Journal of Alloys and Compounds 621 (2015) 116–120

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

# Strength of tungsten triboride under pressure up to 86 GPa from radial X-ray diffraction

Lun Xiong [a,*], Jing Liu [a,*], Ligang Bai [a], Chuanlong Lin [a], Duanwei He [b], Xinxin Zhang [c], Jung-Fu Lin [d]

[a] Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, PR China
[b] Institute of Atomic and Molecular Physics, Sichun University, Chengdu 610065, PR China
[c] State Key Lab of Superhard Materials, Jilin University, Changchun 130012, PR China
[d] Department of Geological Sciences, Jackson School of Geosciences, The University of Texas at Austin, TX 78712, USA

## ARTICLE INFO

*Article history:*
Received 30 July 2014
Received in revised form 6 September 2014
Accepted 8 September 2014
Available online 16 September 2014

*Keywords:*
Tungsten triboride
High pressure
Strength
Radial X-ray diffraction
Diamond anvil cell

## ABSTRACT

The strength of tungsten triboride ($WB_3$) was determined under nonhydrostatic compression up to 86 GPa using an angle-dispersive radial X-ray diffraction technique in a diamond-anvil cell (DAC). Analyze of diffraction data using lattice strain theory indicate that the ratio of differential stress to shear modulus ($t/G$) changes from 0.004 at ambient conditions to 0.078 at 86 GPa. Together with theoretical results on the high-pressure shear modulus, our results here show that $WB_3$ under uniaxial compression can support a differential stress of 26 GPa when it starts to yield to the plastic deformation at 40 GPa. The yield strength of $WB_3$ increases with increasing pressure, reaching a maximum value of 30 GPa at 77 GPa. By comparison, we find that the high-pressure strength of $WB_3$ is comparable to those of $c$-$BC_2N$, $B_6O$, and $\gamma$-$Si_3N_4$.

## 1. Introduction

Many experimental and theoretical studies on boron-tungsten system ($WB_x$) have suggested that tungsten tetraboride ($WB_4$) is potentially a superhard material [1,2]. Gu et al. [1] synthesized the compounds formed by transition metals (TMs) and B, and measured their Vickers hardness ($Hv$) by microindentation tests. The obtained hardness values of $WB_4$ are 46.2(1.2) GPa and 31.8(1.2) GPa under applied loads of 0.49 N and 4.9 N, respectively. Subsequently, Wang et al. [2] calculated the hardness values of $WB_4$ to be 41.1–42.2 GPa, consistent with Gu et al. [1], and they [2] pointed out that $WB_4$ has an ultra-low compressibility with the bulk modulus between 292.7–324.3 GPa. The early works suggested that $WB_4$ is a potential superhard material and has an ultra-low compressibility. Successively, Mohammadi et al. [3] also measured the hardness by microindentation method as 43.3(2.9) GPa and 28.1(1.4) GPa under an applied load of 0.49 N and 4.9 N, respectively, and reported a bulk modulus $K_0 = 339(3)$ GPa at ambient conditions, for $WB_4$ from high-pressure X-ray diffraction (XRD) up to 30 GPa in a DAC with neon as the pressure medium. Liu et al. [4] performed the high-pressure XRD of $WB_4$ up to 51 GPa with silicone oil as the pressure medium and obtained $K_0 = 325(9)$ GPa with $K_0' = 5.1(0.6)$. Both $K_0$ and $K_0'$ are defined in the Birch-Monaghan equation of state (EoS). Xie et al. [5] measured the compression behavior of $WB_4$ with neon as the pressure medium up to 59 GPa and obtained $K_0 = 369(9)$ GPa with $K_0' = 1.2(0.5)$ by fitting the data at pressures lower than 42 GPa. Xiong et al. [6] reported a bulk modulus $K_0 = 319(5)$ GPa with $K_0' = 4.1(0.2)$ at $\psi = 54.7°$ by fitting the radial X-ray diffraction (RXD) nonhydrostatic compression data to 86 GPa.

However, subsequent theoretical studies indicated that the structure of $WB_4$ is unstable and the previously believed $WB_4$ is in fact $WB_3$ [7,8]. Liang et al. [7] evaluated the structure stability of $WB_x$ from first principles, and questioned the stability of $WB_4$ for the first time. They reported that long-believed $WB_4$ is actually $WB_3$ because their Gibbs energy shows that the $WB_3$ is thermodynamically stable and $WB_4$ is not. Subsequently, Liang et al. [9] reported that $WB_3$ is superhard due to its three-dimensional covalent network consisting of boron honeycomb planes interconnected with strong zigzag W–B bonds. Liang et al. [9] calculated the Vickers hardness of $WB_4$ (16.8 GPa) and $WB_3$ (43.1 GPa) using the linear correlation existing between the Vickers hardness and shear modulus for many of the known hard materials and superhard materials. They obtained the Vickers hardness of $WB_4$ (6.8 GPa) and $WB_3$ (39.4 GPa) from theoretical calculation using Chen's model of hardness. The hardness of $WB_4$ (16.8 GPa, 6.8 GPa) is ∼39% of $WB_3$ (43.1 GPa, 39.4 GPa). Zhang et al. [8]

---

* Corresponding authors.

*E-mail addresses:* xionglun@ihep.ac.cn (L. Xiong), liuj@ihep.ac.cn (J. Liu).

http://dx.doi.org/10.1016/j.jallcom.2014.09.076
0925-8388/© 2014 Published by Elsevier B.V.

compared experimental and theoretically calculated XRD patterns between $WB_4$ and $WB_3$, along with the thermodynamic, mechanical, and phonon instabilities of $WB_4$ using density functional theory. They denoted that $WB_4$ with a three-dimensional boron network is identified as $WB_3$ with two-dimensional boron nets. In addition, they suggested that $WB_3$ may not be an intrinsically superhard material due to its much lower ideal shear strengths compared with the superhard material of *c*-BN. Zang et al. [10] calculated the stress–strain relation and the ideal strength of $WB_3$ using the first-principles, leading the authors to conclude that the Vickers hardness of $WB_3$ should be well below that of $ReB_2$, which implies that $WB_3$ cannot be a superhard material. Li et al. [13] examined tungsten borides using a recently developed global structural optimization approach and identified the thermodynamically stable structures. They reported that comparison of experimental and simulated X-ray diffraction patterns leads to the identification of $P6_3/mmc$-4*u* $WB_3$, while *R*-3*m*-6*u* $WB_3$ is thermodynamically stable and thus viable for experimental synthesis. These studies indicate that $WB_4$ is unstable and leaves the issue of whether or not $WB_3$ is a superhard material under debate.

Despite several theoretical calculations for $WB_3$, there are no direct experimental measurements. There are different opinions regarding whether $WB_3$ is a superhard material. Previous studies have shown that the hardness of materials has some relationship with strength which reflects the contributions of both plastic and elastic deformation. In this study, we have investigated the strength of $WB_3$ to 86 GPa under nonhydrostatic compression using radial X-ray diffraction (RXD) in diamond-anvil cell.

## 2. Experimental details

The $WB_3$ powder was synthesized in a DS6 * 8MN cubic press [14] at high-pressure and temperature conditions. The synthesized $WB_3$ sample possesses an average grain size of 0.5–1 μm determined via scanning electron microscopy (SEM). Fig. 1 displays the XRD pattern of the synthesized $WB_3$ and simulated patterns for $WB_4$ and $WB_3$ reported by Zhang et al. [8]. It can be seen that the XRD pattern of synthesized sample matches much better with that of the simulated $WB_3$ from Zhang et al. [8]. The measured XRD pattern shows the highly crystalline and pure phase. At ambient conditions, the synthesized $WB_3$ has a hexagonal structure (space group $P6_3/mmc$, see Fig. 2) with lattice parameters $a = 5.199(0.001)$ Å and $c = 6.347(0.001)$ Å.

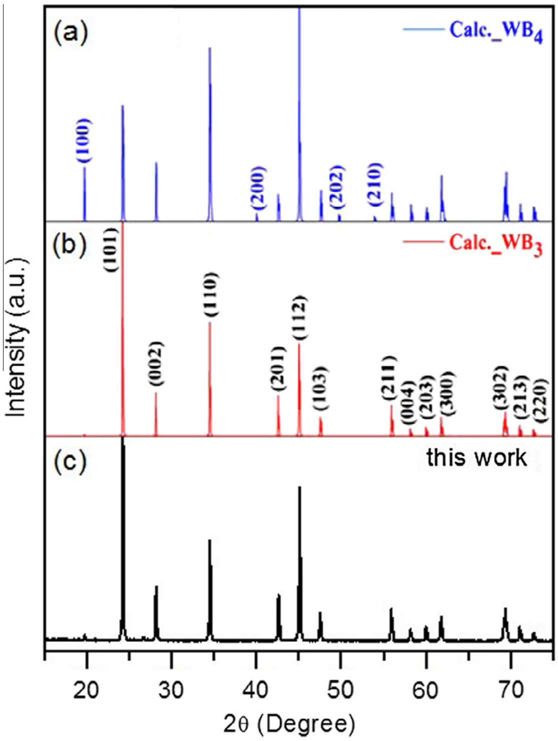

**Fig. 1.** Representative powder X-ray diffraction pattern for tungsten triboride ($WB_3$) at ambient conditions ($\lambda = 1.5406$ Å). The XRD pattern is in agreement with Zhang et al. [8]. The corresponding Miller indices are noted for each peak. X-ray wavelength $\lambda = 1.5406$ Å.

A twofold panoramic DAC with a pair of beveled diamond anvils (150 μm culet diameter) was used to exert uniaxial compression on both the $WB_3$ sample and Mo standard in the RXD measurements. A beryllium gasket was pre-indented to ∼25-μm thickness at ∼20 GPa and a hole of 50-μm-diameter was drilled in the center of the preindented area for use as a sample chamber. Special attention was paid to make sure that the sample hole was well centered with respect to the anvil culet. The $WB_3$ sample was loaded into the gasket hole and a piece of Mo flake with a diameter of ∼20 μm was placed on top within 5 μm of the sample center serving as a pressure standard [15] as well as the positioning reference for X-ray diffraction. No pressure-transmitting medium was used to ensure maximum nonhydrostatic stresses. By design, the DAC was tilted at an angle of 28° to minimize the contribution of Be diffraction to the sample patterns [16]. Angle-dispersive radial X-ray diffraction experiments were performed at the 4W2 beam line of Beijing Synchrotron Radiation Facility (BSRF), Chinese Academy of Sciences. A Si(1 1 1) monochromator was used to tune the synchrotron source to a wavelength of 0.6199 Å, and the incident monochromatic X-ray beam was focused by a pair of Kirkpatrick-Baez mirrors to an approximately 26(vertical) × 8(horizontal) $\mu m^2$ spot of full width at half maximum (FWHM) and directed through the Be gasket and the sample. Two-dimensional diffraction patterns were collected by a Mar345 image plate detector and analyzed with the program Fit2D [17]. The sample-to-detector distance and orientation of the detector were calibrated by a $CeO_2$ standard. At each pressure, the RXD pattern was collected typically for 15–20 min after about 30 min of stress relaxation.

## 3. Theory

The radial X-ray diffraction data was analyzed using the lattice strain theory developed by Singh and co-workers [18,19]. According to the lattice strain theory, the measured *d*-spacing $d_m(hkl)$ is a function of the azimuthal angle $\psi$ between the DAC loading axis and the diffraction plane normal ($hkl$), and can be calculated using the relation as

$$d_m(hkl) = d_p(hkl)[1 + (1 - 3\cos^2\psi)Q(hkl)] \quad (1)$$

where $d_m(hkl)$ is the measured *d*-spacing, $d_p(hkl)$ is the *d*-spacing under the equivalent hydrostatic pressure, and $Q(hkl)$ is the orientation dependent lattice strain.

Under isostress conditions (the Reuss limit), the differential stress, $t$, can be expressed as

$$t = 6G\langle Q(hkl)\rangle \quad (2)$$

where $\langle Q(hkl)\rangle$ represents the $Q$ value averaged over all observed reflections of $Q(hkl)$, and $G$ is the aggregate shear modulus of the polycrystalline sample. The pressure dependence of $G$ can be obtained from extrapolation of ultrasonic or theoretically calculated single-crystal elastic constants. If the differential stress $t$ has reached the limiting value of yield strength at high pressures when

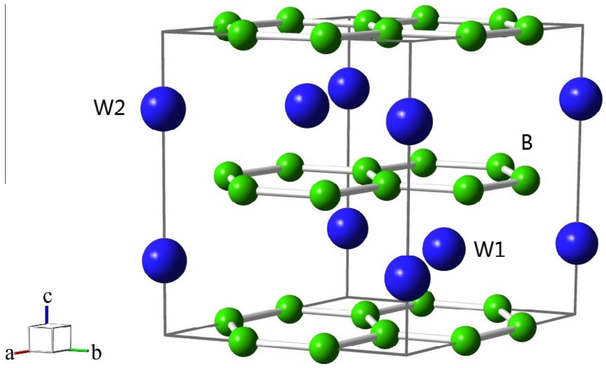

**Fig. 2.** Crystal structure of $WB_3$.