

## Materials potentially harder than diamond: Quenchable high-pressure phases of transition metal dioxides

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The materials with the highest bulk moduli are also the hardest. Diamond has the highest bulk modulus measured, and is the stiffest and also the hardest material known. Our recent pressure–volume measurements indicate that the high-pressure phases of ruthenium and hafnium dioxides formed in a diamond anvil cell at pressures greater than 12 and 42 GPa, respectively, at room temperature, which are at least partly metastable under normal conditions, have bulk moduli similar to or greater than that of diamond, making them the stiffest and possibly therefore the hardest materials known at present.

There is considerable interest in finding other materials that are as hard or harder than diamond. Research has centred on several borides, carbides, nitrides and oxides [1]. Hardness is obtained from mechanical tests using indentors, after which the depth of the indentation is measured. Hardness is therefore related to the linear compressibility, shear strength and plastic flow of a material. Stiffness can be characterized by the bulk modulus, the inverse of the compressibility. In fact, the hardest materials exhibit the highest bulk moduli and hence are also the stiffest materials. This correlation is illustrated in Fig. 1. Metals have been omitted in this figure because even in their hardened state they have lower

hardness than ionic or covalent compounds due to their low shear strength.

In this letter, we present our findings from the pressure–volume relationships obtained by angle-dispersive X-ray powder diffraction on the high-pressure phases of  $\text{RuO}_2$  and  $\text{HfO}_2$ . These phases are found to have bulk moduli at ambient pressure ( $B_0$ ) similar to or greater than that of diamond. As with diamond, which is itself a quenched, high-pressure phase of carbon, these high-pressure oxide phases are also metastable under ambient conditions.

At room temperature the pressure,  $\text{RuO}_2$  and  $\text{HfO}_2$  adopt the rutile and baddeleyite structures, respectively. Rutile- $\text{RuO}_2$ , with a  $B_0$  of 270 GPa [8], is already among the stiffest materials following diamond [2], cubic-BN [4], stishovite- $\text{SiO}_2$  [9], all quenched high-pressure phases and TiN [3]. Apart from diamond, for which  $B_0 = 443$  GPa, these materials have bulk moduli ranging between 369 and 294 GPa.  $\text{HfO}_2$  is moderately incompressible with a  $B_0$  of 145 GPa [10].

Powdered  $\text{RuO}_2$  and  $\text{HfO}_2$  (Alfa Products) were placed in 150–200  $\mu\text{m}$  diameter holes in stainless steel gaskets pre-indented to a thickness of 100  $\mu\text{m}$  along with silver powder or a ruby chip, respectively, between the anvils of a diamond anvil cell. Silicone oil was used as a pressure transmitting medium. Pressures were measured based on the shift of the 111 reflection of silver using the equation of state values of Syassen and Holzapfel [11] and the shift of the ruby  $R_1$  fluorescence line [12] for the  $\text{RuO}_2$  and  $\text{HfO}_2$  experiments, respectively. X-ray diffraction (XRD) patterns were obtained on films placed cylindrically at a radius of 25.10 mm using zirconium-filtered molybdenum radiation from a fine-focus tube. Exposure times were of the order of 24 h. All experiments were performed at room temperature and data were taken upon compression and decompression. Films were analysed using a Molecular Dynamics Personal Densitometer. Observed intensities were integrated as a function of  $2\theta$ , according to the method of Meade and Jeanloz [13]. In addition, standard Debye–Scherrer photographs were obtained on the material recovered after the experiments several days after the complete, and gradual, pressure release, indicating that these phases are metastable under ambient conditions. All figures in parentheses refer to standard deviations.

$\text{RuO}_2$  undergoes two phase transitions at high

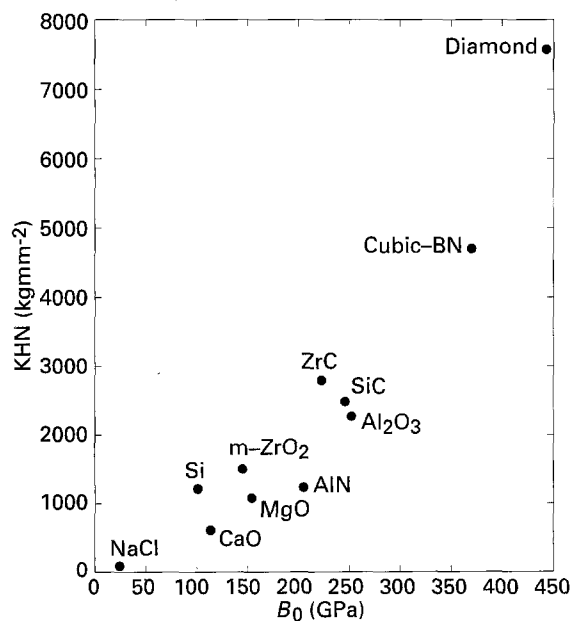


Figure 1 Knoop hardness as a function of bulk modulus for representative materials [1–7].

pressure, [14]; the first from rutile to an orthorhombic distortion of rutile below 8 GPa and the second to a cubic, fluorite-structured phase above 12 GPa. The transition to the fluorite phase is slow at room temperature and some of the orthorhombic phase remained up to 40 GPa, (Fig. 2). The refined lattice parameter of the fluorite-type phase, calculated based upon three to five diffraction lines, is  $a = 0.4836(6)$  nm and  $0.4727(4)$  nm at 0.0001 and 40 GPa, respectively. The relative volume of the fluorite phase at normal pressure is 0.914. The pressure dependence of the volume is shown in Fig. 3.

HfO<sub>2</sub> undergoes three transitions at high pressure [10], culminating in the formation of a tetragonal phase above 42 GPa with cell constants of  $a = 0.498(2)$  nm and  $c = 0.422(1)$  nm at 47.5 GPa and  $a = 0.507(4)$  nm and  $c = 435(2)$  nm at 0.0001 GPa as calculated from five to six diffraction lines. The relative volume of the tetragonal high pressure phase as determined in a standard camera at normal pressure is 0.815. The pressure–volume dependence of this tetragonal phase of HfO<sub>2</sub> is given in Fig. 4.

The pressure–volume data for both oxides were fitted with Birch's equation of state [15] (Figs 3 and 4):

$$P = 1.5B_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}][1 + 0.75(B'_0 - 4)((V/V_0)^{-2/3} - 1)]$$

where  $V_0$  is the volume at ambient pressure and  $B'_0$  the first derivative of the bulk modulus at normal pressure. The fit to the linearized form  $F = B_0 - 1.5B_0(4 - B'_0)f$  where  $F = P/3f(1 + 2f)^{2.5}$

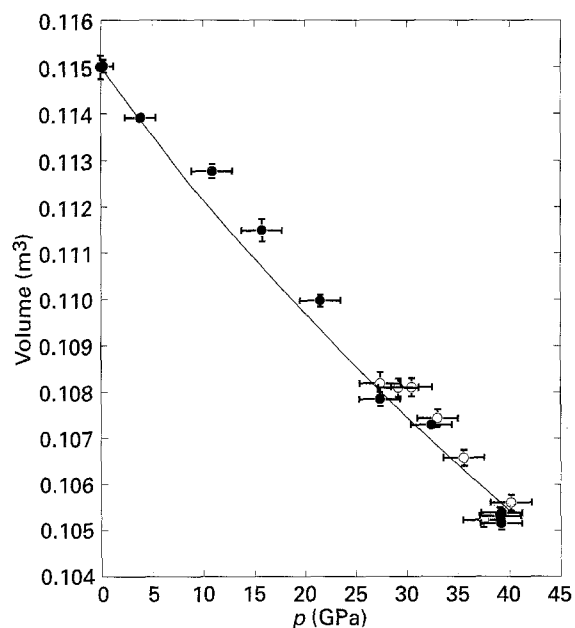


Figure 3 Pressure–volume dependence of cubic-RuO<sub>2</sub>. Open symbols refer to points obtained on compression and solid symbols to those obtained on decompression. The solid line represents a Birch–Murnaghan equation of state fit to the experimental data with  $B_0 = 399(6)$  GPa and  $B'_0 = 3.5$ . (The pressure values between 5 and 20 GPa are less accurate than the others because the 200 reflection of cubic-RuO<sub>2</sub> partially overlapped the 111 reflection of silver.)

and  $f = 0.5[(V_0/V)^{2/3} - 1]$  yields for the high pressure data of both compounds, where  $f$  is not too close to zero, a  $B'_0$  value of  $4 \pm 1.5$ .  $B'_0$  cannot be accurately measured over the pressure range inves-

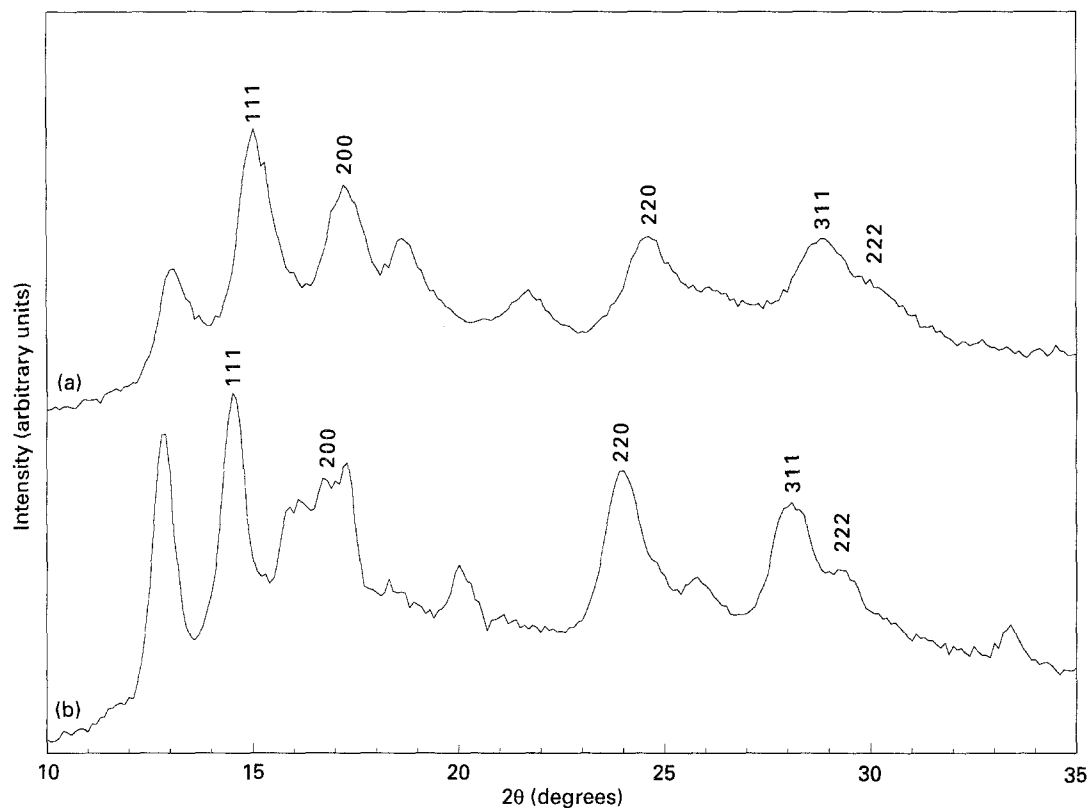


Figure 2 XRD patterns of RuO<sub>2</sub> at (a) 40.2 GPa and (b) 0.0001 GPa after decompression. Reflections due to the cubic phase are indexed; the other reflections arise from the lower pressure phases, silver and iron from the gasket.

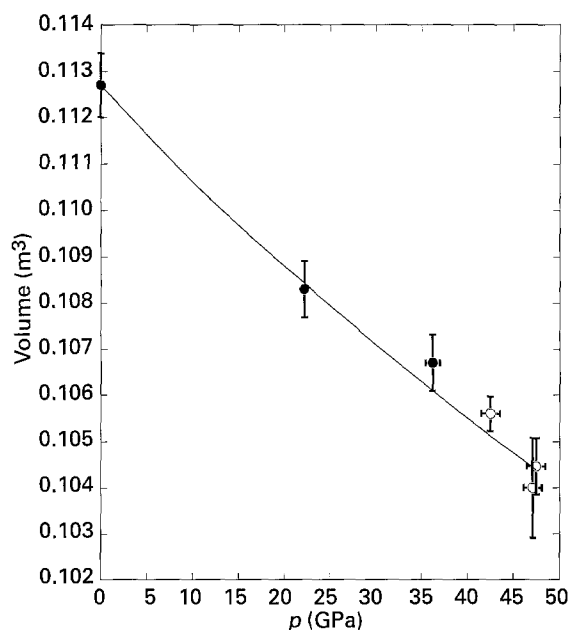


Figure 4 Pressure–volume dependence of tetragonal-HfO<sub>2</sub>. Open symbols refer to points obtained on compression and solid symbols to those obtained on decompression. The solid line represents a Birch–Murnaghan equation of state fit to the experimental data with  $B_0 = 553(17)$  GPa and  $B'_0 = 3.5$ .

tigated although the volume data was obtained from three to six diffraction lines. Accordingly, we set  $B'_0$  to 3.5, the value calculated for cubic boron nitride [4], which similarly is an incompressible, covalently-bonded solid. This value is close to the usual value of 4 to 5 commonly used.

With such a  $B'_0$  value, and using the  $V_0$  values determined under ambient conditions, several days after the pressure experiments, a  $B_0$  of 399(6) GPa is obtained for the high pressure phase of RuO<sub>2</sub>, placing this dioxide in between diamond and cubic-BN, the next hardest and next stiffest material. Under the same conditions, a  $B_0$  of 553(17) GPa is obtained for hafnium dioxide, significantly greater than that of diamond. A reasonable estimate of the accuracy of the bulk modulus is 10% under the above conditions.

The present results indicate that both RuO<sub>2</sub> and HfO<sub>2</sub> are significantly stiffer than cubic-BN and are as stiff or stiffer than diamond. It is the first time that a high pressure phase that can be kept in a metastable state under normal pressure is reported to display a higher bulk modulus than diamond. This

opens up the possibility of finding new stiff materials. From the correlation between bulk modulus and hardness, it is evident that the high-pressure phases of these oxides, and possibly of several other transition metal dioxides, could present a new family of ultra-hard materials.

In both compounds, partial reverse transformation occurred. It is therefore of interest to find means to stabilize these and other high-pressure oxide phases, such as high-pressure phases of silica and zirconia, which could have great potential as ultra-hard materials. This could be achieved by heating these dioxides under high pressure and then quenching. It is interesting to note that the intermediate, orthorhombic phase of RuO<sub>2</sub> was stabilized by the addition of Rh, Ti or Cr [16] and that a similar approach could be taken with the other high-pressure phases.

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