

Introduction

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, T_g, 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/Al₂O₃ = 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 @151/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 Al and Si K-edges and on the D44 station at DCI for the Ca K-edge at LURE (FRANCE).

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 T_g varies of about 400 K between pure SiO₂ (T_g~1500 K) and the center of the ternary system (T_g=1115 K for Ca33.33). For the join R=1, at the bottom of the ternary system, we observe a continuous increase of the T_g with decreasing silica content. The extrapolation of the experimental T_g values for this join yields for the CaAl₂O₄ composition a T_g of 1160±2 K. The increase of T_g as the SiO₂ content decreases (SiO₂ < 30 mol%) indicates that aluminum in tetrahedral coordination plays a role similar to the silicon in the SiO₂-rich 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 T_g 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 Higby et al. [J. Non-Cryst. Solids, 126 (1990) 206]. The explanation for this behavior will be explained below in relation with the structural modifications.

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 : Al K-edge XANES spectra

In Fig. 3a, b, we have plotted the Al 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 Al in 4-fold coordination. From this figure, we can conclude that Al 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 Al in Q³ species. Some multiple scattering calculations are currently carried out in order to verify this assumption.

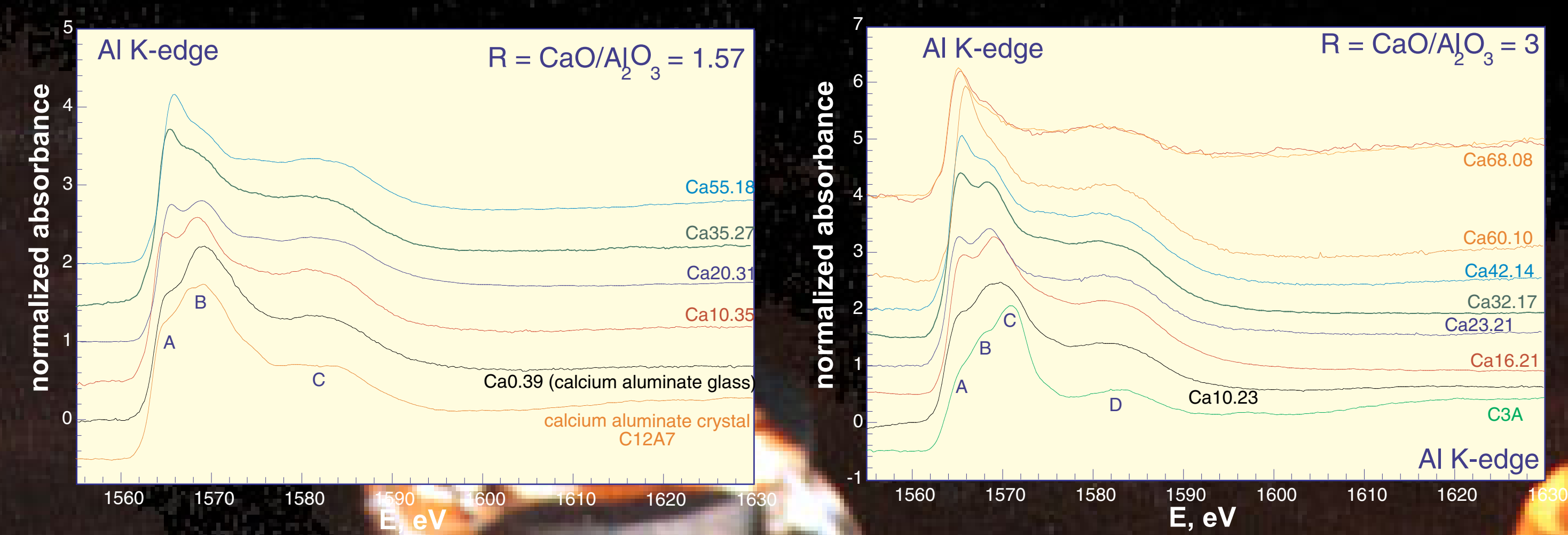


Figure 3a, b : Al K-edge spectra for glasses in the CAS system.

Si K-edge XANES spectra

In Fig. 4, we have plotted the Si K-edge spectra of different glasses along the join R=CaO/Al₂O₃=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 CaO/Al₂O₃, 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.

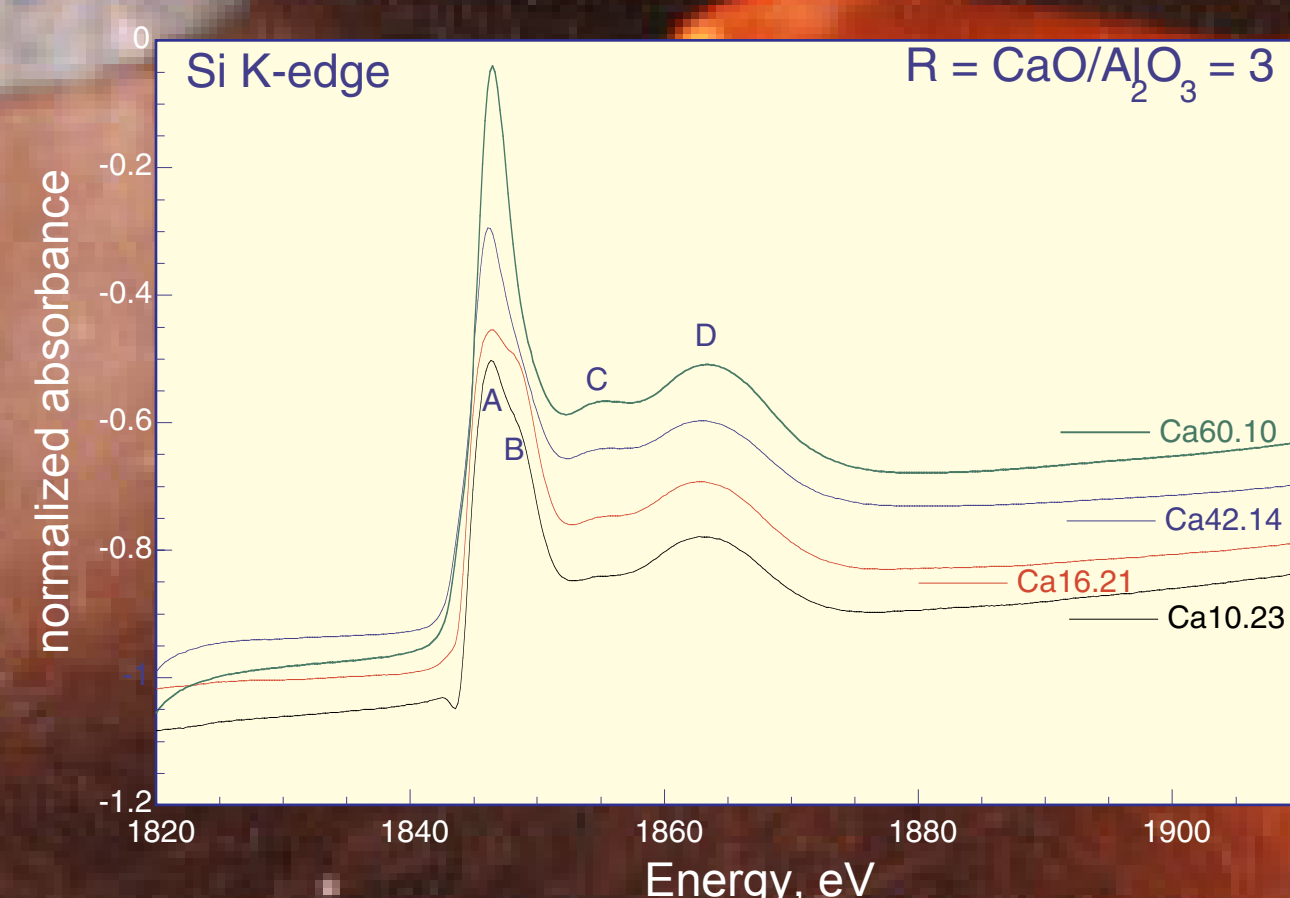


Figure 4 : Si K-edge spectra for glasses in the CAS system

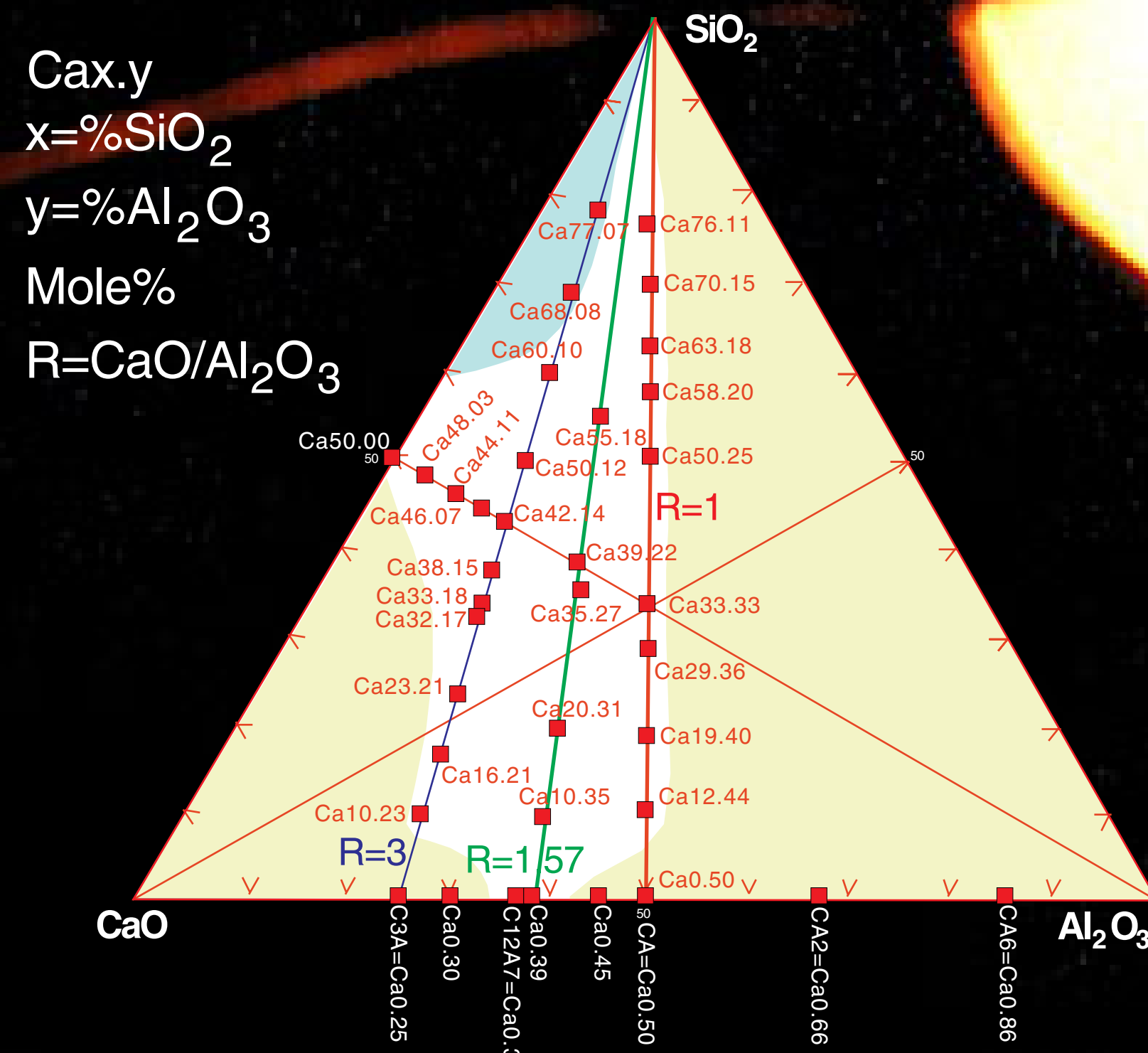


Figure 1 : SiO₂-Al₂O₃-CaO ternary system. Cax.y with x=SiO₂ mole%, y=Al₂O₃ mole% and CaO mole% = 100-(x+y). The blue zone is the unmixing zone and the yellow zone is the high-liquidus and crystallization zone.

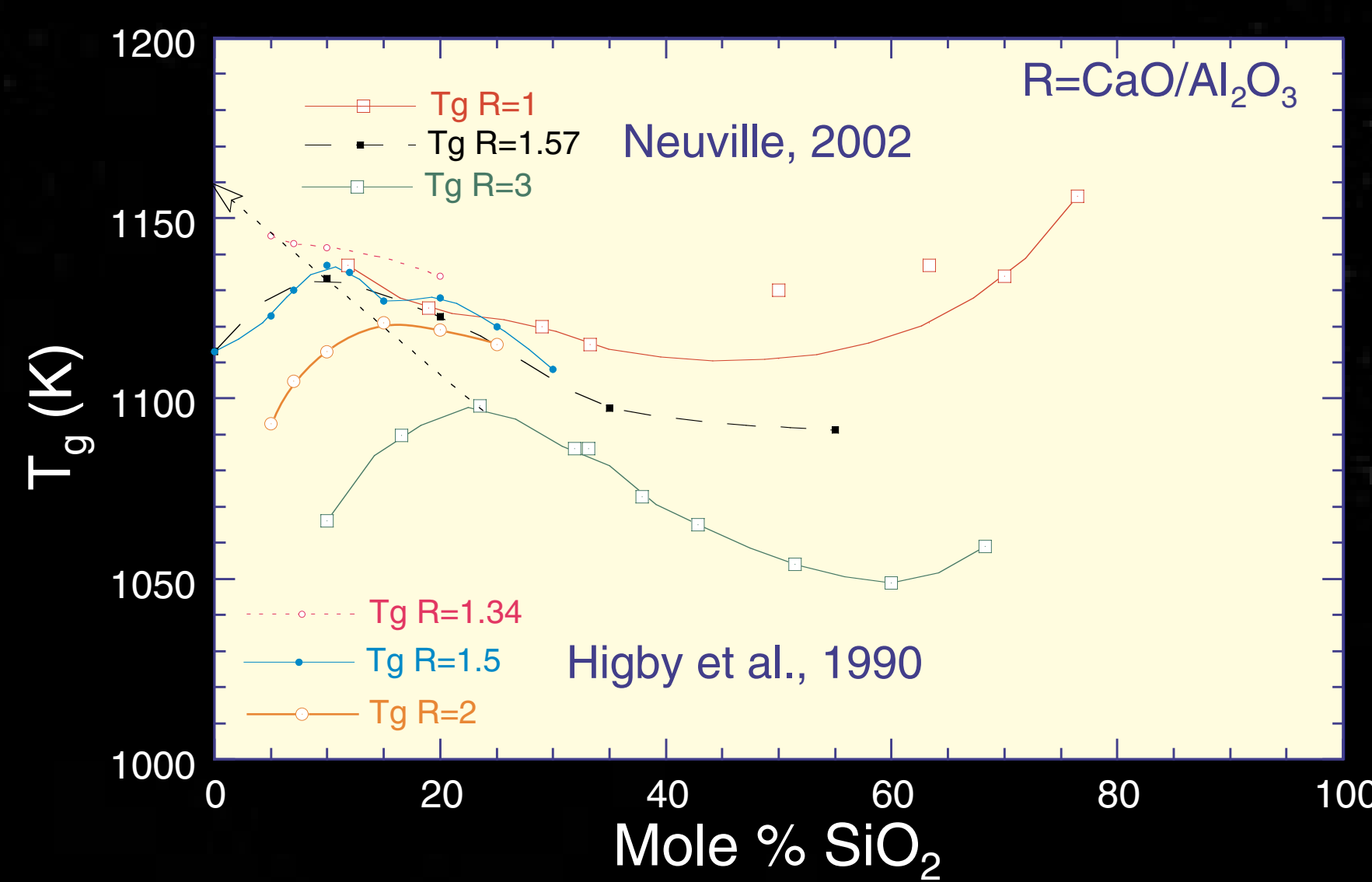


Figure 2 : Glass transition temperature as a function of SiO₂.

Ca K-edge XANES spectra

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 extracted 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 aluminosilicate 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.

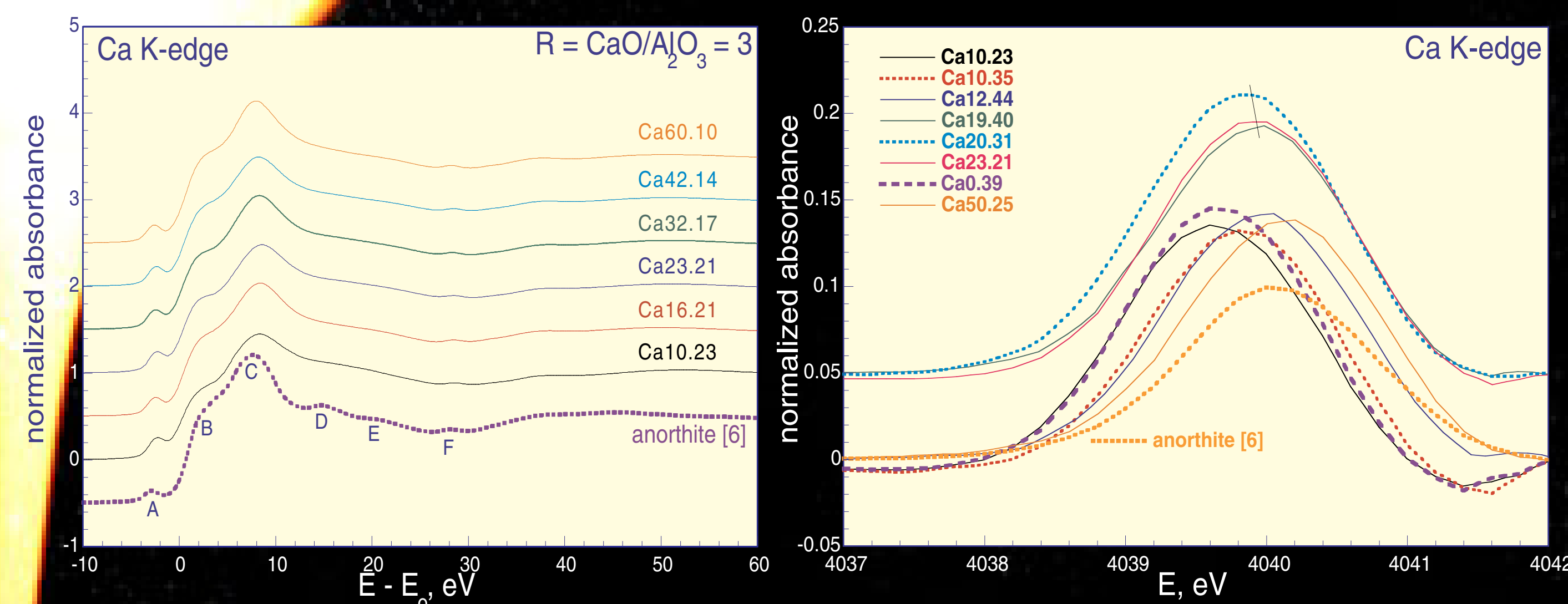


Figure 5a : Ca K-edge spectra for glasses in the CAS system.

Figure 5b : Extracted pre-edge in the Ca K-edge spectra for glasses with low SiO₂ content in the CAS system and for anorthite.

Raman spectra of crystals in the CA system

In Fig. 6, we have plotted the Raman spectra of CA crystals and clintonite (monoclinic, Al in Q³). The Raman spectrum of C3A (cubic, Al 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 between 150 and 400 cm⁻¹. The structure of C3A is based on isolated six-membered rings of AlO₄ tetrahedra. These rings are formed by corner sharing of two oxygens per tetrahedron defined as Al₂ (AlO₂) units. The strong Raman band at 756 cm⁻¹ may be associated with a symmetric stretching vibration of the Al₂ units. The weaker peaks at 508 cm⁻¹ may be associated with the bridging oxygens in the Al-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 corner-shared AlO₄ 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, Al in Q⁴) is based on a fully-polymerized network of AlO₄ 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 Al 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 between 150 and 500 cm⁻¹. The structure of clintonite is based on sheet isolated six-membered rings of AlO₄ tetrahedra. These rings are formed by corner sharing of three oxygens per tetrahedron defined as Al₃ (AlO₃) units. Raman spectra on glasses along the CaO-Al₂O₃ join present similar band than those observed on the Raman spectra of crystal.

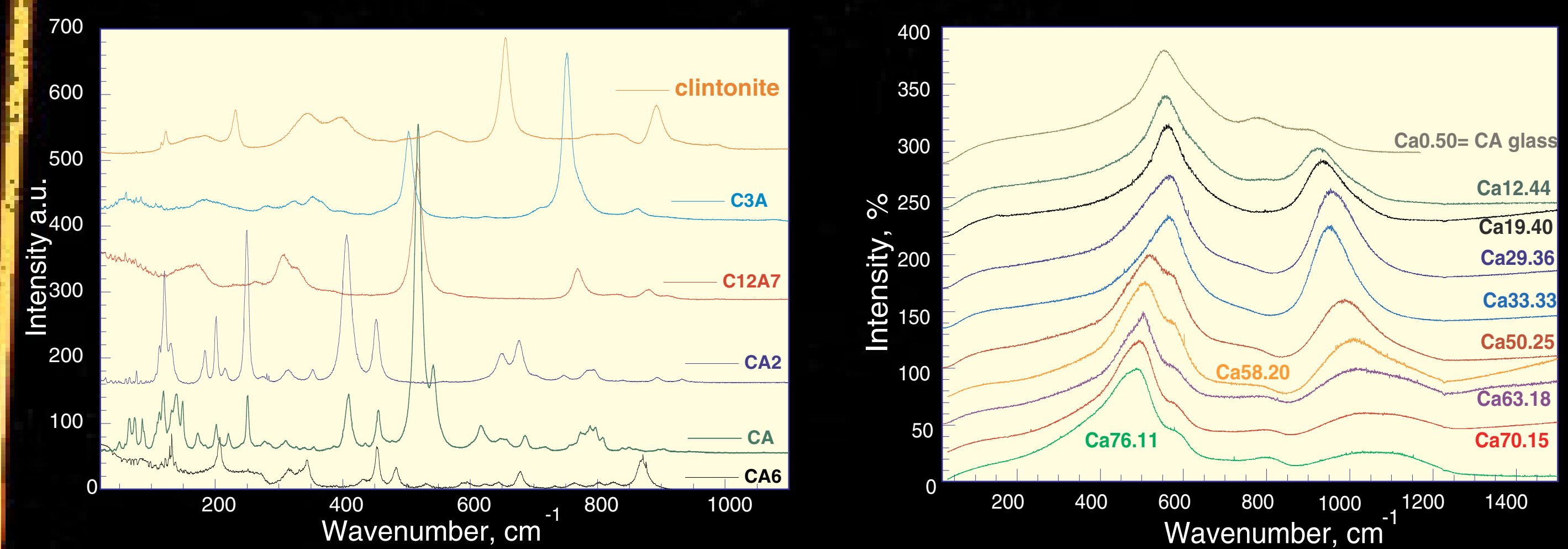


Figure 6 : Raman spectra on crystalline phase between CaO-Al₂O₃ and for clintonite.

Figure 7 : Raman spectra glasses along the join R=1=CaO/Al₂O₃.

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 near 780 cm⁻¹ to Al in Q³ species.

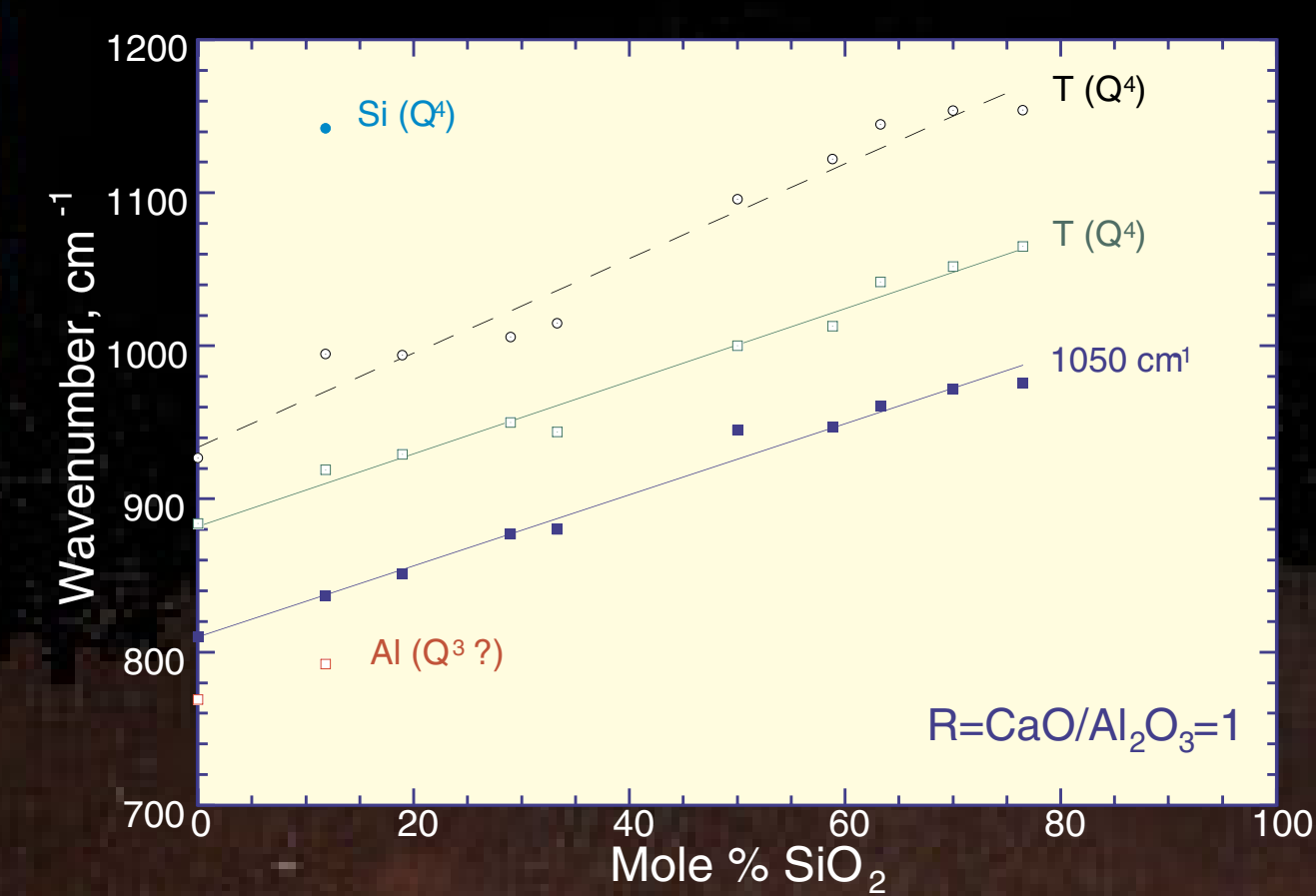


Figure 8 : Frequencies of the deconvoluted bands as a function of SiO₂ for join R=1.

Conclusions

With the addition of silica, there is no evidence of abrupt structural modifications for the glasses presenting the highest T_g. 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 Al atoms are introduced in a different way into the glass structure. Al is usually found in fully-polymerized Q⁴ sites, even in depolymerized aluminosilicate glasses. However for glasses with high CaO content, Al resides in Q³ as well as Q² 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-CaAl₂O₄ system is similar to that observed for the SiO₂-Na₂O-Al₂O₃ system, where three bands are found to evolve linearly with Al/Si substitution. We observed that Al 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 Al in Q species:
- 840 cm⁻¹ band correspond to Al in Q⁴,
- 800-760 cm⁻¹ band, can be attributed to the Al in Q³.

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