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Relationship between short-range order and ease of nucleation in $Na_2Ca_2Si_3O_9$, $CaSiO_3$ and $PbSiO_3$ glasses

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Abstract

A relationship between the short-range order around the modifier cations and the crystal nucleation tendency in silicate glasses is demonstrated. New extended X-ray absorption fine spectroscopy (EXAFS) results on the local structure around calcium and lead atoms were obtained and analyzed for both vitreous and crystalline samples. Three different silicate systems were studied: wollastonite ($CaSiO_3$) and soda-lime–silica ($Na_2Ca_2Si_3O_9$), for which volume nucleation is easily observed and lead metasilicate ($PbSiO_3$) for which nucleation occurs only on the sample surfaces in typical laboratory conditions. In the glasses that have a high nucleation tendency ($Na_2Ca_2Si_3O_9$ and $CaSiO_3$), the local structures of these *modifier* cations are similar to their short-range order in the isochemical crystalline phases, whereas the local structure in the glass that presents a low nucleation tendency ($PbSiO_3$) is quite different from that of its isochemical crystal phase. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Crystal nucleation is a key issue to understanding glass formation. It also plays a fundamental role in the development of advanced glass-ceramics for novel applications.

In the absence of catalyzing agents, most supercooled liquids crystallize heterogeneously from the external surfaces when heated; only a few systems crystallize in the bulk. It has been demonstrated [1] that stoichiometric glass forming systems can be separated into two classes. The first are able to crystallize in the volume (supposedly by homogeneous nucleation) and their temperatures of maximum homogeneous nucleation rate (T_{max}) are close to the experimental glass transition temperatures, T_g (here defined as the point where the viscosity $\eta = 10^{12}$ Pa s). The opposite behavior is observed for the other type of glasses, which only crystallize heterogeneously on the surfaces, i.e., the (calculated) temperatures of maximum homogeneous nucleation rate are substantially lower than T_g ($T_{max} \ll T_g$). For this second family of glasses, the induction periods in the temperature range where nucleation could in principle be detected are

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too long. Alternatively, the homogeneous nucleation rates could be undetectably low.

Although the general trends described above are now firmly established, a crucial question remains [2,3]: *what is the relationship, if any, between the molecular structure of supercooled liquids and their nucleation ability* (*volume or surface nucleation*)? The main assumption is: if the local structure of a glass and its isochemical crystal are similar, only a few interfacial rearrangements will be necessary for crystal nucleation, which then can take place easily, even in the glass volume. If these rearrangements are substantial, nucleation can only occur on the external surfaces, assisted by unsaturated bonds and solid impurities at the surface, or in the volume, only with the aid of nucleating agents.

The objective of this work is to confirm or to refute the proposed relationship between the local structure (the first coordination shell) of the *modifier* cations and the crystal nucleation tendency in silicate glasses. The main backbone of silicate glasses and crystals are composed of identical SiO_4 tetrahedra, thus the Si–O distances and coordination numbers are equal; however the type of linkages between these tetrahedra may be quite distinct. Additionally, it has been proposed [1–3] that for glasses that nucleate in the volume, the local structures of the *modifier cations* are similar to the structures of their isochemical crystal phases. On the other hand, for glasses that only nucleate on the surface, the local order is supposed to be quite different from those of their isochemical crystal phases. A similar short-range order around the *modifier* cations of a given glass and its isochemical crystal phase is assumed to be a necessary, but not a sufficient condition to assure ease of volume nucleation, because only average values of coordination numbers and atomic distances are determined by different structural characterization methods such as X-ray diffraction (XRD) and extended X-ray absorption fine spectroscopy (EXAFS).

In qualitative terms, the degree of structural similarity between parent glass and resulting crystal should affect the main thermodynamic parameters controlling nucleation; liquid–crystal surface energy (σ) and thermodynamic driving force (ΔG), thus affecting the nucleation ability of the system. The homogeneous nucleation rate is given by: $I \sim K'/\eta \cdot \exp(-K'' \cdot \sigma^3/T \cdot \Delta G^2)$, where K', K'' are constants and η is the viscosity; hence the surface energy dominates due to its power-3 against power-2 for ΔG.

The exact relationships of the structural parameters of glass and crystal with surface energy and driving force are not known, however, there should be some *optimum* value of similarity. This idea is clarified if one analyses two limiting cases: (i) when the structures of glass and isochemical crystal are too different, then σ is bound to be large, but ΔG should also be large. On the other hand, in the hypothetical case, (ii) when the structures of glass and crystal tend to be almost identical, σ should be very small, but ΔG should also tend to be zero. In this case, nucleation should not occur!

We present here new EXAFS results on the local structures around calcium and lead, in both vitreous and crystalline samples, in three different systems with well defined nucleation tendencies: soda-lime–silica glass ($Na_2Ca_2Si_3O_9$) and wollastonite ($CaSiO_3$), for which volume nucleation is easily observed and lead metasilicate glass ($PbSiO_3$) for which only surface nucleation is observed [1].

2. Sample preparation, EXAFS measurements and data analysis

The glasses were prepared by melting homogeneous mixtures of analytical grade reagents (Na_2CO_3, $CaCO_3$, Pb_3O_4 and SiO_2) in a platinum crucible. The melting temperatures ranged from 1000 to 1550°C, with a hold time of 2 h. The melts were then cast between two cold steel plates, with an estimated cooling rate of 400°C/s. The amorphous nature of the splat-quenched glasses was confirmed by XRD. To obtain fully crystallized samples, the specimens were submitted to the following nucleation and subsequent development treatments: the $Na_2Ca_2Si_3O_9$ glass sample was heated at 600°C for 24 h and then heated at 690°C for 20 min; the $CaSiO_3$ glass sample was heated at 725°C for 120 h and then heated at 885°C for 12 h

and, finally, the $PbSiO_3$ glass sample was heated at 650°C for 6 h. The crystalline phases were characterized by XRD. Only one crystalline phase was observed in each system: Wollastonite-1A for $CaSiO_3$ [4], Alamosite for $PbSiO_3$ [5] and Combeite for $Na_2Ca_2Si_3O_9$ [6]. The three silicate glasses characterized in this work exhibit widely different volume nucleation rates [1]. The maximum nucleation rates, I_{max} are: $Na_2Ca_2Si_3O_9$ ($\approx 10^{12}$ m^{-3} s^{-1}), $CaSiO_3$ ($\approx 10^6$ m^{-3} s^{-1}) and $PbSiO_3$ undetectably low (< 30 m^{-3} s^{-1}). Experimental values exist for the first two glasses. The limiting value for $PbSiO_3$ was readily calculated because no crystals were observed in the volume after treating samples of $1 \times 10 \times 10$ mm^3 at several temperatures ($T > T_g$) for 100 h. If only one crystal was observed, a nucleation rate of ~ 30 m^{-3} s^{-1} would result.

X-ray absorption experiments (Ca K-edge ≈ 4038 eV, Pb L_{III}-edge ≈ 13055 eV) were carried out on D21 and on D42 beam lines at LURE (France), using a Si(1 1 1) and Si(3 1 1) double-crystal monochromator, respectively. Absorption spectra were recorded in the transmission mode, at 10 K for the experiments made at the Ca K-edge and at room temperature for the Pb L_{III}-edge experiments. The materials were finely ground, then the powders were dispersed in ethanol and finally were cast by drawing the solvent through a polycarbonate filter, to deposit a layer with the required thickness.

The EXAFS function, $\chi(k)$, was extracted from the measured X-ray absorption spectrum following the usual procedure [7]: subtraction of a third-order polynomial drawn through the EXAFS oscillations and normalization to the pre-edge region by fitting to a first-order polynomial extrapolated to the EXAFS region. Then, $k^2\chi(K)$ was Fourier-transformed using a Kaiser window to obtain the radial distribution function of back-scattering atoms around the calcium and lead atoms. The contribution of a particular shell to the EXAFS spectrum was determined by Fourier-filtering the corresponding peak and back transforming to the k space. The back-transformed data were fitted using the Round Midnight program developed by Michalowicz [8]. The fitting parameters were: (i) the mean bond length between the shell and the central atom, (ii) the number and type of atom in each shell and (iii) the structural disorder (mean square displacement between the central and neighboring atoms) described by a Debye–Waller term (σ). The back-scattering amplitude and total phase shift used in the fitting procedure were obtained in two ways: using a reference material having a well-known structure for lead (the red-PbO crystalline compound). As we did not find any appropriate crystalline reference sample for calcium, we used the ab initio functions calculated by the FEFF5 XAS code, developed by Rehr and co-workers [9,10]. The errors were estimated to be ± 0.01 Å in the mean bond length (R) and $\pm 5\%$ in the coordination numbers (N) and in the Debye–Waller factor (σ). The quality of the fit is given by the reduced chi-squared χ^2_ν, defined in [11].

3. Results

3.1. Glassy and crystalline $CaSiO_3$

Fig. 1(a) and (b) show the EXAFS spectra and their Fourier transform of $CaSiO_3$ glassy and crystallized from the glass, respectively.

The first peak at the Fourier transform, situated at approximately 1.8 Å, corresponding to the first Ca–O nearest neighbors, was fitted using ab initio calculated backscattering amplitudes and phase shifts from the FEFF5 XAS code [9,10]. The results of our fittings are given in Table 1 together with the results of other authors. As an example, the agreement between the filtered EXAFS spectra and fitted curve for the $CaSiO_3$ glass is shown in Fig. 2.

3.2. Glassy and crystalline $Na_2Ca_2Si_3O_9$

Fig. 3 shows the EXAFS raw spectra and their Fourier transform of $Na_2Ca_2Si_3O_9$ glassy and crystallized from the glass, respectively. The first peak at the Fourier transform, corresponding to the first Ca–O bonds, presents equal position and amplitude for both materials. However, some difference is observed in the medium range order.

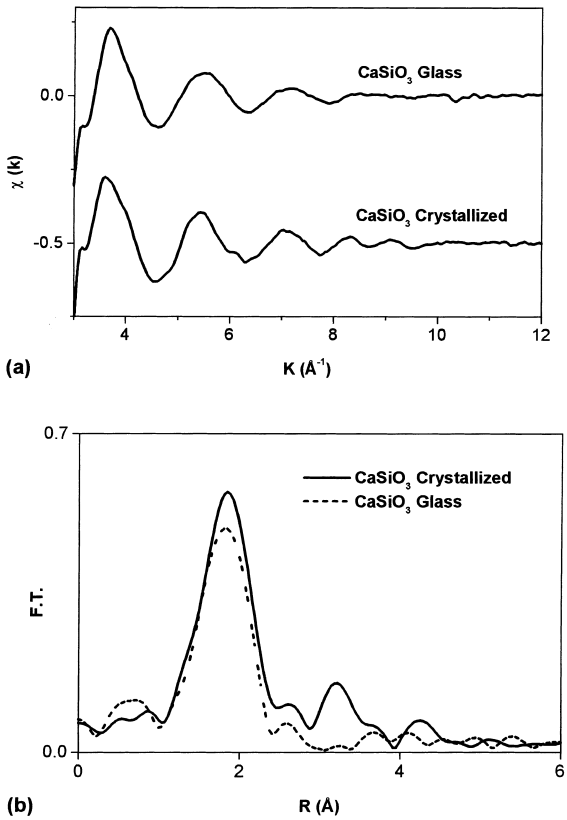

Fig. 1. (a) Ca K-edge EXAFS raw spectra and (b) corresponding Fourier transform for glassy and crystallized $CaSiO_3$.

A quantitative analysis of these samples has been carried out using ab initio back-scattering amplitudes and phase shifts calculated by the FEFF5 XAS code [9,10]. The fitting results are given in Table 2, together with the XRD results of Ohsato and Takeuchi [12] for crystalline Combeite.

3.3. Glassy and crystalline $PbSiO_3$

Fig. 4 shows the raw spectra and their Fourier transform of glassy and crystallized $PbSiO_3$, respectively. The first peak situated at approximately 1.8 Å at the Fourier transform, corresponds the first Pb–O bonding and its intensity is smaller for the crystalline sample. This difference in the first peak intensity can be due to a smaller coordination number or to a higher distortion of the first coordination shell of the crystalline sample. Quantitative results for lead metasilicate glass and crystal were obtained using the red PbO crystal as a model (each Pb atom is coordinated by four oxygen ions situated at approximately 2.31 Å [13]). We have chosen this compound as a reference because the local order around the lead ions is better than that in crystalline $PbSiO_3$ or in yellow PbO. Our fitting results, assuming the existence of only one shell in

Table 1
Structural parameters obtained with different techniques for $CaSiO_3$ compounds[a]

Samples	$N_{Ca–O}$ (±0.3)	$R_{Ca–O}$ (Å) (±0.01) Å	σ_{CaO} Å (EXAFS) (±0.01) Å	χ^2_v	Technique	References
$CaSiO_3$ glass	5.6	2.49	0.24		EXAFS	[14]
$CaSiO_3$ glass	–	2.44	–		XRD	This work
$CaSiO_3$ wollastonite	6.33	2.39	–		XRD	[15]
$CaSiO_3$ wollastonite	6.30	2.40	0.09		EXAFS	[16]
$CaSiO_3$ wollastonite	5.9	2.37	0.08		EXAFS	[17]
$CaSiO_3$ wollastonite	6.4	2.37	0.10		EXAFS	[18]
$CaSiO_3$ wollastonite	6.33	2.39	–		Neutron	
$CaSiO_3$ glass +3% Al_2O_3	6.16	2.37	–		diffraction	[9]
$CaSiO_3$ glass	6.0	2.43	–		XRD	[20]
$CaSiO_3$ glass	6.5	2.40	–		Molecular dynamics	[21]
$CaSiO_3$ crystallized from glass	5.8	2.37	0.11	0.04	EXAFS	This work
$CaSiO_3$ glass	6.0	2.36	0.13	0.06	EXAFS	

[a] In Ref. [14] the number of neighbors, $N_{Ca–O}$, and the mean bond length $R_{Ca–O}$ are the average values of the 3 different calcium sites. Concerning the EXAFS data, N is the total Ca–O coordination number; R is the average Ca–O bond length, σ is the Debye–Waller factor and χ^2_v is the best fit residual factor.

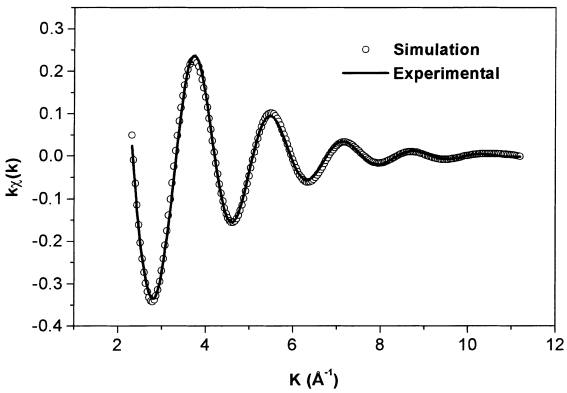

Fig. 2. Fourier filtered experimental signal (line) and best fit (dots) for the $CaSiO_3$ glass.

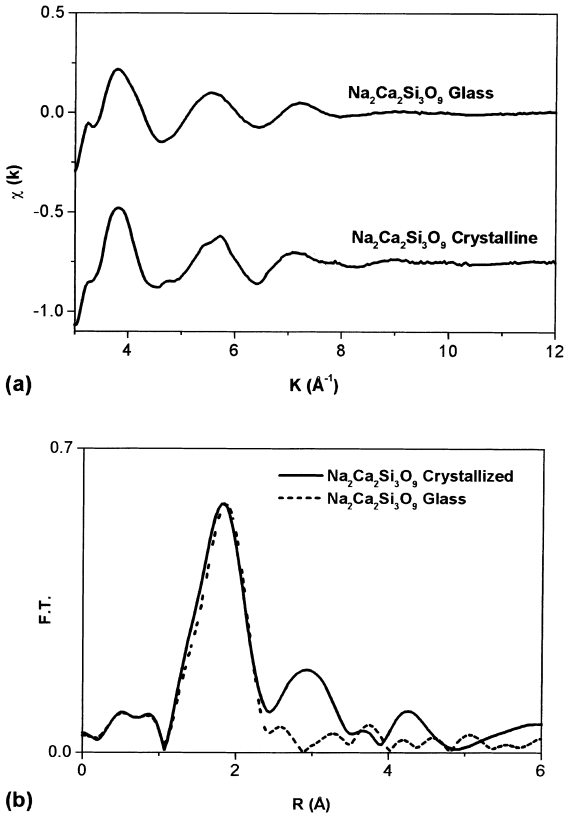

Fig. 3. (a) Ca K-edge EXAFS raw spectra and (b) corresponding Fourier transform for glassy and crystallized $Na_2Ca_2Si_3O_9$.

the first Fourier transform peak, are compared with literature values in Table 3.

4. Discussion

4.1. Glassy and crystalline $CaSiO_3$

Table 1 shows that the results of different studies, using different structural techniques, for the glassy and crystalline samples agree very well, excepting the results of Taniguchi et al. [14] and Yin et al. [15]. Taniguchi et al. reported a mean bond length of 2.49 Å (obtained using EXAFS) and 2.44 Å (obtained using XRD) for the Ca–O pair. Yin et al. [15] reported a mean bond length of 2.43 Å (four pairs of Ca–O at 2.34 Å and two pairs of Ca–O at 2.54 Å). In both cases, the Ca–O mean bond length is larger than all other results presented in Table 1.

We present a local order study of a crystalline $CaSiO_3$ sample, obtained on heat treating a glass for the first time. According to XRD experiments [16] in crystalline $CaSiO_3$, three distinct Ca sites exist; six oxygens lie between 2.22 and 2.54 Å, with a mean $[CaO_6]$ bond length of 2.38 Å, in each site. However, one of the three distinct Ca sites has a further oxygen neighbor at 2.64 Å. Assuming that an equal proportion of the three sites exist, we found an average coordination number of 6.33, with a mean bond length of 2.39 Å. The structural parameters N and R determined by EXAFS are in good agreement with literature data of XRD [16], EXAFS [17–19] and Neutron diffraction [20].

Regarding the glass structure, four different studies should be mentioned; Yin et al. [15] using XRD, the detailed work of Gaskell et al. [20] using neutron diffraction, Abramo et al. [21] using molecular dynamics and Taniguchi et al. [14] using EXAFS and XRD. Our results are in good agreement with the results of neutron diffraction ($N = 6.15$ and $R = 2.37$ Å, respectively) and with the XRD results for the coordination number (6.0). As mentioned before, the values of Ca–O mean bond length found by Taniguchi et al. [14] and by Yin et al. [15] using EXAFS and XRD are larger than those of other studies.

The lower amplitude intensity observed in the first peak of the glass Fourier transform (Fig. 1(b)) is due to a higher disorder of the Ca–O neighborhood (Debye–Waller factor of the glass sample equal to 0.13 Å, Debye–Waller of the crystallized

Table 2
Structural parameters obtained for $Na_2Ca_2Si_3O_9$ samples[a]

Samples	N_{Ca-O} (±0.3)	R_{Ca-O} (Å) (±0.01) Å	σ_{CaO} Å (EXAFS) (±0.01 Å)	χ_v^2	Technique	References
$Na_2Ca_2Si_3O_9$ mineral	5.8	2.40	–		XRD	[12]
Crystallized from glass	5.5	2.34	0.11	0.12	EXAFS	This work
–	–	–	–		–	
Glass	5.5	2.35	0.11	0.15	EXAFS	This work

[a] In Ref. [12] the number of neighbors, N_{Ca-O}, and the mean bond length, R_{Ca-O}, are the average values of the 4 different calcium sites. N is the total Ca–O coordination number; R is the average Ca–O bond length, σ is the Debye–Waller factor and χ_v^2 is the best fit residual factor.

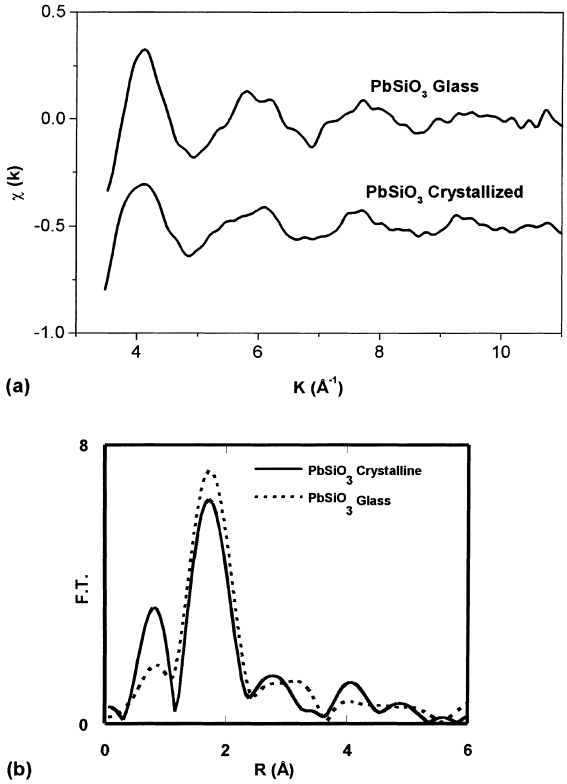

Fig. 4. (a) Pb L_{III}-edge EXAFS raw spectra and (b) corresponding Fourier transform for glassy and crystallized $PbSiO_3$.

sample equal to 0.11 Å). The value of the Debye–Waller factor obtained for the glass is in agreement with that found by Li et al. [22] i.e., $\sigma = 0.14$ Å for a $CaSiO_3$ glass doped with 3% of Al_2O_3. Similar values were reported for other silicate glasses [23].

Summarizing, the EXAFS results show that the $CaSiO_3$ glass and crystal have similar first shells coordination around calcium atoms (6.0 and 5.8, respectively), similar Ca–O mean bond length (2.36 and 2.37 Å, respectively) and that the glass structure presents a higher local disorder when compared to the crystalline one.

Thus, if the assumption of Refs. [1–3] concerning the nucleation tendency is valid, our EXAFS results indicate that volume nucleation should be detected in $CaSiO_3$ glass. Indeed, the work of Gránásy et al. [24] demonstrates that this is the case.

4.2. Glassy and crystalline $Na_2Ca_2Si_3O_9$

The $Na_2Ca_2Si_3O_9$ crystalline sample presents a complex crystallographic structure. According to Ohsato and Takeuchi [12], the calcium ions are distributed between four different sites Ca(1), Ca(2), Ca(3) and Ca(4). Except for the Ca(3) site, which has two oxygens at 2.39 Å, two at 2.31 Å and two at 2.33 Å (6 neighbors), for the three other sites, there are 7 oxygen at different distances, varying between 2.28 and 2.58 Å for the Ca(1) site and 6 oxygen at different distances, varying between 2.31 and 2.51 Å, for the Ca(2) site and 5 oxygen at different distances, varying between 2.21 and 2.55 Å for the Ca(4) site. We did not take into account distances larger than 2.70 Å. Assuming that an equal proportion of the three sites exist, we found an average coordination number of 5.8 oxygen, located at an average distance of 2.40 Å.

Table 3
Structural parameters obtained from different analysis of $PbSiO_3$ samples[a]

Samples	N_{Pb-O} (±0.3)	R_{Pb-O} (Å) (±0.01 Å)	σ_{PbO} Å (EXAFS) (±0.01 Å)	χ_v^2	Technique	References
$PbSiO_3$ crystalline Alamosite	3.0	2.35	–	–	XRD	[25]
PbO–SiO_2 glass	3.0 or 4.0	–	–	–	ESR	[26]
PbO–SiO_2 glass	PbO_3 units	–	–	–	XRD	[27]
$(PbO)_x(SiO_3)_{1-x}$ glasses	4.0	2.30	–	–	EXAFS	[28]
$PbSiO_3$ crystallized from glass	3.0	2.35	0.02	0.20	EXAFS	This work
$PbSiO_3$ glass	4.2	2.34	0.01	0.25	EXAFS	This work

[a] In Ref. [25] the number of neighbors, N_{Pb-O}, and the mean bond length, R_{Pb-O}, are the average of the 3 different lead sites. N is the total Pb–O coordination number; R is the average Pb–O bond length, σ is the Debye–Waller factor and χ_v^2 is the best fit residual factor.

Table 2 shows that the glass and the crystal have similar Ca–O coordination shells. Our EXAFS values are in good agreement with the values for Combeite, determined by XRD [12]. The Debye–Waller factor (σ) of the glass is similar to that found for the $CaSiO_3$ glass and for other silicate glasses having complex structures, such as $CaAl_2Si_2O_8$ ($\sigma = 0.17$) and $CaMgSi_2O_6$ ($\sigma = 0.10$) [23].

In summary, the EXAFS analysis show that the local structures around the Ca atoms in glass and crystal are quite similar: $N = 5.5$ for glass and crystal, the mean bond lengths are quite similar (2.34 and 2.35 Å for glass and crystal, respectively) and the Debye–Waller factors – that gives an idea of the topological disorder – are also similar ($\sigma = 0.11$ Å). Thus, the Ca local structures of glassy $Na_2Ca_2Si_3O_9$ and its homologous crystalline phase are quite similar. This fact confirms the suggestions of [1–3] concerning the nucleation ability, because $Na_2Ca_2Si_3O_9$ clearly crystallizes in the bulk [1]. Our previous experience with this glass and the treatments made for the EXAFS experiments confirmed that volume crystallization is easily observed.

4.3. Glassy and crystalline $PbSiO_3$

According to the work of Boucher and Peacor [25], there are three different lead sites in the $PbSiO_3$ structure: Pb(1), Pb(2) and Pb(3). The coordination numbers for Pb(1), Pb(2) and Pb(3) sites are 3, 4 and 4, respectively. For each of the three Pb atoms, the oxygen distances lie in the range 2.2–2.3 Å, with another one or two in the range 2.45–2.60 Å. If we consider only distances below about 2.50 Å and assuming that an equal proportion of the three sites exists, an average value of 3.0 oxygens as first neighbors for the lead atoms, located at an average distance of 2.35 Å, is found. We believe that the first Pb–O shell accessed by EXAFS contains only Pb–O bonds below 2.50 Å. In fact, as can be observed in Table 3, our EXAFS results for crystalline $PbSiO_3$ agree well with this supposition.

Regarding the local order around lead in $PbSiO_3$ glass, the ESR analysis of Hosono et al. [26] shows that the coordination number of lead in $PbSiO_3$ glass is three or four. No quantitative information about the local structure around lead was given in that work. The structure of $PbSiO_3$ glass was also analyzed by Imaoka et al. using XRD [27]. They found that only PbO_3 pyramidal units, interconnected with several kinds of silicate anions exist. In order to model their XRD data, they assumed two non-equivalent Pb–O distances in the PbO_3 pyramidal units, as being equal to 2.25 and 2.45 Å, respectively. Finally, the local structure around Pb in $(PbO)_x$–$(SiO_2)_{1-x}$ glasses, with composition varying from 38.6 to 83.7 mol% PbO,

were investigated by Montenero et al. [28] using EXAFS. They found that the local structure of these glasses is similar to that of lead oxide, PbO (the Pb ion is fourfold coordinated to oxygen). No information concerning the Debye–Waller factor was given. Therefore, our results for the glass are in good agreement with those obtained by Montenero et al. [28]: lead ions in the glass sample are fourfold coordinated by oxygen at an average distance of 2.34 Å.

In fact, if we consider the experimental error (±0.01 Å), the Pb–O mean bond lengths are equal (2.34 and 2.35 Å, for crystal and glass, respectively). The Debye–Waller factors for glass and crystal are also equal. The coordination numbers, however, are significantly different ($N_{PbO} = 4 \pm 0.3$ for the glass, whereas it is equal to 3 ± 0.3 for the crystalline sample). Thus, due to the different coordination numbers, the Pb environment in the glass and crystalline phase are different.

Therefore, as suggested in [2,3], this glass should nucleate heterogeneously, as it indeed does. Only surface nucleation is observed in heat-treated $PbSiO_3$ glass [1] (see also Section 2). Our previous experience with this glass and the treatments made for the EXAFS experiments confirmed that only surface crystallization occurs in this glass in typical laboratory conditions.

5. Conclusions

Our EXAFS results for the local structures of the modifier cations in glassy and crystalline $CaSiO_3$ and $PbSiO_3$ are in good agreement with published structural EXAFS, XRD and Neutron scattering data. An EXAFS analysis of the local structure of Ca in the $Na_2Ca_2Si_3O_9$ system is presented for the first time.

The relationship between the local structure of the *modifier* cations and the nucleation ability, previously proposed, was corroborated by our EXAFS analysis for the three systems studied. We confirmed that glasses that easily nucleate in the volume present similar local structures to their isochemical crystalline phases, whereas glasses that only nucleate on the surface do not.

Acknowledgements

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