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X-ray study of lithium disilicate glass: High pressure densification and polyamorphism

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ABSTRACT

We have investigated the structural changes induced by high-pressure in lithium disilicate glass with stoichiometric composition $Li_2O.2SiO_2$ (LS_2). Using toroidal type high-pressure chambers, glass samples were processed at 2.5 GPa, 4 GPa, 6 GPa and 7.7 GPa at room temperature. Synchrotron X-ray diffraction measurements were used to obtain the radial distribution functions (RDF) in order to follow the structural changes induced after processing at high pressure. Compared to a pristine sample, the main change observed for the samples processed up to 6 GPa was associated to the distortion of the SiO_4 tetrahedral structure. However, for the sample processed at 7.7 GPa, a drastic change in the RDF indicated the formation of a distinct amorphous phase. The observed polyamorphism is important for a better understanding of the nucleation kinetics of crystalline phases under high pressure.

1. Introduction

Lithium disilicate glass, $Li_2O.2SiO_2$ (LS_2), is a well studied vitreous material because, besides several important technological applications (e.g. biomaterial to produce prostheses and implants), it shows a large difference between the glass transition temperature, Tg, and the crystallization temperature, Tc. This is important for the investigation of the crystallization mechanism on vitreous phases, as it allows the use of the double-stage approach, where the nucleation and growth are considered independent stages [1].

The physical properties of amorphous materials are strongly dependent on the arrangement of the first neighbors. However, the determination of their local atomic structures is a difficult task, which has been overcome by the combination of different diffraction and spectroscopic techniques as also by simulation and modeling [2]. Traditionally, local structure investigations have been viewed as the domain of techniques such as Nuclear Magnetic Resonance (NMR), Extended X-ray Absorption Fine Structure (EXAFS), and X-ray photoelectron spectroscopy (XPS) [3,4]. These techniques are mainly affected by the environment around the probe nuclei in a distance range that is fundamentally different from that sampled by crystallographic methods [3], as neutron diffraction, which was applied by Kitamura et al. [5] to determine the structure of LS_2. They investigated the densification of LS_2 for pressures up to 6 GPa at 400 °C and, based on Raman spectra and radial distribution function, they attributed the observed densification to an increase of the packing density of SiO_4 tetrahedra related to a decrease of both the internal (O – Si – O) and the inter-tetrahedral angle (Si – O – Si), associated to a increase of the Si – O bond length by 0.001 nm.

In a recent work, Buchner et al. [4] investigated by XPS the effect of high pressure on the chemical environments of Si 2p, O 1s and Li 1s in lithium disilicate glass and glass-ceramic with the stoichiometric composition $Li_2O.2SiO_2$. Large shifts of the binding energy toward higher energies were observed after densification at 2.5 and 4 GPa at room temperature. For samples processed at 7.7 GPa, the major component of the binding energy for the Si 2p environment remained practically unchanged compared to the pristine sample, but new components, with smaller intensities, appeared in the spectra, indicating the existence of distinct Q-species induced by high pressure. This behavior may be related to changes in the number of bridged and non-bridged oxygen atoms in the glass structure. The results for the glass-ceramic samples crystallized under high pressure and high temperature showed evidences of three binding energies for the O atoms, one of them related to non-bridged O and two to bridged O atoms. A new component for Li 1s binding energy after processing at 7.7 GPa and room temperature was also observed. According to Adams & De Jong [6,7], this component for Li 1s may be related to a local arrangement that would be favorable to the formation of the metastable phase during heat treatment.

In the past few years, several works have reported the combined effect of pressure and temperature in the structure and properties of lithium disilicate glass-ceramic [4,5,8–15]. Fuss et al. [9] observed the crystallization of $Li_2Si_2O_5$ for lithium disilicate glass samples processed at 4.5 GPa and 608 °C while for samples processed at 6 GPa and

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753 °C they observed the crystallization of a lithium metasilicate solid solution (Li_2SiO_3). Buchner at al. [13] showed that the thermal treatment of LS_2 at 2.5 GPa and 4 GPa induced the crystallization of lithium disilicate phase ($Li_2Si_2O_5$) with orthorhombic phase. The thermal treatment under pressure consisted of heating at 455 °C or 500 °C during 2 h for nucleation followed by heating at 610 °C during 0.5 h for crystal growth. At 7.7 GPa, the same in situ thermal treatment induced the crystallization of lithium metasilicate (Li_2SiO_3). In the pressure range between 4.25 and 6.5 GPa, this thermal treatment induced the formation of crystalline Li_2SiO_3, $Li_2Si_2O_5$, quartz and/or coesite [14]. The obtained phase composition, which is summarized in Fig. 1, is strongly dependent of the processing pressure for the same heating conditions.

Despite all these results about the combined effect of high pressure and high temperature on densification, crystallization and structural changes in LS_2, there is no report about the effects of high pressure densification at room temperature. In this context, in this work we have employed Synchrotron X-ray diffraction (XRD) to investigate possible irreversible structural changes induced by densification at high pressure. The total structure factors, $S(K)$, of LS_2 samples were computed from the XRD measurements and the radial distribution (RDF) functions were obtained through a Fourier transformation of the $S(K)$ factors.

2. Theory

2.1. Faber and Ziman structure factors

According to Faber and Ziman [16], for an amorphous phase containing N chemical elements the total structure factor $S(K)$ is obtained from the normalized scattered intensity on a per atom scale $I_a(K)$ as follows:

$$S(K) = \frac{I_a(K) - \left[\left\langle f^2(K)\right\rangle - \langle f(K)\rangle^2\right]}{\langle f(K)\rangle^2} \tag{1}$$

$$S(K) = \sum_{i=1}^{N}\sum_{j=1}^{N} W_{ij}(K) S_{ij}(K) \tag{2}$$

where $K = \frac{4\pi}{\lambda}\sin\theta$ is the transferred momentum and $W_{ij}(K)$ are the weights of the partial structure factors, $S_{ij}(K)$. The $W_{ij}(K)$ are given by:

$$W_{ij}(K) = W_{ji}(K) = \frac{c_i c_j f_i(K) f_j(K)}{\langle f(K)\rangle^2}. \tag{3}$$

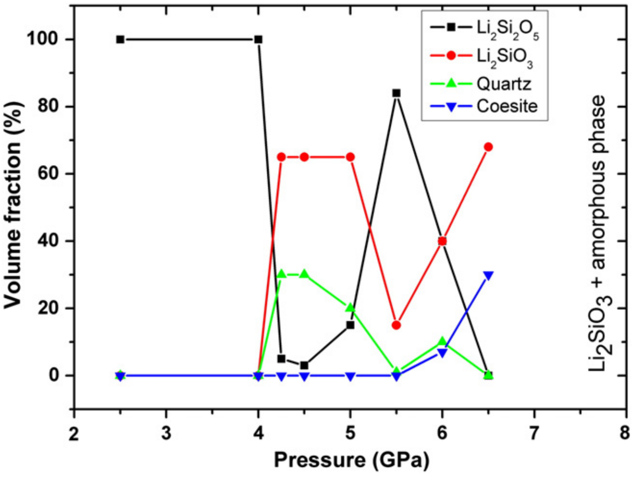

Fig. 1. Phase composition obtained in the literature for samples of crystalline lithium disilicate glass after thermal treatment under pressure: 500 °C during 2 h for nucleation followed by 0.5 h at 610 °C for crystal growth (see Refs. [13,14]).

Here, c_i is the concentration of i-type atoms, and $f_i(K,E) = f_0(K) + f'(E) + if''(E)$ is the atomic scattering factor, for which $f'(E)$ e $f''(E)$ are the real and the imaginary dispersion terms. In these equations, $\left\langle f^2(K)\right\rangle = \sum_i c_i f_i^2(K)$, and $\langle f(K)\rangle^2 = \left[\sum_i c_i f_i^2(K)\right]^2$.

The total pair distribution function $G(r)$ is related to the $S(K)$ through a Fourier transformation, taken into account the atomic density (ρ_0) expressed in atoms/Å^3.

$$G(r) = 1 + \frac{1}{(2\pi^2\rho_0 r)}\int_0^\infty K[S(K)-1]\sin(Kr)dK. \tag{4}$$

The total radial distribution functions $RDF(r)$ are calculated from the $G(r)$ as follows:

$$RDF(r) = 4\pi\rho_0 r^2 G(r). \tag{5}$$

From the maxima of the $G(r)$, or $RDF(r)$, the interatomic distances can be evaluated.

3. Experimental procedure

Lithium disilicate glass of stoichiometric composition $Li_2O.2SiO_2$ was prepared using standard reagent grade Li_2CO_3 (Aldrich Chem. Co., <99%) and ground quartz (<99.9% SiO2). A 200 g batch was melted in a Pt crucible at 1450 °C during 2 h in an electric furnace. The melt was poured on a steel plate, annealed below the glass transition temperature, at 430 °C, during 1 h and cooled down slowly to room temperature. The lithium disilicate glass samples were cut into cylinders of 3 mm diameter and 2.3 mm long for the high pressure experiments.

Using toroidal type high-pressure chambers monolithic lithium disilicate glass samples were processed at 2.5 GPa, 4 GPa, 6 GPa and 7.7 GPa at room temperature (HPRT) during 5 min inside a lead capsule. The specific configuration for the high-pressure processing and calibration procedures is well described in Refs. [4,11–14].

Synchrotron XRD measurements were carried out at the DB12A (XRD1) beam line of the Brazilian Synchrotron Light Laboratory (LNLS). The energy and average current of the storage ring were 1.37 GeV and 150 mA, respectively. The DB12A beam line is equipped with a sagittal focusing double crystal Si(111) monochromator and a Huber diffractometer with an arm that allows an improved stability of the analyzing crystals, slits, detector and a cyberstar scintillation detector [17,18]. A Ge(111) analyzer was used in the secondary beam to suppress the fluorescence signals. However, it did not permit to suppress the contribution of the inelastic scattered intensity. No vacuum cell around the sample was used, but the evaluation of the air scattering contribution to elastic scattered intensity showed that it was not significant.

The XRD measurements were performed in a reflection θ-2θ geometry at $\lambda = 0.888781$ Å, using a fixed step $\Delta K = 0.025$ Å^{-1}, and reaching a maximum value of $K_{máx} = 13.45$ Å^{-1}. The acquisition time by point, typically 4 s, was adjusted to correspond to a fixed counting in a control detector placed in the incident beam. For comparison, a pristine glass sample was also investigated using the same conditions. The $S(K)$ factors were derived from the elastic scattered intensities put on a per-atom scale (normalized to electron units) after the sum of elastic and inelastic scattered intensities was corrected for reabsorption effects, following the procedure described in Ref. [19], and the inelastic scattered intensity was subtracted. The inelastic scattered intensity was calculated according to the analytic approximation given by Pálinkas [20]. At the DB12A beam line the incident radiation polarization is in the horizontal plane, while the acquisition of data was in the vertical plane. Thus, the polarization correction was disregarded. For the Li, Si and O atoms, the f' and f'' values given in table compiled by Sasaki were used [21]. The atomic scattering factor $f_0(K)$ of neutral Li,