

XANES and Raman spectrometry on glasses and crystals in the CAS system

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Ca K-edge



Calcium aluminosilicate glasses are attractive materials for a wide range of technical applications due to their highly refractory nature, their excellent optical and mechanical properties. Some glasses in this ternary system are good candidate to the storage of waste. The CaO-Al₂O₃-SiO₂ system is remarkable since glasses with very few SiO₂ content can be synthesized, contrary to alkali or Mg aluminosilicate glasses.

In a narrow range of composition (70-60 mol% CaO), the calcium aluminate binary glasses can be produced by conventional melt quenching techniques. Compounds in the CaO-Al₂O₃ system can offer fibers for transportation, infrastructure composites and infrared sensor applications and the characterization of the structure of these glasses is necessary to control the vitrification processes. The addition of small amount of SiO₂ allows a broadening of the glass forming ability and a lowering of the liquidus temperature. However, the introduction of silica strongly affects the macroscopic properties and thus the structure of these glasses. For instance, the glass transition temperature, Tg, presents a maximum at 10-20 mol% SiO₂ along constant ratio CaO/Al₂O₃. Several models have been proposed to explain this behavior which result of an increase of the polymerization network but no comprehensive view has yet emerged.

Materials and experiments

Calcium aluminosilicate glasses belonging to the SiO2-Al2O3-CaO ternary system were selected along the joins $R = CaO/Al_2O_3 = 1$, 1.57, 3 (Fig. 1). Samples were prepared from reagent grade CaCO₃, Al₂O₃ and SiO₂. The appropriate quantities of powders were melted at 1900 K during 4 hours in a platinum crucible and then quenched by immersion of the bottom of the crucible in water (classic quenching way). This process was repeated four times to ensure glass homogeneity. The samples have a slightly yellow coloration due to small Pt dissolution. It was recently shown that the solubility of Pt decreases with the addition of silica [Farges et al., Amer. Min., 84 (1999) 1562]. We use the notation Cax.y, where x and y refer to the molar percent of SiO₂ and Al₂O₃, respectively, and 1-x-y is the CaO molar content. Silica glasses and the Ca0.39 glass were prepared by classic quenching with a cooling rate of $\oplus 15\Upsilon$ /s, and CA glasses were prepared by using a laser heating technique developed at the CRMHT (Orléans, France) with a fast cooling rate. Raman spectra were recorded with a new T64000 Jobin-Yvon® spectrometer (Institut de Physique du Globe de Paris) equipped with confocal optics and a nitrogen-cooled CCD detector. A microscope is used to focus the excitation laser beam (514 nm lines of a Coherent® Ar+ laser) to a 2 microns spot and to collect the Raman signal in the backscattered direction. XANES spectra were obtained on the SA32 beamline at SuperACO for the AI and Si K-edges and on the D44 station at DCI for the Ca K-edge at LURE (FRANCE).

Cax.y $x = \% SiO_2$ $y = \% Al_2 O_3$ Mole% R=CaO/Al₂O₃ SiO_2

Ca K-edge XANES spectra

R = CaO/AlO

Ca42.14

Ca32.17

XANES spectra of glasses (Fig. 5a) were similar with those observed for anorthite where six different features can be discerned. The peak B, is a shoulder of the white line (peak C), and its intensity increases with increasing SiO₂ content, which could result from an increase in the Si-Ca linkages. A similar increase was observed for peak C. In Fig. 5b, we have plotted the extrated pre-edge, peak A, for glasses with low silica content, and for the anorthite glass and crystal. The pre-edge is related to the local geometry of the Ca site and can give information on the distortion of the site. At constant silica content, the pre-edge is shifted to higher energy with adding silica. The intensity of the pre-edge decreases with SiO₂, which implies a decrease of the site distortion with adding silica. This result is in good agreement with that observed for anorthite glass and crystal where the pre-edge is smaller for the crystal than for the glass. These results show that the Ca environment is less constrained in silica-rich glasses than in aluminate glasses. XANES spectra and the analysis of the pre-edge feature indicate that Ca is present in a distorted site with 6-7 oxygen neighbors similar to the environment of Ca in crystalline anorthite. This environment is less distorted at high silica content.

Ca10.23

Ca12.44

Ca19.40

Ca20.31 Ca23.21

Ca50.25

---- Ca0.39

Thermodynamics and rheologicals properties

Fig. 2 shows the glass transition temperatures obtained from viscosity measurements (log η = 13 Poises) as a function of SiO₂ content for the three joins SiO₂-R, with R=CaO/Al₂O₃ taken between 1 and 3. For all joins we observe an important decrease of the glass transition with decreasing SiO₂ content, which is the result of the depolymerization of the network. The Tg varies of about 400 K between pure SiO₂ (Tg~1500 K) and the center of the ternary system (Tg=1115 K for Ca33.33). For the join R=1, at the bottom of the ternary system, we observe a continuous increase of the Tg with decreasing silica content. The extrapolation of the experimental Tg values for this join yields for the CaAl₂O₄ composition a Tg of 1160±2 K. The increase of Tg as the SiO₂ content decreases (SiO₂ < 30 mol%) indicates that aluminium in tetrahedral coordination plays a role similar to the silicium in the SiO₂rich part, i.e. a network forming role in a three-dimensional network. A striking behavior is observed for the two other joins R=1.57 and R=3. The Tg values present a maximum at 10 and 20 mol% of silica, respectively. These augmentations are more important for the join R=3 than for the join R=1.57. These results are in good agreement with those of Highby et al.

[J. Non-Cryst. Solids, 126 (1990) 206]. The explanation for this pehavior will be explained below in relation with the structural modifications.



Figure 1 : SiO₂-Al₂O₃-CaO ternary system. Cax.y with x=SiO₂ mole%, $y = Al_2O_3$ mole% and CaO mole% = 100-(x+y). The blue zone is the unmixing zone and the yellow zone is the high-liquidus and crystallization zone.





spectra for glasses with low SiO2 content in the CAS system and for anorthite.

Ca K-edge

Raman spectra of crystals in the CA system

In Fig. 6, we have plotted the Raman spectra of CA crystals and clintonite (monoclinic, AI in Q³). The Raman spectrum of C3A (cubic, AI in Q³) presents a strong peak at 756 cm⁻¹ with several weaker bands also in this region and a medium intensity peak at 508 cm⁻¹ with a shoulder. A group of weaker bands appear betweens 150 and 400 cm⁻¹. The structure of C3A is based on isolated six-membered rings of AIO₄ tetrahedra. These rings are formed by corned sharing of two oxygens per tetrahedron defined as AI2 (AIO₂) units. The strong Raman band at 756 cm⁻¹ may be associated with a symmetric stretching vibration of the AI2 units. The weaker peaks at 508 cm⁻¹ may be associated with the bridging oxygens in the AI-O-Al linkages. The C12A7 (cubic, Al in Q³ and Q⁴) presents a strong peak at 517 cm⁻¹ with several weaker bands also in this region and a medium intensity peak at 764 cm⁻¹. The aluminate framework may be described in terms of fully-polymerized tetrahedral aluminate groups, Q⁴, and tetrahedral AlO₄ groups with one non-bridged oxygen, Q³. The CA (monoclinic, Al in Q⁴) is based on a fully-polymerized three-dimensional network of corned-shared AIO₄ tetrahedra with calcium cation occupying large voids within the network. The Raman spectrum presents a strong band at 520 cm⁻¹ with a shoulder at 545 cm⁻¹, a weak band near 790 cm⁻¹. The 520 and 545 cm⁻¹ bands were related to motions of the bridged oxygen atoms in the Al-O-Al linkages in the plane bisecting the linkage and the 790 cm⁻¹ band is associated with Al-O stretching vibrations. The CA2 (monoclinic, AI in Q⁴) is based on a fully-polymerized network of AIO₄ tetrahedra similar to the feldspar structure. The Raman spectrum is very complex with modes covering the entire frequency range from 100 to 950 cm⁻¹. The CA6 (hexagonal) is based on a spinel structure with AI in six- and four-fold coordination. The Raman spectrum of clintonite presents a strong peak at 656 cm⁻¹ and a medium intensity peak at 894 cm⁻¹. A group of weaker bands appear betweens 150 and 500 cm⁻¹. The structure of clintonite is based on sheet isolated six-membered rings of AIO4 tetrahedra. These rings are formed by corned sharing of three oxygens per tetrahedron defined as AI3 (AIO₃) units. Raman spectra on glasses along the CaO-Al₂O₃ join present similar band than those observed on the Raman spectra of crystal.

clintonite



Structure

X-ray and neutron diffraction techniques have been used to study the structure of these glasses [Cormier et al., J. Non-Cryst. Solids, 274 (2000) 110]. The data indicate that the network is based on SiO₄ and AlO₄ tetrahedra and that Ca atoms are in distorted sites providing charge compensation near AlO₄ tetrahedra.

XANES spectra : AI K-edge XANES spectra

In Fig. 3a,b, we have plotted the AI K-edge spectra of different glasses along the join R=CaO/Al₂O₃ =1.57 and 3 respectively. These spectra are similar to those already published for minerals containing AI in 4-fold coordination. From this figure, we can conclude that AI is in 4-fold coordination in the calcic part of the SiO₂-Al₂O₃-CaO ternary system. The silica-rich glasses present a strong peak, A, at 1566 eV and a shoulder, B, at 1569 eV. The intensity of the peak A decreases rapidly with increasing Al₂O₃ content and, conversely, the intensity of the peak B increases. Another feature is visible for all glasses at higher energy, peak C. A similar behavior was obtained for the join R=1.

From results on crystalline references obtained along the Al₂O₃-CaO join, we suggest that the peak at 1572 eV in the Fig. 3a for the C3A can be attributed to AI in Q³ species. Some multiple scattering calculations are currently carried out in order to verify this assumption.







Figure 8 : Frequencies of the deconvoluted bands as a function of SiO_2 for join R=1.

Raman spectra of glasses in the CAS system

The Raman spectra for CAS glasses were plotted in Fig. 7 for the join R=1. For all glasses two regions were observed, a low frequencies band close to 550 cm⁻¹, and a high-frequencies weak band, between 850 and 1200 cm⁻¹. For silica-rich glasses, the bands are at 500 and 1150 cm⁻¹. With decreasing silica content, these two bands are shifted to two bands near 600 and 850 cm⁻¹. On the two joins (R=1.57 and 3), a similar behavior is observed. In Fig. 7, we observed a strong band centered near 500 cm-1, with a shoulder near 550 cm⁻¹ and a weak band centered at 1100 cm⁻¹. These results are similar to those observed by Seifert et al., [Amer. Min., 67 (1982) 696]. These 3 peaks evolve into 2 peaks near 550 and 925 cm⁻¹ when SiO₂ is decreased from 76 to 0 mole %.

The high frequency region of the Raman spectra were deconvoluted using Igor® software. We find three Gaussians bands, near 1050, 1150 and 1200 cm⁻¹, in the Raman spectra of SiO₂ glass. The same number of bands occurs in all spectra for glasses with high silica content. In the Raman spectra of glasses along the join SiO₂-CaAl₂O₄, we observe a continuous shift of these bands as a function of CaAl₂O₄ (see Fig. 8). These observations are consistent with continuous substitution of Al³⁺ for Si4+ in tetrahedral coordination in the two structural units for all compositions. There is evidence of new bands forming with decreasing SiO₂. At low silica content, we observed a band at 870 and 890 cm⁻¹ for respectively Ca0.50 and Ca12.44, and for the Ca12.44 a band at 1140 cm⁻¹. We can propose that the band at 1140 cm⁻¹ in the Ca12.44 correspond to isolated Si in Q⁴ species in the glasses and that the band

Si K-edge XANES spectra

In Fig. 4, we have plotted the Si K-edge spectra of different glasses along the join $R=CaO/Al_2O_3 = 3$. Similar spectra were obtained for the joins R=1 and R=1.57. The silica-rich glasses present a noticeable white line, A, with a shoulder B and two others peaks C and D. The intensity of peak A decreases rapidly with increasing Ca₃Al₂O₆, while the intensity of peak B increases. Peaks C and D are little affected by the chemical variations. Multiple scattering calculation will provide a relationship between these peaks and the polymerized network.



Figure 4 : Si K-edge spectra for glasses in the CAS system

near 780 cm⁻¹ to AI in Q³ species.

Conclusions

With the addition of silica, there is no evidence of abrupt structural modifications for the glasses presenting the highest Tg. This indicates that the variations in properties of these glasses with the addition of silica are not due to changes in the environment around Si atoms. We have shown that Si and AI atoms are introduced in a different way into the glass structure. AI is usually found in fully-polymerized Q⁴ sites, even in depolymerized aluminosilicate glasses. However for glasses with high CaO content, AI resides in Q³ as well as Q⁴ sites. The number of Q³ positions increases with CaO which implies a rapid decrease of the viscosity and of the glass transition temperature for low silica content.

Ca is in distorted sites with 6-7 oxygen neighbors in all glasses. The site distortion decrease with increasing SiO₂ content. Al is in 4-fold coordination in all glasses.

We have presented the Raman spectra of glasses and crystal in the CAS ternary system. From Raman deconvolution, the bands position observed for the SiO₂-CaAIO₄ system is similar to that observed for the SiO₂-Na_{0.5}AlO₂ system, where three bands are found to evolve linearly with Al/Si substitution. We observed that AI can be substituted to Si in Q⁴ position in two structural unit with different intertetrahedral angle. This substitution corresponds to a decrease in frequencies with decreasing SiO₂ content in aluminosilicate glasses. We proposed the attribution of some band to AI in Q species: - 840 cm⁻¹ band correspond to AI in Q⁴, - 800-760 cm⁻¹ band, can be attributed to the AI in Q³.

We woud like to thank Dominique Ghaleb (CEA-Marcoule) for Molecular Dynamics calculations, François Farges (University of Marne-la-Vallée), and Valerie Briois (LURE) for their help in the data collection of the XANES at the Ca K-edge, and Georges Calas for fruitful discussions.