BL04B2: Structure of High-Temperature Levitated Liquids Probed by High-energy X-ray Diffraction – The Relationship between Liquid Structure and Glass Forming Ability

Introduction

High-brilliance and high-energy X-rays are one of the greatest advantages of SPring-8. The use of high-energy X-rays allows us to measure diffraction patterns up to high values of the momentum transfer in reciprocal space in transmission geometry, using small scattering angles and small correction terms. This fortunate combination provides more detailed and reliable structural information of disordered materials (glasses, liquids and amorphous materials) than it has hitherto been available. On the other hand, use of the levitation technique allows us to achieve deeply supercooled states, because there is no interface between the liquid and a container wall. Hence we can obtain new metastable materials (glasses) from the supercooled levitated liquid. In this practical session, we will try to levitate an oxide melt at a temperature beyond 2,000 ˚C by using a conical nozzle levitator. We will learn how we can obtain reliable diffraction data and how we analyze the data. Furthermore we will try to perform structure modelling of disordered materials on the basis of diffraction data employing a computer simulation technique, in order to understand the relation between the structure of a liquid and its glass forming ability.

High-energy X-ray diffraction technique

In this practical session, we measure diffraction from disordered materials, that do not exhibit Bragg peaks due to the lack of long-range periodicity. We will use the two-axis diffractometer dedicated for disordered materials (see Fig. 1 [1]). The energy of incident X-rays is 61.4 keV obtained by a Si 220 monochromator. The scattered X-rays from the sample are collected by a Ge detector using a conventional θ - 2θ step scan method. We analyze the diffraction pattern and obtain Faber-Ziman total structure factor $S(Q)$ [2] by the following equation,

$$
\begin{aligned}
S(Q) &= \frac{I(Q) - \left\langle |f(Q)|^2 \right\rangle}{|\langle f(Q) \rangle|^2} + 1 \\
&= \sum_{ij} c_i c_j \frac{\mathrm{Re}\left[f_i(Q) f_j^*(Q)\right]}{|\langle f(Q) \rangle|^2} S_{ij}(Q) = \sum_{ij} w_{ij}(Q) S_{ij}(Q),
\end{aligned}
\tag{1}
$$

where $S(Q)$ can be obtained by a normalization of the corrected X-ray scattering intensity $I(Q)$. The pair distribution function $g(r)$ and total correlation function $T(r)$ are obtained by a Fourier transformation of $S(Q)$,

$$
\begin{aligned}
g(r) &= 1 + \frac{1}{2\pi^2 \rho r} \int_0^{Q_{\max}} Q\left[S(Q) - 1\right] sin(Qr) \mathrm{d}Q \\
&= 1 + \sum_{ij} \frac{1}{\pi r} \int_{-\infty}^{\infty} \int_0^{Q_{\max}} r'[g_{ij}(r') - 1] \cdot w_{ij}(Q) \cos[Q(r - r')] \mathrm{d}r' \mathrm{d}Q
\end{aligned}
\tag{2}
$$

$$
T(r) = 4\pi\rho r \cdot g(r) \tag{3}
$$

where Q is the absolute value of wave number ($Q = (4\,\pi/\lambda)\sin\theta$, 2θ: scattering angle, λ: wavelength of incident x-rays) and < > means the average per one atom; c_i and $f_i(Q)$ represent the atomic fraction and the atomic form factor of component i, respectively. $w_{ij}(Q)$, $S_{ij}(Q)$, and $g_{ij}(r)$ are the weighting factor of i-j correlations for X-rays, partial structure factor for i-j correlations, and the partial pair distribution function for i-j correlations, respectively. ρ is the atomic number density. We can assign atomic correlation peaks and derive the coordination number by integrating the area under the peak in the real-space function.

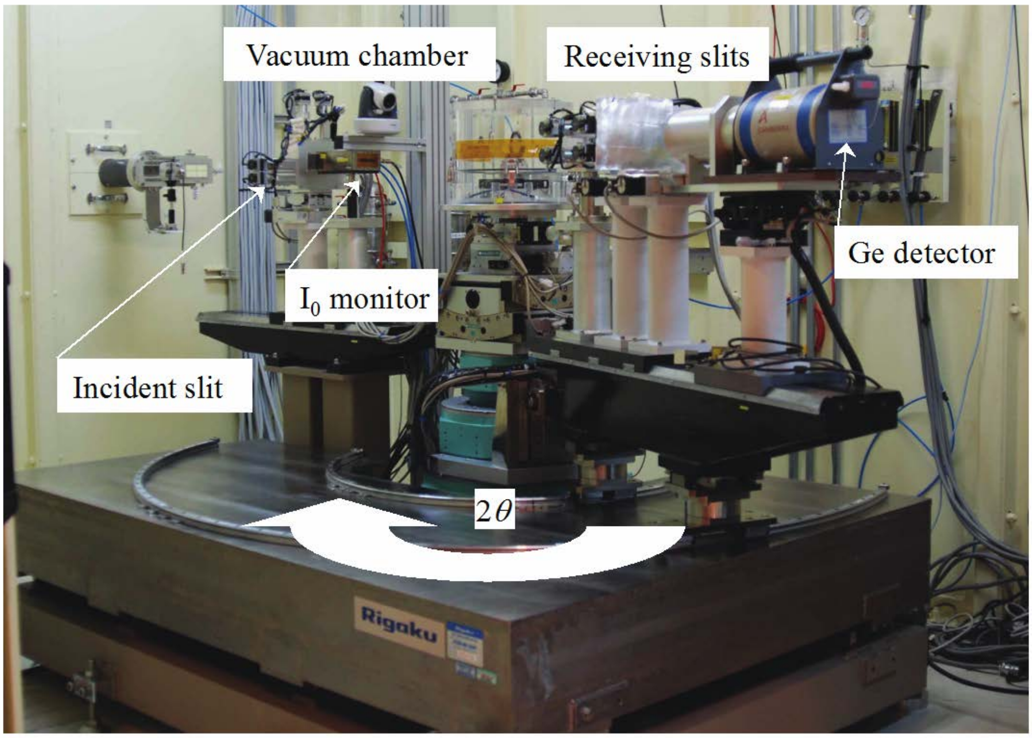

Fig. 1 Photograph of the two-axis diffractometer for disordered materials for typical room temperature measurement.

Aerodynamic levitation technique

One of the major experimental difficulties in studying materials at extremely high temperatures is unwanted contamination of the sample through contact with the container. This can be avoided by suspending the samples through levitation. This technique also makes metastable states of matter accessible, opening up new avenues to new materials for technological applications.

In the aerodynamic levitation technique [3], a sample is levitated by gas flow in a convergent-divergent nozzle in which Bernouilli forces push the sample back to the axis of the nozzle. Stable levitated samples can then be heated by a CW CO_2 laser. The condition for levitation is derived from the law of momentum conservation applied to a control volume that contains the sample:

$$\int\left[\frac{1}{2}\rho\mu^2+p\right]dA=Mg, \tag{4}$$

where ρ, μ and p are the gas density, vertical gas flow velocity and gas pressure, respectively, and Mg is the sample weight. The integral is performed over the surface A

of the control volume.

Figure 2(a) shows a schematic view of conical nozzle used for aerodynamic levitation. Typical size of the sample is ~ 2 mm in diameter. The typical experimental set up for oxide melts is shown in Fig. 2(b). During this practical session, we will try to levitate a liquid Al_2O_3 droplet at a temperature above 2000 ˚C.

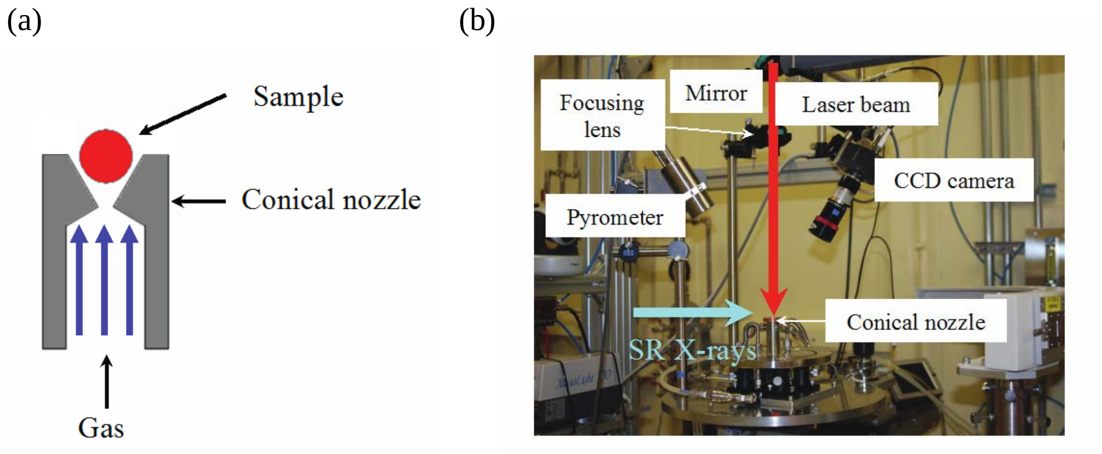

Fig. 2 Schematic view of the conical nozzle (a) and photograph of the aerodynamic levitation apparatus (b).

Reverse Monte Carlo simulation

One may realize after the experiment that diffraction data yield only one-dimensional structural information. To reveal the complicated structure in disordered materials, it is necessary to construct 3-dimensional atomic configurations on the basis of diffraction data. The reverse Monte Carlo (RMC) method [4,5] has been shown to be a useful tool to construct a three-dimensional structural model of disordered materials using mainly experimental diffraction data. In the RMC simulation technique the atoms of an initial configuration are moved so as to minimize the deviation from the experimental diffraction data, using a standard Metropolis Monte Carlo algorithm [6]. Here, we try to generate a 3-dimensional atomic configuration of liquid Al_2O_3 that is consistent with diffraction data. Then we will try to understand the reason why we cannot synthesize Al_2O_3 glass, from the point of view of glass forming ability.

References

[1] S. Kohara, M. Itou, K. Suzuya, Y. Inamura, Y. Sakurai, Y. Ohishi, and M. Takata, *J. Phys.*: *Condens. Matter*, **19**, 506101 (2007).

[2] T.E. Faber and J.M. Ziman, Phil. Mag. **11**, 153 (1965).

[3] D.-L. Price, “High-Temperature Levitated Materials”, Cambridge University Press, 2010.

[4] R. McGreevy and L. Pusztai, Mol. Simul. **1**, 359 (1988).

[5] R. McGreevy, *J. Phys.*: *Condens. Matter* **13**, R877 (2001).

[6] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller, and E. Teller, *J. Phys. Chem*. **21**, 1087 (1953).