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ABSTRACT

$2\text{Na}_2\text{O} \cdot 0.1\text{CaO} \cdot 0.3\text{SiO}_2$ glass and glass-ceramics are investigated by conventional and microprobe Raman spectroscopy. The glass spectrum can be deconvoluted into 6 gaussian bands located at 860, 920, 975, 1030 cm^{-1} attributed to stretching of Si-nonbridging oxygen (NBO) bond and at 625, 660 cm^{-1} attributed to Si-O-Si bond vibrations. Partially crystallized glass is formed as spherulites imbedded in the amorphous phase. Their Raman activities show that during crystallization the number of SiO_4 tetrahedra having 2 NBO increases and that the Si-O-Si bonds soften. Highly crystallized samples still contain a small amount of amorphous phase.

1. INTRODUCTION

Raman and infrared spectroscopic techniques are powerful tools to investigate the nature of vibrational modes of interatomic bonds and the local atomic structure of crystalline and amorphous solids. Raman spectroscopy has been applied to gain such information in glass and glass-ceramics with the molar composition $2\text{Na}_2\text{O} \cdot 0.1\text{CaO} \cdot 0.3\text{SiO}_2$, hereafter called N_2CS_3 .

N_2CS_3 glass belongs to the metasilicate class. SiO_4 tetrahedra have a mean number of 2 nonbridging oxygens (NBO); as the bridging oxygens (BO) are shared, the glass is formed into a chain-like structure built up of $\text{Si}_2\text{O}_6^{4-}$ units. Tetrahedra with 1, 3 and 4 NBO form $\text{Si}_2\text{O}_5^{2-}$ (sheet), $\text{Si}_2\text{O}_7^{6-}$ (dimer) and SiO_4^{4-} (monomer) structural units, respectively, which coexist in a small degree in metasilicate glasses [1].

N_2CS_3 glass undergoes homogeneous nucleation between 440 and 570°C: crystals also grow in this temperature range [2]. The structure of these crystals is not known [3], but it is expected that the crystallized N_2CS_3 phase contains only $\text{Si}_2\text{O}_6^{4-}$ units (2NBO/ SiO_4), forming chains linked together by modifier cations.

2. EXPERIMENTAL PROCEDURE

N_2CS_3 glasses were obtained by conventional melting in a Pt crucible

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at 1350°C and cast onto an iron plate at a cooling rate > 400°C/min to avoid nucleation. Partially crystallized samples were obtained after heat treatment at 590°C for 15 minutes; and highly crystallized samples were produced at 513°C after 16 hours. SEM micrographs are shown in Figure 1. Conventional Raman spectra were obtained at 90° scattering geometry with a SPEX 1402 monochromator, at 488 nm. Microprobe spectra were recorded in backscattering with a 1.XY.00.C DILOR confocal spectrometer, at 514.5 nm (100mW).

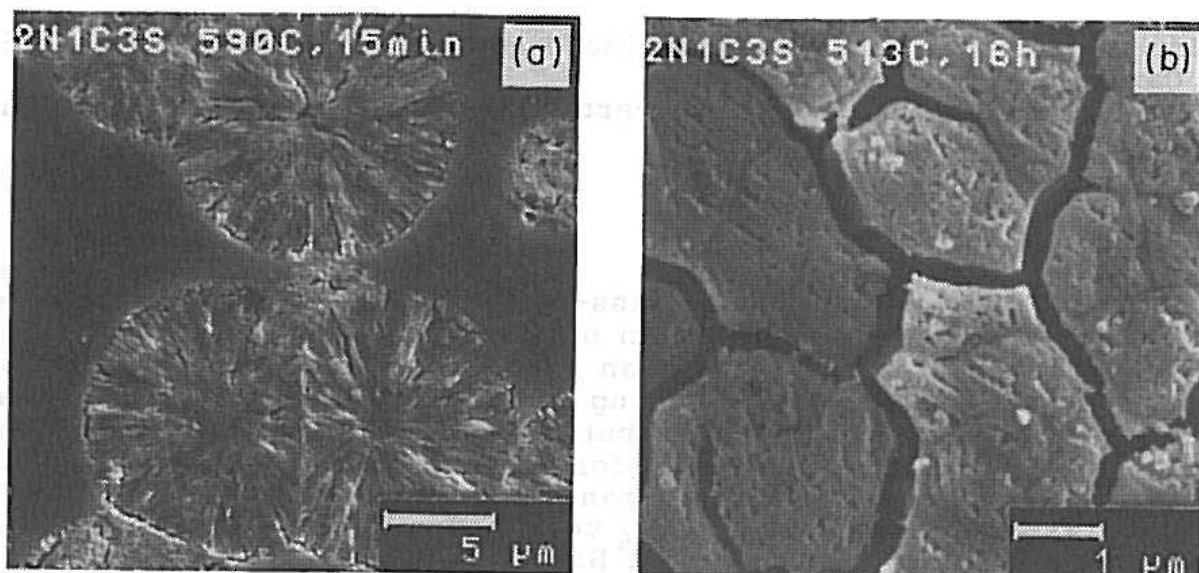


Figure 1. SEM (Zeiss 960) micrographs of N_2CS_3 (a) partially crystallized (590°C, 15 min), (b) highly crystallized (513°C, 16h).

3. RESULTS AND DISCUSSIONS

Figure 2 shows the conventional Raman spectrum of N_2CS_3 glass, deconvoluted into 6 gaussian bands, I_i . Their sum is superposed for comparison.

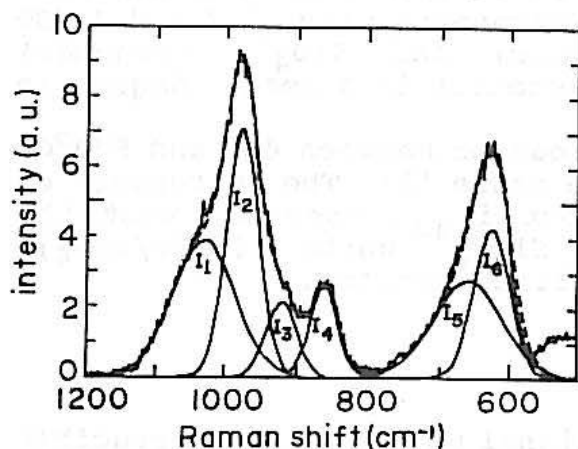


Figure 2. Conventional Raman spectrum of N_2CS_3 glass (—) deconvoluted into 6 gaussian bands, I_i . Their sum (---) is superposed onto the experimental spectrum.

The bands I_1 to I_4 located between 800 and 1100 cm^{-1} are attributed to stretching of Si-NBO bonds in SiO_4 tetrahedra having 1, 2, 3 and 4 NBO respectively [1]. The I_5 and I_6 gaussians at $\sim 625 \text{ cm}^{-1}$ are attributed to BO vibrational motion in Si-O-Si bonds, resulting from in-phase symmetric stretching vibrations of SiO_4 tetrahedra [4].

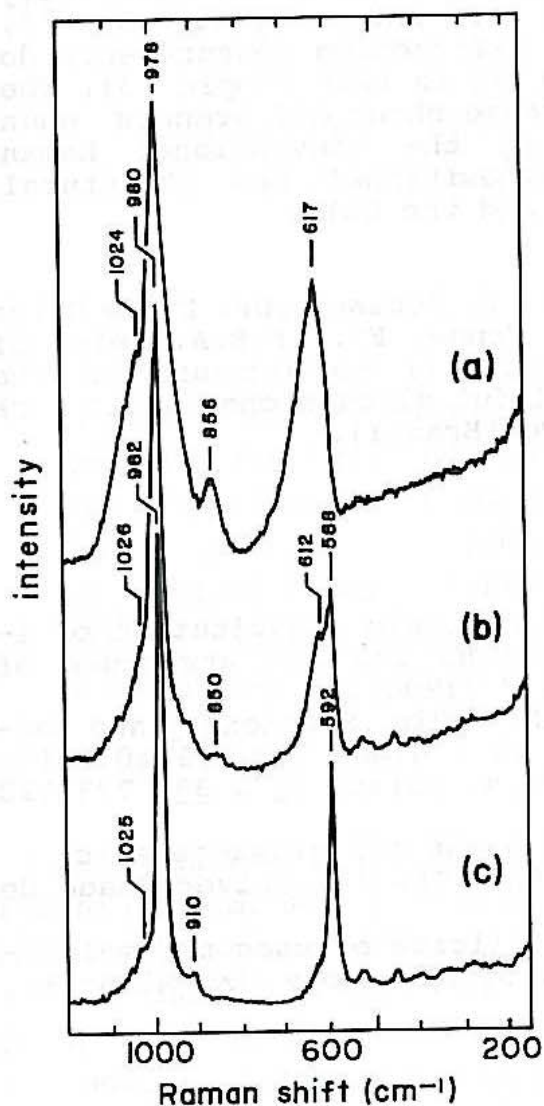


Figure 3. N_2CS_3 microprobe Raman spectra:
 a) amorphous phase,
 b) crystallite of partially, crystallized sample,
 c) highly crystallized (see Fig. 1 for sample textures).

Figure 3 compares 3 typical spectra of (a) amorphous, (b) partially and (c) highly crystallized samples of the N_2CS_3 glass obtained using the Raman microprobe spectrometer. Spectrum (c) shows two intense bands at 592 and 982 cm^{-1} related to Si-O bond vibrations in the crystalline metasilicate chains. According to the above assignment, the 982 cm^{-1} band is due to the stretching of Si-NBO bonds of SiO_4 tetrahedra having 2 NBO (I_2). Its high relative intensity indicates that the number of these tetrahedra increases during crystallization at the expense of tetrahedra with 1, 3 and 4 NBO, which present correspondingly low intensities at 1030 cm^{-1} (I_1) and 920 cm^{-1} (I_3), and even complete disappearance of the I_4 band at 850 cm^{-1} . Moreover the I_4 band at $\sim 620 \text{ cm}^{-1}$ shifts toward lower frequency as the crystallinity increases, indicating that Si-O-Si bonds soften during the process. This behavior is compatible with the observation that the material density increases with increasing crystallinity from 2,661 g/cm^3 (glass) to 2,759 g/cm^3 (highly crystallized) [3]. As the increase in density is related to reduction in the Si-O bond lengths the Si-O-Si vibrations consequently weaken.

Spectrum (b) is an intermediate between spectra (a) and (c). Its normalized intensity I_b can be expressed as a linear combination of the intensities I_a and I_c , respectively: $I_b = xI_a + (1-x)I_c$, with $0 \leq x \leq 1$, where $(1-x)$ is a measure of the degree of crystallinity of the spherical microcrystals. For $x=0.45$, the calculated I_b curve is similar to spectrum (b).

4. CONCLUSIONS

The analysis of SEM and Raman spectra of N_2CS_3 glass and glass-ceramics indicate that the spherical crystallites in partially crystallized samples are spherulites made up of a mixture of crystalline and amorphous phases. The crystals in each crystallite are randomly oriented. Highly crystallized samples still contain a small amount of the amorphous phase as indicated by the relatively large base of the Raman bands, the low band intensity at 910 cm^{-1} , and the shoulder at 1025 cm^{-1} . X-ray diffraction measurements do not indicate any residual amorphous phase in this sample [3]. The microprobe spectrum of the amorphous phase shows differences when compared to the spectrum measured by the conventional Raman technique. These are related to compositional and structural differences between the glass surface and the bulk.

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