

An *In Situ* High Temperature Investigation of Cation Environments in Aluminate and Silicate Glasses and Liquids at the LUCIA Beamline

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Abstract. The structure of crystals and melts were obtained at high temperature using X-ray absorption at the Ca *K*-edge on CaMgSi₂O₆ (diopside), CaAl₂Si₂O₈ (anorthite), Ca₃Al₂O₆ (C3A) and CaAl₂O₄ (CA) compositions. Important changes are observed above the liquidus temperature particularly for the C3A composition where all oscillations in the XANES spectra disappear. Important changes in the Ca *K*-edge XANES are also visible in the pre-edge region, with increasing temperature, for crystalline CaMgSi₂O₆.

Keywords: XANES, calcium, aluminate, melts.

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INTRODUCTION

Aluminosilicates are of importance in the glass and ceramic industries, as well as, in geological melts. Previous experiments [1] have shown that Al *K* edge XANES is very sensitive to structural variations of aluminosilicates glasses containing Ca or Na, and to the degree of polymerization (Q^n) of the (AlO₄) tetrahedra.

Temperature-induced changes in the Al environment can contribute to the total configurational entropy of the system, which has been correlated with viscosity of silicate magmas through Adam-Gibbs theory [2]. Structural information at high temperature are thus required to provide atomic-level constraints on models of mantle melting, and to better understand the configurational, thermodynamic and crystallization/nucleation properties of melts. However, determination of liquid structures at high temperature is a challenging endeavor, especially for highly refractory materials. *In situ* NMR measurements are possible for determining the Al environment in melts but are limited due to quadrupolar broadening effects. However, XAS is able to give us complementary information, regarding both

the local and medium range organization. Furthermore, information on non-network forming elements, such as Ca, can be obtained and is essential to understand the structural modifications taking place in the liquid state.

In this paper, we present Ca *K*-edge XANES spectra obtained on CaMgSi₂O₆ (diopside), CaAl₂Si₂O₈ (anorthite), Ca₃Al₂O₆ (C3A) and CaAl₂O₄ (CA) in the crystalline, glassy, and liquid states, using a home-made heating device.

EXPERIMENTAL SET-UP

XAS measurements were made using the LUCIA beam-line at SLS (Switzerland) [3]. This line is dedicated to micro X-ray absorption spectroscopy in the 0.8-8 keV energy range. Si (111) monochromator was used for Ca *K*-edge. The heating wire-furnace, previously described [4], was adapted to fit within the vacuum chamber. Temperatures were measured with an optical pyrometer. The beam size was set to 20*20 μm. A small chunk of glass is placed in a hole drilled in the Pt-Ir10% heating wire (800 μm in diameter). The XAS spectra were recorded in the fluorescence mode using a silicon drift diode detector protected by a

beryllium cap. The glasses and crystals used in this study have been analyzed and described previously[1].

RESULTS AND DISCUSSION

Four compositions, $\text{CaMgSi}_2\text{O}_6$ (diopside), $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite), $\text{Ca}_3\text{Al}_2\text{O}_6$ (C3A) and CaAl_2O_4 (CA), were studied from room to high temperature at the Ca *K*-edge and the results are plotted in figures 1, 2 and 3. In all three figures significant changes in the XANES spectra can be observed with increasing temperature.

High Temperature XANES Spectra of Diopside

Significant changes in the pre-edge XANES region were observed between crystal and liquid states (Fig. 1) of $\text{CaMgSi}_2\text{O}_6$ (diopside). In crystalline $\text{CaMgSi}_2\text{O}_6$, Ca is in 8 fold-coordination [5,6]. This spectrum is characterized by a pre-edge at 4041.1 eV (line y), and five peaks *a*, *b*, *c*, *d* and *e*. These five peaks, characteristic of a crystal with a periodic three-dimensional network structure, disappear after increasing the temperature up to the liquidus. This change is a direct illustration of the melting effect on the structure of the mineral. Moreover, a noticeable shift is observed for the pre-edge of the glass and the liquid localized at 4040.8 eV (line x), and peak *b* disappears between the crystal and amorphous states. This corresponds to a change in the nearest neighbor environment of Ca on going from a crystal to a glass, where Ca is in a more distorted polyhedron (6-7 fold coordination) [6,7].

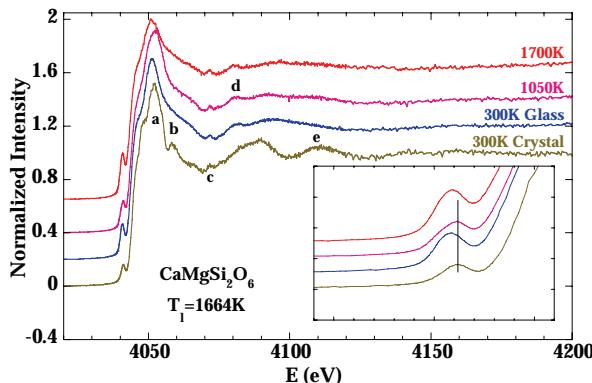


FIGURE 1. XANES spectra of $\text{CaMgSi}_2\text{O}_6$ at the Ca *K*-edge, glass, crystal and liquid at different temperature.

After heating the $\text{CaMgSi}_2\text{O}_6$ glass up to 1050 K, the pre-edge peak energy is the same as that observed for the crystal at 4041.1 eV. This indicates the onset of rapid crystallization just after the glass transition

temperature ($T_g = 991$ K, [8]). In this spectra, the XANES oscillations are the same as those in the glass.

At higher temperature, 1700 K, the XANES spectrum of the liquid show a great similarity with the XANES spectrum of the glass at room temperature, with a pre-edge at 4040.8 eV. The intensity of the XANES pre-edge for both crystalline and amorphous phases increases with temperature. This increase of the intensity of the pre-edge corresponds to an increase in the distortion of the Ca site with temperature.

High Temperature XANES Spectra of Anorthite

The XANES spectra of anorthite crystal (triclinic), $\text{CaAl}_2\text{Si}_2\text{O}_8$ (figure 2) shows a peak *a* at 4051.0 eV and a shoulder at 4045.9 similar to diopside. These results are in good agreement with those previously observed [6]. In anorthite crystal and glass, Ca is localized in a distorted polyhedron with 7 oxygen neighbours at an average distance of 2.49 Å, but with Ca-O distances ranging from 2.29 to 2.83 Å [9]. Such an environment agrees with Molecular Dynamics (MD) simulations obtained on various CAS glasses [9]. An increase of temperature close to the liquidus temperature does not modify the peak position for the mean resonance *a*, but peak *b* disappears and EXAFS oscillations are less visible for amorphous phase. The pre-edge feature for glass and liquid at 1900 K is at 4040.9 eV (line x) and for the crystal is at 4041.1 eV (line y).

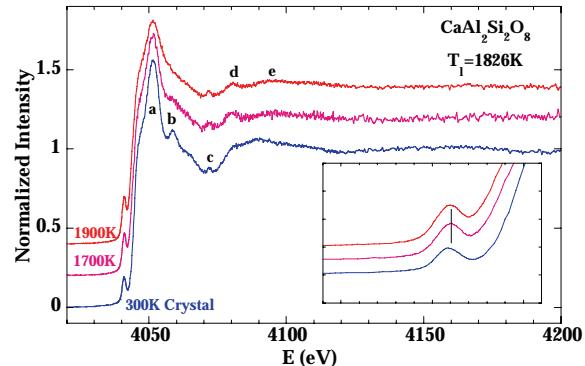


FIGURE 2. XANES spectra of $\text{CaAl}_2\text{Si}_2\text{O}_8$ at the Ca *K*-edge, crystals and liquid at different temperature.

In agreement with past results [6], significant differences can be observed between the XANES spectra of crystal and glass at room temperature. However, when the glass spectrum at room temperature is compared to that of the liquid at 1900 K the spectra are similar. Conversely, comparison of the glass spectrum and that obtained at 1700 K shows differences: at 1700 K the pre-edge is at slightly higher energy than for the anorthite crystal and melt, peak *b*

disappears slowly and a strong peak *d* appears. This spectrum corresponds to a new anorthite phase observed below the liquidus temperature and described previously [10].

High Temperature XANES Spectra of CA and C3A

In figure 3, XANES spectra for the two calcium aluminate crystals and liquids, CA ($\text{CaO}\text{-}\text{Al}_2\text{O}_3$) and C3A ($3\text{CaO}\text{-}\text{Al}_2\text{O}_3$), are plotted at room temperature and 1950 K respectively. XANES spectra of the CA and C3A crystals show important oscillations after the main resonance, indicating a well-ordered structure for Ca atoms. The C3A crystal is cubic, and its spectrum exhibits more oscillations than the CA crystal which is monoclinic.

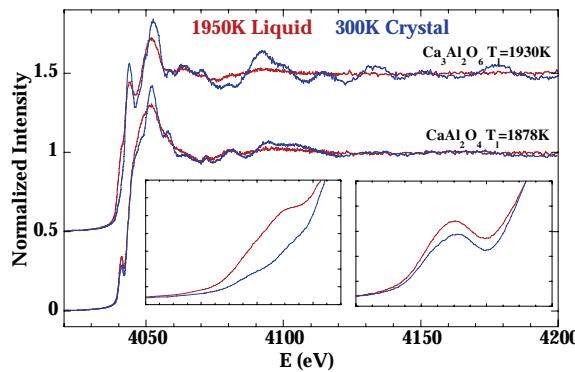


FIGURE 3. XANES spectra of calcium aluminate at the Ca *K*-edge, crystal and liquid at room temperature and 1950 K.

In C3A crystals, Ca is in regular octahedral sites, and the spectrum is characterized by the absence of a pre-edge feature contrary to CA where a pre-edge peak is observed at 4041.0 eV and shows a slight evolution with increasing temperature. In the liquid state, the regularity of the Ca sites in C3A is maintained as indicated by the lack of a significant pre-edge feature. This indicates a surprisingly ordered state for the cation in the liquid state. This differs from Ca sites observed previously in glasses [1,6] that exhibit a pre-peak in their XANES at 4041.0 eV.

In the liquid state at 1900 K, the medium range organization for CA and C3A undergoes a spectacular reorganization as indicated by the decrease in intensity and loss of the structural oscillations resulting from both thermal and topological disorder.

CONCLUSIONS

Using a home-made Pt-heating device we have obtained XANES spectra at the Ca *K*-edge on the LUCIA beamline at temperatures up to 2000 K on Ca silicates, aluminosilicates and aluminates. Significant differences are observed in the Ca environment between the crystal, glass and liquid phases. The pre-edge intensity and position present an important temperature dependence related to the site geometry of Ca. These spectra show that *in situ* XAS experiments at high temperature are sensitive tools for studying crystals and melts and obtained direct *in-situ* structural information.

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