The Pressure-Volume Equation of State of the High-Pressure B2 Phase of NaCl

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Introduction

The structure of NaCl transforms from the rock salt structure (B1 phase) into the CsCl structure (B2 phase) at about 30 GPa.[1,2] The equation of state (EOS) of the NaCl-B1 phase has been well studied for its importance as one of simplest ionic crystals and a commonly used pressure calibrant at pressures below 30 GPa. Detailed information on the NaCl-B2 phase would be useful in extending the useable pressure range of the calibrant, however, such data are limited.[3-5] We performed high-pressure experiments to measure the volume-pressure relations of the NaCl-B2 phase up to 68 GPa with the use of the diamond anvil cell (DAC) and laser heated annealing techniques at GeoSoilEnviroCARS (sector 13).

Experiment

A diamond anvil cell, with cullet size of 300 µm, was used to generate high-pressure conditions. The rhenium gasket was pre-indented to 30 µm in thickness and a hole of 120 µm was drilled to form a sample chamber. Four disks of powdered samples (NaCl, 2 Pt+MgO mixtures and NaCl) were placed in the sample chamber. To avoid any moisture, the whole assembly was put in a vacuum furnace at 120°C before pressure was applied. Our experimental procedure was as follows: increase pressure at room temperature to a desired point; obtain x-ray diffraction patterns before and after laser annealing; increase pressure to the next level and repeat until the anvil failed at 68 GPa. The YLF lasers in 13-ID-D were used for annealing. The laser heating spot size at the sample position was about 20 µm in diameter. A 45-µm-square area at the central position was scanned by the heating laser for a total time of about 3 minutes for each annealing. Annealing at a temperature around 1200K helps to release sample stress. No clear crystal growth was observed by keeping the temperature below 1200K. We used monochromatic x-rays (0.4246 Å) with a CCD detector (Bruker-2k) for diffraction measurements in 13-BM-D. CCD exposure time was 5 minutes.

Results

Strong 111, 200 peaks of Pt (denoted Pt 111 and Pt 200), 110 peak of the B2 phase of NaCl (NaCl-B2 110) and 200 peak of MgO (MgO 200) were observed in the diffraction patterns. Weak NaCl-B2 100, MgO 111 peaks were also observed. Pressure was obtained from lattice parameters of Pt[6] and MgO[7] and denoted as P_{Pt} and P_{MgO}, respectively. MgO 111 and NaCl-B2 100 peaks were used only for estimating errors due to the weakness in intensity. The unit cell volume was determined from NaCl-B2 110 (V_{B2}). Figure 1 shows both P_{Pt} and P_{MgO} after annealing plotted against V_{B2} together with literature data (DAC experiments[3,4] and pseudo-potential calculation[8]).

Discussion

We found that it was difficult to fit our data with the Birch-Murnaghan EOS,[9] because of the lack of the zero pressure volume of the B2 phase. The universal EOS[10] is widely accepted for large compressible solids. Although this EOS contains the zero-pressure volume term, it is not as critical as treated with the Birch-Murnaghan EOS. We assumed a zero pressure volume V_0 and then minimized the residual between the observed and calculated data. When we used P_{Pt} , the residual decreases as V_0 increased to infinity. We modified the universal EOS in order to adopt the infinite zero pressure volume.

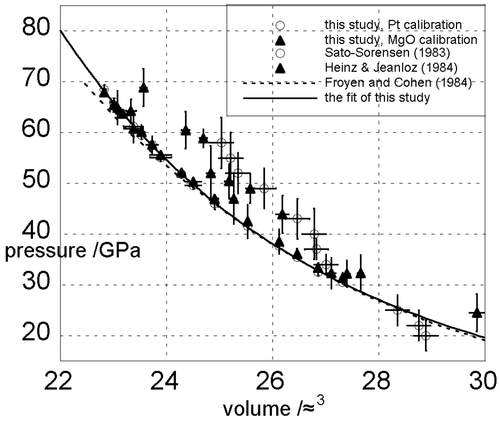

FIG. 1. Volume-pressure relation of the B2 phase. Solid circles and triangles are our observations. Open circles and triangles are reported experimental observations.[3,4] Dashed line is the psuedo-potential calculation.[8] Solid line is the fit with the modified universal EOS (eq. 1) with V_r=27.17 Å^3: P_r =31.14(13) GPa, and K_r = 143.5(6) GP.

$$P = P_r \cdot \left(\frac{V}{V_r}\right)^{-2/3} \times \exp\left\{-\left(\frac{3K_r}{P_r} - 2\right)\left[\left(\frac{V}{V_r}\right)^{1/3} - 1\right]\right\} \qquad (1)$$

P(V) is obtained from the pressure P_r and the bulk modulus K_r at the reference volume V_r. The free energy does not depend on the value of the reference volume V_r. As a result, we obtain the same *V* - *P* relation from any reference volume even if the parameters are different. We assumed a reference volume of V_r =27.17 Å^3, which is the value reported by Bassett et al.[1] as the volume of the NaCl-B2 phase at the B1-B2 transition point. In this case, P_r and K_r correspond to the pressure and bulk modulus at the transition point. The fitting results were P_r = 31.14 (14) GPa, K_r = 143.5 (6) GPa using the data of P_{Pt} and P_r = 32.15 (13) GPa, K_r =141.0 (6) using the data of P_{MgO} .

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