific structural units.[7,12,14,15] The small band at 870 cm^{-1} can be attributed to the *Si-O*$^-$ stretching with three Non-Bridging Oxygen per Silicon (NBO/Si = 3; Q^1). The band near 950 cm^{-1} is mainly due to a band in the frequency range assigned to *Si-O*$^-$ stretching in structural units with two Non-Bridging Oxygen per Silicon (NBO/Si) (equal at Q^2). The prominent band centred near 1050 cm^{-1} is due to the *Si-O*$^-$ stretching in unit with one Non-Bridging Oxygen per Silicon (NBO/Si = 1; Q^3). The high frequency band at 1150 cm^{-1} results from the presence of fully polymerised units (Q^4). The large band (1000 cm^{-1}) at slightly lower frequency is considered to represent a vibrational frequency assignable to a *Si-O*^{0} bridging oxygen stretching mode[7] or alternatively to a vibration in structural units associated with the metal cation.[16]

A decrease in frequency can be observed for all bands with increasing Al_2O_3 content. These observation can be attributed to the addition of Al in the polymerised network in the various Q^n species.

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