TEMPERATURE DEPENDENCE OF c-Si_3N_4 LATTICE PARAMETER IN THE RANGE 65-295 K

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The family of IV-V spinel-type nitrides is widely studied because of their theoretically predicted and experimentally confirmed extreme physical properties. These compounds, Si_3N_4, Ge_3N_4, Sn_3N_4, can be prepared at high temperatures and pressures by transformation of ambient-pressure polymorphs, by reaction of elements or by other chemical reactions, as well as by shock compression. They preserve the spinel structure in a broad temperature range. For example, the metastability range of Si_3N_4 extends up to about 1670 K or 1673 K (as reported in Refs. [1] and [2], respectively) for HP-HT synthesised compound and up to 1620 K for shock synthesised compound [3]. The reported values of hardness (35.31 GPa [4], 43 GPa [5]) show that Si_3N_4 is the third of the hardest phases known (after diamond and borazon, see [6]). The high hardnesss is accompanied by a high value of bulk modulus (experimental values are 308 GPa [7], 290 GPa [8], 309 GPa [9], for review of the theoretical ones see Ref. [9]).

Earlier work on thermal expansion of Si_3N_4 is limited to high-temperatures (range 295-1075 K) [9]. In the present study, unit-cell parameter was studied in the temperature range 65-300 K. The crystals studied in this paper were grown at Technical University of Denmark using the high-pressure high-temperature conditions. The low-temperature XRD measurements were carried out at a powder diffractometer (for construction details see [10]) at the B2 beamline using Debye-Scherrer geometry. A scintillation counter was applied for the data collection. The lattice parameter was determined from the position of the 773 diffraction line.

The sample in the form of a sintered plate of about 1 mm radius was mounted within a thin-wall glass capillary together with a small quantity of diamond powder which served as a standard for monitoring of possible X-ray wavelength fluctuations. The He-closed-cycle cryostat allowed capillary rotation. Experimental thermal-expansion data for pure diamond were taken from Ref. [11]. The diamond standard was chosen because of its small thermal expansivity making that the possible effect due to impurities or to defect structure of the standard on the final result is also small. The experiment consisted in data collection using temperature steps starting from the lowest applied temperature, 65 K. The wavelength was determined by least-squares refinement of five reflections of silicon (NIST 640b diffraction standard, a=5.43094 Å). The present results of investigation of the unit-cell dimensions in the 65-300 K range are presented in Fig. 1. The obtained dependence of the lattice parameter on temperature shows that there is a vanishing tendency of the thermal expansion at the lowest temperatures.

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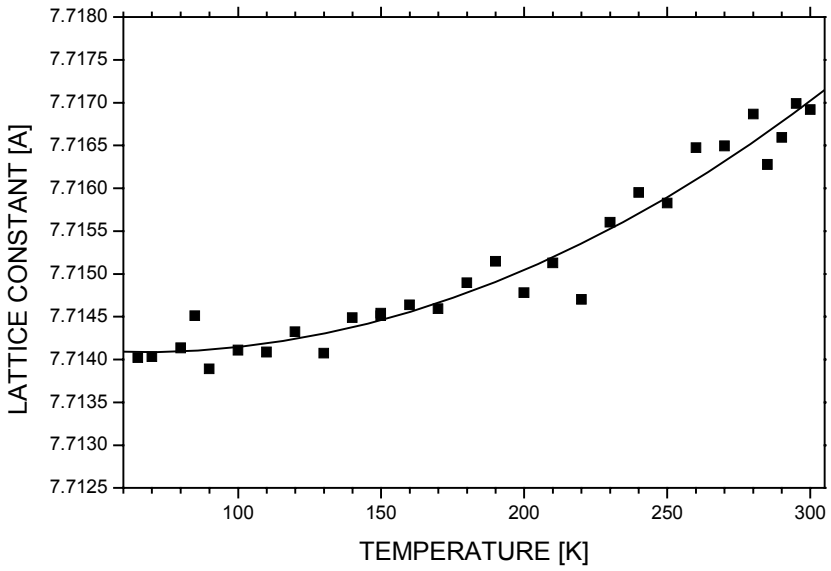

Figure 1: Lattice parameter dependence on temperature for spinel-type Si_3N_4.

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