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Densification of Lithium Disilicate under High Pressure Investigated by XPS

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ABSTRACT

The aim of this work was to investigate by X-ray photoelectron spectroscopy the effect of high pressure on the chemical environments of Si 2p, O 1s and Li 1s in lithium disilicate glass ceramic with stoichiometric composition $Li_2O{\cdot}2SiO_2$ (LS_2). A group of samples was processed at 2.5 GPa, 4 GPa and 7.7 GPa at room temperature and a second group was crystallized under high pressure and high temperature. Large shifts of the binding energy toward higher energies were observed in the X-ray photoelectron spectroscopy spectra for samples of the first group after densification at 2.5 and 4 GPa. 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 second group of samples, crystallized under high pressure, showed evidences of three binding energies for the O atoms, one of them related to non-bridged and two of them to bridged O atoms.

Keywords: XPS; Glass Ceramic; Lithium Disilicate; High Pressure; Binding Energy

1. Introduction

Structural analysis of glasses under high pressure is important to understand the effect of densification mechanisms on the glass properties [1]. Bridgman *et al.* [2] pointed out that the permanent densification after applying high pressure and high temperature (HPHT) is a phenomenon observed only for glassy materials due to their structural freedom.

Kitamura *et al.* [1] investigated the densification of lithium disilicate $Li_2O{\cdot}2SiO_2$ (LS_2) glasses at 6 GPa and 400˚C. Based on Raman spectroscopy and radial distribution function, they attributed the densification to an increase of the packing density of SiO_4 tetrahedra due to a decrease of the Si-O-Si bond angle between the tetrahedra. They showed the Si-O-Si bond angle decreased from 109.8˚ to 108.8˚ and the Si-O length increased by 0.001 nm.

Schmelzer *et al.* [3] discussed the pressure dependence of viscosity and free volume of liquids in frozen systems in non-equilibrium states. According to them, the viscosity of simple liquids typically increased with pressure.

The crystallization of LS_2 under HPHT has been studied in the past few years [1,4-11]. In previous works, the effect of densification on the crystallization process and thermal properties of LS_2 glass was investigated [4], as well as the effect of pressure and temperature on the mechanical [5] and optical [6] properties. It was observed that the hardness and elastic modulus of the sample processed at HPHT increased noticeably compared to the samples crystallized at atmospheric pressure. The refractive index of LS_2 was also significantly affected by HPHT.

Nuclear Magnetic Resonance (NMR) results obtained by Fuss *et al.* [9] indicated the formation of lithium metasilicate solid solution (LS-ss) for samples submitted to 6 GPa and thermal treatment below 750˚C. According to the authors, the difference between lithium metasilicate (MS) and LS-ss was not detectable by X-ray diffraction since there were no changes in the crystal symmetry of both structures. The difference would be related to the number of bridged (BO) and non-bridged (NBO) oxygen atoms. Buchner *et al.* [6], on the other hand, showed the formation of crystalline MS after processing LS_2 at 7.7 GPa and 455/500˚C for nucleation followed by 610˚C for crystal growing.

Adams & De Jong [12] investigated the early stages of crystallization of a slightly hyper stoichimetric LS_2 sample (34.5 mol% Li_2O) at 450˚C using X-ray photoelectron spectroscopy (XPS) and they ascribed the presence of an extra Li 1s peak in the XPS spectrum (~51.7 eV) to the formation of a MS phase. Soares *et al.* [13], however, repeated the XPS analysis at the same conditions and concluded that this extra Li 1s peak was related to contamination. Moreover, they concluded that XPS was not a suitable technique to detect structural changes in LS_2 when the volume fraction of the crystals was very low. On the other hand, the formation of the MS phase in the early stages of nucleation was confirmed by them using TEM analysis [14].

Nesbitt *et al.* [15] investigated the chemical environment around Na 1s, O 1s and Si 2p atoms in Na_2O-SiO_2 glass as a function of the glass composition. Six compositions of Na_2O-SiO_2 glass ranging from 100 to 45 mol% SiO_2 were investigated by XPS and NMR. The Si $2p_{3/2}$ peak maximum shifted to lower binding energy (BE) with increasing Na_2O content. According to the authors, the BE shift indicated increased valence electron density on the Si nuclei with increased Na_2O concentration. Each Q-species should yield a peak at slightly different BE since the electron density over each Si atom should be different, depending on the number of BO and NBO bonded to it.

According to Sawyer *et al.* [16], the BE of the Q-species are strongly affected by the number of NBO bonded to the Si atom, with BE decreasing systematically from Q^4 to Q^0 species. They observed the shift of the peak toward lower BE with increasing K_2O content in K_2O-SiO_2 glass. Two doublets in the Si 2p spectra of different glass compositions were identified. According to the authors, the strongly asymmetric nature of the Si 2p spectra of the potasic glasses may result from two or more Q-species contributions to the Si 2p spectra and the intensity of the doublet would depend on the amount of the particular Q-specie.

In this context, the aim of this work was to investigate the effect of high pressure on the chemical environment of Si 2p, O 1s and Li 1s atoms of the LS_2 glass structure using XPS to help elucidate the mechanisms responsible for the early stages of the formation of the metasilicate structure induced by densification. For comparison, the chemical environment of these atoms was also investigated after complete crystallization of the glass structure under high pressure and high temperature.

2. Experimental Procedure

2.1. Sample Preparation

Lithium disilicate glass of stoichiometric composition $Li_2O{\cdot}2SiO_2$ (LS_2) was prepared using standard reagent grade Li_2CO_3 (Aldrich Chem. Co., 99+%) and ground quartz (<99.9% SiO_2). The 200 g batch was melted in a Pt crucible at 1450˚C during 2 hours 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.

2.2. High Pressure Experiments

The HP experiments were performed in a toroidal high pressure apparatus. The specific configuration and type of high-pressure chamber used in the experiments were optimized for providing quasi-hydrostatic pressure [17]. The pressure calibration was carried out by the "fixed-points" technique using Bi and Yb, which permitted the calibration of the pressure at the following points: Bi with phase transitions at 2.5 GPa and 7.7 GPa, and Yb with a phase transition at 4.0 GPa. A detailed description of the high-pressure calibration method has been provided elsewhere [17].

During the HPHT experiments, a monolithic LS_2 sample was placed inside a hexagonal boron nitride (hBN) capsule which acted as a soft pressure transmitting medium. The hBN capsule was placed inside a graphite cylinder which acted as a heater element. For experiments performed at HP and room temperature (HPRT), the capsule of hBN was replaced by a lead capsule, which is a softer pressure transmitting compared to hBN.

In the first group, the samples were submitted to 2.5 GPa, 4 GPa and 7.7 GPa at room temperature during 5 min inside the lead capsule. In the second group, the samples were submitted to HP (2.5, 4.0 and 7.7 GPa) inside the hBN capsule and, simultaneously, to the following thermal treatment: 500˚C during 2 h for nucleation followed by 610˚C during 0.5 h for crystal growing. For comparison, a pristine glass sample and a sample submitted to the same heat treatment at 1 atm were also investigated.

According to a previous work [6], the processing at 2.5 GPa and high temperature induced the crystallization of the monoclinic phase of lithium disilicate ($Li_2Si_2O_5$). At 4.4 GPa it was observed the formation of the orthorhombic phase with the same stoichiometry and, at 7.7 GPa the glass structure crystallized as MS (Li_2SiO_3).

After HPRT and HPHT processing, the surface of the samples was grounded on SiC abrasive paper up to #1200 and polished with CeO_2 slurry for XPS analyses.

2.3. Analytical Techniques—XPS

XPS analyses were performed in an Omicron-SPHERA station using Al Kα radiation (1486.6 eV). The anode was operated at 225 W (15 kV, 15 mA). Survey spectra were recorded with a 50 eV pass energy. Si 2p, O 1s, and Li 1s regions were recorded with high resolution (pass

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energy of 20 eV). The detection angle of the photoelectrons (Θ) with respect to the sample surface (take-off angle) was fixed at 53˚ for all measurements. The C 1s signal from adventitious carbon at 284.6 eV was used as an internal energy reference. All spectra were fitted assuming a Shirley background. Lines were fitted by 70% Gaussian + 30% Lorentzian functions with set values of full width at half maximum for each line.

3. Results and Discussion

3.1. Densification at Room Temperature (HPRT)

Figures 1-3 show high resolution XPS spectra for Si 2p, O 1s and Li 1s, respectively, after processing at high pressure compared to the pristine sample. It is clearly seen that the BE of the three elements changed irreversible after densification, revealing the strong influence of high pressure in the chemical environment due to the structural freedom of the glassy LS_2.

According to **Figure 1**, Si 2p presents two doublets from 2.5 to 7.7 GPa, corresponding to Si $2p_{3/2}$ and Si $2p_{1/2}$. However, the intensity and BE of each doublet changed with pressure. **Figure 2** shows that there is practically only one BE component for O 1s up to 2.5 GPa,

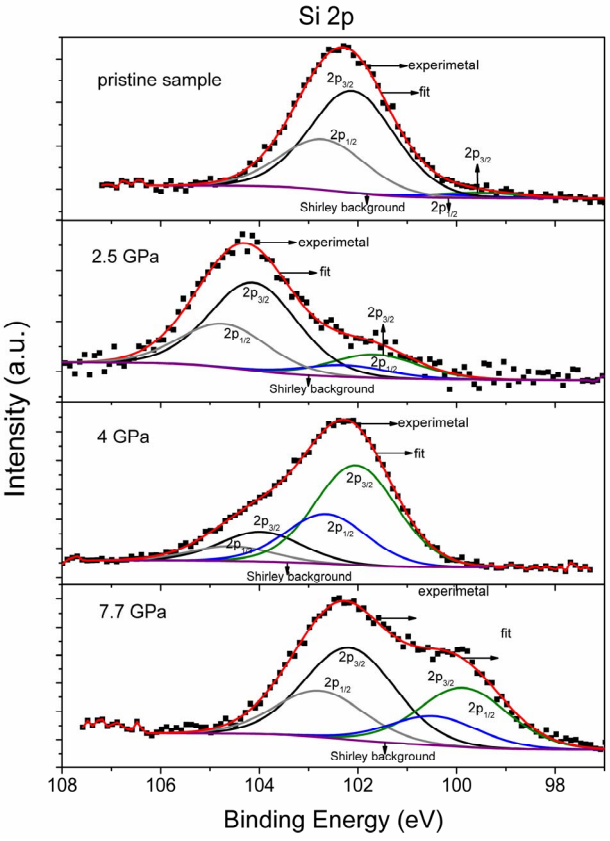

Figure 1. Si 2p region of XPS spectrum of the LS_2 pristine sample and after processing at 2.5 GPa, 4 GPa, and 7.7 GPa at room temperature.

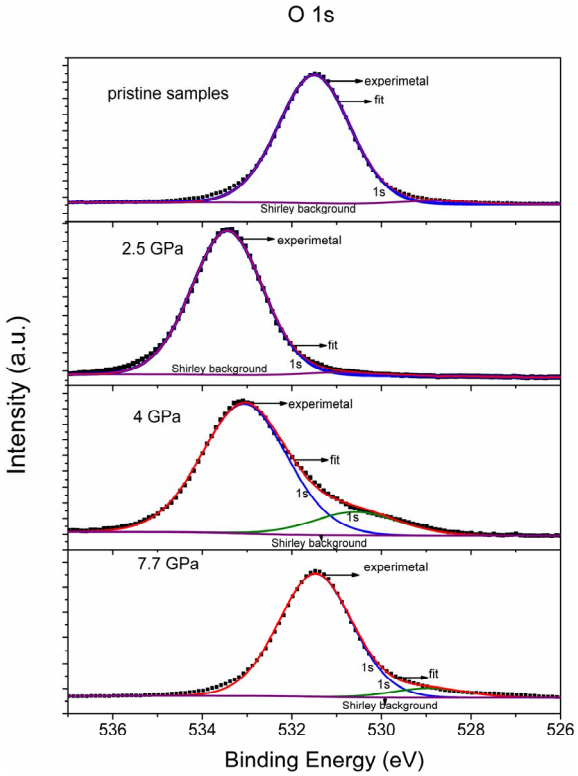

Figure 2. O 1s region of XPS spectrum of the LS_2 pristine sample and after processing at 2.5 GPa, 4 GPa, and 7.7 GPa at room temperature.

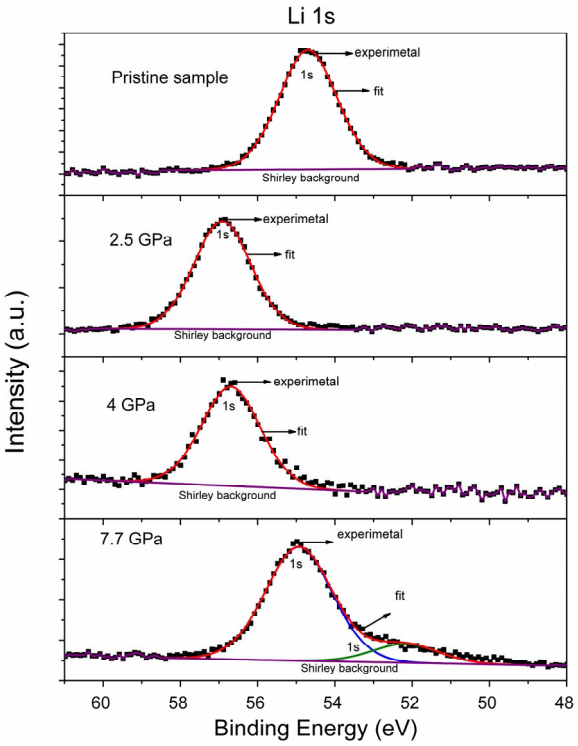

Figure 3. Li 1s region of XPS spectrum of the LS_2 pristine sample and after processing at 2.5 GPa, 4 GPa, and 7.7 GPa at room temperature.

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while after processing at 4 and 7.7 GPa there are two components. In these cases, the component with higher intensity corresponds to BO while the lower intensity component corresponds to NBO. For Li atoms (**Figure 3**), only at 7.7 GPa it is possible to identify a second component of BE.

Table 1 shows the values of the BE obtained in this work by fitting the experimental data compared to the results found in the literature for LS_2.

3.2. Crystallization under High Pressure (HPHT)

Figures 4-6 show the XPS results for the samples crystallized under high pressure. In this case there was practically no shift in the BE as a function of pressure.

Figure 4 shows that the formation of doublets for Si $2p_{3/2}$ and Si $2p_{1/2}$ now happens only after processing at 7.7 GPa. **Figure 5** shows that there were three components of BE for O 1s up to 7.7 GPa, one associated to NBO and two associated to BO. The intensity of the component with higher BE decreases with increasing pressure. For Li atoms (**Figure 6**), only at 7.7 GPa it was possible to identify a component of the BE. Soares *et al*. [18] already reported that the detection of the Li 1s XPS signal from crystalline samples of LS_2 was difficult.

The BE measured for the pristine glass sample and for the crystalline sample obtained at atmospheric pressure are similar to the results found in the literature [12,13,18], as shown in **Table 1**. The permanent shift of the BE toward higher energy and the change in the intensity of the peaks for Li 1s, O 1s and Si 2p observed in **Figures 1-3** indicated that the densification affects irreversibly the glass structure, even without crystallization.

The large shift of the BE toward higher energies observed for Si 2p after processing at 2.5 and 4 GPa (**Figure 1**) suggests a stronger interaction with the surrounding oxygen atoms compared to the pristine glass. According to Sawyer *et al.* [16], the BE decreases systematically from Q^4 to Q^0 species for Si 2p. According to **Figure 1**, two Q-species were observed in all samples for Si 2p, but for pristine samples the intensity of the Q-species of lower energy was very small. Probably in pristine glass samples the Q^3 specie was dominant and the small peak of lower energy corresponded to residual Q^2 species.

Table 1. Binding energy values obtained from the fitting of the XPS experimental data for the samples processed under high pressure at room temperature (glass) and processed under high pressure and high temperature (glass ceramic) compared to the results found in the literature at 1 atm.

Glass									
Pressure	Heat treatment	Binding Energy (eV)						Ref.	Obs
		Si 2p		O 1s		Li 1s			
1 atm	Room temperature	102.1	99.5	531.4	528.8	54.7	-	This work	
2.5 GPa		104.1	101.6	533.4	530.9	56.9	-	This work	
4.0 GPa		104.0	102.1	533.0	530.5	56.7	-	This work	
7.7 GPa		102.2	99.8	531.5	528.9	54.9	52.1	This work	
1 atm		102.7	-	530.7	532.4	51.6	55.7	[13]	$Li_2O{\cdot}2SiO_2$
1 atm		103.2		530.1	531.6	51.0	54.9	[18]	$Li_2O{\cdot}2SiO_2$ 32.0/32.5 %mol Li_2O
1 atm		102.1		530	532.01	-	-	[15]	$Na_2O{\cdot}SiO_2$
1 atm		102.93	101.73	531.86	529.71	-	-	[16]	$K_2O{\cdot}SiO_2$
Glass ceramic									
Pressure	Heat treatment	Binding Energy (eV)						Ref	Obs
		Si 2p		O 1s		Li 1s			
1 atm	455˚C/2 h + 610˚C/2 h	101.95		533.01	531.70	529.51	-	-	This work	$Li_2Si_2O_5$
2.5 GPa	500˚C/2 h + 610˚C/0.5 h	102.56		533.43	531.87	529.67	-	-	This work	$Li_2Si_2O_5$
4.0 GPa	500˚C/2 h + 610˚C/0.5 h	102.55		533.13	531.70	529.44	-	-	This work	$Li_2Si_2O_5$
7.7 GPa	500˚C/2 h + 610˚C/0.5 h	102.36	99.56	532.94	531.60	529.75	55.2	-	This work	Li_2SiO_3 + amorphous SiO_2
1 atm	450˚C/5 h	102.7		532.2		530.4	55.6	51.7	[13]	$Li_2Si_2O_5$

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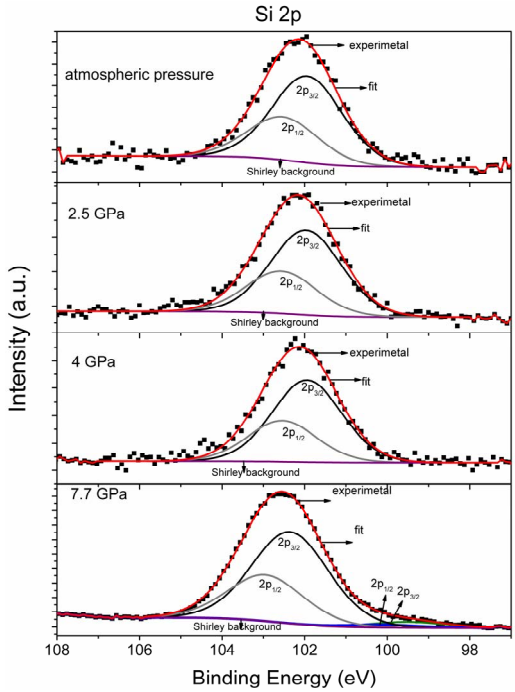

Figure 4. Si 2p XPS spectra obtained from crystalline samples produced at atmospheric pressure, 2.5 GPa, 4 GPa, and 7.7 GPa. The thermal treatment was: 500˚C during 2 h for nucleation followed by 610˚C during 0.5 h for crystal growing.

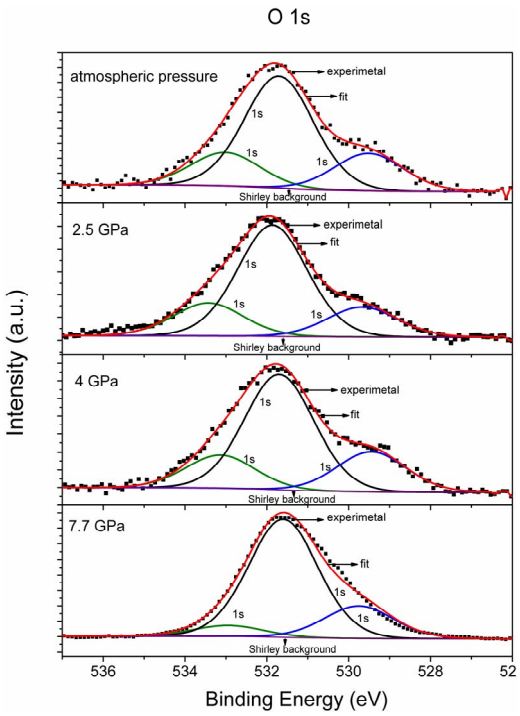

Figure 5. O 1s XPS spectra obtained from crystalline samples produced at atmospheric pressure, 2.5 GPa, 4 GPa, and 7.7 GPa. The thermal treatment was: 500˚C during 2 h for nucleation followed by 610˚C during 0.5 h for crystal growing.

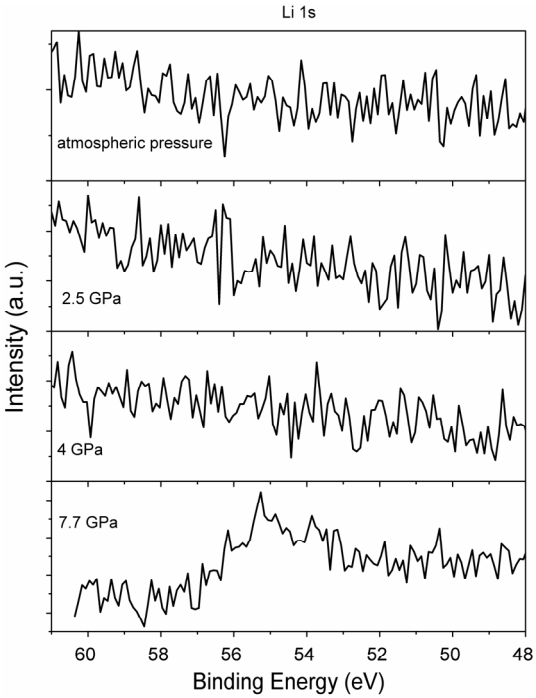

Figure 6. Li 1s XPS spectra obtained from crystalline samples produced at atmospheric pressure, 2.5 GPa, 4 GPa, and 7.7 GPa. The thermal treatment was: 500˚C during 2 h for nucleation followed by 610˚C during 0.5 h for crystal growing.

In the case of O 1s atoms (**Figure 2**), the peak at higher energy (~531 eV) for the pristine sample corresponds to BO atoms (Si-O-Si) while the other component (~528.8 eV) corresponds to the NBO atoms (Si-O-Li) [13,19]. After processing at 2.5 and 4 GPa the BE of the BO atoms shifted irreversibly to higher energies, indicating a larger interaction with the Si atoms, in agreement with the behavior of the Si 2p XPS spectrum. The intensity of the peak related to the NBO atoms was very low for the pristine sample and after processing at 2.5 GPa the intensity of this peak slightly increased after processing at 4 and 7.7 GPa, probably indicating a decomposition of the Q^3 into the Q^2 species at higher pressure.

Figure 3 shows that the BE for Li 1s also shifted after processing at 2.5 GPa and 4 GPa, and a second component at 52.1 eV was detected after processing at 7.7 GPa. According to Adams & De Jong [12,20], this component may be related to a local arrangement that would be favorable to the formation of the metastable phase during heat treatment.

Considering the XPS spectra for crystalline samples produced under high pressure, **Figure 4** shows that the Si 2p presents only one chemical environment related to Q^3 species formed during crystallization of lithium disilicate ($Li_2{\cdot}Si_2O_5$). The Si $2p_{3/2}$ spectrum for the sample crystallized at 7.7 GPa, however, presents a doublet indicating

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the formation of two structures, one of them related to lithium metasilicate $Li_2{\cdot}SiO_3$ and the other, to residual SiO_2 to satisfy stoichiometric restrictions [6].

For O 1s (**Figure 5**), the smaller BE corresponds to the NBO atoms (Si-O-Li) [13,19] and it was observed for all pressure range investigated. For pressures up to 4 GPa, the intensity and energy of this peak remained practically unchanged, compatible with the formation of crystalline lithium disilicate. At 7.7 GPa, it was observed a small shift of this component toward higher energy and a slight decrease of its intensity. This result is in agreement with the changes observed in the spectrum for Si 2p at the same pressure, indicating a distinct configuration of Q-species at higher pressures.

Two peaks related to BO atoms, of higher BE, were observed for all pressure range in the crystalline samples. The most intense component was probably related to Si-O-Si and the other one may be related to BO-Li. Ching *et al.* [21] also observed two types of BO atoms in crystalline Na disilicate. According to them, one type was assigned to Si-O-Si as in vitreous silica whereas the other type of BO atom was also bonded to a Na atom with the BO-Na bond length being similar to the NBO-Na bond length [22]. Du and Cormack [23] and Mountjoy [24] investigated by molecular dynamics simulations the formation of two BO in sodic glasses. The experimental results obtained by Nesbitt *et al.* [15] for sodic glass also provided evidences for two types of BO, one bonded to two Si atoms and one bonded to a Na atom as well as to two Si atoms. Sawyer *et al.* [16] reported that the width of the O 1s XPS peak was highly variable and wider than that of the NBO peak for potasic glass. The variable width would be a consequence of the presence of two types of BO atoms with somewhat different BE; one type bridged to two Si atoms while the other type bridged to three atoms, two Si and one K atom. According to the authors, the abundance of the two types of BO atoms was similar to the abundance of Q^4 and Q^3 species of previous NMR studies.

Fuss *et al.* [9] observed that at 4.5 GPa and high temperature, LS_2 crystallized as the lithium disilicate phase, consisting only of Q^3 tetrahedra, but the NMR results indicated the presence of a small amount of Q^2 SiO_4 tetrahedra, which could be a glassy or crystalline phase acting as imperfections. In the present work, the crystallization at 4 GPa induced the formation of only the Q^3 species in the Si 2p spectrum, without any evidence of residual Q^2. At 6 GPa, the results obtained by Fuss *et al.* suggested that the LS_2 glass densified under pressure and crystallized as a single new phase with a higher density, resembling a slightly deformed MS phase. For this sample, they observed one sharp Q^2 peak in the NMR spectrum associated with crystalline MS, a broad Q^4 band related to glassy SiO_2 and a broad Q^3 band associated with the residual glass. Additionally, they found four more peaks related to Q^3 and Q^4 tetrahedra that could not be related to residual glass. Based on the NMR, Raman and IR results, they suggested the formation of a crystalline lithium metasilicate solid-solution having the same symmetry of MS but formed out of three different tetrahedral species. In this solid solution, four Li ions from the metasilicate structure would be statistically replaced by one Si ion and three vacancies, without changing the crystal symmetry. This replacement would be detected by a shift of the peaks in the XRD pattern related to the change in lattice parameters that was, in fact, observed by the authors and corroborated by the NMR results about the amount of BO and NBO atoms. The XPS results found in the present work for the sample crystallized at 7.7 GPa indicated two chemical environments around Si atoms, associated with Q^3 species of lithium metasilicate (Li_2SiO_3) and Q^2 associated to residual SiO_2. No evidences of other Q species were observed. Maybe the reason for the differences between the consistent results found by Fuss *et al.* [9] and the results found in this work is related to the thermal treatment: they investigated temperatures from 608˚C during 20 min up to 753˚C during 60 min at 6 GPa. In this work we considered 500˚C during 2 h for nucleation followed by 0.5 h at 610˚C for crystal growing, both under high pressure. Probably the higher temperatures used by Fuss *et al.* [9] were not suitable for nucleation of the crystalline phases, resulting in a solid solution favored at higher temperatures where the average Si-O-Si bonding angle would decrease and there would be at least four different Si sites, according to the NMR results.

4. Conclusion

Densification of lithium disilicate at room temperature under high pressure induced large and irreversible modifications in the chemical environment of Si 2p, O 1s and Li 1s. These modifications would be related to the rearrangement of the atoms induced by high pressure due to the structural freedom of the glass structure, even at room temperature. XPS showed to be a suitable technique to detect the structural changes induced by densification at room temperature. For samples crystallized under high pressure, it was observed that a similar behavior for pressures up to 4 GPa, related to the formation of monoclinic and orthorhombic lithium disilicate. The in- terpretation of the XPS results for Si 2p and O 1s for the sample crystallized at 7.7 GPa was consistent with the formation of lithium metasilicate and SiO_2.

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