Hardness and elasticity in cubic ruthenium dioxide

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The Knoop hardness of the highly incompressible cubic phase of ruthenium dioxide was found to be 19–20 GPa from indentation tests. This value scales well with the shear modulus approximated by the elastic constant C_{44} of 144 GPa obtained from Brillouin scattering measurements. This work provides evidence that the shear modulus is a better indicator of hardness than the bulk modulus for ionic and covalent materials. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1401786]

Ruthenium dioxide, which has a rutile-type structure under ambient conditions, transforms into cubic phase with a modified-fluorite-type structure above 12 GPa.[1–3] This dense, high-pressure, cubic form of RuO_2, which can be recovered at ambient pressure and temperature, was found to have a measured bulk modulus[1] of $B=399$ GPa, which is only 10% less than that of diamond, the least compressible and hardest material known. There is a general trend toward greater hardness with increasing bulk modulus for ionic and covalent materials[4–10] (Fig. 1). This cubic form of RuO_2 was thus considered a possible candidate as a hard material. The results of *ab initio* calculations[11,12] also indicate a very high bulk modulus for cubic RuO_2 ranging from 299 to 380 GPa, which are among the highest values known. The calculated value of $C_{44}=147$ GPa, however, was found to be lower than that for many hard materials, such as cubic carbides, which have C_{44} values of typically 150–270 GPa. We have thus undertaken to directly measure both the hardness, H, and C_{44} of cubic RuO_2 in order to further the understanding of the physical origin of mechanical hardness.

The cubic form of ruthenium dioxide was prepared at 20 GPa and 1100 °C in a MA-8 multianvil device described elsewhere.[3] The recovered samples with volumes of the order of 1 mm³ were polished prior to further study. Knoop hardness measurements were performed using a Shimadzu-type M microhardness tester with loads of 490, 980, and 1960 mN. The resulting hardness values of 19–20 GPa were independent of the load, and control measurements made on an alumina sample were in excellent agreement with previous studies.

Brillouin spectra were obtained using a six-pass tandem Fabry–Pérot interferometer. The efficient mechanism for light scattering in opaque materials is the so-called ripple mechanism, which involves surface elastic excitations. These excitations, in the case of a semi-infinite solid such as RuO_2, are directly related to the bulk elastic constants of the material. Analysis of the Brillouin spectra requires a Green's function approach of the equation of motion of elasticity, which leads to the spectral density of the perpendicular displacement $u_z(z)$ of the free surface (at $z=0$).[13] The scattered intensity at frequency ω depends upon the wave vector $k_\parallel$ of the excitation, where $k_\parallel$ is the **k** component parallel to the surface of the sample and is defined by the experimental geometry: for backscattering geometry, it becomes $k_\parallel = 2k_i \sin\theta$, where $k_i = 2\pi/\lambda_i$ is imposed by the incident wavelength λ_i of the laser and θ is the angle between the incident beam and the normal to the sample. The intensity is then proportional to $\langle |u_z(0)|^2 \rangle$, which exhibits a pole at ω_R corresponding to the Rayleigh surface wave with velocity
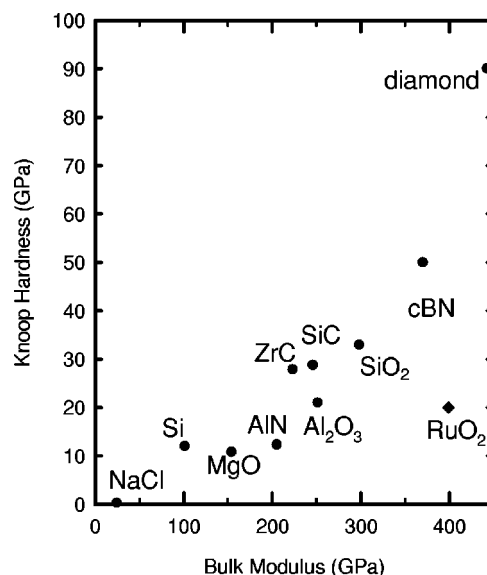

FIG. 1. Hardness as a function of the bulk modulus for a representative selection of ionic and covalent materials.

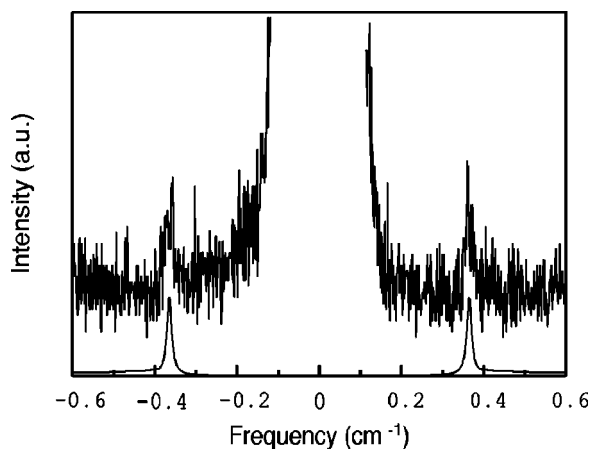[a)]Electronic mail: leger@cnrs-bellevue.fr

FIG. 2. Brillouin spectrum of cubic RuO_2. The solid line below the spectrum represents the best fit of $\langle |u_z(0)|^2 \rangle$ to the Rayleigh line.

FIG. 3. Hardness as a function of the shear modulus for a representative selection of ionic and covalent materials.

$V_R = \omega_R / k_\parallel$. Figure 2 shows a typical Brillouin spectrum and the best fit of $\langle |u_z(0)|^2 \rangle$ to the Rayleigh line. The frequency ω_R is closely related to the transverse C_{44} elastic constant, whereas other characteristic elastic features in the spectra should in principle permit the determination of C_{11}. Such additional contributions could not be observed in the present experiments on this black phase of RuO_2 due to the relatively poor signal to noise ratio. Our measured value of C_{44}, 144 GPa, is in very good agreement with the theoretical value[11] of 147 GPa. The values of C_{11} and C_{12} were obtained from *ab initio* calculations[11] and the value of the Voigt averaged shear modulus, $G = (3C_{44} + C_{11} - C_{12})/5$, of 140 GPa is very close to that of C_{44}. In general for cubic materials the shear modulus is slightly lower than the value of C_{44}. Since the theoretical calculations indicate that G is only 5% lower than C_{44} in cubic RuO_2, the experimental value of C_{44} is used to approximate G in the following discussion.

The measured hardness of cubic RuO_2, which ranges from 19 to 20 GPa, is very similar to that of alumina, but is much lower than what might be expected based on the general trend between the hardness and bulk modulus (Fig. 1). There have been proposals that the shear modulus may be a better indicator of hardness.[14] If the values for cubic RuO_2 are added to a plot of hardness as a function of shear modulus (Fig. 3), it can be seen that the point fits in well with the values of other materials. It can be noticed that in this latter plot that there is less scatter. In the present case, the shear modulus thus gives a good indication of the hardness of cubic RuO_2.

The shear modulus of RuO_2 is close to that of alumina ($G = 163$ GPa),[15,16] and the hardness values are similar (Fig. 3). Cubic RuO_2 is thus among the hardest oxides, but it is not superhard and it is significantly less hard than stishovite (SiO_2),[17] which is the hardest oxide known with $H = 33$ GPa. The bulk modulus of cubic RuO_2 does not scale well with the measured hardness of this material and is very high with respect to the shear modulus. The bulk moduli of high-pressure phases in oxides are typically very high due to the number of short oxygen–oxygen contacts present in their structures.[10,18] A detailed study of the structure of cubic RuO_2 by neutron diffraction[3] indicated a large number of short O–O contacts of 2.6208 Å in the rhombohedral coordination polyhedron and even shorter interpolyhedral O–O
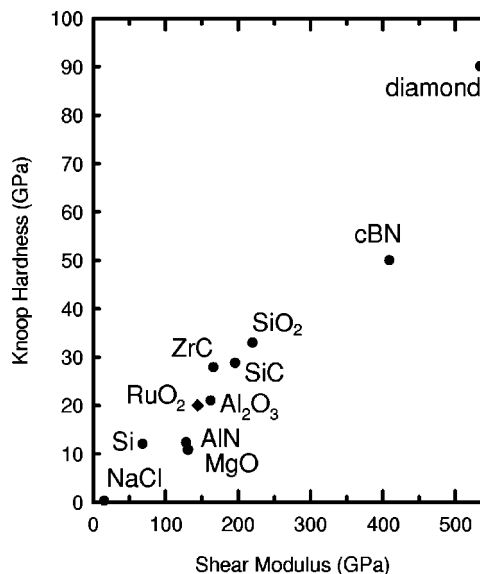
distances of 2.5054 Å, which are shorter than in any other oxide. These short O–O distances play an important role in the high bulk modulus of this material. In alumina,[19] in contrast, the average intrapolyhedral O–O distance is 2.719 Å in the AlO_6 octahedron and the bulk modulus is significantly lower,[14,15] $B = 251$ GPa. A second major difference, which should have an influence on the shear modulus, is that the polyhedra in cubic RuO_2 are entirely linked by shared corners, whereas in alumina all polyhedra share faces and edges and the structure can be expected to be more rigid with respect to shear stress. This provides added evidence that the structural topology[20] plays an essential role in determining the hardness of a material in addition to the required short interatomic distances.

Cubic ruthenium dioxide is found to be a hard material with hardness of 19–20 GPa, but it is not as superhard as what could be inferred from correlations between hardness and the bulk modulus. Instead, the hardness scales well with the shear modulus thereby providing evidence that the latter is a better indicator of potential hardness for ionic and covalent materials.

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