Investigations of high temperature liquid oxides with synchrotron radiation

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Introduction

Most of the physical properties of a high temperature liquid are related to its atomic structure. Thus it is important to develop devices to probe the local environment of the atoms in the sample. At very high temperature, it is difficult to use conventional furnaces, which present major problems. In particular, the sample can be polluted by the container and the structural properties of the materials can be affected by the crucible. This led to the development of containerless techniques and their use at synchrotron sources for structural investigations on molten materials. We have chosen to work with the aerodynamic levitation method associated with CO_2 laser heating [1]. The advantages are the simplicity and compactness of the device, making it possible to integrate it easily in different beamlines at synchrotron sources.

Over the past ten years, synchrotron radiation techniques such as total and anomalous x-ray diffraction [2,3] and x-ray absorption [4] have been frequently used on levitated samples above the melting point and in the supercooled state and have provided structural information not previously available. More recently, the inelastic x-ray scattering technique has been applied to study the dynamics of high temperature levitated liquids [5].

Research is now underway to study the structural behavior of materials during their solidification (crystallisation or glass transition). Since solidification occurs very quickly after the laser shutdown, these dynamical studies require measurements with acquisition times of 100 ms of less. The development of fast detectors and their use at intense synchrotron sources make it now possible to perform time-resolved measurements of structural changes in materials as the liquid-crystal or liquid-glass transitions are approached.

We present here some preliminary résults obtained with the spinel $MgAl_2O_4$ in the liquid state and during its solidification.

Methods and Materials

As opposed to crystals, liquids are disordered systems whose structure is generally described in terms of distribution functions for interatomic distances and bond angles. In particular, the pair correlation function g(r) is proportional to the probability of finding an atom at a distance r from another taken at the origin. Such pair correlation functions are directly obtained with a Fourier transform of the structure factor S(Q) which can be measured by x-ray diffraction techniques:

$$g(r)-1=\frac{1}{2\pi^2\rho}\int_0^{Q_{max}} Q(S(Q)-1)\frac{\sin Qr}{r}dQ$$

$MgAl_2O_4$ is a refractory oxide with a melting point of 2408 K. At room temperature, it presents a spinel cubic structure (Fd3m space group). Aluminium sites are octahedral with a distance Al-O of 1.91 Å. Mg atoms are surrounded by 4 oxygen atoms with a bond length of 1.94 Å.

Small spherical samples, 2.0-2.7mm in diameter, were prepared by melting weighed pieces of compacted $MgAl_2O_4$ powder under levitation conditions and cooling them to room temperature.

A detailed description of the experiment can be found elsewhere [6] and we give here only a short description of the set-up. The spherical sample is situated on a levitator in the center of the chamber. This device is equipped with a convergent-divergent nozzle enabling the diffusion of a regulated gas flow onto the sample from below. This enables the sample to remain in a stable position during the heating phase without any contact. For these experiments, the samples were levitated with an argon or oxygen gas flow and heated by a CO_2 laser beam. The temperature was measured on the upper part of the sample at the point illuminated by the x-ray beam by means of optical pyrometers. The absolute temperature scale of the pyrometers was checked by comparing the freezing point of the same sample with its known melting point.

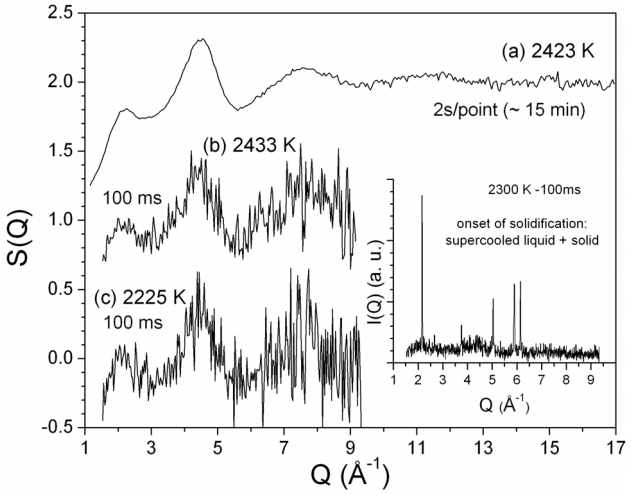

Fig 1.
Structure factor of $MgAl_2O_4$ measured in the liquid state at (a) 2423 K for 15 min, (b) 2433 K for 100 ms and (c) 2225 K for 100 ms. The inset is the diffraction pattern recorded at the onset of the crystallization at 2300 K.

Fast diffraction measurements were carried out with counting times of 100 ms at the 6.2 Beam Line [7] at the Synchrotron Radiation Source (SRS) at Daresbury (UK), using the 60°-aperture Rapid2 detector [8] developed at SRS. We used monochromatic x rays with an energy of 16.9keV.

Additional measurements with wider *Q* range and longer counting times were performed at the 12-ID-B beam line at the Advanced Photon Source (APS) in Argonne (IL, USA). In this case, the scattered intensity was measured at an energy of 25keV using a solid-state detector with 300 eV resolution over a 2θ angular range of 5-85°.

Results

Fig. 1. shows (a) the x-ray weighted average structure factor *S(Q)* for liquid $MgAl_2O_4$ at 2423 K, obtained in a 15 min measurement with the scanned solid state detector, and the *S(Q)*'s obtained in short (100 ms) measurements at (b) 2433 K (b) and 2225 K (c). With the 15 min measurement, *S(Q)* exhibits four main peaks between 1 and 15 $Å^{-1}$ The first three peaks peaks are also visible in the fast measurements (b and c) but with poorer statistics. All structure factors are very similar showing that no obvious structural change occurs between the stable liquid above the melting point and the supercooled state.

The figure inset shows the diffraction pattern corresponding to the onset of solidification where crystallites start to appear in the supercooled liquid. A profile matching of this pattern using the spinel Fd3m structure gives a lattice parameter a = 8.198 Å. The poor statistics do not make it possible to detect additional phases.

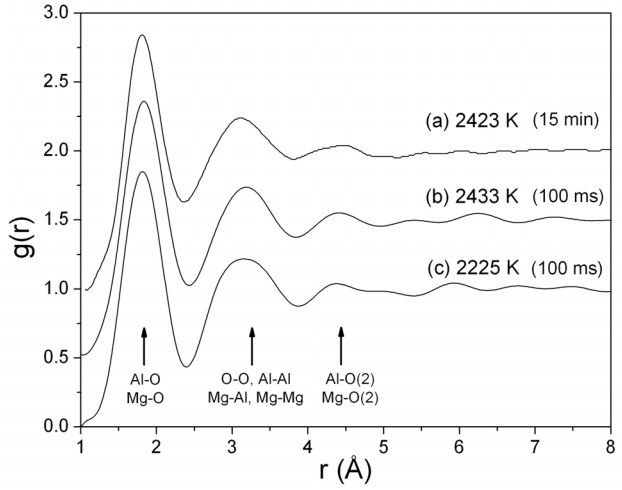

Fig 2.
Pair correlation function of liquid $MgAl_2O_4$ measured in the liquid state at (a) 242 3K for 15 min, (b) 2433 K for 100 ms and (c) 2225 K for 100 ms.

Fig 2 shows the average pair correlation functions *g(r)* obtained by the Fourier transform of the three structure factors *S(Q)* presented previously in Fig. 1. All curves are very similar and exhibit three peaks between 1 and 5 Å. The peak assigment has been done with help of Molecular Dynamics (MD) simulations [9] in which the first peak at 1.8 Å was identified as a combination of Al-O and Mg-O correlations. The second peak at 3.1 Å is a combination of several correlations including O-O, Al-Al, Al-Mg and Mg-Mg. The third peak at 4.4 Å arise from the next nearest neighbor Al-O and Mg-O correlations.

As the first peak corresponds to Al-O and Mg-O correlations, the area *A* under this peak in $RDF(r)=4\pi\rho r^2 g(r)$ is a weighted sum of the Al-O and Mg-O coordination numbers and at 25 keV we have: $A=3.95=0.594C^{Al\text{-}O} + 0.274C^{Mg\text{-}O}$.

An initial MD simulation [9] gives coordination numbers of about 4.4 for Al-O and 5.1 for Mg-O, corresponding to a peak area *A*=4.01 in good agreement with the experimental results. A nuclear magnetic resonance study of liquid $MgAl_2O_4$ gives a Al^{3+} coordination number of about 4.67 [10].

Discussion

Time resolved measurements enabled us to follow the solidification of the $MgAl_2O_4$ from the liquid state to room temperature. It was shown that the sample crystalizes directly into the cubic spinel structure. No additional phases were apparent. The pair correlations funtions obtained above the melting point during 15 min (Fig 2-a) and 100 ms (Fig 2-b) are very similar and show that the counting time has a low influence on these results, as observed previously [1]. The structure factors measured above the melting point and in the supercooled state are also very similar and do not show any obvious structural changes (Fig 1.). However, while the first peak is similar for all pair correlation functions in Fig 2, the second peak exibits a different shape in the supercooled measurements (Fig 2-c) which could reflect some changes.

The interperetation of the results is difficult due to the combination of various correlations in the peaks in g(r), and with these single x-ray measurements it is not possible to go further with the analysis. Since the absorption edges for Mg, Al and O are very low, it is not possible to use more selective techniques like anomalous x-ray scatering or x-ray absorption spectrocopy.

In order to complete this study, we have recently performed neutron scattering measurements on liquid $MgAl_2O_4$. The data analysis is in progress and will give us additional information. Both x-ray and neutron data will be modeled by MD simulations in order to determined all the partial S(Q) and g(r).

Modeling techniques are essential for obtaining reliable structural information in the liquid state and this is well illustrated with this study of liquid $MgAl_2O_4$.

Acknowledgments

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