

Correlation between hardness and elastic moduli of the ultraincompressible transition metal diborides RuB₂, OsB₂, and ReB₂

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The ultraincompressible transition metal diborides RuB₂, OsB₂, and ReB₂ were synthesized by arc melting the elemental metals and boron under an argon atmosphere at ambient pressure. The hardness and Young's modulus were measured using nanoindentation with a Berkovich diamond indenter. The bulk modulus and shear modulus were derived based on an isotropic model and then plotted as a function of hardness. A strong correlation is observed between the hardness and shear modulus for these transition metal diborides. © 2008 American Institute of Physics.

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Hard and superhard materials are of great interest because of their widespread industrial applications as abrasives, cutting tools, and in wear prevention. Superhard materials are often defined as having a microhardness exceeding 40 GPa.¹ However, hardness is a complex parameter involving elasticity and plasticity and is governed by both intrinsic properties, i.e., bond strength, cohesive energy and crystal structure, and extrinsic properties, i.e., defects, stress fields, and morphology. In general, a superhard material possesses a high bulk modulus, a high shear modulus, and a high shear strength.² A material with a high bulk modulus tends to elastically resist volume compression, while a material possessing a high Young's modulus tends to elastically resist linear compression. A material having a high shear modulus tends to resist elastic deformation in a direction different from that of the applied load thus resisting shape change rather than volume change. A material is considered to be hard if it resists plastic deformation involving irreversible motion of atoms with respect to each other via the creation and movement of dislocations. The activation and mobility of dislocations are governed by the resolved shear stress. However, the shear strength of a material is difficult to measure. Therefore, considerable effort has been devoted to correlate hardness with other physical properties such as bulk modulus^{1,3,4} and shear modulus.^{2,5,6}

A promising approach to design superhard materials is to combine transition metals possessing a high bulk modulus with small, covalent bond-forming atoms such as boron, carbon, nitrogen or oxygen.⁷ Recently, both OsB₂ and ReB₂ have been experimentally demonstrated to have high bulk moduli of 365–395 (Ref. 8) and 360 GPa,⁹ respectively, which are not that far from diamond (443 GPa).^{10,11} The theoretical bulk moduli for OsB₂ and ReB₂ based on first-principles calculations have also been recently determined.^{12–16} In order to elucidate possible relationships between hardness and elastic moduli, we report here on the hardness values and Young's moduli of three ultraincom-

pressible transition metal diborides—RuB₂, OsB₂, and ReB₂—measured using nanoindentation techniques. The bulk and shear moduli are then calculated using an isotropic model and the correlation between hardness and stiffness is further examined.

RuB₂, OsB₂, and ReB₂ were synthesized by arc melting elemental boron with the metals Ru, Os or Re with an applied current of 80 A under an argon atmosphere at room temperature. The arc-melted crystals were crushed into powder and then characterized using a PANalytical XPert Pro x-ray powder diffractometer with Cu K α radiation. The experimental details are described in Ref. 9. The nanoindentation testing was performed using a MTS Nano Indenter XP instrument with a diamond Berkovich indenter. The hardness (H) and Young's modulus (E) were calculated using the method developed by Oliver and Pharr.¹⁷

The load-displacement curves with a 0.05 s⁻¹ strain rate and 720 mN maximum load were performed on single grains for each of the three different transition metal diborides (Fig. 1). Under the same load, the diamond indenter penetrated deeper in OsB₂, and RuB₂ than into ReB₂, implying that ReB₂ is the hardest substance among these three transition

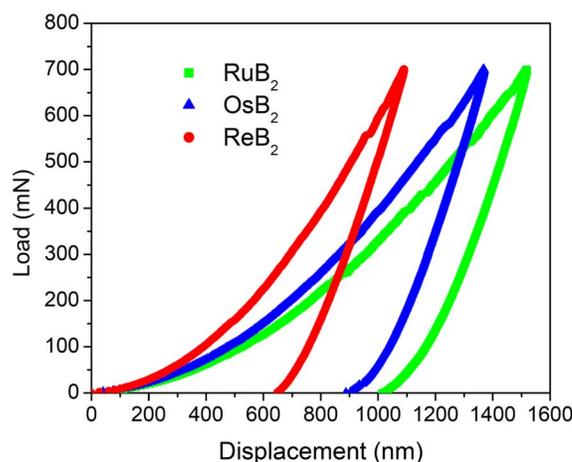


FIG. 1. (Color online) Load-displacement curves for RuB₂, OsB₂, and ReB₂ with the maximum load of 720 mN.

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TABLE I. The hardness H , Young's modulus E , and Poisson's ratio ν , for RuB₂, OsB₂, and ReB₂.

Material	H (GPa)	E (GPa)	$E_{\text{first-principles calculation}}$ (GPa)	ν
RuB ₂	19.2 ± 2.1	366 ± 45	...	0.27 ^a
OsB ₂	21.6 ± 3.0	410 ± 35	426–444 ^a	0.27 ^a
ReB ₂	37.0 ± 1.2	712 ± 43	683–699 ^b	0.18 ^b

^aReference 12.^bReference 16.

metal diborides. The average measured hardness values are 19.2 ± 2.1, 21.6 ± 3.0, and 37.0 ± 1.2 GPa for RuB₂, OsB₂, and ReB₂, respectively. Clearly, ReB₂ is significantly harder than RuB₂ and OsB₂ and we believe it is the hardest of the known transition metal diborides. Note that the nanoindentation data for ReB₂ differ from our previously reported microindentation values,⁹ since the Vicker's technique measures the residual indent without taking into account the material's elastic response.

Since the Poisson's ratios (ν) of these three transition metal diborides have not been experimentally measured yet, the theoretical values recently reported, 0.27 for RuB₂ and OsB₂ (Ref. 12) and 0.18 for ReB₂,¹⁶ were used to calculate the Young's moduli. The value of the Poisson's ratio is indicative of the degree of directionality of the covalent bonds. The smaller Poisson's ratio for ReB₂ compared to OsB₂ and RuB₂ indicates a stronger degree of covalent bonding resulting in the higher hardness. The measured Young's moduli are compared with those predicted from first-principles calculations, as given in Table I. Both of the experimental Young's moduli for OsB₂ and ReB₂ are in good agreement with the theoretical values. In addition, ReB₂ possesses the highest measured Young's modulus, 712 ± 43 GPa, of any known transition metal diboride. This can be compared to, for example, the Young's modulus of TiB₂, 446–540 GPa.¹⁸

As seen in Fig. 1, the loading curves for RuB₂, OsB₂, and ReB₂ contain multiple pop-in events. The mechanisms of pop-in events observed in other materials are associated with a burst of dislocations, cracking, and elastic-plastic deformation transitions.^{19–22} However, the discontinuities reported here result from crack initiation and propagation around the indentations, since there are no cracks observed near the indentation when the applied load is lower than that for the first pop-in event. In OsB₂, cracks form in grains oriented with the {010} planes at the lower critical force.²³ In contrast, a higher critical force is needed to produce cracks for grains less oriented with the {010} planes. In ReB₂, the critical force for the first pop-in event is about 600 mN and

the deviation is not significant due to less asymmetry in hexagonal ReB₂ when compared to orthorhombic OsB₂. Additionally, the length of the crack surrounding the indentation impression is much shorter for ReB₂ than that observed within OsB₂. In RuB₂, there are few visible cracks found around the residual indentation impression. These results indicate that the critical forces needed to cause pop-in events depend on the materials, crystallographic orientation, and quality (i.e., impurities, defects, etc.) of the grains.

Gou *et al.*¹² and Wang²⁴ have demonstrated that OsB₂ and ReB₂ have little elastic anisotropy; therefore, an isotropic model is used to estimate the bulk modulus (B) and shear modulus (G) based on the Young's modulus (E) derived from nanoindentation experiments carried out on these three transition metal diborides. The calculated bulk and shear moduli are compared with first-principles calculations and x-ray experimental data in Table II. Both the bulk modulus and shear modulus of ReB₂ calculated from an isotropic model are in excellent agreement with those based on x-ray measurements and first-principles calculations. The measured bulk modulus for OsB₂ ranges from 365–395 GPa depending on the value of B'_0 used in the Birch–Murnaghan equation of state.⁸ Theoretical calculations of the bulk modulus for OsB₂ based on first-principles calculations are reported to be 307–365 GPa.^{12–15} However, the bulk modulus derived from an isotropic model is 297 ± 25 GPa which is 18%–25% smaller than the x-ray measurement and lies within the lower bound of the first-principles calculation. Additionally, the shear modulus reported here is also within the lower bound of the first-principles calculation. For RuB₂, the isotropically calculated (265 ± 33 GPa) and experimentally measured bulk modulus (281 GPa when B'_0 is set to 4) are consistent with each other. However, the bulk modulus (335 GPa) based on first-principles calculation is 16%–21% higher since the exchange-correlation energy function is treated with the local density approximation, resulting in an underestimation for the equilibrium volume, and thus an overestimation for the bulk modulus.¹³

As mentioned earlier, many attempts have been made to correlate hardness with other physical properties for a wide range of hard materials.^{1–6} The hardness as a function of bulk modulus and shear modulus for the transition metal diborides RuB₂, OsB₂, and ReB₂ are plotted in Figs. 2(a) and 2(b), respectively. The data of hardness versus shear modulus lie along the same straight line, while the data of hardness versus bulk modulus scatter away from a linear relationship. This is likely due to the bulk modulus' dependency on the spatially averaged electron density within the three-dimensional densely packed networks without respect to the

TABLE II. The bulk modulus B and shear modulus G for RuB₂, OsB₂, and ReB₂.

	B (GPa)	$B_{\text{x-ray measurement}}$ (GPa)	$B_{\text{first-principles calculation}}$ (GPa)	G (GPa)	$G_{\text{first-principles calculation}}$ (GPa)
RuB ₂	265 ± 33	281	335 ^c	144 ± 18	...
OsB ₂	297 ± 25	365–395 ^d	307–365 ^{a,c,e,f}	161 ± 14	168–254 ^{a,c}
ReB ₂	371 ± 22	360 ^g	347–377 ^b	302 ± 18	285–299 ^b

^aReference 12.^bReference 16.^cReference 13.^dReference 8.^eReference 14.^fReference 15.^gReference 9.

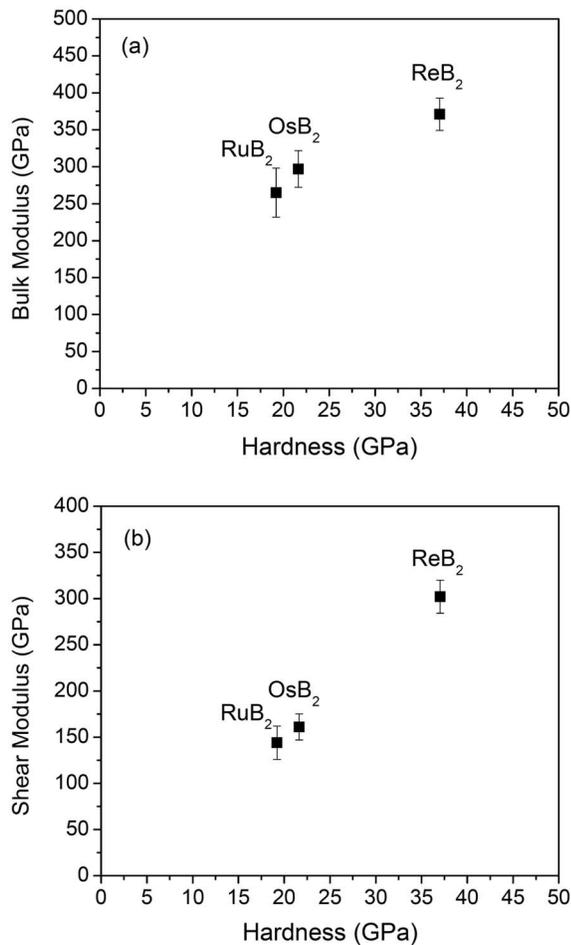


FIG. 2. Hardness as a function of the (a) bulk modulus and (b) shear modulus for selected transition metal diborides.

type of bonds formed, i.e., metallic, ionic or covalent. On the other hand, the shear modulus is sensitive to the nonuniform distribution of valence electron density corresponding to the kind of directional bonds that in turn act as barriers for dislocation movement. Therefore, the shear modulus is a significantly better qualitative predictor of hardness than the bulk modulus. This result therefore may provide a guiding principle for seeking superhard transition metal borides since incompressibility (the reciprocal of bulk modulus) is a necessary but insufficient attribute of a hard material.

In summary, three ultraincompressible transition metal diborides—RuB₂, OsB₂, and ReB₂—were synthesized by arc melting at ambient pressure. The hardness and Young's modulus of ReB₂ measured using nanoindentation are 37 and

712 GPa, respectively. Thus, ReB₂ is currently the hardest known transition metal diboride. Bulk and shear moduli were derived using an isotropic model and then plotted versus hardness. A strong correlation is observed between the hardness and shear modulus for the transition metal diborides resulting from the sensitivity of shear modulus on the directionally nonuniform distribution of valence electron density.

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