Journal of
Synchrotron Radiation

ISSN 0909-0495

Received 20 March 2009
Accepted 31 August 2009

Stress measurement under high pressure using Kawai-type multi-anvil apparatus combined with synchrotron radiation

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A system for stress measurement under high pressure has been developed at beamline BL04B1, SPring-8, Japan. A Kawai-type multi-anvil apparatus, SPEED-1500, was used to pressurize polycrystalline KCl to 9.9 GPa in a mechanically anisotropic cell assembly with the KCl sample sandwiched between dense Al_2O_3 pistons. The variation of deviatoric stress was determined from the lattice distortion measured using two-dimensional X-ray diffraction with monochromatic synchrotron X-rays. The low-pressure B1 phase transformed to the high-pressure polymorph B2 during compression. The deviatoric stress increased with increasing pressure in both the B1 and B2 phases except for the two-phase-coexisting region at a pressure of 2–3 GPa. This new system provides one of the technical foundations for conducting precise rheological measurements at conditions of the Earth's lower mantle.

Keywords: stress measurement; two-dimensional X-ray diffraction; high pressure; KCl; phase transition.

1. Introduction

Rheological properties of minerals are important parameters for understanding the Earth's dynamics. As physical conditions in the Earth's interior are extreme [including pressures (P) and temperatures (T) up to P = 360 GPa and $T = \sim$5000–8000 K, respectively, at the Earth's centre], experimental studies at high pressure are required to investigate the rheology of deep Earth. Several deformation mechanisms are considered to be active in the Earth's interior (*e.g.* dislocation creep, diffusion creep), and rheology (viscosity) relies on stress quite differently depending on active deformation mechanisms (Frost & Ashby, 1982; Karato, 2008). The characterization of stress has fundamental importance in experimental studies on rheological properties.

The analytical method developed by Weidner *et al.* (1998) determines the microscopic stress in powder samples by deconvoluting X-ray diffraction peak broadening at pressures up to 20 GPa. However, the nature of deformation at grain contacts is highly complicated and its relevance of derived stress to deep Earth rheology is questionable. On the other hand, stress measurements based on the orientation dependence of lattice strain have been performed using the following high-pressure apparatus: diamond-anvil cell (DAC) (*e.g.* Duffy *et al.*, 1995; Merkel *et al.*, 2002), deformation-DIA apparatus (D-DIA) (*e.g.* Li *et al.*, 2006; Nishiyama *et al.*, 2007), Kawai-type apparatus (*e.g.* Chen *et al.*, 2004; Li *et al.*, 2004*a*) and rotational Drickamer apparatus (RDA) (*e.g.* Nishihara *et al.*, 2008; Kawazoe *et al.*, 2009). In this technique, the lattice strain is measured using X-ray diffraction data collected at different azimuth angles with respect to stress direction. The measured stress can be adequately compared with macroscopic traditional stress measurements.

Among the different high-pressure apparatus, the Kawai-type multi-anvil benefits from the advantage of the generation of well controlled high-pressure and high-temperature conditions. The DAC enables very high pressure conditions of greater than 300 GPa, but a homogeneous and stable heating of the samples is difficult to achieve owing to small (and thin) sample sizes. Even though the situation is better for RDA than for the DAC, the thin sample and the thin pressure medium in the RDA make homogeneous heating difficult too. In addition, pressure is generally limited to <10 GPa in experiments using single-stage multi-anvil apparatus, such as DIA and D-DIA apparatus, which is insufficient for studying the material behavior at the Earth's lower mantle (>23 GPa). Chen *et al.* (2004) established a high-pressure stress measurement system using the Kawai-type apparatus with synchrotron white X-rays

based on the orientation dependence of the lattice distortion. The guide-block system used in their system is less suitable for generating very high pressures of >20 GPa owing to the low symmetry of the guide-block system [(111) type] compared with that of the DIA-type guide-block system [(100) type]. Therefore, the development of a technique for stress measurements using the Kawai-type apparatus with a DIA-type guide-block is highly desirable.

In this study, we have developed a system for stress measurements under high pressure at beamline BL04B1, SPring-8, Japan. In the new system, the sample is pressurized with a Kawai-type multi-anvil apparatus, SPEED-1500, which has a DIA-type guide-block system, and the stress is determined from the lattice distortion measured using two-dimensional X-ray diffraction with monochromatic synchrotron X-rays. As the maximum pressure in a Kawai-type apparatus with a DIA-type guide-bock is ∼30 GPa using conventional WC second-stage anvils (*e.g.* Katsura *et al.*, 2009) and ∼80 GPa using sintered diamond second-stage anvils (Tange *et al.*, 2008), the new system provides one of the technical foundations for conducting precise rheological measurements at lower mantle conditions (P > 23 GPa).

We conducted stress measurements of polycrystalline KCl at room temperature to examine the capacity of the new system. In this article, we report specifications of the new high-pressure stress measurement system and first results from the test experiments.

2. Experimental procedures

2.1. High-pressure stress measurement system

In situ stress measurements under high pressure and high temperature were conducted using a Kawai-type multi-anvil apparatus, SPEED-1500, at the bending-magnet beamline BL04B1 at SPring-8, Japan (Utsumi *et al.*, 1998), in conjunction with a two-dimensional X-ray diffraction system. A schematic illustration of the high-pressure stress measurement system is shown in Fig. 1. The white X-rays from a bending-magnet source were monochromated by a water-cooled Si (111) monochromator which is installed in the same hutch as the SPEED-1500 and is capable of selecting monochromatic energies up to ∼50 keV. In this study, X-ray diffraction was carried out using X-rays of energy 50 keV. The monochromatic X-ray beam was collimated to 200 µm × 200 µm by horizontal and vertical slits (Fig. 1). Two-dimensional diffraction patterns were recorded using an imaging plate (FUJI, 200 mm × 250 mm) placed at a distance of 520 mm from the sample. The two first-stage anvils at the detector side have conical bores to provide a pathway for diffracted X-rays (Fig. 1). The observable maximum diffraction angle 2θ using the present system is 10°.

2.2. Sample assembly

An octahedral Cr_2O_3-doped MgO pressure medium with 10 mm edge length was compressed by six WC and two cubic BN (cBN) anvils with a 5 mm truncated edge length. The two

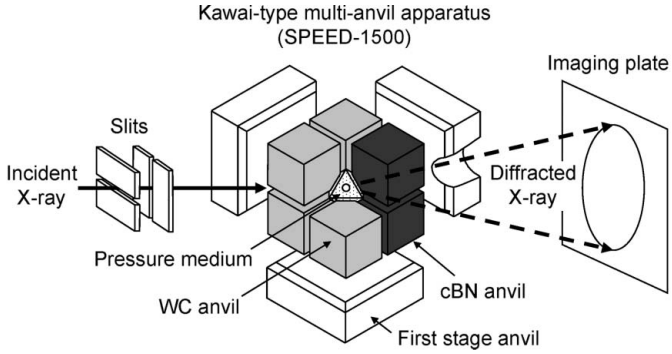

Figure 1
Schematic illustration of the system of two-dimensional X-ray diffraction at high pressure and high temperature at BL04B1, SPring-8. The sample is packed within an octahedral pressure medium which is placed at the centre of eight cubic anvils. Monochromatic synchrotron X-rays irradiate the sample through the gap in the WC anvils. Diffracted X-rays pass through cBN anvils. The conical holes carved in the first-stage anvils enable the diffracted X-rays to reach the two-dimensional detector (imaging plate).

cBN anvils were used as windows for diffracted X-rays because cBN is transparent to high-energy X-rays. The size of the cubic second-stage anvils (14 × 14 × 14 mm) used in this study is smaller than those of the standard size in SPEED-1500 (26 × 26 × 26 mm). Therefore, six additional first-stage anvils (thickness 12 mm, truncation edge length 27 mm) were used to fill the gaps behind the second-stage anvils.

The materials along the X-ray path were replaced by a mixture of amorphous B and epoxy resin to avoid diffraction from gaskets and pressure medium and to maximize the intensity of the diffracted X-rays. Details of the B + epoxy parts are shown in Fig. 2(*a*). Because deformation of the sample is not controllable in the present system, high deviatoric stress was applied to the sample by uniform compression of the mechanically anisotropic cell assembly. Fig. 2(*b*) shows the design of the cell assembly in the octahedral pressure medium used for the experiment. A polycrystalline KCl rod (diameter 2.1 mm, height 1.5 mm) formed by cold-press was used as the sample. This sample was inserted between dense Al_2O_3 pistons to yield high stress by compression of the pressure medium. The crushable Al_2O_3 with porosity of ∼50% was used to optimize the magnitude of deformation.

2.3. X-ray diffraction

The typical exposure time for obtaining X-ray diffraction patterns using an imaging plate was 20 min. The imaging-plate data were transferred off-line and were digitized using a FUJI BAS2000 reader using a resolution of 100 µm × 100 µm. Fig. 3 shows representative diffraction patterns. The program *PIP* (*Powder Pattern Analyzer for an Imaging Plate*) developed for DAC imaging-plate systems (Fujihisa & Aoki, 1998) was used for the data analysis.

The energy of the monochromatic X-rays (E) was calibrated using a Ge solid-state detector (SSD). Monochromatic X-rays were diffracted by CeO_2 powder (diameter 0.3 mm) to reduce the X-ray flux received by the SSD. The sample-to-detector (imaging-plate) distance (L) was calibrated using diffraction

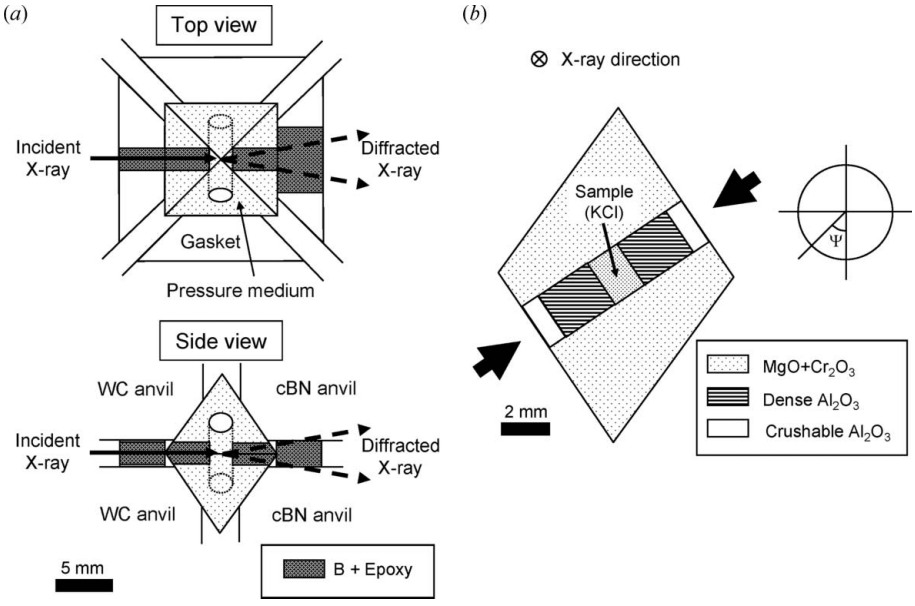

Figure 2
Schematic illustrations of the cell assembly. (*a*) Illustration of the X-ray path in the pressure medium and in the gaskets. Materials along the X-ray path are replaced by a mixture of amorphous boron and epoxy resin to avoid diffraction from materials other than the sample and to maximize the intensity of the diffracted X-rays. (*b*) Cross section of the cell assemblies. Large arrows show the compression direction in this assembly ($\Psi = 54.7^\circ$).

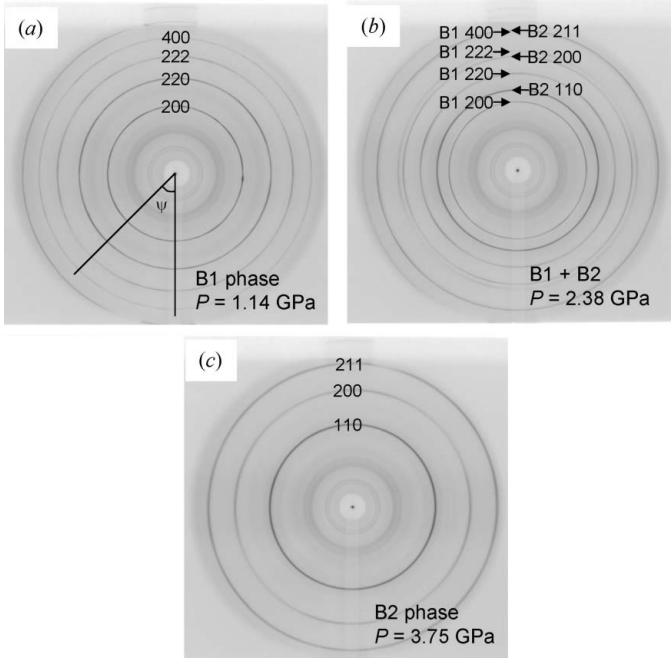

Figure 3
Two-dimensional X-ray diffraction patterns of KCl: (*a*) at $P = 1.1$ GPa (B1 phase), (*b*) at 2.4 GPa (coexisting B1 and B2 phases) and (*c*) at 3.8 GPa (B2 phase).

of a CeO_2 standard. One of the most common calibration methods of E and L is the so-called 'double-cassette method' (*e.g.* Ono *et al.*, 2006). In this method, E and L are determined simultaneously from the diffractions of a standard material recorded at two different sample-to-detector distances, L and $L + \Delta L$ (ΔL is a known distance). In this study, because E was determined with high precision (± 0.01 keV) using the SSD independent of L, calibration of L was highly reliable compared with that by the double-cassette method. The diffraction peaks of (200), (220) and (222) of the B1 phase of KCl and (110), (200) and (211) of the B2 phase were used to determine stress and pressure.

2.4. Stress analysis

Stress within the KCl sample was determined from the two-dimensional diffraction patterns of the sample based on the orientation dependence of the lattice strain. The two-dimensional diffraction patterns recorded on the imaging-plate were subdivided into 16 equal angular sectors of 22.5° of azimuth angle Ψ (Figs. 2 and 3). Each sector was integrated and d-spacings were determined by fitting each integrated pattern. This procedure yields a set of 16 d–Ψ data at each pressure condition. Stress was calculated by fitting the following equation of Singh (1993) to the d–Ψ data set,

$$d_{hkl}(\Psi) = d^0_{hkl}\left[1 + \left(1 + 3\cos^2\chi\right)\frac{t}{6\langle G_{hkl}\rangle}\right], \qquad (1)$$

where $\cos\chi = \cos\theta\cos(\Psi - \Psi_{\max})$, $d_{hkl}(\psi)$ is the observed d-spacing as a function of angle Ψ, d^0_{hkl} is the d-spacing corresponding to the hydrostatic pressure, t is the deviatoric stress, $\langle G_{hkl}\rangle$ is the effective shear modulus for a given Miller index hkl at the corresponding P–T condition, χ is the angle between the diffracting plane normal and the maximum principal stress direction, θ is the diffraction angle, Ψ is the azimuth angle on the detector, and $\Psi_{\max}$ is the Ψ angle at which $d_{hkl}(\psi)$ is minimum (corresponding to the maximum principal stress direction). $\langle G_{hkl}\rangle$ was calculated from the elastic constants of KCl at high pressure (Haddadi *et al.*, 2008) for both the B1 and B2 phases using equations described by Singh *et al.* (1998) with the assumption of uniform stress conditions. A more detailed description of the equation is given elsewhere (*e.g.* Singh *et al.*, 1998; Merkel *et al.*, 2002). Pressure was determined from the unit-cell volume, which in turn was calculated from the d^0_{hkl} values and the equation of state of KCl (Walker *et al.*, 2002).

3. Results and discussion

Diffraction patterns of the sample were recorded at 12 different pressure conditions during compression up to $P = 9.9$ GPa at room temperature. As shown in Fig. 3, the Debye–Scherrer rings from the sample were observed very clearly. The low-pressure B1 phase transformed to the high-pressure B2 phase during compression. Coexistence of both

phases was observed at P = 2.3 and 2.4 GPa. The transition pressure is fairly consistent with that determined by Vaidya & Kennedy (1971): P = 1.9 ± 0.2 GPa. The small difference between the determined transition pressures is presumably related to reaction kinetics. The volume reduction by the B1–B2 phase transformation (∼12%; Walker *et al.*, 2002) caused pressure generation to be less efficient at the pressure range of the two-phase coexistence.

Significant lattice distortion was observed during the compression by two-dimensional X-ray diffraction. Figs. 4 and 5 show variations of the normalized d-spacing (d/d_0, where d_0 is the d^0_{hkl} value in the lowest pressure data for each phase) of the B1 and B2 phases, respectively, as a function of Ψ angle. The minimum d/d_0 value was observed at close to the compression direction (Ψ = 54.7°) of the cell assembly (Fig. 2*b*) and the maximum occurred close to the dilatation direction (144.7°). Lattice distortion increases with increasing pressure in both B1 and B2 phases except at P = ∼2–3 GPa where the two phases coexist owing to the phase transition. The magnitude of the lattice distortion in both phases was significantly different depending on the diffraction planes (as shown in Figs. 4 and 5). For the B1 phase, the lattice distortion of the (220) and (222) planes is much larger than that of the (200) plane. For the B2 phase, the lattice distortion of the (200) plane is much larger than that of the (110) and (211) planes. These lattice plane dependences of the lattice distortion are considered to be primarily due to stress heterogeneity in the sample and partly due to elastic anisotropy.

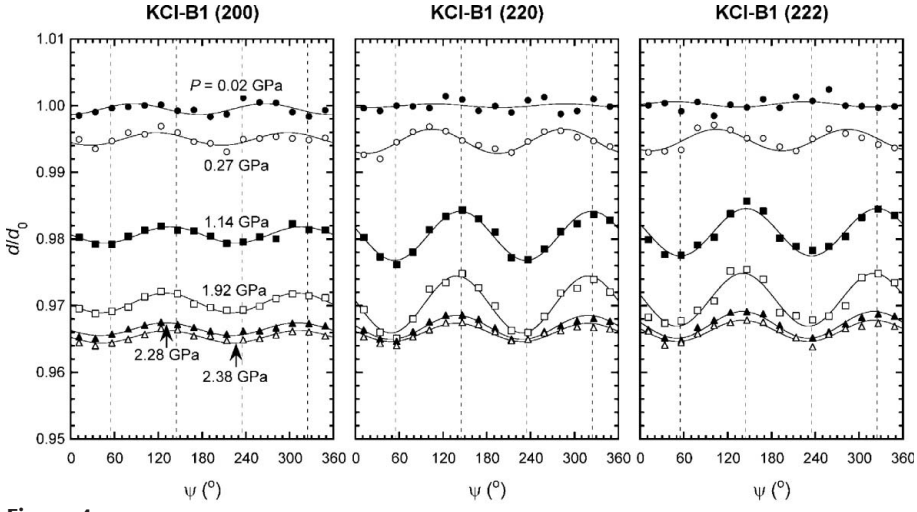

Figure 4
Variation of the normalized d-spacing (d/d_0) of the B1 phase of KCl as a function of Ψ angle upon compression. Lattice distortion increases with increasing pressure for each diffraction plane at lower pressures (P < 2 GPa) and the lattice distortion of the (220) and (222) planes is much larger than that of the (200) plane. Curves are fits of equation (1).

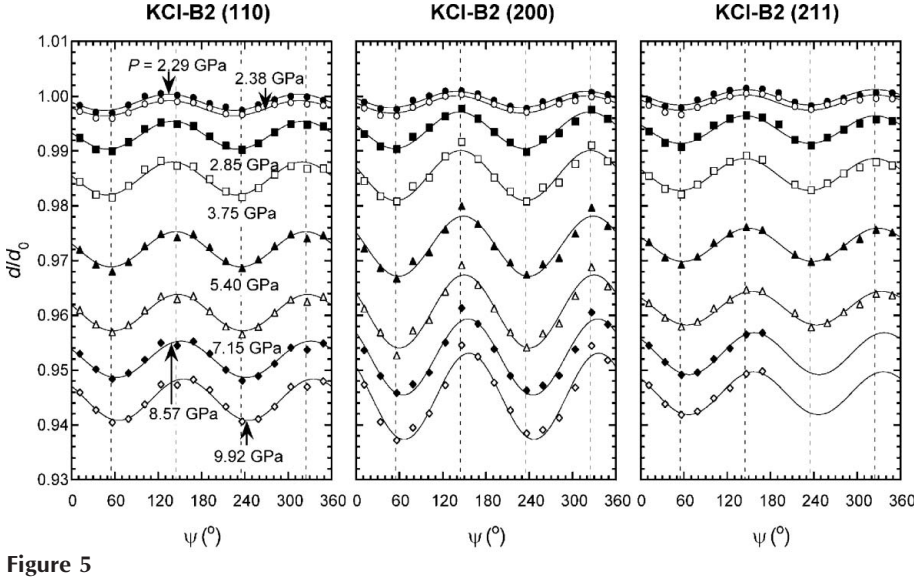

Figure 5
Variation of the normalized d-spacing (d/d_0) of the B2 phase of KCl as a function of Ψ angle upon compression. Lattice distortion increases with increasing pressure for each diffraction plane and the lattice distortion of the (200) planes is much larger than that of the (110) and (211) planes. Curves are fits of equation (1).

Fig. 6 shows variations of deviatoric stress in KCl up to P = 9.9 GPa. The deviatoric stress increased with increasing pressure in both B1 and B2 phases except for the two-phase-coexisting region at P = ∼2–3 GPa. This low stress in the two-phase region is considered to be due to a large volume reduction (∼12%) associated with the B1–B2 phase transition. The difference in the deviatoric stress between diffractions was more significant in the B2 than in the B1 phase within the experimental conditions of this study. Further analyses based on elastic plastic self-consistent (EPSC) models are needed to understand more accurately the macroscopic stress applied to the bulk sample (*e.g.* Li *et al.*, 2004*b*; Burnley & Zhang, 2008). This issue is beyond the scope of this study.

Bridgman (1937) determined the shear strength of KCl at pressures of 1–5 GPa in a series of torsion experiments using thin discs on 250 inorganic materials. For comparison with this study, Bridgman's (1937) data of shear stress (σ_S) were converted to equivalent stress (σ_E) using the equation $\sigma_E = (\sqrt{3}/2)\sigma_S$ and plotted in Fig. 6. Although the strain rate of the sample in this study is not known, the strain rate of the KCl of Bridgman (1937) is considered to be significantly higher than that in this study. Thus the stress values are expected to be higher for Bridgman (1937). However, Bridgman's (1937)

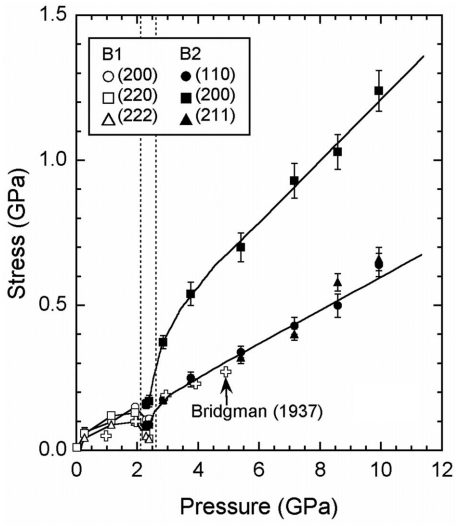

Figure 6
Variation of the deviatoric stress in KCl upon compression to P = 9.9 GPa. The deviatoric stress increases with increasing pressure in both the B1 and B2 phases except for at $P = \sim$2–3 GPa where the two phases coexist owing to pressure-induced phase transition. Coexistence of the B1 and B2 phases was observed at the pressure range between the two dotted lines. Solid lines are guides for the eye.

results are close to the lowest stress values among three diffractions determined in this study for both B1 and B2 phases. One of the possible reasons for the inconsistency is inaccuracy in stress measurements by Bridgman (1937) owing to a radial stress gradient in the sample.

4. Concluding remarks

In this study we have established a technique for high-pressure stress measurement using a Kawai-type multi-anvil apparatus with a DIA-type guide-bock and two-dimensional X-ray diffraction with monochromatic synchrotron X-rays at beamline BL04B1, SPring-8. Through the high-pressure measurements of KCl, we confirm that the capacity of the stress measurement is sufficient for quantitative rheological measurements. Although pressure and temperature conditions in this study were limited to 10 GPa and room temperature, similar measurements are potentially possible up to 80 GPa and $\sim$2000 K using smaller cell assemblies, resistive heaters and sintered diamond second-stage anvils (*e.g.* Tange *et al.*, 2008). This new system provides one of the technical foundations for conducting precise rheological measurements at conditions of the Earth's lower mantle (P > 23 GPa).

In the present system, deformation of the sample is not controllable. The stress can only be generated by cold compression of a mechanically anisotropic cell assembly (or by thermal stress through heating), and achievement of steady-state deformation is difficult. These limitations can be severe for quantitative rheological experiments. Therefore, in order to investigate deep Earth rheology, it is desirable to use high-pressure deformation apparatus such as Kawai-type multi-anvil apparatus with mechanisms of deformation (Nishihara, 2008).

The X-ray diffraction experiments were performed using the SPEED-1500 system at BL04B1, SPring-8 (proposal Nos. 2007B1246, 2008A1180). We thank Layachi Louail for providing the numerical data of elastic constants of KCl reported by Haddadi *et al.* (2008), and Dirk Spengler for reading the manuscript. We also thank two anonymous reviewers for constructive reviews. This work was supported by a Grant-in-Aid for Young Scientists (B) (No. 20740307) to YN, and the 21st Century COE Program and Global COE Program of the Japan Society of the Promotion of Science.

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