Thermal Expansion of α and β Silicon Nitride

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Silicon nitride, Si_3N_4, belongs to the family of group-IV nitrides exhibiting unique physical and chemical properties. Its low density, low (but tunable) electrical conductivity, superior mechanical properties at high temperatures, wear resistance, oxidation resistance, fracture toughness, mechanical fatigue and creep resistance lead to numerous applications. There exist three most known crystallographic structures of silicon nitride α, β and γ. α-Si_3N_4 (nierite) has a trigonal ($P3_1c$) structure, β-Si_3N_4 (phenacite-type) has a hexagonal ($P6_3/m$ or $P6_3$) structure, and γ-phase has a cubic spinel-type structure. Thermal expansion of α and β phases is not well recognised up to now, that for γ phase has been determined recently (see Ref. [1] and references therein). The published results for the β phase were determined for limited ranges of temperature (see e.g. Refs. [2, 3]).

Two commercial (ALDRICH) α and β samples were studied. The X-ray characterisation was realized at a laboratory diffractometer using $CuK\alpha_1$ radiation. The thermal-expansion study was performed under low- and high-temperature conditions by powder X–ray diffraction. Lattice parameters and thermal expansion coefficients for α- and β-Si_3N_4 phases were determined in broad temperature ranges: 10-1073 K for α-Si_3N_4 and 20-1103 K for β-Si_3N_4 phase. The diffraction measurements were carried out at a powder diffractometer at the B2 bending–magnet beamline, using the Debye–Scherrer geometry and suitable temperature heating and cooling stages [4]. Diamond powder was added to the samples as internal standard permitting to eliminate the wavelength fluctuations occurring during the measurement session. The Rietveld-refinement program Fullprof 2.k (v. 2.7) was used for the structural analysis. The thermal-expansion coefficients were calculated using the Debye-Grüneisen model.

Phase analysis showed that both samples were Si_3N_4 mixtures with 92:8 and 29:71 of α:β weight proportions, as established by quantitative Rietveld analysis. The diffraction data collected for both samples permitted for precise determination of thermal expansion coefficients for α and β phases. The observed temperature variation of the expansion coefficient generally confirms the trends reported in [2, 3]. In the temperature range studied, the volume of unit cells of both Si_3N_4 phases varies by about 0.7%. The value of volume thermal-expansion coefficient at temperature 300 K for the α-Si_3N_4 is 3.747×10^{-6} K^{-1} is marginally higher than for β phase, 3.554×10^{-6} K^{-1}. It is by 17% lower than the previously publihed value (4.4×10^{-6} [3]).

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