



Neutron diffraction study of molten calcium aluminates

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ABSTRACT

We use the aerodynamic levitation technique combined with CO₂ laser heating to study the structure of liquid calcium aluminates using neutron diffraction. We determine the structure factors and corresponding pair correlation functions describing the short-range order in the liquids above the melting points. The combination of the experiments with *ab initio* molecular dynamics simulations makes possible to get a detailed description of the liquid structure. We find that ordered tetrahedral sites around the Al atoms become more prevalent with increasing CaO concentration, while the Ca atoms present highly distorted environments at all compositions studied.

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1. Introduction

Most of the physical properties of a high-temperature liquid are related to its atomic structure. It is therefore important to develop specific devices to probe the local environment of the atoms in the sample. In the study of the molten state, most experiments must be conducted at high temperatures and it is often difficult to use conventional furnaces, which present several problems. Firstly, it is very difficult to attain and work at very high temperatures, and when this is possible there is always the risk that the material of the container pollutes the sample. These problems can be avoided by using containerless techniques like the aerodynamic levitation method associated with CO₂ laser heating [1], the method we have chosen for our study.

In this paper, we present results on the structure of levitated liquid calcium aluminates (CaO)_x(Al₂O₃)_{1-x} as obtained by neutron diffraction (ND). Using conventional techniques, these binary compounds can be vitrified to colourless transparent glasses in a narrow range of composition (0.6 < x < 0.7) [2]. These glasses present a high transparency in the mid-IR range up to 6 μm and in the past they were considered for technological applications such as waveguides for infrared lasers [3]. By using levitation techniques, it is possible to extend the vitreous domain to a range of composition between x = 0.37 and x = 0.75. This is roughly the zone between the two

compounds CA2 (CaAl₄O₇, x = 0.33, melting point: ~2050 K) and C3A (Ca₃Al₂O₆, x = 0.75, mp: ~2050 K).

This paper is divided into two parts. First we present a ND study of 3 compositions including CA2, C3A and also the equimolar composition CA (CaAl₂O₄, mp: ~1900 K). As we will see, the interpretation of the results is not easy and requires the modelling of the experimental data using *ab initio* molecular dynamics simulations (AIMD), which is presented in the second part.

2. Neutron diffraction

2.1. Experiments

The three samples, CA2, CA and C3A, were made from high-purity powders prepared using a sol–gel method [4]. The powders were first pressed under a pressure of 200 MPa, then melted in an aerodynamic levitator with a CO₂ laser beam and finally cooled to room temperature. In this way we prepared spherical samples with a diameter of 2.7 mm and about 30 mg.

Neutron scattering experiments were carried out at the D4c instrument at the Institut Laue Langevin (ILL) in Grenoble (France). This two-axis neutron diffractometer is dedicated to the structure determination of liquid and amorphous systems [5], some of its main characteristics being its wavelength, high flux and good stability. In this study we used the Cu[220] monochromator and a working wavelength of 0.5 Å. The diffracted beam was measured over a 1.3–135° angular range corresponding to a Q-range of 0.3–23.2 Å⁻¹ with an average resolution ΔQ/Q = 2.5 × 10⁻². As usual, Q is the modulus of the scattering vector.

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We used the levitation setup integrated into the D4C instrument which is described elsewhere [6], so here we are just giving a short description of its principle. The spherical sample is placed on a levitator that contains a convergent–divergent nozzle enabling the diffusion of a regulated gas flow onto the sample from below. This enables the sphere to remain in a stable position without any contact with the nozzle. When the system operates, two CO₂ lasers directed from the top and one from the bottom through the hole in the nozzle melt the levitated sample. The temperature is measured with a one-colour optical pyrometer and several video cameras are used to monitor the sample during the heating process.

2.2. Experimental results

The method used in this paper for the data processing is described briefly in Hennet et al. [6]. Recent descriptions of the technique and theoretical background for X-ray and neutron diffraction from liquids and glasses are given elsewhere [7,8].

Fig. 1 shows the neutron-weighted average structure factors $S^N(Q)$ for liquid CA2, CA and C3A measured at 2100 K. These curves are compared with the corresponding X-ray-weighted average structure factors $S^X(Q)$ measured at the ID11 beamline at the European Synchrotron Radiation Facility (Grenoble, France). In all three compositions, the first sharp diffraction peak (FSDP) at 2.15 \AA^{-1} in $S^X(Q)$, due mainly to cation–cation correlations, is much smaller and appears as a shoulder of the first main peak in $S^N(Q)$. From the X-ray measurements, one can see a sharpening and an intensity increase of this peak, implying an enhanced medium-range order when the CaO content is increased. The first main peak in $S^N(Q)$ at 2.73 \AA^{-1} is primarily due to O–O correlations and is not clearly visible in $S^X(Q)$. The broadening of this peak suggests an evolution of the oxygen environment in the liquid when the CaO content is increased.

Using high-energy X-rays, Mei et al. have studied in detail calcium aluminate melts for compositions x above 0.5 [9], so in this paper we will concentrate on the neutron results. Fig. 2 shows the neutron-weighted average pair correlation functions $g^N(r)$ obtained by the Fourier transform of the structure factors $S^N(Q)$. For all compositions,

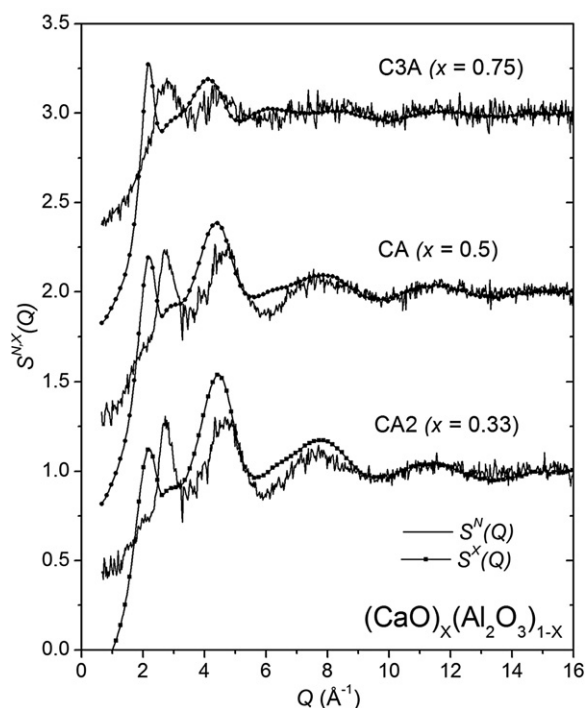


Fig. 1. X-ray and neutron structure factors $S^X(Q)$ and $S^N(Q)$ for liquid CA2, CA and C3A at 2100 K. Curves are shifted up by 1 for clarity.

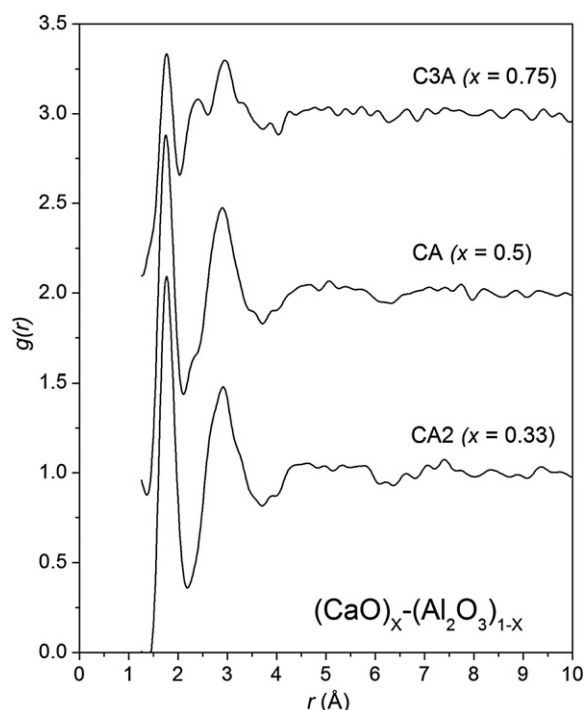


Fig. 2. Neutron total pair correlation functions for liquid CaAl_2O_4 at 2100 K. The upper curve is shifted up by 1 for clarity.

the first peak found at $1.82 \pm 0.03 \text{ \AA}$ corresponds to the nearest-neighbour Al–O distance. The second peak due to Ca–O correlations and found at about $2.30 \pm 0.03 \text{ \AA}$ for the sample C3A (having the highest CaO content), is not visible in CA2 and is just a shoulder of the third peak in CA. From a Gaussian fit to the three first peaks, it is possible to evaluate the Ca–O distance as $2.32 \pm 0.03 \text{ \AA}$. The third peak at $2.90 \pm 0.05 \text{ \AA}$, mostly due to the O–O correlations, is much lower for the composition CA2 and shifted to higher r ($2.95 \pm 0.05 \text{ \AA}$) for C3A. This confirms that we have an evolution of the O–O local structure when the CaO content is increased. In order to determine the coordination numbers, we performed a Gaussian fit to the total correlation functions $T^N(r) = 4\pi r \rho_0 g^N(r)$ where ρ_0 is the atomic number density taken as 0.073, 0.074 and 0.077 atom/ \AA^3 for CA2, CA and C3A, respectively [10]. The area under the first peak gives Al–O coordination numbers of 4.1 (CA2), 4.4 (CA) and 4.5 (C3A) ± 0.5 in good agreement with previous NMR [11] and X-ray scattering measurements [12,13]. The slight increase of the coordination number is not significant since it falls inside the error bar and no associated increase of the Al–O bond distance is observed.

The determination of the Ca–O coordination number for the CA and CA2 compositions is not easy since the peak is not well defined. For the C3A composition, the second Gaussian gives a Ca–O coordination number of 5.7 ± 0.5 . Fixing the Ca–O distance at 2.30 \AA , the distance found in C3A, the Ca–O coordination number is 5.4 ± 0.5 for the CA sample. This value obtained in the liquid state is similar to that given for the glass in Ref. [14], indicating that the Ca–O coordination number does not change significantly between the liquid and glass with the same composition. This has been also observed in the X-ray work of Mei et al. [9,13]. All these experimental parameters are summarized in Table 1.

Experimental errors were determined following an analysis discussed elsewhere [15]. The main source of uncertainty is the limited Q -range used for the Fourier transform and the resulting appearance of additional artificial features in $g(r)$, minimized by using the Lorch modification function. Additional errors in the coordination numbers could arise from uncertainties in the number density and from imperfect normalization of $S(Q)$.

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