PHYSICAL REVIEW B **78**, 224106 (2008)

Thermal equation of state of rhenium diboride by high pressure-temperature synchrotron x-ray studies

Yuejian Wang,[*] Jianzhong Zhang, Luke L. Daemen, Zhijun Lin, and Yusheng Zhao[†]
LANSCE Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

Liping Wang
Mineral Physics Institute, State University of New York, Stony Brook, New York 11794, USA

(Received 10 September 2008; published 16 December 2008)

The unit-cell volume of rhenium diboride (ReB_2) has been measured by synchrotron x-ray diffraction at pressures and temperatures of up to 7.5 GPa and 1100 K with a cubic anvil apparatus. From the pressure (P)-volume (V)-temperature (T) measurements, thermoelastic parameters were derived for ReB_2 based on a modified high-T Birch-Murnaghan equation of state and a thermal-pressure approach. With the pressure derivative of the bulk modulus, K_0', fixed at 4.0, we obtain: the ambient bulk modulus $K_0=334(23)$ GPa, temperature derivative of bulk modulus at constant pressure $(\partial K/\partial T)_P=-0.064(6)$ GPa K^{-1}, volumetric thermal expansivity $\alpha_T(\mathrm{K}^{-1})=a+bT$ with $a=1.33(25)\times 10^{-5}$ K^{-1} and $b=1.48(64)\times 10^{-8}$ K^{-2}, pressure derivative of thermal expansion $(\partial\alpha/\partial P)_T=-5.76(95)\times 10^{-7}$ GPa^{-1} K^{-1}, and temperature derivative of bulk modulus at constant volume $(\partial K/\partial T)_V=-0.049(11)$ GPa K^{-1}. The ambient bulk modulus derived from this work is comparable to previous experimental and theoretical results. These results, including the ambient bulk modulus and other thermoelastic parameters determined in present study, extend our knowledge of the fundamental thermophysical properties on ReB_2 and are important to the development of theoretical and computational modelings of hard materials.

DOI: 10.1103/PhysRevB.78.224106 PACS number(s): 62.50.−p, 64.30.−t, 61.05.cp

I. INTRODUCTION

Materials with three-dimensional covalent-bonded networks of light elements, including boron, carbon, nitrogen, and oxygen, are generally expected to exhibit simultaneously low compressibility, good thermodynamic and chemical stabilities, large hardness, and high wear resistance.[1–4] Typically, these materials (e.g., diamond, cubic boron nitride, and BC_2N) have been synthesized at high pressure.[2–4] This places severe limitations on the production volume and the cycle rate of the apparatus and hence presents disadvantages in large scale industrial manufacturing.

An alternative path to the development of ultrahard materials is to make use of high electron densities in noble metals in combination with the short and strong covalent bonds normally formed by B, N, and O. This approach restricts the creation and propagation of defects, which would in turn lead to higher resistance to plastic deformation.[5] As a result a number of noble-metal borides, nitrides, and oxides have been investigated by optimizing the valence-electron density in metals and bonding properties of light elements.[6–9] Recently much theoretical and experimental attention has been focused on the synthesis and characterization of rhenium diboride, ReB_2, at ambient pressure.[10–14]

Thermoelastic properties are of fundamental importance to understand the mechanical properties of materials. Though there is no direct correlation between the elastic bulk modulus and a material's hardness, superhard materials usually have a high bulk modulus, e.g., diamond with $K_0=442$ GPa and c-BN with $K_0=400$ GPa. In the case of ReB_2, previous studies reported a value of 360 GPa for the bulk modulus, suggesting that ReB_2 is potentially a superhard material.[10] However all previous theoretical and experi-

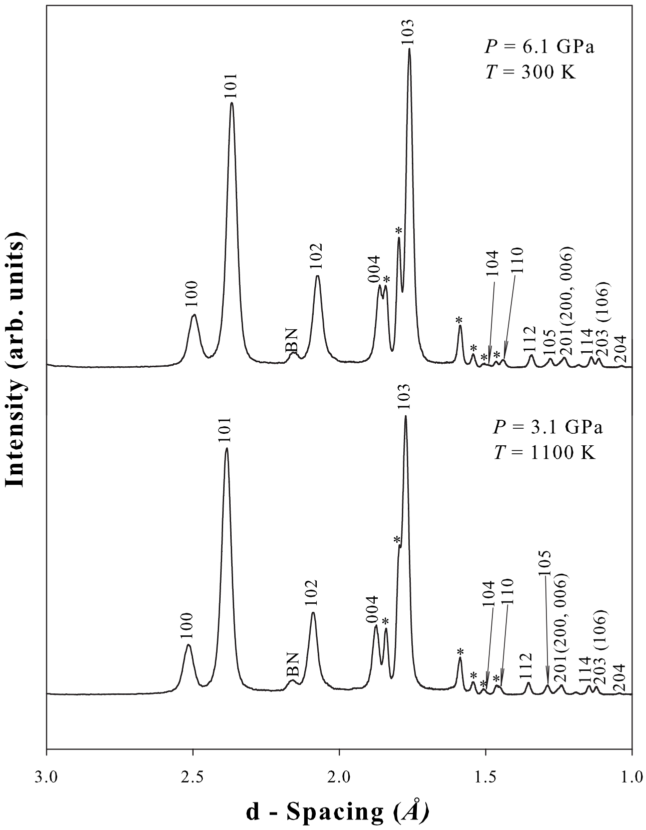

FIG. 1. Representative x-ray diffraction patterns used for the refinement of unit-cell parameters of ReB_2 under high P-T conditions. The peaks marked with stars are fluorescence lines of Re. The BN peaks were observed because of the BN cylinder surrounding the sample.

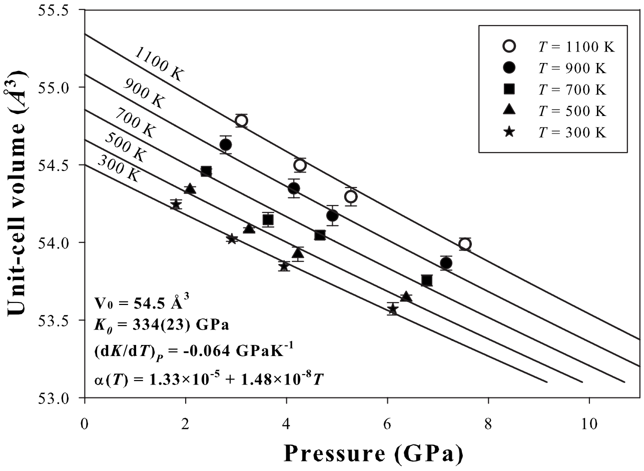

FIG. 2. P-V-T data measured for ReB_2. The curves represent results of the least-squares fitting using Eq. (1). The ambient unit-cell volume (V_0) determined from the P-V-T fit is in good agreement with the reported value in the JCPDS file 00-011-0581 (Ref. 15).

mental investigations were conducted without concerning the temperature dependence of compressibility. This dependence is embedded in the thermoelastic equation of state (EOS), which describes the relationship between pressure, volume, and temperature (P-V-T). The EOS gives access to temperature-dependent properties such as the temperature derivative of the bulk modulus and the pressure derivative of thermal expansion, which are very important to understand better correlations between crystal structure and mechanical behavior, as well as to benchmark theoretical and computational modelings.

In the present study, we performed an *in situ* high P-T x-ray diffraction experiment to investigate the thermoelastic properties of ReB_2. Thermal EOS parameters, such as bulk modulus, temperature derivative of the bulk modulus, volumetric thermal expansion, and pressure derivative of thermal expansion, were derived by fitting the P-V-T data sets to a modified high-temperature Birch-Murnaghan EOS. A thermal-pressure approach was also used to produce the temperature derivative of the bulk modulus at constant volume—a thermoelastic parameter that is experimentally difficult to measure. From these analyses an internally consistent thermal equation of state is obtained for ReB_2.

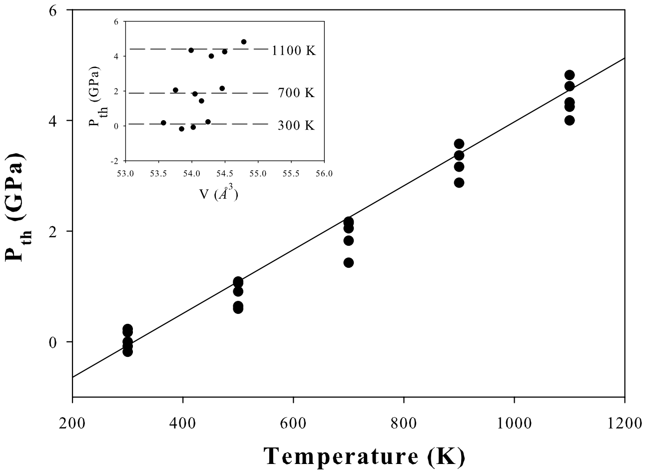

FIG. 3. Thermal pressure (P_{th}) of ReB_2 as a function of temperature. The spread of the data points at any given temperature corresponding to thermal pressures at different volumes, which is plotted in detail in the inset. The dashed lines in the inset plot show approximate constant values of thermal pressure for a given temperature, indicating that thermal pressure is independent of volume for ReB_2. The scattering of the data points at room temperature is representative of the uncertainties in thermal-pressure calculations from the present P-V-T measurements.

II. SAMPLE PREPARATION AND HIGH-PRESSURE EXPERIMENTAL METHOD

At ambient conditions, ReB_2 has a primitive hexagonal structure (space group $P6_3/mmc$, No. 194) with two ReB_2 units per unit cell. This structure can be depicted in terms of alternative layers of rhenium (Re) and boron (B) atoms.[15] The starting ReB_2 powders were synthesized by using the methodologies published in Ref. 10. The mixture of Re and amorphous B powders with molar ratio of 1:5 was first pressed into tablets and sealed into a silica tube under vacuum. The tube was then heated at 1200 °C for 5 days, followed by cooling to room temperature. X-ray diffraction data of the reacted powders reveal a single phase material with a diffraction pattern that is consistent with JCPDS file 00-011-0581.[15] At room temperature and ambient pressure, the lattice parameters were determined to be $a=2.900$ Å and $c=7.478$ Å after a Rietveld refinement of the data.

The high P-T experiment was conducted using a cubic anvil apparatus at beamline X17B2 of the National Synchro-

TABLE I. Summary of thermoelastic parameters for ReB_2. Except for $(\partial\alpha/\partial P)_T$, the numbers in parentheses are standard deviations from the least-squares fits and refer to the last digit(s) of the parameter values. For $(\partial\alpha/\partial P)_T$, the uncertainties are estimated from the error propagation of K_0 and $(\partial K/\partial T)_P$.

Ref.	K_0 (GPa)	K_0'	$(\partial K/\partial T)_P$ (GPa K^{-1})	$\alpha_T(K^{-1})=a+bT$ $a, 10^{-5}$	$b, 10^{-8}$	$(\partial\alpha/\partial P)_T$ (10^{-7} GPa^{-1} K^{-1})	$(\partial K/\partial T)_V$ (GPa K^{-1})
This work[a]	334(23)	4.0	−0.064(6)	1.33(25)	1.48(64)	−5.76 ± 0.95	
This work[b]	334(23)	4.0	−0.071(11)			−6.36 ± 1.32	−0.049(11)
10	360	4.0					
14	359	4.09					

[a] Based on the measured P-V-T data and Eqs. (1) and (2).

[b] Thermal-pressure approach based on the measured data and Eqs. (3) and (4).

tron Light Source, Brookhaven National Laboratory. The white radiation from the superconducting wiggler magnet was used for energy-dispersive measurements. The diffracted x-rays were collected with a 13-element detector at a fixed Bragg angle of $2\theta=6.4757°$. The cell assembly used in the present experiment has been described elsewhere.[16] Briefly, a cube made up of a mixture of amorphous B and epoxy resin was employed as pressure-transmitting medium, and amorphous carbon was used as furnace material to achieve high temperatures. The ReB_2 sample, sandwiched by NaCl powder, was packed into a cylindrical container of boron nitride (BN), 1.0 mm inner diameter and 2.0 mm length.

In the present study NaCl was used as an internal pressure marker and the sample pressure was calculated from Decker's EOS for NaCl.[17] At each experimental condition, four NaCl diffraction peaks, 111, 200, 220, and 420, were used for the determination of pressure. The uncertainty in pressure measurements is mainly due to the statistical variation in the positions of different diffraction peaks and is less than 0.2 GPa in the P-T range investigated here. Temperatures were measured by a W/Re25%–W/Re3% thermocouple that was in direct contact with the sample. Diffraction patterns were obtained for the sample and NaCl in close proximity to the thermocouple junctions. Errors in temperature measurement were estimated to be around 10 K. Temperature gradients over the entire sample length were on the order of 20 K at 1500 K, and the radial temperature variations were less than 5 K at this condition.[16]

The ReB_2 sample was first compressed at room temperature to a desired pressure, followed by heating to the maximum temperature of 1100 K and then stepwise cooling to 900, 700, 500, and 300 K. Similar run cycles were repeated several times at progressively higher pressures of up to ~ 7.5 GPa. To minimize deviatoric stress built up during the room-temperature "cold" compression using a solid pressure medium, all diffraction patterns in the experimental P-T space were collected after temperature reached 1100 K and during subsequent cooling cycles. Our data analysis indicates that peak widths observed under high P-T conditions are similar to those at ambient conditions, confirming that the present experiment was conducted near the hydrostatic conditions. In addition, all the P-V-T data reported here were collected from a single high P-T experiment to eliminate the systematic errors which are typically present among different measurements.

III. THERMAL EQUATION OF STATE OF ReB_2

Figure 1 shows x-ray diffraction patterns at selected P-T conditions. The lattice d spacings were determined by Gaussian peak fitting of the diffracted intensity, and the unit-cell parameters were calculated by least-squares fitting based on a hexagonal unit cell using 8–10 diffraction lines. The relative standard deviations in determination of the unit-cell volumes, as plotted in Fig. 2 as a function of pressure and temperature, are typically less than 0.1%.

We employ a modified high-T Birch-Murnaghan EOS,[18–20] truncated to third order, to derive the thermoelastic parameters based on the measured P-V-T data for ReB_2. A general form of this modified EOS is formulated by

$$P = 3K_T f(1+2f)^{5/2}[1 - 3/2(4-K')f + \ldots], \qquad (1)$$

where

$$K_T = K_{To} + (\partial K/\partial T)(T-300),$$

$$K' = \partial K/\partial P,$$

and

$$f = \frac{1}{2}[(V_T/V_{PT})^{2/3} - 1],$$

$$V_T = V_0 \exp\left[\int \alpha(0,T)dT\right].$$

In Eq. (1), K_{To} and K_T represent the isothermal bulk modulus at 300 K and a higher temperature T, and $(\partial K/\partial T)$ and $(\partial K/\partial P)$ stand for the temperature and pressure derivatives of the bulk modulus, respectively. V_0, V_T, and V_{PT} correspond to the unit-cell volumes at ambient conditions, at atmospheric pressure and temperature T, and at high P-T conditions, respectively. $\alpha(0,T)$ is the volumetric thermal expansion at atmospheric pressure, commonly represented by $\alpha(0,T)=a+bT-c/T^2$ (for T in kelvin, see Ref. 21). In the modified high-T Birch-Murnaghan EOS, the temperature effects were taken into account by replacing K_0 with K_T and substituting V_0/V_P with V_T/V_{PT} in the isothermal EOS. Because of the limited pressure coverage that restricts an accurate constraint on K' for ReB_2, we assume $K'=4$ in Eq. (1) throughout the data analysis. Similarly, we ignore the term of c/T^2 in $\alpha(0,T)$ as well as higher-order terms and cross derivatives of the bulk modulus such as $\partial^2 K/\partial T^2$ and $\partial^2 K/\partial P\,\partial T$. From a least-squares fit to all P-V-T data using Eq. (1), we obtain $K_0=334(23)$ GPa, $(\partial K/\partial T)_P=-0.064(6)$ GPa K^{-1}, and $\alpha(0,T)=a+bT$ with $a=1.33(25)\times 10^{-5}$ K^{-1} and $b=1.48(64)\times 10^{-8}$ K^{-2}. Errors on the thermoelastic parameters in the present study are those of the least-squares fitting. Uncertainties in the P-V-T measurements were not included in the error estimation. From the thermodynamic identity,

$$(\partial\alpha/\partial P)_T = (\partial K/\partial T)_P K_{To}^{-2}. \qquad (2)$$

The pressure derivative of the volume thermal expansivity, $(\partial\alpha/\partial P)_T$, is found to be $-5.76\pm 0.95\times 10^{-7}$ K^{-1} GPa^{-1}. The uncertainty in $(\partial\alpha/\partial P)_T$ is estimated from the error propagation of K_0 and $(\partial K/\partial T)_P$.

The thermal-pressure approach to process P-V-T data has been widely applied for its thermodynamic importance.[20,22–25] This method is also useful for deriving thermoelastic parameter $(\partial K_T/\partial T)_V$, the temperature derivative of bulk modulus at constant volume, which is experimentally difficult to measure. In this approach, thermal pressure P_{th} is calculated as the difference between the measured pressure at a given temperature and the calculated pressure from Eq. (1) at room temperature, with both pressures corresponding to the same volume. Following this definition, thermal pressures were calculated for ReB_2 and are plotted in Fig. 3. An inspection of Fig. 3 demonstrates that thermal pressure varies linearly with temperature, which is consistent with the linear trend revealed in many different classes of condensed matter.[22–26] Thermal pressure at any temperature above 300 K for a given volume can also be analyzed from thermodynamic relations. Following the method of Anderson[22,23] and his subsequent studies, thermal pressure was calculated by

$$P_{\mathrm{th}} = \int_{300}^{T} (\partial P/\partial T)_V dT = P_{\mathrm{th}}(V,T) - P_{\mathrm{th}}(V,300)$$
$$= [\alpha K_T(V_{300},T) + (\partial K_T/\partial T)_V In(V_{300}/V)](T-300). \qquad (3)$$

From the least-squares fit of the thermal pressure versus temperature shown in Fig. 3, we obtain average values of $\alpha K_T(V_{300},T)$ and $(\partial K_T/\partial T)_V$ that are 0.0055(2) and −0.049(11) GPa K^{-1}, respectively, for ReB_2. From the thermodynamic identity,

$$(\partial K_T/\partial T)_V = (\partial K_T/\partial T)_P + (\partial K_T/\partial P)_T \alpha K_T(V_{300},T). \qquad (4)$$

We obtain a value of −0.071(11) for $(\partial K_T/\partial T)_P$, which is in agreement with the results derived from Eq. (1). The value of $(\partial\alpha/\partial P)_T$ derived from Eq. (2) is $-6.36 \pm 1.32 \times 10^{-7}\ \mathrm{K}^{-1}\ \mathrm{GPa}^{-1}$. Internally consistent thermal EOSs for ReB_2, as summarized in Table I, are thus obtained using different analysis methods. Within the experimental uncertainties, the K_0 value we obtained is comparable to those of previous studies (see Table I), whereas the thermoelastic parameters $(\partial K/\partial T)_P$, $(\partial K/\partial T)_V$, and $(\partial\alpha/\partial P)_T$ for ReB_2 can be found in previous literatures.

IV. AXIAL COMPRESSIBILITY OF ReB_2

In addition to the study of thermal EOS, the high *P-T* diffraction data also allow us to determine the compressibilities along different crystallographic axes in hexagonal ReB_2. The relations between pressure, lattice parameters, and corresponding c/a ratios at different temperatures are illustrated in Fig. 4. Like most materials, ReB_2 exhibits lattice expansion under high temperature and lattice contraction under high pressure. Consistent with our *P-V-T* analysis using Birch-Murnaghan EOS, our results reveal that axial compressibilities for both the *a* and *c* axes increase linearly with temperature. For example, the values of β_a vary from $1.07(8)\times 10^{-3}$ at room temperature to $1.22(3)\times 10^{-3}$ at 1100 K. The lattice compression in ReB_2 is highly anisotropic, with the *c* axis being significantly more compressible than the *a* axis. As a consequence of this, the c/a ratios increase with increasing pressure, raising gradually from 2.5778 at ambient pressure to 2.5862 around 7.5 GPa, which is in agreement with a recent study using diamond-anvil cells (DACs) and synchrotron radiation.[10] Within the experimental uncertainties, however, the variation in c/a ratios with pressure does not show observable dependence on temperature (Fig. 4). The gradual increase in the c/a ratio with pressure suggests an increasingly isotropic interatomic potential, which is an important finding because it validates the isotropic force potential used in some theoretical modeling for elastic modulus of hexagonal metals under high pressures.[27]

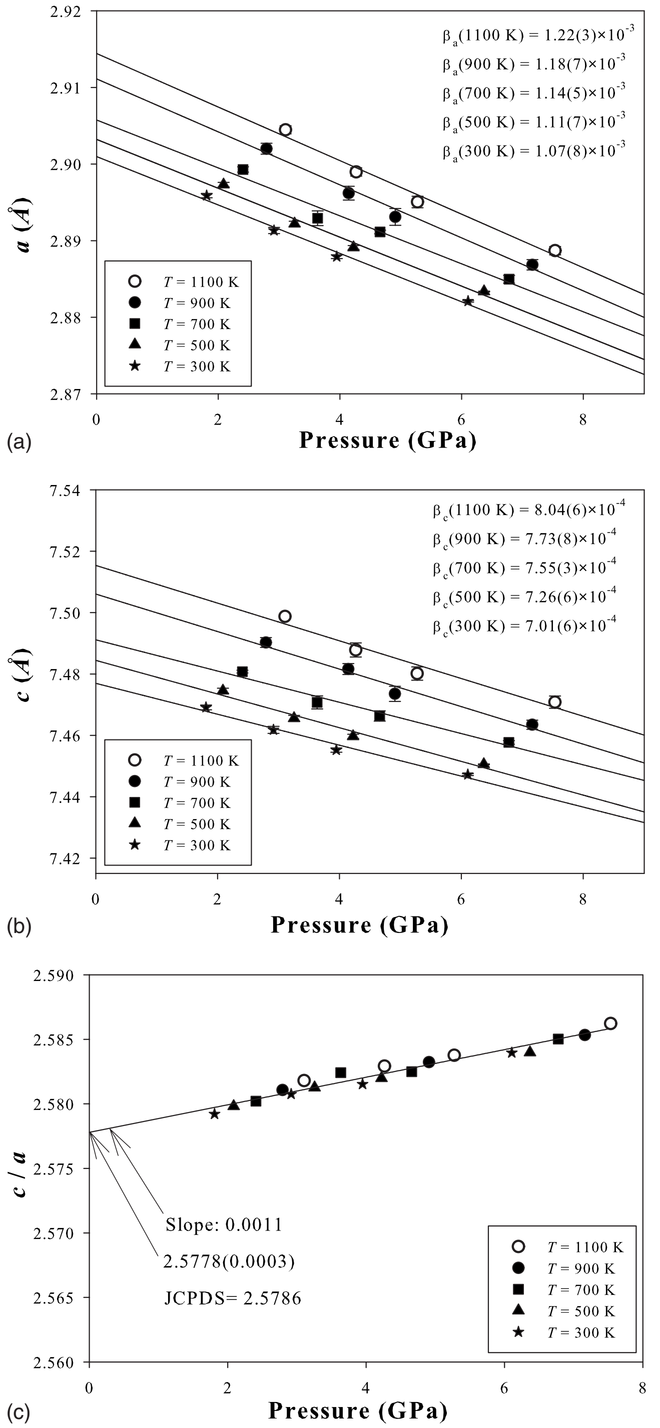

FIG. 4. Variation in lattice parameters as a function of pressure for ReB_2. The β values, obtained from the linear fits of normalized lattice parameters, indicate the axial compressibilities at given temperatures.

In conclusion, we have conducted *in situ* x-ray diffraction experiments for ReB_2 at pressures of up to 7.5 GPa and temperatures of up to 1100 K. From these measurements a complete thermal EOS of ReB_2 has been derived. Different methods, namely, high-*T* EOS and thermal pressure, have been applied in the data reduction process. The overall thermoelastic parameters, including temperature and pressure derivatives of thermal expansion and elastic bulk modulus, are consistent with each other. Within the experimental uncertainty, the bulk modulus obtained in our study is in good agreement with the value determined with DACs. A noticeable anisotropic axial compressibility was observed in $\mathrm{ReB_2}$ at high pressure. The pressure dependence of the c/a ratio is important for the theoretical modeling of the mechanical properties of $\mathrm{ReB_2}$. Finally we note that at a pressure of up to 7.5 GPa and temperature of up to 1100 K, x-ray diffraction does not show evidence of any structural phase transition.

ACKNOWLEDGMENTS

This research was supported by the Los Alamos National Laboratory, which is operated by Los Alamos National Security LLC under DOE (Contract No. DEAC52-06NA25396). The experimental work was carried out at beamline X17B2 of the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the Consortium for Materials Properties Research in Earth Sciences (COMPRES) under NSF (Cooperative Agreement No. EAR 01-35554).

---

[*] wang_yuejian@hotmail.com

[†] yzhao@lanl.gov

[1] J. C. Zheng, Phys. Rev. B **72**, 052105 (2005).

[2] D. W. He, M. Akaishi, and T. Tanaka, Diamond Relat. Mater. **10**, 1465 (2001).

[3] V. L. Solozhenko, D. Andrault, G. Fiquet, M. Mezouar, and D. C. Rubie, Appl. Phys. Lett. **78**, 1385 (2001).

[4] T. Irifune, A. Kurio, S. Sakamoto, T. Inoue, and H. Sumiya, Nature (London) **421**, 599 (2003).

[5] R. B. Kaner, J. J. Gilman, and S. H. Tolbert, Science **308**, 1268 (2005).

[6] R. W. Cumberland, M. B. Weinberger, J. J. Gilman, S. M. Clark, S. H. Tolbert, and R. B. Kaner, J. Am. Chem. Soc. **127**, 7264 (2005).

[7] A. F. Young, C. Sanloup, E. Gregoryanz, S. Scandolo, R. J. Hemley, and H. K. Mao, Phys. Rev. Lett. **96**, 155501 (2006).

[8] D. A. Dzivenko, A. Zerr, V. K. Bulatov, G. Miehe, J. Li, B. Thybusch, J. Brötz, H. Fueß, G. Brey, and R. Riedel, Adv. Mater. (Weinheim, Ger.) **19**, 1869 (2007).

[9] E. Gregoryanz, C. Sanloup, M. Somayazulu, J. Badro, G. Fiquet, H.-k. Mao, and R. J. Hemley, Nature Mater. **3**, 294 (2004).

[10] H.-Y. Chung, M. B. Weinberger, J. B. Levine, A. Kavner, J.-M. Yang, S. H. Tolbert, and R. B. Kaner, Science **316**, 436 (2007).

[11] X. Q. Chen, C. L. Fu, M. Krcmar, and G. S. Painter, Phys. Rev. Lett. **100**, 196403 (2008).

[12] X. Zhu, D. Li, and X. Cheng, Solid State Commun. **147**, 301 (2008).

[13] X. Hao, Y. Xu, Z. Wu, D. Zhou, X. Liu, X. Cao, and J. Meng, Phys. Rev. B **74**, 224112 (2006).

[14] Y. Liang and B. Zhang, Phys. Rev. B **76**, 132101 (2007).

[15] S. J. La Placa and B. Post, Acta Crystallogr. **15**, 97 (1962).

[16] D. J. Weidner, M. T. Vaughan, J. Ko, Y. Wang, X. Liu, A. Yeganeh-haeri, R. E. Pacalo, and Y. Zhao, in *High-Pressure Research: Application to Earth and Planetary Sciences*, edited by Y. Syono and M. H. Manghnani (American Geophysics Union, Washington, DC, 1992), p. 13.

[17] D. L. Decker, J. Appl. Phys. **42**, 3239 (1971).

[18] S. K. Saxena and J. Zhang, Phys. Chem. Miner. **17**, 45 (1990).

[19] Y. Zhao, D. Schiferl, and T. J. Shankland, Phys. Chem. Miner. **22**, 393 (1995).

[20] Y. Zhao, A. C. Lawson, J. Zhang, B. I. Bennett, and R. B. Von Dreele, Phys. Rev. B **62**, 8766 (2000).

[21] I. Suzuki, J. Phys. Earth **23**, 145 (1975).

[22] O. L. Anderson, *Equations of State of Solids for Geophysics and Ceramic Science* (Oxford University Press, Oxford, 1995).

[23] O. L. Anderson, J. Geodyn. **1**, 185 (1984).

[24] J. Zhang and F. Guyot, Phys. Chem. Miner. **26**, 206 (1999).

[25] J. Zhang and P. Kostak, Phys. Earth Planet. Inter. **129**, 301 (2002).

[26] J. Zhang, Y. Zhao, R. S. Hixson, G. T. Gray, L. Wang, W. Utsumi, S. Hiroyuki, and H. Takanori, Phys. Rev. B **78**, 054119 (2008).

[27] W. J. Evans, M. J. Lipp, H. Cynn, C. S. Yoo, M. Somayazulu, D. Häusermann, G. Shen, and V. Prakapenka, Phys. Rev. B **72**, 094113 (2005).