

Atomic structural and thermal expansion of novel silicon nitride

During our beamtime (15 shifts) in 26-31 Oct. 2000, the atomic structure and thermal expansion behavior of the cubic silicon nitride have been studied in situ angle-dispersive XRD at beamline BM16. The powder sample, ground from the recovered sample, was placed in an amorphous quartz capillary, pumped down to 10^{-5} mbar and then sealed, and rotated during data collections with a multichannel detector and a wavelength of 0.71031 Å. A hot air gun was used for high temperature measurements. The temperature at sample was calibrated using the known temperature dependence of lattice parameter for pure silicon powder in place of the sample position.

Structural characterization of the third polymorph of silicon nitride, synthesized under high-pressure and high-temperature conditions, has been obtained by Rietveld structure refinements¹ of X-ray powder diffraction data recorded using synchrotron radiation.² The material has a cubic spinel structure at 295 K 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. The complete structural data obtained should offer a firm basis for understanding the properties of the novel material.

High-temperature XRD patterns, recorded in steps of 40 K from 295 to 1075 K for the cubic Si₃N₄ phase, are identical except for the thermal expansion.³ All refinements converged to small residual values. No phase transformation was detected in this temperature range 295-1075 K in vacuum, in agreement with previous data reported for the c-Si₃N₄ sample annealed in air in a temperature range from 295 to 1673 K.⁴ The lattice parameter, a , and the linear thermal expansion coefficient, α , of the c-Si₃N₄ phase are obtained. A non-linear increase of the lattice parameter with temperature can be seen. The data are fitted with a polynomial function, $a=7.72740(\text{Å}) + 2.08932 \times 10^{-5} T + 1.55371 \times 10^{-8} T^2$. Here α is defined as $\alpha=(da/dT)/a$. It is clear that α increases linearly with temperature and can be described with $\alpha=2.71576 \times 10^{-6} \text{ K}^{-1} + 0.00398 \times 10^{-6} T$. The linear thermal expansion coefficient at 295 K for the c-Si₃N₄ phase is $\alpha=3.89 \times 10^{-6} \text{ K}^{-1}$, which is almost four times larger than $1.05 \times 10^{-6} \text{ K}^{-1}$ at 300 K for diamond.⁵ The temperature dependences of the bond lengths for the tetrahedral and octahedral sites were obtained from the Rietveld structural refinements. It is clear that the octahedral Si-N bond length increases with temperature, $d=1.871(\text{Å})$

$+1.610 \times 10^{-5} T$, while the length for the tetrahedral Si-N bond remains almost unchanged within the experimental uncertainty. Both octahedral N-N bond lengths, shared $N-N_{\text{oct,sh}}$, $d=2.558(\text{\AA}) + 3.197 \times 10^{-5} T$, and unshared $N-N_{\text{oct}}$, $d=2.733(\text{\AA}) + 1.404 \times 10^{-5} T$, edges of the Si-N octahedral, increase with temperature while the length for the tetrahedral N-N bond remains almost unchanged.

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