Hardness and thermal stability of cubic silicon nitride

LETTER TO THE EDITOR

Hardness and thermal stability of cubic silicon nitride

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Abstract
The hardness and thermal stability of cubic spinel silicon nitride (c-Si_3N_4), synthesized under high-pressure and high-temperature conditions, have been studied by microindentation measurements, and x-ray powder diffraction and scanning electron microscopy, respectively. The phase at ambient temperature has an average hardness of 35.31 GPa, slightly larger than SiO_2 stishovite, which is often referred to as the third hardest material after diamond and cubic boron nitride. The cubic phase is stable up to 1673 K in air. At 1873 K, α- and β-Si_3N_4 phases are observed, indicating a phase transformation sequence of c-to-α-to-β-Si_3N_4 phases.

(Some figures in this article are in colour only in the electronic version; see www.iop.org)

A third polymorph of silicon nitride synthesized recently by Zerr *et al* [1] under high-pressure and high-temperature conditions was, from theoretical calculations, predicted to have a hardness to be comparable to that of the hardest known oxide (stishovite, a high-pressure phase of SiO_2, hardness of 33 GPa) and significantly greater than the hardness of the two long-established hexagonal polymorphs α- and β-Si_3N_4, offering considerable industrial scope for the material [1]. Since then there has been considerable interest in this field [2–10]. In our previous work [3], we performed Rietveld structure refinements of x-ray powder diffraction data recorded using synchrotron radiation of the novel silicon nitride phase and determined the structure of the material to be a cubic spinel structure at ambient temperature with a space group Fd-$3m$, $Z = 8$, a unit cell of $a = 7.7339 \pm 0.0001$ Å, nitrogen position $x = 0.2583 \pm 0.0001$, and density $\rho = 3.75 \pm 0.02$ g cm^{-3}, while Schwarz *et al* [5] reported a unit cell of $a = 7.7381 \pm 0.0002$ Å and nitrogen position $x = 0.259\,68 \pm 0.000\,01$. At the moment, experimental determination of the hardness and the thermal stability of the new phase at temperatures above 1230 K are still lacking [3], which, however, are fundamental data for industrial applications of the material. In this letter, the hardness at ambient temperature and the thermal stability of the cubic silicon nitride (c-Si_3N_4) up to 1873 K in air were investigated by microindentation hardness measurements, and x-ray powder diffraction (XRD) and scanning electron microscopy (SEM), respectively. A hardness of about 35.31 GPa and a phase transformation sequence of c-to-α-to-β-Si_3N_4 phases were determined.
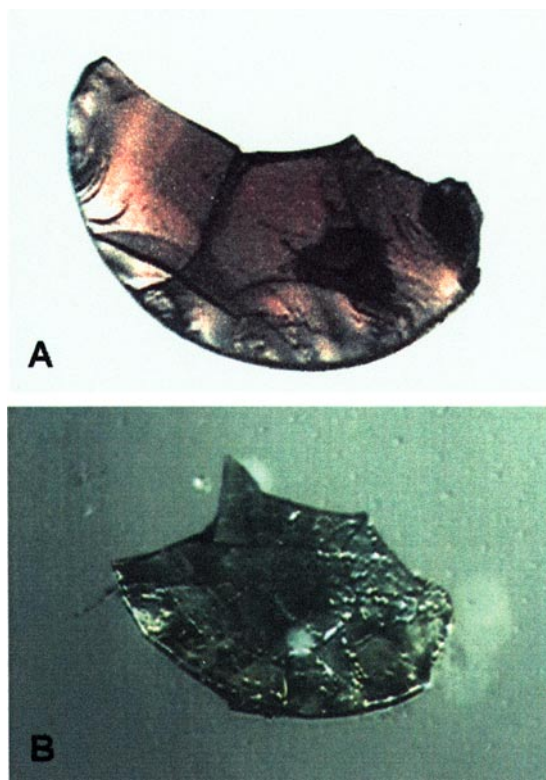
Figure 1. Optical micrographs of the as-prepared cubic spinel Si_3N_4 phase (a) and the sample annealed at 1873 K in air for 30 min (b).

A multi-anvil octahedra pressure assembly was employed in synthesis of the cubic spinel Si_3N_4 phase. A mixture of α- and β-Si_3N_4 powders was packed into 3.5 mm long platinum capsules of 2 mm outside diameter that were previously welded closed at one end. In order to exclude oxygen from the samples the capsules were placed in a vacuum chamber that was pumped down to 0.01 mbar and then flushed through several times with argon gas. The capsules were then removed from the chamber and quickly welded closed. Each capsule was placed at the centre of an 18 mm edge length MgO octahedral pressure assembly containing a $LaCrO_3$ stepped furnace. The MgO pressure assembly was placed in the octahedral cavity created by truncating corners of eight tungsten carbide cubes. Each cube was of 54 mm edge length with truncations of 11 mm edge length. The set of eight cubes was compressed between six hardened steel guide blocks over a period of 3 hours to a maximum force of 2000 tones, equivalent to 17 ± 0.5 GPa. The experiments were then heated to 2100 K for 1 hour and then quenched by turning off the power to the furnace. The temperature of the experiment was monitored using a W 3% Re–W 25% Re thermocouple. Heat treatments of the as-prepared c-Si_3N_4 were performed with a furnace up to 1873 K in air.

We performed hardness tests on a polished polycrystalline slice of the rod sample with 1.37 mm in diameter using a LECO microindentation hardness tester with a Vickers diamond. The surface of the sample was polished using diamond paste down to 1 μm. Four sets of indentation measurements were performed, in which more than ten measurements were carried out to estimate an average value for each set. They gave harnesses of 32.78, 35.94, 35.25 and
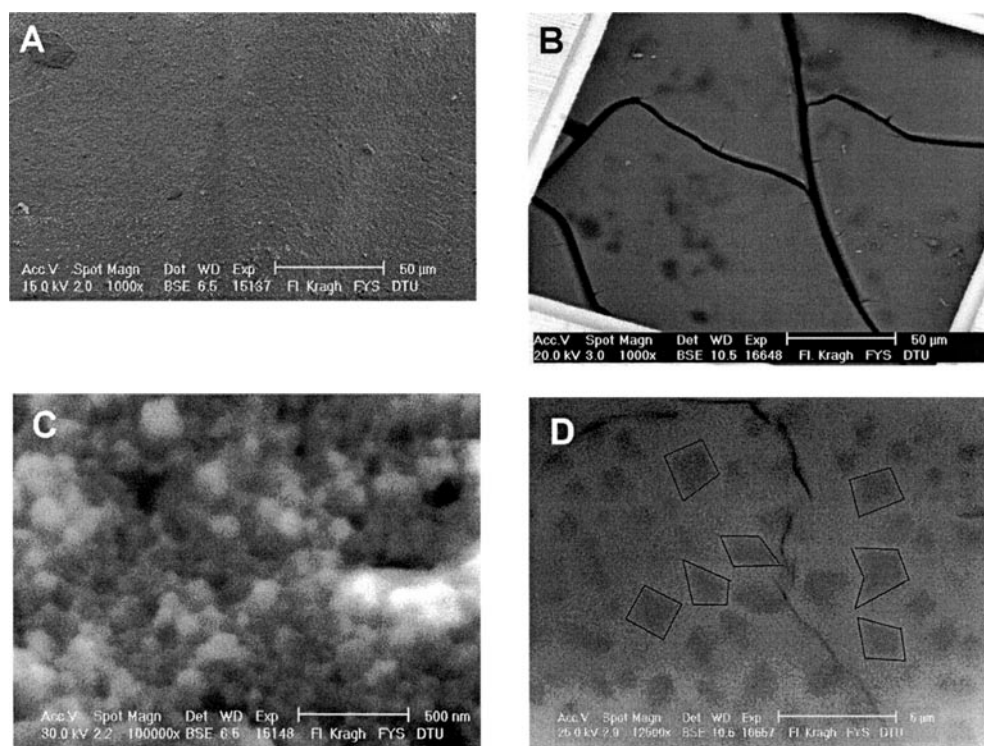
Figure 2. SEM micrographs of the as-prepared cubic spinel Si_3N_4 phase (a and c) and the sample annealed at 1873 K in air for 30 min (b) and (d).

37.27 GPa with an average of 35.31 GPa. These measurements, although of a polycrystalline sample, for the first time experimentally indicate that the c-Si_3N_4 phase is a very hard material with a hardness slight higher than SiO_2 stishovite (33 GPa), which is often referred to as the third hardest material after diamond and cubic boron nitride [11].

Figure 1 shows the optical micrographs of the as-prepared c-Si_3N_4 sample and the sample annealed at 1873 K in air for 30 min. The as-prepared sample is light yellow and transparent while the annealed sample becomes light black with cracks. The microstructures of both samples were further examined by scanning electron microscopy as depicted in figure 2. Cracks were observed in the annealed sample (figure 2(b)) while a smooth surface with no cracks was detected in the as-prepared sample (figure 2(a)). The as-prepared sample is composed of sintered crystals with an average grain size of approximately 140 nm (figure 2(c)) while light–dark domains (around a few micrometres in size) appear in the annealed sample (figure 2(d)). Most of the domains have a distinct squarelike morphology, whereas some are of elongated shape. It was reported that α-Si_3N_4 grains are equiaxed, whereas β-Si_3N_4 grains are elongated [12]. Thus, the square-like and elongated domains observed in figure 2(d) could be attributed to α- and β-Si_3N_4 grains, respectively, which were confirmed by XRD measurements. Secondary ion mass spectroscopy (SIMS) measurements of both the as-prepared and annealed samples reveal that the oxygen impurity is only detected at the top surface layer (<30 nm) and becomes negligible in the interior of both samples. To quantitatively determine the oxygen content, other measurements, e.g., Auger electron spectroscopy or secondary neutral mass spectroscopy, are required. This result indicates that the c-Si_3N_4 phase possesses excellent oxidation resistance.
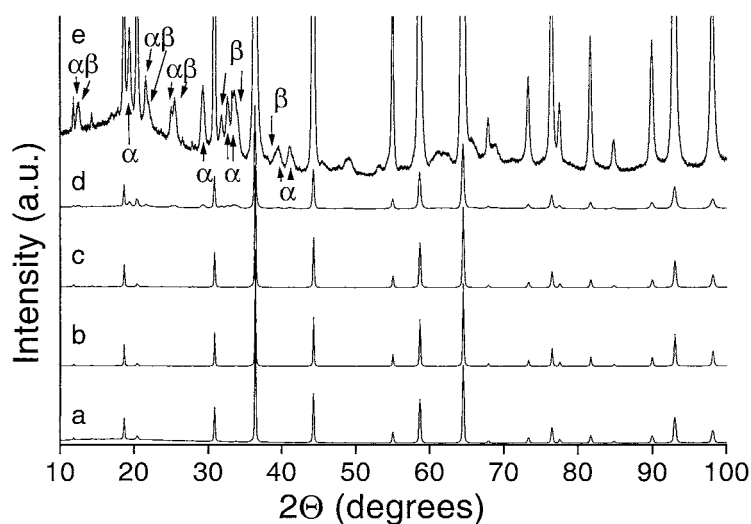
Figure 3. XRD patterns recorded for the cubic spinel Si_3N_4 phase annealed at 1423 (a), 1523 (b), 1673 (c) and 1873 K (d) in air for 30 min. The α- and β-Si_3N_4 phases are marked in the XRD pattern (e) 20× (d) for the sample annealed at 1873 K.

We further performed x-ray powder diffraction measurements on the as-prepared c-Si_3N_4 sample and the samples annealed at various temperatures up to 1873 K at beamline I711 at the MAX II synchrotron in Lund, Sweden, utilizing a Huber G670 imaging plate Guinier camera. The wavelength, 1.462 90 Å, was determined using a Si standard. The sample was mounted on the top of a glass capillary and rotated during data collections. The diffraction patterns were all collected in the range 8.6 to 100 degrees in 2θ-steps of 0.005 degrees, and accumulated for 5 min. The Rietveld refinement program is a local variation of the LHMP1 program [13], using the Voigt profile function and Chebyshev polynomial background fitting. Data in a 2θ-range of 18–99 degrees were used for structural refinements. Figure 3 shows some XRD patterns recorded from the samples annealed at 1423, 1523, 1673, and 1873 K in air for 30 min. Results for the cubic spinel Si_3N_4 phase obtained from structure refinements are summarized in table 1. Up to 1673 K, no obvious difference between the as-prepared sample and the annealed samples was observed. The XRD patterns are mainly composed of the cubic spinel phase together with some weak peaks from as yet unidentified phase(s). It should be stressed that no α- and β-Si_3N_4 phases were detected for the as-prepared sample and the samples annealed at temperatures below 1673 K. At 1873 K, some new tiny peaks can be detected and indexed to α- and β-Si_3N_4 phases. The α-to-β-Si_3N_4 phase transformation was reported to occur at temperature above 1673 K [14]. Thus, on the basis of our observation and the reported data, one might suggest a phase transformation sequence of c-to-α-to-β-Si_3N_4 phases for the cubic silicon nitride at temperature above 1673 K in air. High temperature differential scanning calorimeter measurements will be useful for further investigation of the phase transformation. The resistivity of the c-Si_3N_4 material at ambient temperature was estimated by direct resistance measurements of an as-prepared sintered cylinder (1.37 mm in diameter and 0.75 mm in length). It is larger than 2×10^{10} Ω m.

In conclusion, large-volume Si_3N_4 material with a cubic spinel structure has been synthesized using a multi-anvil press. The hardness of the cubic silicon nitride was experimentally determined to be 35.31 GPa as the third hardest material after diamond and cubic boron nitride, which is in agreement of the theoretical prediction. The thermal stability

Table 1. Structural data for the as-prepared cubic spinel Si_3N_4 sample and the samples annealed at various temperatures in air for 30 min.

	295 K	1423 K	1523 K	1673 K	1873 K[a]
a (Å)	7.7339(1)	7.7335(1)	7.7339(1)	7.7344(1)	7.7362(8)
X	0.2583(1)	0.2573(1)	0.2580(1)	0.2574(1)	0.2571(3)
g Si(1)	0.210(1)	0.209(2)	0.211(2)	0.211(2)	0.211(3)
Si(2)	0.454(4)	0.426(5)	0.434(5)	0.428(5)	0.437(7)
B (Å^2) Si(1)	0.83(1)	0.97(1)	0.60(1)	1.03(1)	0.75(2)
Si(2)	1.03(1)	0.83(1)	0.52(1)	0.88(1)	0.83(2)
N	1.67(3)	1.90(3)	1.50(3)	1.93(3)	1.79(6)
ρ (g cm^{-3})	3.75(2)	3.66(5)	3.69(5)	3.67(5)	3.69(8)
Si(1)–N (Å)	1.7849(16)	1.7723(16)	1.7817(16)	1.7735(17)	1.7706(23)
Multiplicity	4	4	4	4	4
Si(2)–N (Å)	1.8718(9)	1.8785(9)	1.8736(9)	1.8782(9)	1.8804(12)
Multiplicity	6	6	6	6	6
N–N (Å)	2.5539(21)	2.5743(21)	2.5591(21)	2.5729(22)	2.5789(29)
Multiplicity	3	3	3	3	3
N–N (Å)	2.7373(9)	2.7365(9)	2.7371(9)	2.7369(10)	2.7374(13)
Multiplicity	6	6	6	6	6
N–N (Å)	2.9148(21)	2.8941(21)	2.9096(21)	2.8962(22)	2.8914(29)
Multiplicity	3	3	3	3	3
Si(2)–Si(2) (Å)	2.7343(1)	2.7342(1)	2.7343(1)	2.7345(1)	2.7352(1)
Multiplicity	6	6	6	6	6
R_P	4.12	3.43	4.84	4.09	8.30
R_{WP}	6.43	5.36	7.56	6.45	12.12
R_B	0.84	1.25	1.20	1.38	1.58

[a] The α- and β-Si_3N_4 phases were not taken into account by the Rietveld structure refinement of the XRD pattern. Numbers in parentheses are estimated standard deviations in the last decimal places quoted. The positions of Si and N atoms were described by Si(1), 8a (1/8, 1/8, 1/8); Si(2), 16d (1/2, 1/2, 1/2); N, 32e (x, x, x) with $x = 0.25 + \delta$. We found that the value of δ is around 0.008. g is the occupancy factors for Si(1) and Si(2) sites assuming nitrogen has an occupancy factor of one. B is the equivalent isotropic temperature factor.

of the material was studied by x-ray powder diffraction and scanning electron microscopy. It was found that the material is stable up to 1673 K in air, which makes the material suitable for engineering superhard ceramics for high temperature structural applications. At 1873 K, α- and β-Si_3N_4 phases are observed, which indicates a phase transformation sequence of c-to-α-to-β-Si_3N_4 phases.

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