

## Determination of the Phase Boundary Between the B1 and B2 Phases in NaCl by *In Situ* X-ray Diffraction using a New High Pressure Apparatus, SPEED-Mk II, with an Oscillation System

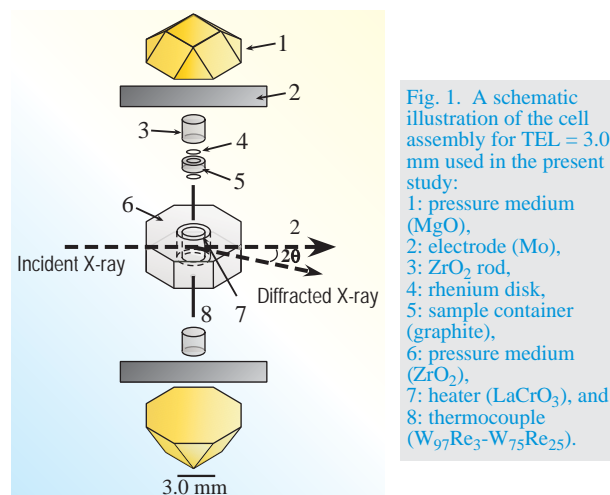
NaCl is one of the simplest and most thoroughly studied ionic crystals. Thus, the physical properties of NaCl such as its phase transformation, compressibility, and thermal expansivity can provide a basic model for understanding the physical properties of more complex ionic crystals. It has been well established that NaCl with a rock salt structure (the B1 phase) transforms into a CsCl structure (the B2 phase) at about 30 GPa and room temperature [1]. However, transition pressures at high temperatures have neither been well established nor well studied experimentally. The accurate location of this phase boundary in P-T space is useful for high-pressure earth science because the B1 phase of NaCl is frequently used as a pressure gauge in *in situ* X-ray diffraction experiments because it is very compressible and its P-V-T equation of state has been well established [2]. Pressure corresponds to depth, which is the most essential variable when physical properties of mantle minerals are studied. However, under P-T conditions above the B1-B2 phase boundary, NaCl is unusable as a pressure gauge because of its transformation to the B2 phase. Thus, this phase boundary sets a limit to the P-T conditions where the B1 phase can be used as a pressure gauge.

To elucidate the phase boundary between B1 and B2 phases of NaCl at high temperatures, we carried out a series of *in situ* X-ray diffraction experiments using a new Kawai-type apparatus, SPEED-Mk II, installed in **BL04B1**. To our knowledge, this is the first Kawai-type apparatus with an oscillation system [3]. It has been reported that grains of the B2 phase grow very fast even at temperatures below 673 K [4]. Thus it has been difficult to obtain a powder X-ray diffraction pattern of the B2 phase particularly at high temperature because of a shortage in the number of grains contributing to the X-ray diffraction pattern. Since the new apparatus, SPEED-Mk II, has a press-oscillation system, the sample under high pressure and temperature conditions can be oscillated during data collection, which increases the number of grains contributing to the diffraction pattern and reduces the effect of grain growth of the sample on the diffraction pattern. Figure 1 shows a schematic illustration of the cell assembly used in the present study. At temperatures above 1100 K, the press was oscillated within the

angular range from  $-4^\circ$  to  $7^\circ$  during data collection.

Figure 2 shows a comparison between a diffraction pattern collected without press oscillation and that collected with press oscillation. These diffraction patterns were collected under the same P-T conditions of 24.7 GPa and 1150 K. In the pattern obtained without press oscillation, only two peaks of the B2 phase, indexed as (111) and (222), were observed; these are minor peaks in the X-ray diffraction patterns obtained in a previous study. In the X-ray diffraction pattern obtained with press-oscillation, we observed an intense peak of B2 phase indexed as (110), which is the most intense peak of B2 phase. Two other diffraction peaks of the B2 phase [those indexed as (111) and (220)] were also observed in this profile. The relative intensities of these peaks are reasonably consistent with those observed in the previous study. According to these results, it is obvious that the press-oscillation system helped us to identify the B2 phase under these P-T conditions, because the most intense peak of this phase was clearly observed in the diffraction pattern obtained with press oscillation, whereas this peak was not observed in the diffraction pattern obtained without press oscillation.

A summary of the experimental results is shown in Fig. 3. At temperatures below 1500 K, the B1 to B2 (forward) and B2 to B1 (backward) transitions were observed; above this temperature, we observed complete transitions from one phase to the other, which



placed some restrictions on the phase boundary. The equilibrium phase boundary determined in the present study is represented by a dashed line, and is given by  $P(\text{GPa}) = 30.6 - 0.0053 T (\text{K})$ . At the highest temperature of 2100 K and at a pressure of about 20 GPa, no diffraction peaks of either the B1 or the B2 phase were observed. Thus, we concluded that NaCl melted under these P-T conditions. Taking all the experimental data obtained in the present study into consideration, the triple point between B1, B2, and liquid NaCl would be located at a pressure of about  $19.7 \pm 0.5 \text{ GPa}$  and a temperature of about  $2050 \pm 50 \text{ K}$ .

According to the results of the present study, the B1 phase of NaCl cannot be used as a pressure gauge under P-T conditions corresponding to those at the bottom of the mantle transition zone and the lower mantle. Thus, we have to use other pressure gauges for *in situ* X-ray diffraction experiments to study properties of lower mantle minerals. MgO can be the

best pressure gauge under lower mantle conditions because of its wide stability field. Many studies including those using MD simulations have been performed to establish the P-V-T equation of state of MgO [5].

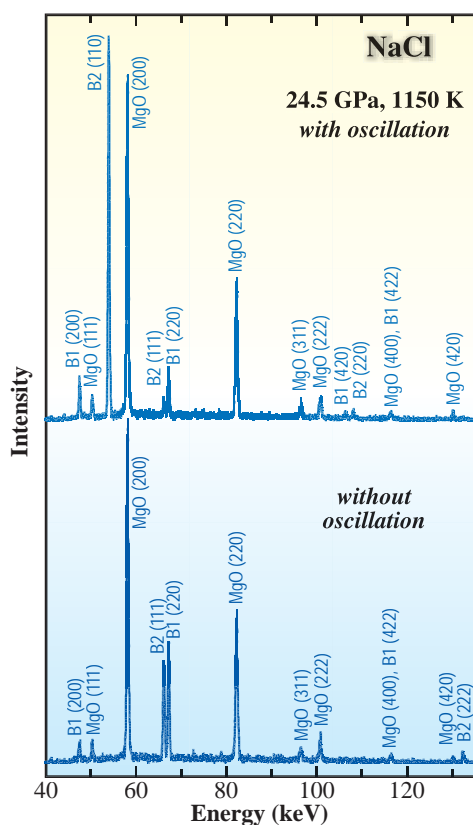


Fig. 2. Comparison between a diffraction pattern collected without press oscillation and that collected with press oscillation. These diffraction patterns were collected under the same P-T conditions of 24.7 GPa and 1150 K using the energy dispersive method with a fixed angle of approximately 6 degrees. The most intense peak of the B2 phase indexed as (110) was observed in the diffraction pattern obtained with press oscillation, whereas this peak was not observed in that obtained without press oscillation. The press oscillation dramatically reduces the effect of NaCl grain growth at high temperature on diffraction patterns obtained using the energy-dispersive method.

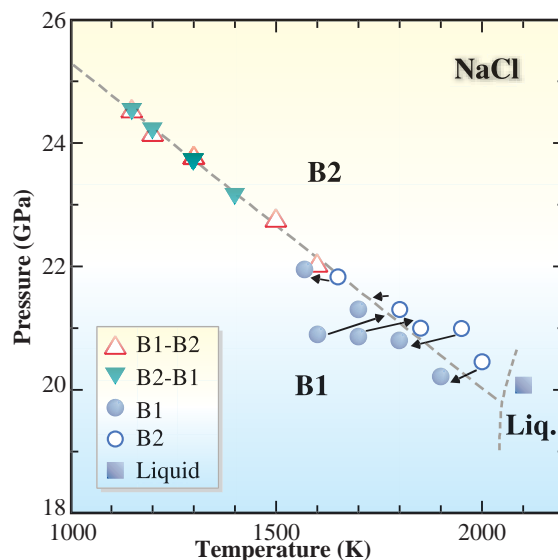


Fig. 3. The equilibrium phase boundary between the B1 and B2 phases in NaCl determined in the present study (dashed line between the B1 and B2 phases). Open and closed triangles represent P-T conditions where the B1 to B2 (forward) and B2 to B1 (backward) transitions were observed, respectively. Open and closed circles represent P-T conditions where single phases of B1 and B2 were observed, respectively. Under P-T conditions of 20.1 GPa and 2100 K, liquid NaCl was observed (a solid square). Upward and downward arrows represent complete transitions from B1 to B2 and those from B2 to B1, respectively. According to the present experimental results, the triple point between B1, B2, and liquid NaCl would be located at a pressure of  $19.7 \pm 0.5 \text{ GPa}$  and at a temperature of  $2050 \pm 50 \text{ K}$ .

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