

In situ high temperature investigation of cation environments in glasses at the LUCIA beamline (SLS)



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INTRODUCTION

The knowledge of structures at high temperature is of fundamental importance for earth and material sciences. Aluminosilicates are major constituents in glass and ceramic industry and significant components in geological melts. Important efforts have been made to determine the structure of aluminosilicate glasses containing Ca or Na. In peralkaline earth glasses, we have shown that Al K-edge XANES spectra exhibit remarkable structural variations with chemical composition [1]. The spectra of the glasses are compared to those of calcium aluminate crystals. The analysis reveals a correlation between some peaks and the degree of polymerization (Q^n) of the (AlO_4) tetrahedra. Al is distributed in Q^2 , Q^3 , and Q^4 species at low silica content and progressively enters only Q^4 as SiO_2 or Al_2O_3 content increases. This change can be related to some thermodynamical variations [2-4].

Temperature-induced changes in 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 [5]. Structural information at high temperature are thus required to provide atomic-level constraints in models of the mantle melting, and to better understand the configurational, thermodynamic and crystallization/nucleation properties. However, determination of the liquid structures at high temperature is a challenging endeavour, especially for refractory materials. NMR *in situ* measurements are possible to determine the Al environment in melts but are limited due to the quadrupolar broadening. XAS will be 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 are essential to understand the structural modifications taken place in the liquid state.

EXPERIMENTAL PART

Heating furnace

Our heating device consists in a Pt-Ir10% wire that can be heated from ambient up to more than 2000 K. This cell was already used on microbeam lines at LURE and ESRF and it is relatively easy to handle. A small chunk of glass ($<1mm^2$) is placed in the 1-mm hole drilled in the heating wire. We have verified the calibration, intensity-temperature of the Pt-cell in the vacuum chamber used to perform low energy experiments. Changes were observed in the $I=f(T)$ curves compare to air conditions. Figure 1 presents the furnace into the vacuum chamber with a sample heated at 1973 K. XANES spectra were acquired at the Swiss Light Synchrotron (SLS) on the LUCIA beamline in the fluorescence mode at the Al and Ca K-edges on aluminosilicate glasses and crystals which were heated up to the liquid state.

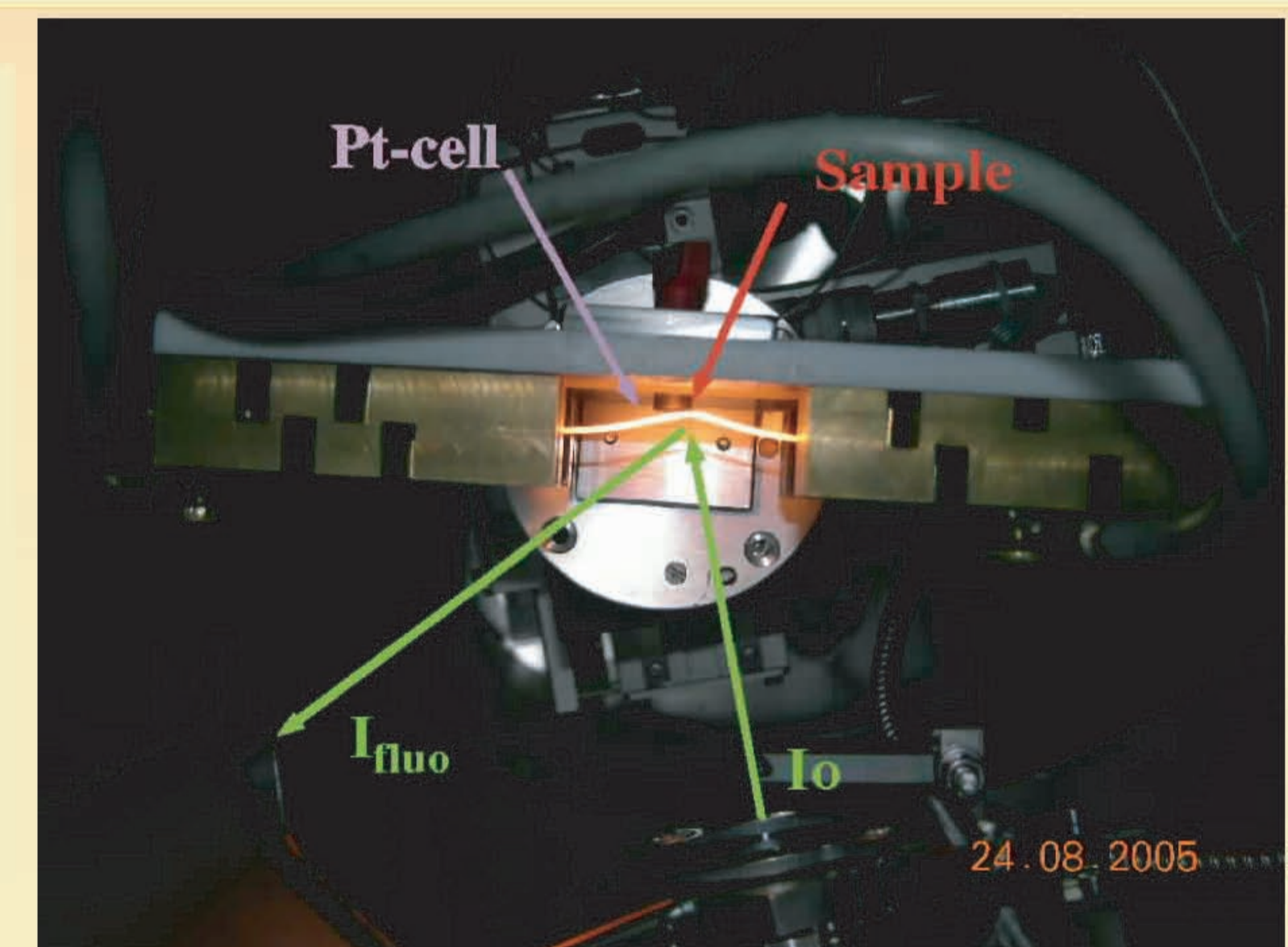


Figure 1: Furnace into the vacuum chamber with a sample heated at 1973 K.

Ca K edge

The first set of experiments at high temperature was acquired at the Ca K-edge using Si (111) crystal as a monochromator. These measurements on calcium aluminate and calcium aluminosilicate samples give information on the alkali position within the aluminate or aluminosilicate networks.

Significant changes in the pre-edge XANES spectra were observed for the $CaMgSi_2O_6$ (diopside) composition between solid and liquid (Figure 2). In the $CaMgSi_2O_6$ crystal, Ca is in 8 fold-coordination with a pre-edge at 4040.9 eV (line a). A noticeable shift is observed for the pre-edge of the glass and the liquid localized at 4041.2 eV (line b). This corresponds to a different coordination, and a more distorted polyhedron (6-7 fold coordination) [6].

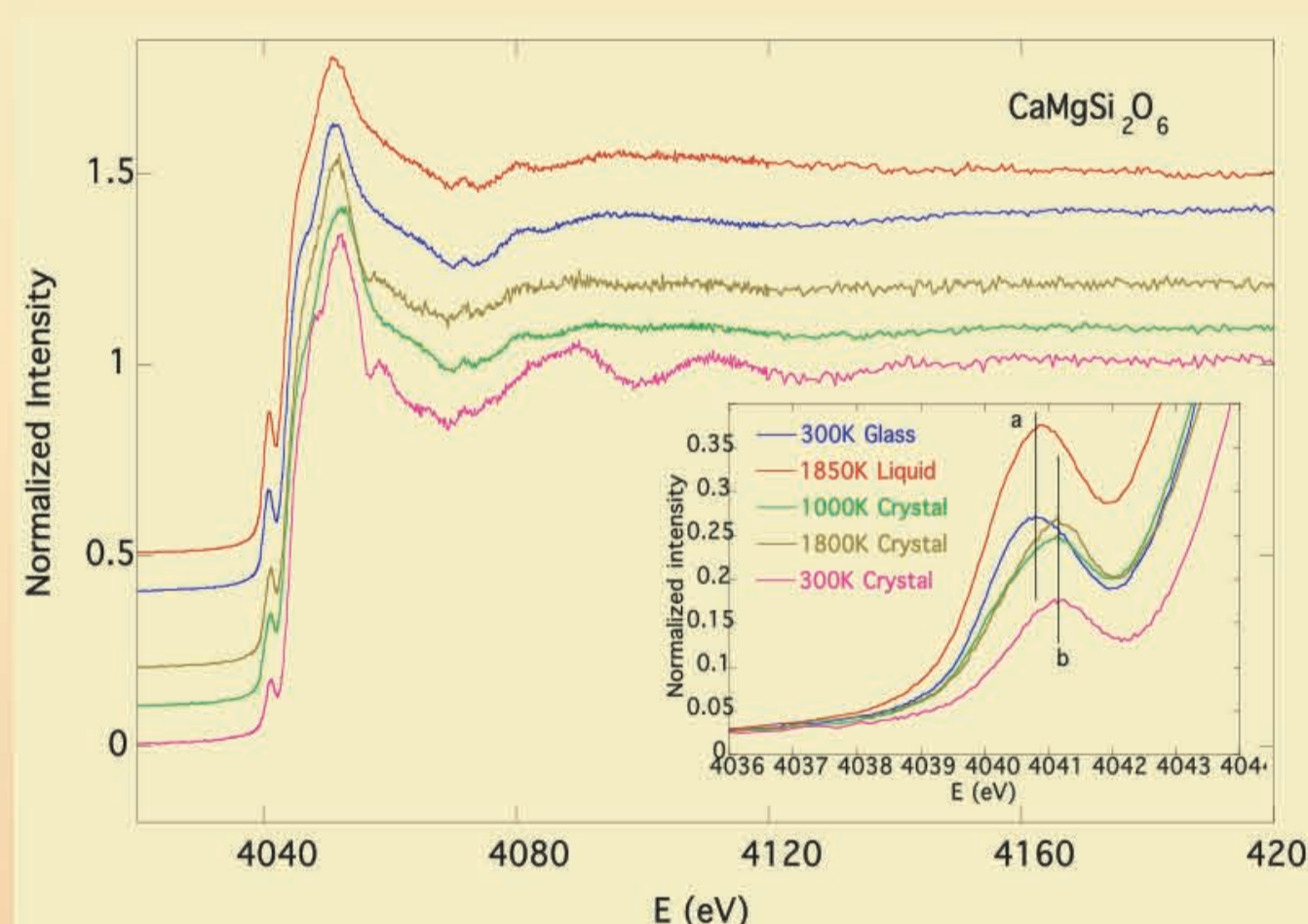


Figure 2: XANES spectra at the Ca K-edge at different temperature for $CaMgSi_2O_6$. Insert: Pre-edge of XANES spectra (the lines a and b indicates the pre-edge position in the glass and in the crystal, respectively).

In figure 3, XANES spectra of two calcium aluminate crystals (blue curves) and liquids (red curves), CA ($CaO \cdot Al_2O_3$) and C3A ($3CaO \cdot Al_2O_3$), were plotted at room temperature and 1950 K respectively. XANES spectra of CA and C3A crystals at RT show strong oscillations after the main resonance indicating a well-ordered structure for Ca. In C3A crystal, Ca is in a regular octahedral site, characterized by the absence of pre-edge at the contrary of CA where a pre-edge is observed for crystal at 4041.0 eV and stays constant with temperature. In the liquid state, the regularity of the Ca sites in C3A is maintained as evidenced by the lack of significant pre-edge, which indicates a surprisingly ordered state for a cation in liquids. This differs from Ca sites observed in calcium aluminosilicate glasses [2] that present a pre-peak at 4041.0 eV, clearly distinguishable in CA liquid (Fig. 3). In the liquid state at 1950K, the medium range organization disappears for CA and C3A, as evidenced by the important decrease in the structural oscillations resulting from both thermal and topological disorder.

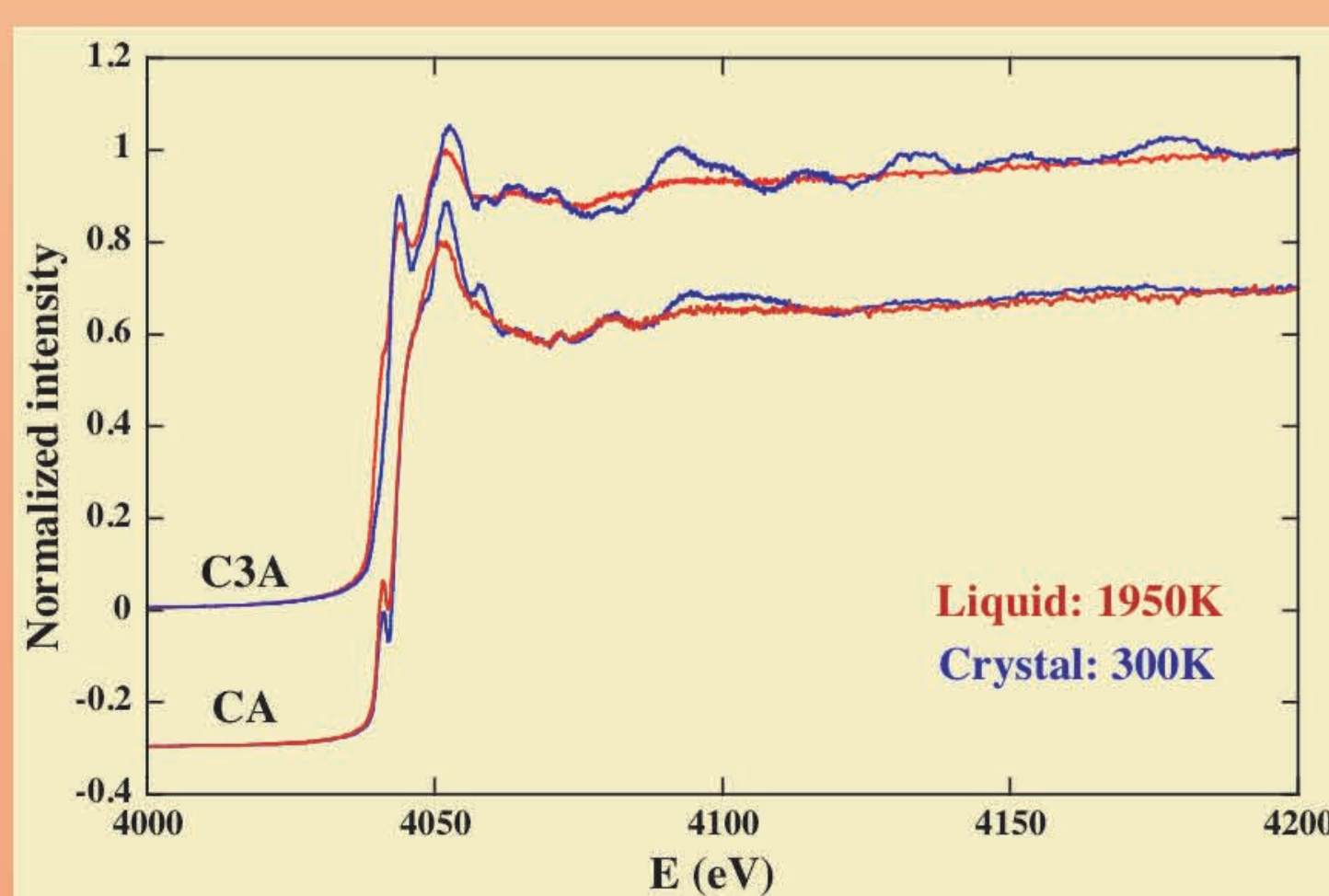


Figure 3: XANES spectra at the Ca K-edge for CA and C3A crystal at room temperature and liquid at 1950K.

Al K edge

XANES spectra of two crystal phases CA and C3A were acquired using a KTP monochromator and are reported in figures 4 and 5 as a function of temperature, up to the liquid state.

The spectra at room temperature are similar with those obtained on the SA32 beamline (SUPER-ACO, LURE) [2,3] but the resolution has improved in the present experiment. In both crystals, Al is present in a tetrahedral site but in distinct polymerized species. Al is in Q^4 position for CA and in Q^2 position for C3A [2,3]. A first intense peak a is observed for the CA crystal that rapidly decreases in intensity as the temperature increases. This peak is smaller than peak b in the liquid state. The peak c almost vanishes in the liquid state. These changes can be attributed to an increase of the distortion of the Al site between crystal and liquid and/or modification at medium range order (opening of the ring structure).

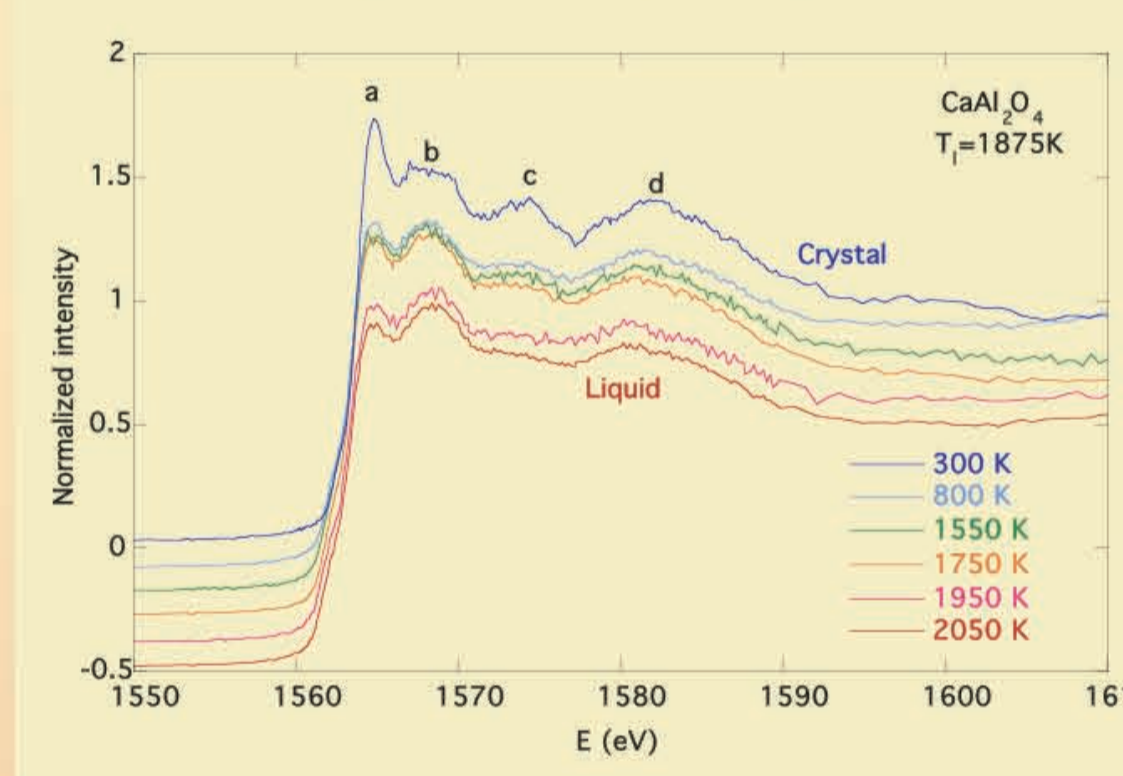


Figure 4: XANES spectra at the Al K-edge for Ca ($CaAl_2O_4$) crystal and liquid.

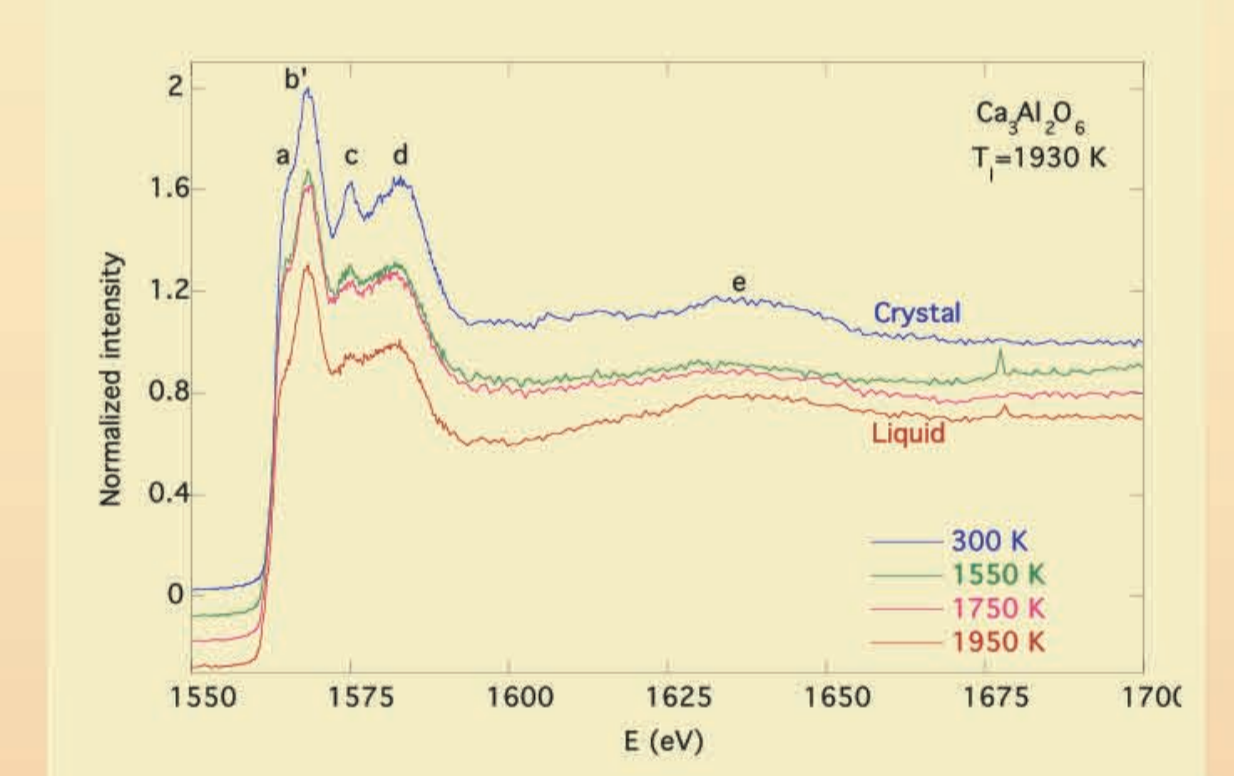


Figure 5: XANES spectra at the Al K-edge for C3A ($Ca_3Al_2O_8$) crystal and liquid.

There is, qualitatively, a striking resemblance in the evolution of XANES features of liquid and crystals with composition. Therefore, we can consider that the Al environment in these two liquids is similar to the Al environment in the corresponding crystals. These results indicate that Al K-edge XANES spectra are likely sensitive to the local geometry and to its connection with other AlO_4 tetrahedra though other contributions such as mean Al-O bond length and intertetrahedral angle can also modify the XANES shape.

CONCLUSIONS

We have demonstrated we can measure XANES spectra at Al and Ca K-edges up to temperatures as high as 2100 K, using a home-made Pt-furnace and the micro beam available at the LUCIA beamline. We have shown important modifications of the XANES spectra between crystals and glasses at room temperature and melts above the liquidus temperature. Such experiments will be used to characterize refractory materials and investigate the structural modifications between glasses, crystals and melts at high temperature.

References:

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