

Reaching the ionic limit in the $(1 - X)[Ca_{0.5}Mg_{0.5}]O-XSiO_2$ pseudo binary glass system with $0.5 < X < 0.27$: Glass formation and structure

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ABSTRACT

Container-less levitation techniques and CO₂-laser heating were used to prepare a series of silicate glasses along the compositional join $(1 - X)(0.5Ca-0.5 Mg)O-XSiO_2$ with X ranging between 0.50 and 0.27; thus reaching compositions beyond the orthosilicate limit ($X = 0.33$). Polarized and depolarized Raman spectra measured at ambient conditions for all these glasses show systematic and smooth band intensity changes with composition. Q¹-species analysis of the isotropic Raman spectra shows the presence a) of bridging oxygens in all glasses studied with silica mole fractions down to $X = 0.33$ and b) of free oxygen at all compositions. Beyond the $X = 0.33$ limit, the connectivity between the SiO₄ tetrahedra decreases drastically and the corresponding glass structures are characterized by isolated negatively charged “tetrahedral” SiO₄⁴⁻ and O²⁻ anions with M²⁺ (M = Mg, Ca) as counter cations, held together by pure Coulombic (ionic) interactions. The Boson peak appears in the low-frequency range 70–90 cm⁻¹ and its polarization characteristics and frequency shifts with glass composition are pointed out and discussed.

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1. Introduction

The research activities on silicate glasses involving the oxides of alkali and alkaline earth metals have been limited to glasses with silica contents above the orthosilicate limit {i.e. SiO₂ mole fraction $X > 0.33$ } [1]. Glasses with X below 0.4 are difficult to almost impossible to prepare especially as X is approaching 0.333. However, with aerodynamic levitation techniques and CO₂-laser heating/melting Tangeman et al. were able to glassify forsterite (Mg₂SiO₄) thus reaching the orthosilicate limit [2].

Very recently, with the use of similar techniques it was possible to glassify the mixed alkaline earth system $(1 - X)[0.5MgO-0.5CaO]-XSiO_2$ system (denoted in this paper as CMSX) with silica mole fraction as low as 0.27 [3]. Systematic structural Raman [4] and NMR [5] spectroscopic studies of the glasses formed in the $(1 - X)MgO-XSiO_2$ (denoted in this paper as MSX) system with $0.5 < X < 0.33$ have indicated that even at the orthosilicate composition bridging oxygens as well as free oxygens are present due to the formation of Q¹ species, which are in equilibrium with the predominant Q⁰-species (i.e. $Q^1 = 2Q^0 + O^{2-}$). On the other hand, structural Raman [3] and NMR [6] spectroscopic studies of the glasses formed in the CMSX system with compositions $X < 0.29$ have shown that the glass structure is fully ionic consisting of isolated SiO₄⁴⁻ tetrahedra, Ca²⁺ and Mg²⁺ cations as well as O²⁻ anions. No bridging oxygens are present,

while the cation coordination is determined by the oxygens on the faces, the edges and/or the apexes of the SiO₄ tetrahedra and by the available free oxygen anions [3,6] according to the stoichiometry requirements. As expected, the charge of the O²⁻ anions is balanced by the Ca²⁺ and Mg²⁺ cations.

In the present work we have used container-less aerodynamic levitation techniques and CO₂-laser heating/melting to synthesize glasses in the CMSX pseudo binary system with compositions from $X = 0.5$ to $X = 0.27$. Raman spectra of the prepared glasses were measured extensively and are discussed in relation to their structural peculiarities.

2. Experimental

The starting materials for the synthesis of the glasses were reagent grade SiO₂ (99.999% pure, Puratronic powder), MgO (99.95% pure, powder) and CaO (99.95% pure, powder), all purchased from Alfa Aesar. The oxides were first dried in a furnace at ~400 °C for 24 h and then mixed to prepare the compositions $(1 - X)(0.5Ca/0.5 Mg)O-XSiO_2$ with $X = 0.5$ to 0.46, 0.42, 0.40, 0.38, 0.36, 0.34, 0.33, 0.32, 0.30, 0.29, 0.28 and 0.27. The procedures for the glassification of these oxide mixtures by CO₂-laser melting and aerodynamic levitation methods have been described in detail elsewhere [3,4,7]. Glasses with compositions from CMS50 to CMS32 were easily and quickly prepared by this method. On the other hand glasses with silica composition below the CMS32 composition were rather difficult to prepare and a series of “trial and error” experiments were conducted with a success rate of about 10%. In the final step of rapid quenching

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via sudden shutdown of the CO₂-laser spherical, completely colorless and transparent amorphous beads of about 1–1.5 mm in diameter were obtained. The “lifetime”, before crystallization of the CMS27 glass was rather short and we were not able to measure its Raman spectrum. For each composition 5 to 10 spherical samples were prepared. Chemical analyses by electron microprobe indicated that the stoichiometry of the prepared glass samples was within 1 wt.% of the nominal compositions.

Stokes-side Raman spectra were recorded with a 90° scattering geometry using a collecting lens system (80 and 260 mm FL) coupled to a triple monochromator (T-64000 Jobin-Yvon) and equipped with a CCD detector. The wavelength resolution of the instrument was 2 cm⁻¹ and the frequencies are associated with an error <2 cm⁻¹ for the whole set of measurements. The ~1 mm diameter spherical glass beads were placed on an X–Y–Z stage and the 514.5 nm laser line was focused on the sample using 145 mm focal length (FL) lens. Laser power of 300 mW (measured on the sample) was used with the beam passing along the diameter and focused at the center of the glassy sphere, thus, minimizing light reflections and permitting confocal measurements close to the excitation line thereby resolving the Boson peak.

For all spectroscopic measurements, the sample position, optical geometry, and laser power were kept constant allowing relative intensity measurements at different compositions with an error of less than 3%. Uncertainties in further calculations were estimated using the standard error-propagation methodology.

3. Results

Representative room temperature polarized (VV) Raman spectra for ten of the prepared compositions are shown in Fig. 1. The conventional Stokes Raman intensities in the two standard polarization configurations I_{VV} and I_{VH} were also measured and sample spectra studied at three selected compositions (the two end (X = 0.5 and 0.28) and one intermediate (X = 0.38)) are shown in Fig. 2.

The reduced Raman intensities R_σ(ω) at frequency shift ω/cm⁻¹ were also calculated for all compositions according to the relations [8]:

$$R_{\sigma}(\omega) = I_{\sigma}(\omega)\omega(\omega_0 - \omega)^{-4} [n(\omega) + 1]^{-1} \quad (1)$$

where ω₀ is the excitation laser frequency, [n(ω) + 1] is the Boltzmann thermal factor with n(ω) = [exp(hωc/kT)]⁻¹ and σ stands for either the VV or VH configurations. For isotropic materials such as the CMSX glasses, the two polarization configurations VV and VH permit

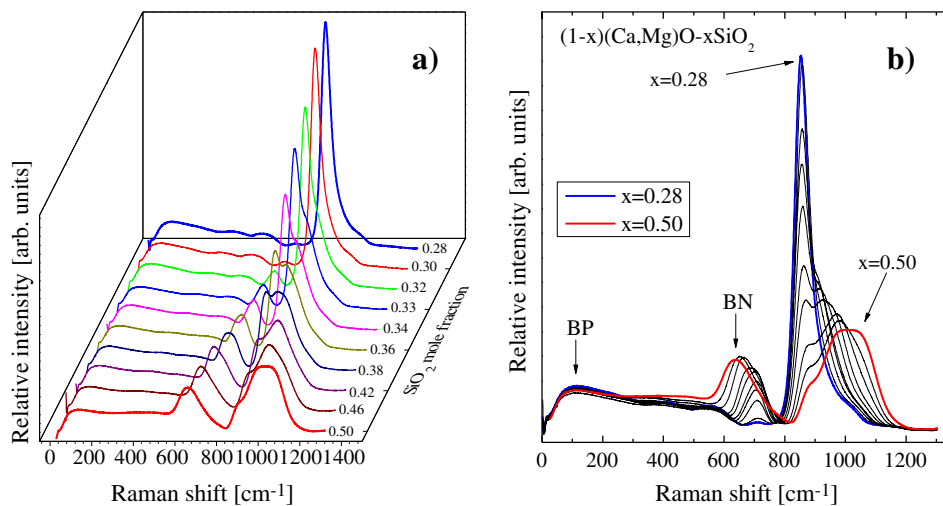


Fig. 1. Raman spectra of the CMSX glasses at different X compositions. (a) Raw polarized (VV) spectra with normalized intensities and (b) the same spectra projected on a plane. The two end compositions CSM28 and CMS50 are indicated by arrows. In the normalization procedure, the intensity at each frequency in the spectrum is divided by the square root of the sum of the squares of all the intensities, where the sum is over all frequencies. Spectral conditions: excitation line 514.5 nm; laser power 300 mW; spectral resolution 2 cm⁻¹; and CCD detector.

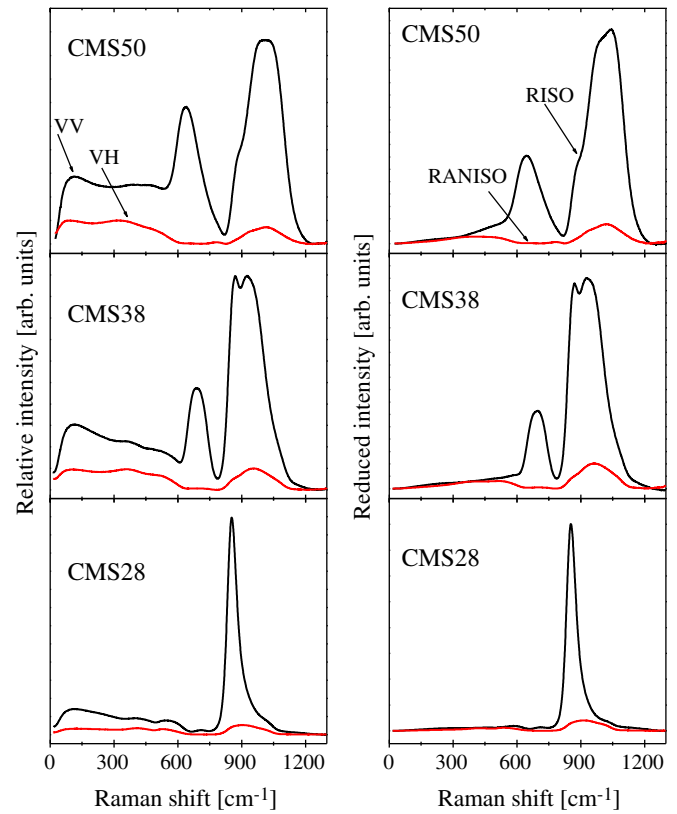


Fig. 2. Comparison of the polarized (VV) and depolarized (VH) Raman spectra of the CMSX glasses for two end and one intermediate SiO₂ compositions: (a) CMS28, (b) CMS36 and (c) CMS50. (e), (d) and (f) show the corresponding reduced isotropic and reduced anisotropic spectra to these compositions, respectively. Spectral conditions as in Fig. 1.

the calculation of the reduced isotropic and anisotropic scattering intensities through the relations:

$$R_{ISO}(\omega) = R_{VV}(\omega) - (4/3)R_{VH}(\omega); R_{ANISO}(\omega) = R_{VH}(\omega). \quad (2)$$

The isotropic spectra are related to scattering arising from the diagonal elements of the polarizability tensor and consequently show only the totally symmetric A-type vibrations.

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