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We report high-pressure synthesis of chromium monoboride (CrB) at 6 GPa and 1400 K. The elastic and plastic behaviors have been investigated by hydrostatic compression experiment and microindentation measurement. CrB is elastically incompressible with a high bulk modulus of 269.0 (5.9) GPa and exhibits a high Vickers hardness of 19.6 (0.7) GPa under the load of 1 kg force. Based on first principles calculations, the observed mechanical properties are attributed to the polar covalent Cr-B bonds interlinked with strong zigzag B-B covalent bonding network. The presence of metallic Cr bilayers is presumably responsible for the weakest paths in shear deformation. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4922147]

Transition-metal borides (TMB) have been extensively studied over the past decades because of their high hardness, excellent corrosion resistance, and relatively high electrical conductivity.1–3 As commonly accepted, the high hardness is attributed to strong directional covalent bonds between the TM and the light elements boron.4,5 The high valence-electron density in transition metals is responsible for the high value of bulk modulus under hydrostatic pressure, while the introduction of light elements such as boron can significantly increases the resistance to plastic shear due to the formation of strong covalent metal-boron and boron-boron bonding networks.5

Because metallic bonds in TMB may induce the lattice softening under shear deformation, much effort has been made to increase the shear plastic resistance by incorporating high boron content to form three dimensional (3D) networks of covalent bonds. Consequently, a series of diborides and tetraborides of transition metals have been synthesized and investigated by both experiments and theoretical calculations.6–11 Of the transition metal diborides, OsB2,6 RuB2,7 and ReB27 are typical examples that can be synthesized at ambient pressure. OsB2 possesses high elastic moduli but a low hardness due to the presence of weak metallic bonds.12 ReB2 was believed to be superhard,13 but the measured asymptotic hardness (i.e., load-independent) is less than 30 GPa because of the electronic instabilities of 5d orbitals under finite shear strain, which results in transformation to phases with lower plastic resistance.14 Since Os, Ru, and Re are all noble metals, the high cost of these materials will also hinder their large scale production and a broad application in industry.

Transition metal tetraborides, TMB4, are promising candidates of ultraincompressible and hard materials. In general, higher boron content incorporates additional B-B covalent bonds, which would in principle lead to improved hardness. This correlation, although currently still under debate, appears to hold well for some tetraborides such as WB3 (originally reported as WB4),9 FeB4,10 and CrB410,11 all of which exhibit superior mechanical properties. Besides intrinsic mechanical properties, synthesis condition is another factor that must be considered because the current techniques for the synthesis of TMB4 require either very high temperature such as arc melting or extreme pressure conditions. For massive and industrial-scale production, the use of earth-abundant and inexpensive materials along with modest synthesis P-T conditions is highly desired. Tungsten monoboride, WB, which can be synthesized under 3 GPa and 1000 °C and exhibits a high hardness of ~28 GPa,15 is a good example of ultraincompressible and hard materials based on transition metal monoboride.

In this letter, we studied systematically the hardness and elastic and electrical properties of monoboride CrB, by means of experiments and first principles calculations. The observed mechanical behaviors are found to be closely related to the formation of polar Cr-B bonds interlinked with strong zigzag B-B covalent bonding network in the crystal structure of CrB. The presence of Cr-Cr bimetallic layers should provide a unique combination of metal and ceramic properties.

Commercially available crystalline powders of Cr (>99.9% pure) and B (>99.5% pure) in a molar ratio Cr:B = 1:1.05 were homogeneously mixed for the synthesis of CrB. In each experimental run, a pre-pressed pellet was placed in an MgO capsule, which was then sealed in a graphite heater. High-P experiments were performed in a DS 6 × 600 T cubic press. At the target pressure of 6 GPa, the temperature was gradually increased to 1400 K at a heating rate of 360 K/min, and the sample was soaked for 15 min before quenching to room temperature. After turning off the...
electric power, the sample temperature can be rapidly dropped under 373 K in 60 s because the anvils are surrounded by the cooling water tubing.

The final products were characterized by x-ray diffraction with Cu Kα radiation. The crystal structure was refined based on XRD data using Rietveld refinements and the GSAS software. The Vickers hardness was measured using a micro-hardness tester on well-sintered bulk samples under different applied loads of 10–1000 g. Under each load, the measurement was repeated 10 times with a dwelling time of 15 s, and the reported Vickers hardness is the mean value of 10 data points. The uncertainty σ is calculated from: $\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (x_i - \bar{x})^2}$, where $N = 10$ in our case, $x_i$ is the hardness value from each individual indentation, and $\bar{x}$ is the mean value of the measured hardness.

High-P synchrotron x-ray diffraction experiments using a diamond-anvil cell (DAC) were performed at the Beijing Synchrotron Radiation Facility (BSRF), China. The obtained boride was ground into powders and loaded into the sample hole in a stainless steel gasket with neon as pressure-transmitting medium. A few ruby balls were also loaded into the same sample chamber to serve as internal pressure standard. The collected angle-dispersive diffraction data were analyzed by integrating 2D images as a function of 2θ using the program Fit2D to obtain conventional, one-dimensional diffraction profiles.

Figure 1(a) shows the crystal structure of CrB with space group of Cmcm (No. 63) refined from XRD pattern. The refined lattice parameters and atom positions are in good agreement with Ref. 18, and listed in Table S1. As shown in Figure 1(a), each Cr atom is surrounded by seven B atoms with three type denoted as B1, B2, and B3. The B1 atoms, which form a tetragonal plane parallel to the a-c plane, are closest to Cr atoms with a distance of ~2.19 Å, representing the strongest bonding between the Cr and B atoms. Cr-B2 and Cr-B3 bonds have longer distances of ~2.22 Å and 2.29 Å, respectively, suggesting that weaker interactions. On the other hand, the B1-B2 bonds form zigzag boron chains with a bonding distance of ~1.78 Å in the b-c plane, which is much shorter than that in WB. This may play an important role in resisting the plastic deformation.

Phase stability and compressibility of CrB were investigated by synchrotron x-ray diffraction in a DAC. Figure 1(b) shows selected XRD patterns collected under room-temperature compression. The orthorhombic CrB is structurally stable up to 16 GPa and no phase transition was observed. The derived pressure-volume data for CrB are fitted to the second order Birch-Murnaghan equation of state as shown in Figure 1(c), and the obtained bulk modulus, B, is 269.0 (5.9) GPa. Figure S2 shows the relative cell parameters as a function of pressure; CrB displays more nearly isotropic compressibility compared to CrB2. As expected, the c-axis is slightly less compressible than the a and b axes because the zigzag boron-boron chains are primarily along the c direction. While along the a and b directions, the axial compressibility is mainly determined by the strength of Cr-B and Cr-Cr bonds.

The density of the sintered pellet was measured by using the Archimedes method. The measured density is ~5.4 g/cm³, which is ~89% of the theoretical density (~6.1 g/cm³), indicating that a small amount of porosity and/or unreacted boron may be present in the sintered sample, the latter of which is insensitive to x-ray diffraction measurement. The Vickers hardness measurements were performed on the bulk sample. As shown in Figure 2, the determined asymptotic hardness of CrB is ~19.6 (0.7) GPa, which is comparable to that of the well-known WC and OsB2. However, CrB shows higher hardness over CrB2 (16 GPa under the load of 500 g), indicating that the boron content is not necessarily a determining factor for the design of hard and superhard materials. As will be discussed later in the paper,
the enhanced mechanical behavior of CrB is mainly attributed to the strong 3D Cr-B and zigzag B-B bonding networks.

Figure S3 shows a typical electrical resistivity-temperature curve of metallic behavior of CrB. The resistivity at room temperature is about 2.3 \( \mu \Omega \) m, comparable to some metal alloy. The resistivity decreases linearly with decreasing temperature in the range of 300–60 K, and then flattens out and approaches a plateau value of 0.4 \( \mu \Omega \) mK as temperature further decreases to 2 K. The upturn of resistivity at low temperatures due to the Kondo effect was not observed, suggesting that the scattering of conduction electrons due to magnetic impurity is negligibly weak. The data from 2 to 60 K are fitted by a formula \( \rho = \rho_0 + AT^n \), where \( \rho_0 \) is the residual resistivity, and the observed data can be well described by \( \rho_0 = 0.4 \mu \Omega \) m and \( n = 2.7 \). The residual resistivity ratio RRR, defined as \( \rho(300 K)/\rho(0) \), is 5.7, which is very small for the large contribution of impurity (extra boron) or grain boundary to the resistivity.

First principles calculations were performed using the VASP code with the generalized-gradient approximation proposed by Perdew and Wang for exchange-correlation functional. The optimized lattice constants of orthorhombic CrB (referred as oS8 later in the manuscript, \( a = 2.925 \) Å, \( b = 7.839 \) Å, \( c = 2.915 \) Å, listed in Table I) are in good agreement with the experimental results and previous Density Functional Theory (DFT) calculations. Meanwhile, single-crystal elastic constants of CrB were calculated using the efficient strain-energy method. The obtained elastic constants of oS8 are listed in Table S2. By means of the Voigt averaging method, we obtained the Voigt bulk modulus \( B_V = 304.8 \) GPa, shear modulus \( G_V = 225.4 \) GPa, and Poisson ratio \( \nu = 0.203 \). The Voigt bulk modulus from simulation is comparable to our experiment value ~269 GPa. In addition, the tetragonal phase of CrB (referred as t116 later) was also calculated for comparison, and the calculated results are summarized in Tables I and S2. Surprisingly, even with different crystal structures and compliance parameters, the oS8 and t116 CrB phases show very similar bulk modulus and shear modulus. The calculated shear moduli are even comparable to hard ReB2 and WB3, indicating that they have similar shear stiffness.

In order to gain deeper understanding into the mechanical properties of oS8 and t116-CrB, the orbital decomposed electronic density of states (DOS) is calculated and shown in Figure 3. It is found that both CrB phases show finite DOS at the Fermi level and hence exhibit metallic behavior. Another important feature in Figure 3 is the presence of the so-called “pseudo-gap” for t116-CrB, which is the difference between the bonding and anti-bonding states. This suggests a strong “pseudo-covalent” contribution due to the hybridization between Cr d orbital and B p orbital. However, the “pseudo-gap” does not exist in oS8-CrB, indicating that the oS8 phase should exhibit a conventional metallic-type electrical conductivity, consistent with the experimental results discussed above. Figure 4 shows the bond structures and isosurface of the valence charge density difference (VCDD) of t116 and oS8-CrB.

![FIG. 2. Measured Vickers hardness as a function of applied loads from 10 g to 1000 g.](image)

![FIG. 3. Partial density of states for (a) t116-CrB and (b) oS8-CrB. The red solid and blue dashed curves are from Cr d orbital and B p orbitals, respectively. The vertical dashed lines indicate the Fermi level.](image)

| TABLE I. Experimental and simulated results of lattice parameters, bulk modulus, shear modulus, and Poisson’s ratio of orthorhombic (No. 63) and tetragonal (No. 141) phase CrB. |
|---|---|---|---|---|---|---|
| CrB | a (Å) | b (Å) | c (Å) | B (GPa) | G (GPa) | \( \nu \) |
| Experiment | 2.959 | 7.846 | 2.919 | 269.0 |
| oS8 | 2.925 | 7.839 | 2.915 | 304.8 | 225.4 | 0.203 |
| t116 | 2.919 | 15.673 | 306.4 | 230.5 | 0.199 |
the presence of metallic Cr bilayers would be responsible for the weakest shearing paths in a similar manner to that shown in WB₃.

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19See supplementary material at http://dx.doi.org/10.1063/1.4922147 for the refined XRD pattern, relative cell parameters as a function of pressure, and the electrical resistivity of CrB.