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High-pressure X-ray diffraction study on the structure of NaCl melt using synchrotron radiation

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ABSTRACT

Molten NaCl was analyzed by high-pressure X-ray diffraction experiments using synchrotron radiation up to 5 GPa and 1600 °C along the melting curve. The interference function $Qi(Q)$ and the correlation function $g(r)$ were derived from the diffraction data. The first-neighbor distance r_1 is about 2.7 Å and the second-neighbor distance appears around $1.4r_1$–$1.5r_1$. The coordination number, CN, of the nearest neighbor ions increases with pressure from 3.5 at 0.1 MPa to 4.5 at 5 GPa. This is the evidence that the NaCl melt has a B1-like structure with large vacancies over this pressure range and becomes densified by an increase in CN as a result of second neighbor compaction.

INTRODUCTION

Molten alkali halides are examples of typical ionic liquids. Elucidation of the structure of alkali halide melts at high pressure forms the key to solving the densification process of ionic liquids. Many alkali halides have been known to transform from the NaCl-structure (B1 structure) to the CsCl-structure (B2 structure) at high pressure. The molten alkali halides appear to undergo a structural change corresponding to this solid-state transformation (Kawai and Inokuchi 1970; Tallon 1979). This hypothesis has been examined by computer simulations such as Monte Carlo calculations (e.g., Ross and Rogers 1985; Boehler et al. 1996). However, the structural description of alkali halide melts under pressure is still incomplete. Experimental approaches such as X-ray diffraction (XRD) analysis are very useful as complements to the computer calculations.

Urakawa et al. (1996, 1998) first revealed the pressure-induced structural transition in KCl and KBr melt in a high-pressure XRD study using synchrotron radiation. Up to a pressure of 4 GPa, the structure of molten KCl and KBr changes from an open B1-like structure to an open B2-like one. A systematic study is needed for complete understanding of pressure-induced structural changes in molten alkali halides. Here we focus our attention on NaCl, which has a smaller cation-anion radius ratio ($r_c/r_a = 0.53$) than KCl and KBr (0.79 and 0.68) and a higher B1-B2 transition pressure (30 GPa) than potassium halides (about 2 GPa). In this study, we performed XRD experiments on molten NaCl up to 5 GPa using synchrotron radiation to reveal its static structure.

EXPERIMENTAL METHOD

High pressure and temperature were generated by using the cubic type apparatuses, MAX80 and MAX90, at Photon Factory, KEK, Japan. The high-pressure cell assembly was described in detail by Urakawa et al. (1998). The sample of NaCl was a reagent powder with a purity of 99.99%, which was enclosed in the BN sample container. Pressure was calculated by the volume of hBN using the equation-of-state determined by Zhao et al. (1997) and our unpublished data. Temperature was measured by a W3%Re-W25%Re thermocouple. XRD patterns were acquired at 50–100 degrees above the melting temperature of NaCl up to 5 GPa.

High-pressure XRD experiments were carried out by the energy dispersive method in transmitting geometry using the white X-ray from the vertical wiggler of BL14C and the bending magnet of AR-NE5 in Photon Factory. The white X-ray in both beamlines is available from 10 to 100 keV. XRD profiles were collected at several fixed 2θ angles between 1.5° and 24° with a Ge solid-state detector. A typical exposure time was 1000 s. By using a sharp slit system and a large sample (3mm in diameter), the X-ray beam was focused on the sample and the diffracted X-rays from the sample capsule were eliminated completely, except for 2θ lower than 4°.

Some problems still remain with reduction of the intensity data for the structure factor $S(Q)$. In high-pressure experiments, the density and the size of the pressure cell assembly change with compression, which increases the uncertainty in the absorption correction. Thus it is difficult to evaluate these corrections properly at high pressure and temperature. For the first-order approximation, we used the initial value before compression for absorption correction. Another difficulty is the evaluation of the energy profile of the incident X-ray. The oscillation of

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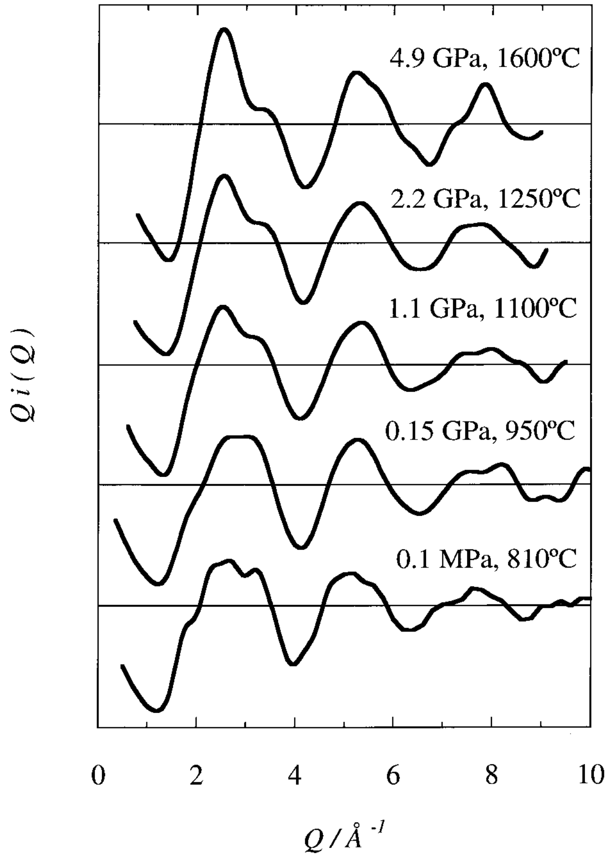

FIGURE 1. The interference function $Qi(Q)$ of molten NaCl at high pressure. $Qi(Q)$ at 0.1 MPa (Ohno and Furukawa 1981) is also shown for comparison.

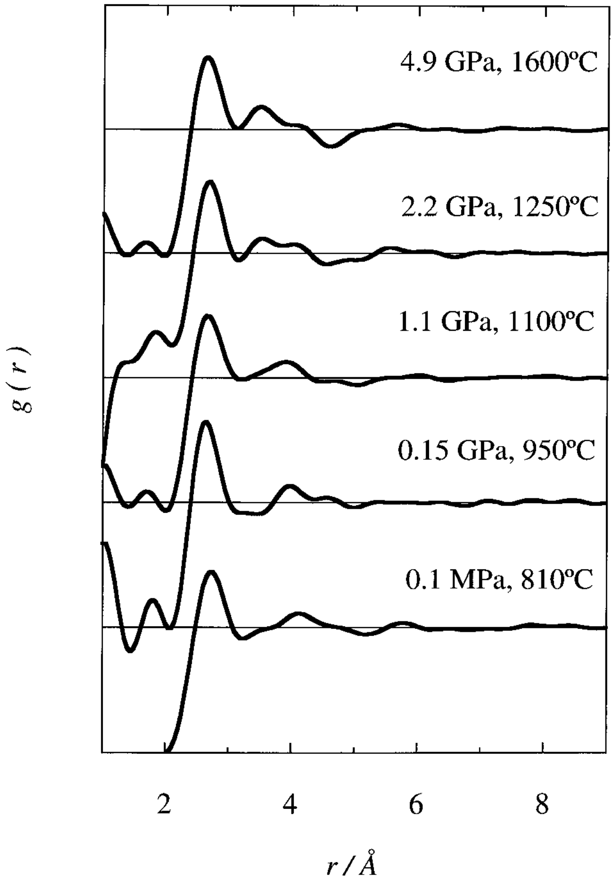

FIGURE 2. The correlation function $g(r)$ for molten NaCl at high pressure. The first peaks at 2.7–2.8 Å and the broad second peaks around 4 Å are obvious. The oscillation of $g(r)$ damps out rapidly and becomes close to unity above 6 Å. The ripples observed on both sides of first peaks are ghost peaks. The plot of $g(r)$ at 0.1 MPa (Ohno and Furukawa 1981) is also shown for comparison.

$S(Q)$ is damped quickly with increasing Q (= $4\pi E\sin\theta/12.398$) and becomes nearly unity above 10 Å^{-1} for an NaCl melt. Thus the energy profile of the incident X-ray must resemble that of the diffracted X-ray from melt at high 2θ. We inferred it from the diffraction profile obtained at $2\theta = 24°$. Using these approximations, the intensity data were corrected for absorption, polarization, and incoherent scattering to deduce the structure factor $S(Q)$ based on the procedure proposed by Tsuji et al. (1989) and Urakawa et al. (1998).

The radial distribution function $D(r)$ and the correlation function $g(r)$ are given by Fourier transformation of $Qi(Q) = Q[S(Q) - 1]$. The density of the NaCl melt used in the derivation of $D(r)$ is unknown at high pressure. We estimated the density of the melt based on the Clausius-Clapeyron relation with the assumption of a constant entropy change at fusion. We used the thermal equation-of-state for crystalline NaCl (Yamamoto et al. 1987) and the melting curve of NaCl (Akella et al. 1969) for calculating the density of the NaCl melt.

RESULTS

The interference function $Qi(Q)$ is shown in Figure 1 and the correlation function $g(r)$ in Figure 2. $Qi(Q)$ and $g(r)$ at 0.1 MPa and 810 °C obtained by the angle dispersive XRD experiment using θ-θ X-ray diffractometer (Ohno and Furukawa 1981) are also shown in Figures 1 and 2, respectively. $Qi(Q)$ and $g(r)$ at 0.15 GPa and 950 °C are very similar to those at 0.1 MPa and 810 °C, indicating not only the structural similarity but also the advantage of our energy dispersive method compared to the angle dispersive method.

The $g(r)$ curve of molten NaCl is characterized by a sharp first peak at about 2.7 Å and a broad second peak around 3.5–4 Å. The first peak denotes the position of the nearest neighbor unlike ion pair Na^+-Cl^-, and the second peak position shows the distance between the like ions, Na^+-Na^+ or Cl^--Cl^-. The $g(r)$ curve becomes unity around 6 Å, which is interpreted as a result of complete charge cancellation (Biggin and Enderby 1982). There are some ghost peaks on both sides of the first peak in $g(r)$, which originate from terminating the Fourier integral at

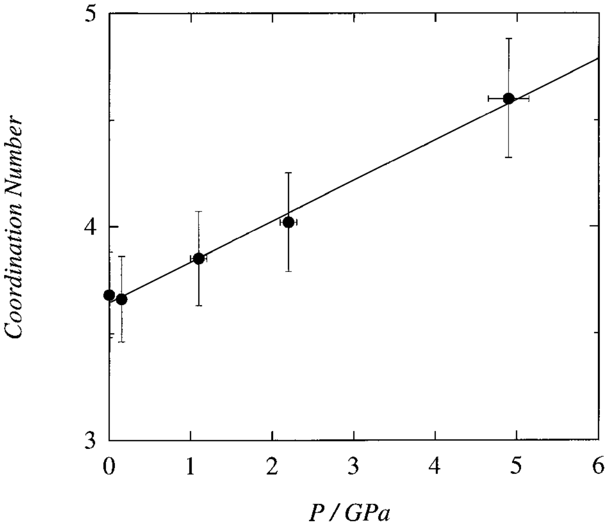

FIGURE 3. The coordination number of nearest neighbor ions, CN, in molten NaCl as a function of pressure. The CN increases linearly with pressure (solid line is for reference only).

Q_{max} (Ohno et al. 1994). These ghost peaks overlap the second peak and make its position unclear.

Near atmospheric pressure, $Qi(Q)$, is characterized by the triplet first peak (Fig. 1), and the $g(r)$ curve shows the first peak at 2.7 Å and the second peak around 4 Å (Fig. 2). The pre-peak at 1.8 Å^{-1} and the subsequent peak at 3.2 Å^{-1} in $Qi(Q)$ are interpreted as a contribution of the second neighbor like-ions pair. With increasing pressure, these subpeaks are depressed and become weaker, whereas the main first peak at 2.5 Å^{-1} becomes sharp and stronger, which indicates movement of the second neighbor ion toward the nearest neighbor. The $g(r)$ curve also shows the second peak closer to the first peak at high pressure than at low pressure (Fig. 2).

The nearest neighbor ionic distance r_1 in NaCl melt is nearly constant as a function of pressure within the present experimental conditions. This phenomenon was also found in the KCl and KBr melts and is understood as the result of the compensation effect between the pressure compression and the thermal expansion (Urakawa et al. 1998). It is of interest that r_1 is very close to the sum of the ionic radii of Na^+ and Cl^- reported by Shannon and Prewitt (1969).

The coordination number of the nearest neighbor ions (CN) in NaCl melt is shown as a function of pressure in Figure 3. The CN was calculated by integrating the first peak in the $D(r)$ curve, and its accuracy depends on the estimation of melt density at high pressure. Our results show that the CN increases linearly with pressure up to 5 GPa.

DISCUSSION

Aspects of the structure of molten NaCl determined by XRD analysis at atmospheric pressure were summarized in Ohno et al. (1994) as follows: (1) the nearest ionic distance r_1 in the liquid is shorter than that in the crystal at the melting point; (2) the first CN in the crystal decreases from 6 to about 4 at fusion; (3) the second peak of $g(r)$ is broad and its position r_2 is located at around $1.5r_1$. Point 2 is confirmed by the partial correlation function $g(r)_{Na\text{-}Cl}$ determined by the neutron diffraction study of Biggin and Enderby (1982). Thus the structure of NaCl melt is loose and the volume increase of 24% that accompanies melting can be explained by the large vacant sites in its local structure.

These prominent features of an NaCl melt are also found at high pressure, whereas some changes by compression are observed. Although the differences of the r_1 and the CN between solid and liquid decrease with increasing pressure, the r_1 and the CN of the melt are still smaller than those of crystal at 5 GPa. The second peak of $g(r)$ shifts toward the first peak with increasing pressure from $1.5r_1$ at 0.1 MPa to $1.4r_1$ at 5 GPa. These shifts imply that the size of vacancies in the NaCl melt decrease with pressure. Thus, NaCl melt is thought to be densified by compression with an increase of the CN and compaction of second-neighbor ions. However, throughout the pressure range up to 5 GPa, the ratio of the second-neighbor to the first-neighbor distances, r_2/r_1, is close to that of B1 structure (1.41). This indicates that the general feature of the local structure of NaCl melt resembles a B1-like structure with many vacant sites.

Urakawa et al. (1998) showed that KCl and KBr melts take on a structure correlated with its crystalline state. KCl and KBr transforms into the B2 structure from the B1 structure at ~2 GPa, and the corresponding structural change is also observed in melts. KCl and KBr melts change from an open B1-like structure to an open B2-like structure. This structural change is accompanied by an increase of the CN and a decrease of r_2/r_1.

NaCl also undergoes a phase transformation into the B2 structure at ~30 GPa and room temperature (Bassett et al. 1968). This transition pressure is one order of magnitude higher than those of potassium halides. The pressure of the present experiments is still in a range of B1 structured-NaCl. When $Qi(Q)$ and $g(r)$ of an NaCl melt at 5 GPa are compared with potassium halides at several hundred MPa, we notice the similarity in their shape. These similarities suggest the possibility that the NaCl melt also transforms into a B2-like structure above 30 GPa.

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