Discovery of hardest known oxide

SIR — Microhardness measurements on synthesized samples of stishovite, a high-pressure phase of silica, show that it is the hardest oxide yet discovered. Among polycrystalline materials, its hardness (33 gigapascals, GPa) rivals those of the hardest materials. Despite many searches[1–4], no material with a measured hardness comparable to diamond or cubic boron nitride has been identified until now.

Hardness (H) of ionic and covalent materials increases with bulk modulus[1–5]. Diamond has the highest known bulk modulus, B = 444 GPa, and is also the hardest material known, with single-crystal H = 90 GPa. It is followed by cubic boron nitride (cBN), with corresponding values of B = 369 GPa and single-crystal H = 48 GPa (refs 2, 4).

Theoretical calculations have been used in this search for hard materials, principally by looking for high-bulk-modulus compounds. A semi-empirical theory[1] was applied to group IV elements and III–V and II–VI compounds: $B = N/4\ (1{,}971-220I)d^{-3.5}$ (where N is the average coordination number, I is an empirical ionicity parameter and d the bond length). However, no superhard material has been synthesized as a result of these calculations and the stability of the predicted compounds has not been verified.

Under ambient conditions, the bulk modulus of ionic compounds is given by a general relationship: $B \propto Z_a Z_c/V$, where Z_a and Z_c are the formal anion and cation charges respectively, and V is the specific volume per ion pair[6]. High bulk moduli require high charges and small volumes; thus tetravalent cation dioxides could be hard. Under pressure, packing efficiency increases at phase transitions at which the cation coordination number (N_c) rises. As structures become more compact, compression becomes increasingly difficult and the bulk modulus rises. High-pressure phases may thus be hard materials. The transformation from graphite to diamond is the archetypical example.

Although silicon is the smallest tetravalent cation, the common forms of silicon dioxide are not hard because of their open structures in the cristobalite or quartz phases ($N_c = 4$). However, the high pressure phase[7] of silica, stishovite ($N_c = 6$), could potentially be a hard material. It is much denser than quartz, and is metastable under normal conditions[7]; its bulk modulus, 298 GPa (ref. 8), is significantly greater than that of alumina, 252 GPa, which is itself a hard oxide. Here, we report microhardness measurements on synthesized stishovite.

We performed synthesis experiments using a 1,200-ton uniaxial MA-8 multi-anvil apparatus (see ref. 9 for method), taking Raman and X-ray diffraction (see ref. 10 for image plate system) measurements. Microprobe analysis showed only silicon in the investigated region. We did the hardness tests, using a Knoop microhardness tester (Shimadzu type M) with loads of 490, 980 and 1,960 mN, on quenched samples after polishing. The hardness values obtained are independent of load and those of a test sample of alumina are in excellent agreement with values cited in the literature (see table).

Bulk moduli and Knoop hardness for polycrystalline hard materials

Material	B (GPa)	H (GPa)
B_4C	200	30
B_6O	200	30
SiC	248	29
Al_2O_3	252	21; 19*
SiO_2	298	33*
Sintered cBN	369	32
Sintered diamond	444	50

Values from ref. 4, except for B_6O (ref. 12) and asterisks (this work).

We treated a sample of α-quartz at 14 GPa and 1,000 °C; X-ray diffraction indicated that the sample was >99% stishovite. Micro-Raman spectroscopy indicated the presence of coesite and possibly quartz (line around 490 cm^{-1}) at various places on the sample surface; the lines of stishovite were observed in all cases. The hardness measurements ranged between 19 and 33 GPa. This scatter was attributed to the presence of small amounts of quartz or coesite, both of which have very low hardness, on the surface of the sample, as revealed by the Raman spectroscopy.

To test this hypothesis, we synthesized another sample at higher pressure: 20 GPa and 1,100 °C, using amorphous silica as the starting material. The transformation to polycrystalline stishovite was complete and we could detect no foreign phase by Raman spectroscopy or X-ray diffraction. The seven indentation measurements indicated a very high hardness ranging from 30.9 to 34.7 GPa, with an average value of 33 GPa, irrespective of the orientation of the indentor and the load. We noticed no change in the Raman spectrum before and after indentation.

The second experiment definitely shows that stishovite is very hard. The hardness of stishovite has been reported to be 17–20.8 GPa along different directions[7], but the sample used in this case had been synthesized at about 9.5–10 GPa and 1,200–1,400 °C. The transformation was not complete at this pressure, as later shown[11]. The small amount of lower-pressure phases present drastically modified the indentation results.

Polycrystalline stishovite is now the hardest oxide known; it is harder than alumina and boron oxides[12]. Other superhard polycrystalline materials include diamond and cubic boron nitride compacts; their hardness is much lower than that of single crystals, with hardness values of 50 and 32 GPa, respectively[4]. Thus, stishovite is among the hardest polycrystalline materials known.

Stishovite is thus potentially an important technological material. It may be the first member of a new family of superhard materials: the metastable high-pressure phases of high-valence cation oxides with high bulk moduli induced by an increase of the coordination number.

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