Isotropic Thermal Expansivity and Anisotropic Compressibility of ReB_2 *

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We experimentally investigated some of the mechanical properties of ReB_2 under high temperature/pressure (T/P) conditions. High-T experiments (up to 600°C at 1 atm) were carried out in a high-T oven attached to a conventional x-ray diffractometer whereas high-P experiments (up to about 42 GPa at 25°C) were conducted in a diamond-anvil cell using synchrotron x-ray radiation. High-T data suggest a highly isotropic thermal expansivity whereas high-P data suggest a highly anisotropic compressibility for ReB_2.

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Superhard rhenium diboride (ReB_2)[1−3] may find itself many industrial applications from cutting and polishing tools to wear-resistant coatings in the near future. As demonstrated by Chung *et al.*,[1] it can be synthesized at 1 atm; the traditional method of manufacturing superhard materials is using high-P techniques, which makes the product expensive. The possibility of generating reasonably cheap superhard materials has made ReB_2 the subject of numerous experimental and theoretical investigations.[1−31]

ReB_2 has a primitive hexagonal structure ($P6_3/mmc$; a=2.900 Å and c=7.478 Å) with two ReB_2 units per unit cell.[32] This structure can be described as alternating layers of hexagonally close-packed Re and puckered hexagonal networks of B along the c-axis.[1] To be a superhard material, therefore, the bond Re-B and its properties between these alternating layers are critical; graphite also has a layered structure, and with very weak van der Waals interaction among the layers, it is essentially a very soft material.[33] In ReB_2, Re atoms provide very high electron concentration, and the bonds between Re and B atoms show strong directional covalent nature,[4,7,17] so that ReB_2 has the potential to be a superhard material.

To be a superhard material, the mechanical properties are critical, and two of them are thermal expansivity and elastic compressibility. So far there have been only one experimental investigation on the thermal expansivity of ReB_2 at ambient P,[17] one compression investigation on the bulk modulus at room temperature,[1] and one compression investigation on the thermal equation of state of ReB_2.[19] Other indirect experimental methods were used, but the number of investigations have remained to be small; for example, Qin *et al.*[24] used the ultrasonic method to investigate the elasticity of ReB_2 but generated very different result. Apparently, more direct experimental investigations on the mechanical properties of ReB_2 are desirable.

Our polycrystalline ReB_2 sample was synthesized in a DS6×8MN cubic press from a mixture of powders of rhenium and amorphous boron (in a molar ratio of 1:2.5) at 5 GPa and 1600℃ for 60 min. The synthesized material was pulverized, and its XRD pattern was taken using a powder x-ray diffractometer at Sichuan University (X'Pert Pro MPD system). The XRD data revealed a single crystalline phase, ReB_2, with its XRD pattern consistent with the JCPDS file 00-011-0581. This material was also checked by a JEOL 6490 SEM, and was found of the grain size of ∼3 μm. In addition, the material readily absorbs moisture from air, resulting in some surface contamination. This surface contamination was well demonstrated by our tentative Raman data taken on some ReB_2 single crystals, which by no means agree with the theoretically-calculated Raman characteristics of ReB_2.[17] For more experimental techniques and detailed characterization, Qin *et al.* and Chen *et al.* are recommended.[24,34]

The high-T XRD experiments at 1 atm were conducted using an X'Pert Pro MPD system at Peking University, which was attached with an Anton Paar HTK-1200N oven (Eurotherm 2604 T controller; type S thermocouple). The maximum T achievable with this heating system is 1200℃, and the accuracy in the T measurement is about ±2℃. The diffractometer system was equipped with a Cu target, and operated at 40 kV and 40 mA with a scanning step length of $2\theta = 0.017°$. The experimental procedure was as follows: after collection of the XRD data at a given T, the sample was heated up by 10℃/min to the next T

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target, then allowed to relax for 5 min, and finally x-rayed. Data were collected at 2θ=10–80°. According to Liu *et al.*,[35] this experimental procedure secures the quality of the XRD data, which lead to unit-cell parameters with high accuracy.

The high-P angle dispersive XRD experiments with a diamond-anvil cell (DAC) were conducted at beamline X17C, NSLS, BNL. A 250 μm thick T301 stainless steel plate was used as gasket. The central area of the plate was pre-indented to a thickness of about 40 μm, and a hole of 120 μm in diameter was drilled through it. The ReB_2 powder, plus two tiny ruby balls, was loaded with the P medium (a 16:3:1 methanol-ethanol-water mixture) into the hole. To minimize the deviatoric stress in the DAC, the volume ratio of the solid material (ReB_2 + ruby balls) to the liquid P medium was kept very low, about 1:2. The experimental P was determined by the P-induced fluorescence shift of ruby.[36] The incident x-ray beam was monochromatized to a wavelength of 0.4066 Å, and its beam size was collimated to $\sim 25\times 20\,\mu m^2$ in diameter. The XRD pattern at certain P was collected for 10–20 min using an online CCD detector, and later integrated to give the conventional one-dimension profile using the Fit2D program.[37]

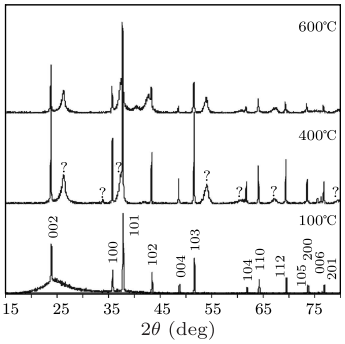

Fig. 1. Examples of XRD patterns of ReB_2 at high T.

Our high-T experiments at 1 atm were conducted up to 1000℃, but only the data collected in the experiments up to 600℃ are reported here. Typical XRD patterns are shown in Fig. 1. Sharp XRD peaks from ReB_2 occurred at T up to 600℃, but completely disappeared at 700℃, suggesting a potential phase transition at somewhere in between. This observation apparently disagrees with the previous experimental investigations, which demonstrated the stability of ReB_2 up to 1000℃ both in vacuum and in air.[17,18,25] Additionally, some broad diffraction peaks occurred in the XRD pattern at 200℃ and persisted to higher T, suggesting the presence of a poorly crystallized phase which might be α-boron or β-boron, since our material contained some amorphous boron.[24,26,31] We checked these broad diffraction peaks against the PDF cards 12-0377 (α-boron) and 11-0618 (β-boron), but found no agreement in either case.

The unit-cell parameters of ReB_2 at different T are listed in Table 1 and shown in Fig. 2. The room-temperature unit-cell parameters are a=2.8998(2) Å, c=7.4754(6) Å, and V=54.437(8) Å^3, consistent with the JCPDS file 00-011-0581.[32] Fig. 2 shows that the unit-cell parameters vary almost linearly with T, suggesting that the expansion coefficients are generally independent to T; this linearity, however, might be resulted from the narrow T interval covered by our experiments. Consequently, the axial/volumetric thermal expansion coefficients ($\alpha_j = l_j^{-1}\partial l_j/\partial T$ or $\alpha_V = V^{-1}\partial V/\partial T$) were calculated by a linear regression; they are $\alpha_a = 8.5(5)\times 10^{-6}$℃$^{-1}$, $\alpha_c = 8.1(5)\times 10^{-6}$℃$^{-1}$ and $\alpha_V = 2.5(1)\times 10^{-5}$℃$^{-1}$.

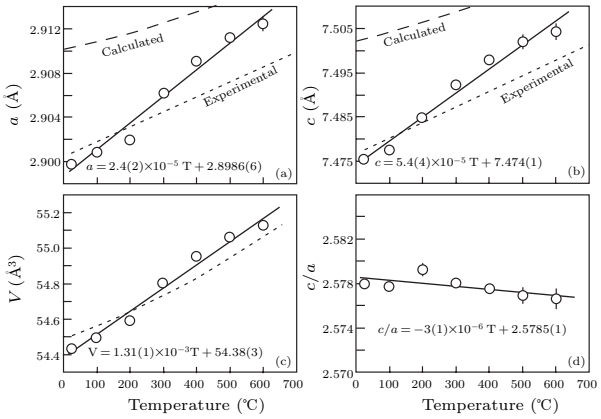

Fig. 2. Unit-cell parameters versus T: (a) axis a; (b) axis c; (c) volume; (d) a/c ratio. Data from Zhou *et al.*[17] are sketched in (a) and (b) whereas the extrapolated result from Wang *et al.*[19] is plotted in (c). For most data points their error bars are approximate to or smaller than the symbols.

Table 1. Unit-cell parameters at different T (1 atm).

T (℃)	a (Å)	c (Å)	V (Å^3)
27	2.8998(2)[a]	7.4754(6)	54.437(8)
100	2.9008(2)	7.4775(7)	54.492(9)
200	2.9020(4)	7.4848(11)	54.588(14)
300	2.9062(1)	7.4921(3)	54.801(4)
400	2.9091(3)	7.4979(8)	54.951(10)
500	2.9112(5)	7.5019(14)	55.061(19)
600	2.9125(7)	7.5024(18)	55.125(25)

[a] Numbers in parentheses represent one standard deviation in the right-most digit.

With first-principles calculation and neutron-scattering method, Zhou *et al.*[17] investigated the thermal expansivity of ReB_2 and found that the effect of T on the unit-cell parameters is not only nonlinear, but also much smaller than ours (Figs. 2(a) and 2(b)). Due to the dependence of the axial expansion coefficients on T (Fig. 3(a)), their axial expansion coefficients are significantly smaller than ours at relatively low T, but approach ours at high T. Since they did not report any experimental details, it is difficult to find out the cause of this conflict. Anyhow, both investigations have found that the axial thermal expansion coefficients along the a- and c-axes are almost

identical, indicating an isotropic thermal expansivity for ReB_2. Wang *et al.*[19] experimentally studied the thermal equation of state of ReB_2 under high P-T conditions, and the extrapolation of their results to 1 atm appears in good agreement with ours (Fig. 2(c)). The negligible influence of T on the c/a ratio of ReB_2 determined by Wang *et al.* also supports this study (Fig. 2(d)), suggesting an isotropic thermal expansivity for ReB_2.

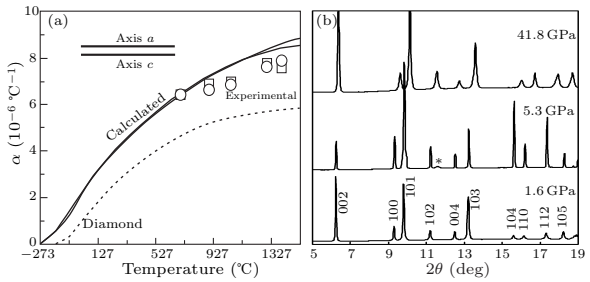

Fig. 3. (a) Axial thermal expansion coefficients of ReB_2 versus T. The top two thick solid lines are from this study whereas thin solid ones from Zhou *et al.*[17] Empty squares (axis a) and circles (axis c) represent experimental data collected by neutron diffraction.[17] Calculated thermal expansion coefficients of diamond are also sketched.[17] (b) Examples of XRD patterns of ReB_2 at high P. Peak indicated by the star probably belongs to the gasket.

The thermal expansivity of ReB_2 is compared to that of diamond in Fig. 3(a). The thermal expansion coefficients of ReB_2 appear significant larger than those of diamond, which might undermine the value of ReB_2 as a material for cutting tools and abrasion-resistance coating.

Our high-P experiments suggest that at room temperature, ReB_2 is stable (or metastable due to potential kinetic reason) up to at least 41.8 GPa (Fig. 3(b)). The XRD pattern at 41.8 GPa shows slight peak-broadening (for example, the FWHM value of the peak 101 is about twice of that at 1 atm), which might indicate the built-up differential stress in the cell, as manifested by the large uncertainty of the measured P (Table 2).

The effect of P on the unit-cell parameters of ReB_2 is summarized in Table 2 and shown in Fig. 4. Apparently both the a- and c-axes have a nonlinear dependence on P over this P range, in disagreement with previously reported linear dependence.[1,19] Moreover, the c/a ratio of ReB_2 over the investigated P range also has a nonlinear dependence (Table 2 and Fig. 4), which disagrees with previously reported linear dependence.[19]

The P–V data were fitted to the third-order Birch–Murnaghan equation of state (BM-EoS) by a least-squares method:[38]

$$P = 3K_T f_E(1+2f_E)^{5/2}\left[1+\frac{3}{2}(K_T'-4)f_E\right],$$

where K_T is the isothermal bulk modulus, K_T' the first P derivative of K_T, and f_E the Eulerian definition of finite strain, which is $[(V_0/V)^{2/3}-1]/2$. In the Eulerian definition of finite strain, V_0 is the volume at zero P whereas V the volume at high P. When K_T' is set as 4, K_T is determined as 361(27) GPa whereas V_0 as 54.48(5) Å^3. If only the data at P less than 13 GPa are used in the data-fitting process, the results are K_T=372(46) GPa and V_0=54.48(7) Å^3, which are essentially the same. If K_T' is not fixed, the results for the whole data set are K_T=392(57) GPa, K_T'=0.9(43) and V_0=54.47(6) Å^3, indicating no significant improvement.

Table 2. Unit-cell parameters at different P (25℃).

P (GPa)	a (Å)	c (Å)	V (Å^3)
0.0001[a]	2.8991(3)[b]	7.472(1)	54.39(1)
1.6(1)[c]	2.8970(1)	7.472(0)	54.31(0)
2.4(1)	2.8982(6)	7.473(4)	54.34(3)
5.3(1)	2.8884(3)	7.461(1)	53.90(1)
8.6(1)[c]	2.8764(7)	7.434(4)	53.26(3)
12.9(2)	2.8613(3)	7.420(1)	52.61(1)
19.3(6)	2.8399(6)	7.385(1)	51.58(2)
26.7(7)	2.8300(6)	7.366(6)	51.09(4)
41.8(10)	2.7954(9)	7.312(4)	49.48(1)

[a] Data were collected on the ReB_2 powder sample loosely packed into a small hole (400 μm cross-section) in a stainless steel plate.
[b] Numbers in parentheses represent one standard deviation in the right-most digit.
[c] Data were collected during decompression.

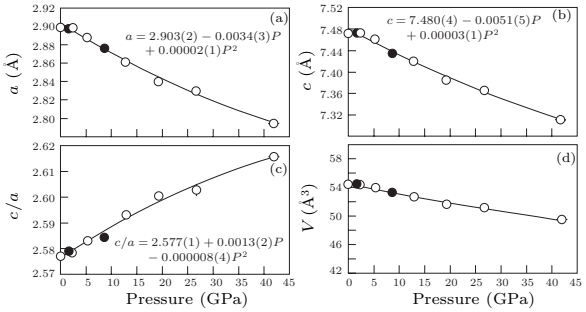

Fig. 4. Unit-cell parameters versus P: (a) axis a; (b) axis c; (c) a/c ratio; (d) volume. Empty circles, except the one at 1 atm, represent data collected during compression while filled circles represent data collected during decompression. For most data points their error bars are approximate to or smaller than the symbols.

A linearized third-order BM-EoS was used to obtain the axial EoS parameters,[39] and the derived values are a_0=2.9021(10) Å, $K_T(a)$=301(41) GPa and $K_T'(a)$=2.2(43) for the a-axis; c_0=7.4796(11) Å, $K_T(c)$=523(81) GPa and $K_T'(c)$=3.0(73) for the c-axis. The elastic anisotropy of ReB_2 thus appears to be significant ($K_T(c)$:$K_T(a)$=1.74), which is in excellent agreement with the result from theoretical calculation.[4] If a and c are fixed at 4, we obtain $K_T(a)$=286(16) GPa and $K_T(c)$=513(33) GPa.

The bulk modulus of ReB_2 (either adiabatic or isothermal) has been constrained by several methods, including theoretical calculation[4–6,8,10,17] and

experimentation.[1,19,24] The adiabatic bulk modulus K_S is related to the isothermal bulk modulus K_T by the equation $K_S = K_T(1 + \alpha\gamma T)$, where α is the volumetric thermal expansivity and γ the Grüneisen parameter. According to the data in the literature,[10,19] the difference between the K_S and K_T of ReB_2 at room temperature is about 1%. The K_S values from the theoretical calculations range from 335 to 377 GPa, showing excellent consistency despite the difference in the calculating methods. The K_T values from the experiments, however, show some scattering.[1,19,20,24] In general, our result (K_T=361(27) GPa, with K'_T=4) agrees well with Chung *et al.* (DAC; synchrotron x-ray radiation; K_T=360 GPa, with K'_T=4),[1] Wang *et al.* (multi-anvil press; synchrotron x-ray radiation; K_T=334(23) GPa, with K'_T=4)[19] and Chung *et al.* (K_S=371(22) GPa, which, assuming an isotropic model, was calculated from the Young's modulus derived from their nanoindentation experiments).[20] However, the agreement between these experimental studies and Qin *et al.* (K_S=210 GPa, calculated from their ultrasonic measurements) is relatively poor.[24] Several factors such as effect of grain size, non-random distribution of the grains, presence of amorphous boron and underestimation of the porosity in the sample might have affected the ultrasonic measurements.

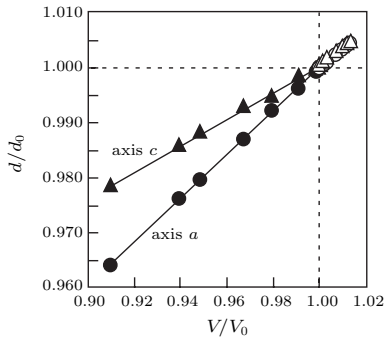

Fig. 5. Unit-cell dimensions (d/d_0) versus V/V_0.

Usually thermal expansivity and compressibility are simultaneously isotropic or anisotropic for most materials. It is surprising that ReB_2 has a nearly isotropic thermal expansivity and a significantly anisotropic compressibility (Fig. 5). In the lattice of ReB_2, strong and directional covalent B-B and Re-B bonds form a rigid three-dimensional network,[17] efficiently preventing any atom thermally displacing away from its equilibrium position. This might result in the nearly isotropic thermal expansivity. On the other hand, the anisotropic compressibility of ReB_2 might be caused by the special atom arrangement in the crystal structure of ReB_2: in the *ab* plane, the atoms B and Re are in planes offsetting from each other, so that the electrostatic repulsion does not push each other directly; along the *c*-axis, however, the atoms B and Re are located right as one on top of the other, leading to highly directional repulsive electronic interactions.[4]

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