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The lattice parameter and thermal expansion coefficient (TEC) for the spinel-type Si$_3$N$_4$ phase prepared under high-pressure and high-temperature conditions are determined for 14 K$<T<$302 K by x-ray diffraction, at a synchrotron-radiation source, and for 0 K$<T<$1683 K by first-principles calculations. The low- and high-temperature experimental TEC data are in excellent agreement with the calculations. Our results provide the first experimental evidence that the linear expansion coefficient tends to vanish for $T<$100 K. The experimental temperature dependence of the TEC is accurately represented by polynomials over the complete T range.

Since the discovery of the formation of the spinel Si$_3$N$_4$ phase (c-Si$_3$N$_4$) under high-pressure (HP) and high-temperature (HT) conditions,[1] the structural, physical, and chemical properties of c-X_3N$_4$ nitrides ($X=$Si,Ge,Sn) have been intensively studied.[2–33] The thermal expansion is one of these properties. Experimental values for the lattice parameter and thermal expansion coefficient (TEC) for a temperature range of about 300–1000 K were reported by Jiang *et al.*[27] for c-Si$_3$N$_4$ samples prepared under static HP-HT conditions, as well as by Hintzen *et al.*[31] for samples prepared by shock compression. Fang *et al.*[32] performed the first-principles calculations of the TEC over 0–1000 K. Their HT results agree, within experimental uncertainty, with the experimental data reported so far.[27,31] They found that the TEC steeply increases with temperature in the range 50–400 K and that it virtually vanishes below 50 K. To the best of our knowledge, these theoretical results for the low-temperature regime have not yet been experimentally confirmed, while neither experimental nor theoretical values are known above 1073 K. In this paper, we report the experimental results of the low-temperature (LT) thermal expansion of the c-Si$_3$N$_4$ phase obtained by *in situ* x-ray powder diffraction measurements, using a synchrotron beam, and theoretical results deduced from first-principles simulations for 0 K$<T<$1683 K. Thus, the complete stability range of this compound is now covered.

In the present study we have used the same sample as that of Ref. 27. A multianvil octahedral pressure assembly was employed in the synthesis of the cubic spinel Si$_3$N$_4$ phase. A mixture of α- and β-Si$_3$N$_4$ powders was compressed at 17 ±0.5 GPa and 2100 K for 1 h. The temperature of the experiment was monitored using a W 3% Re–W 25% Re thermocouple. Further details of the sample preparation are given in Ref. 13. The recovered sample (about 10 mg in weight) was composed of light-yellow transparent sintered crystals with an average grain size of approximately 140 nm determined by optical and scanning electron microscopy and x-ray powder diffraction. Secondary ion mass spectroscopy measurements on the recovered sample revealed an oxygen impurity of less than 1 at. %.

The LT x-ray diffraction studies were carried out with a powder diffractometer[34] at the B2 (Hasylab/DESY) bending-magnet beamline, using the Debye-Scherrer geometry. A scintillation counter was applied for the data collection. The apparatus configuration (involving an analyzer) allowed for high resolution and low background at the expense of intensity. The beam spot size was 1 mm×15 mm. The closed-circuit He cryostat ensures temperature stability and accuracy better than 0.5 K. The Si$_3$N$_4$ sample was mounted within a thin-wall glass capillary (external diameter 0.8 mm) together with an internal sealed capillary (diameter 0.5 mm) containing diamond powder with a purity of 99.9%. The experiment consisted of data collection for 440 peak for c-Si$_3$N$_4$ using 4–8 K temperature steps starting from the lowest applied temperature 14 K. The average position of the
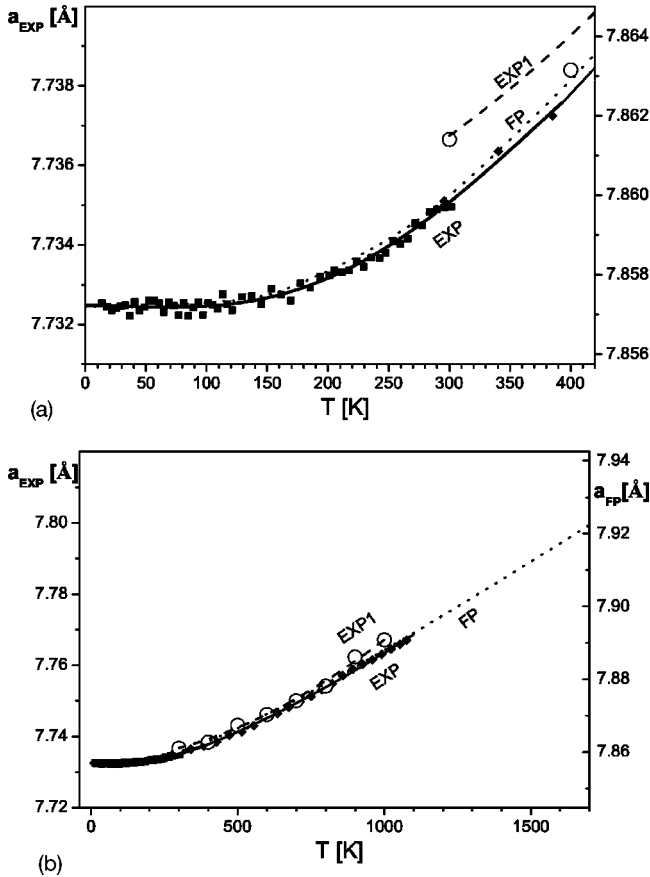
FIG. 1. Temperature dependence of the lattice parameter of c-Si_3N_4 in the LT range (a) and in the whole temperature range (b). Experimental LT data from this work: "EXP," solid squares. HT data for the same sample (Ref. 27): solid diamonds. HT data from a shock-prepared sample (Ref. 31): "EXP1," open circles and dashed line. First-principles results from this work for 0–1673 K: FP, dotted lines. The absolute scale of the theoretical points has been slightly shifted (see the right axis) to show the good agreement in the $a(T)$ curve shape.
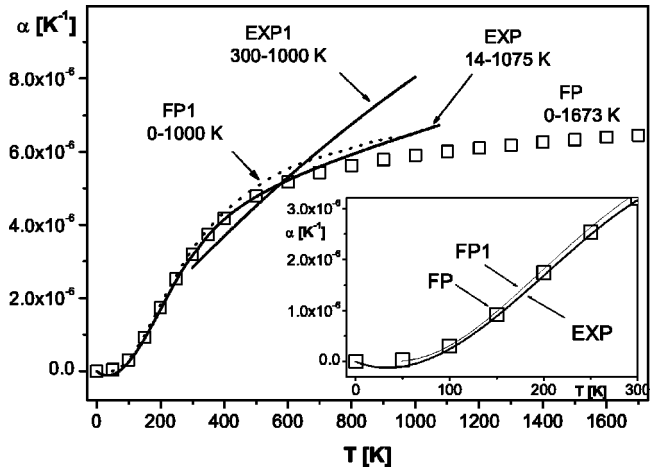

FIG. 2. Thermal expansion coefficient of c-Si_3N_4 as a function of temperature. The inset shows the magnified LT part. Experimental data: the experimental data for 14–1075 K ("EXP," solid line) were derived from the fitted $a(T)$ dependence; the literature data for a shock-prepared sample for 300–1000 K range (Ref. 31) are shown for comparison ("EXP1," solid line). First-principles data: present data ("FP," squares) for 0–1673 K and literature data (Ref. 32) ("FP1," dotted line) are shown.

neighboring 220 diffraction line of the diamond before and after the measurement of Si_3N_4 peak served as an internal x-ray-wavelength standard on the basis of $a(T)$ polynomial dependence for pure diamond.[35]

Theoretical calculations were performed following a two-step procedure. First, the total all-electron energy of the crystal was computed at selected volumes surrounding the experimental equilibrium geometry and allowing the nitrogen internal position to be optimized. Si and N basis sets of triple-ζ quality were adapted to this crystalline structure. Nonlocal exchange (Becke) and correlation (Perdew-Wang) functionals[36] were employed in the density functional theory approach implemented in the CRYSTAL package.[37] Second, thermal effects were incorporated in the electronic energy using a quasiharmonic Debye model that accounts for the dependence of the Debye temperature Θ_D on the crystal volume by means of the isotropic approximation.[38] The good performance of this nonempirical model has been checked in c-Si_3N_4 by comparing our results with those obtained after the evaluation of the vibrational contributions from the dis-

persion phonon curves.[32] We found very good quantitative agreement with all the thermal properties reported by Fang et al.,[32] including entropy, specific heat at constant volume, zero-point vibrational energy, and Grüneisen parameter.

Figure 1 shows the lattice parameter of the c-Si_3N_4 phase in the temperature range 14–302 K together with HT experimental and full-range calculated data. The lattice parameter a of the c-Si_3N_4 phase is 7.7325 Å at 0 K and 7.7351 Å at 300 K. The precision of determination of a is 0.0002 Å while the accuracy is evaluated to be 0.0005 Å. It remains almost constant up to $\sim$ 100 K and then increases with temperature. In order to find simple analytical expressions describing the experimental $a(T)$ curve, separate fittings for the LT and HT ranges were carried out: $a_{LT}(T) = 7.73248 - 2.809 \times 10^{-8} T^2 + 3.002 \times 10^{-10} T^3 - 3.679 \times 10^{-13} T^4$ in the range 0–393 K and $a_{HT}(T) = 7.72026 + 3.204 \times 10^{-5} T + 9.911 \times 10^{-9} T^2 + 1.256 T^{-1}$ in the range 393–1673 K. The relative change of a in the range (14–302 K) is about 0.034%. This value is about twice as small as the 0.062% observed in the range 80–300 K for the prototype spinel $MgAl_2O_4$ phase,[39] indicating a stronger bonding for c-Si_3N_4. The absolute theoretical values of a are somewhat higher than the experimental ones, as already observed in the literature,[4,9,22,23,32] although the calculated $a(T)$ curve shape is consistent with the experimental one. This can be seen in Fig. 1.

The TEC defined as $\alpha(T) = (da/dT)/a(T)$ was derived from the fitted $a(T)$ expressions. Merging the data from the LT and HT ranges in a single curve shows a smooth temperature dependence for the whole range. This picture improves the simpler approach adopted for the HT range in Ref. 27. The experimental $\alpha(T)$ curve is presented in Fig. 2, with details for the range 14–302 K given in an inset. The LT experimental TEC data obtained here do confirm the theoretical calculations of Ref. 32 and of our present work. The

experiments, when performed in a broad temperature range, give results fully consistent with theoretical evaluations. From these experimental and theoretical results we conclude the following.

(1) The TEC in the range from 0 to ~ 100 K is negligible. The experimental curve in Fig. 2 exhibits a very shallow minimum. Due to the very low magnitude of this effect, it is not possible to judge whether it has any physical meaning. In the range from ~ 100 to ~ 300 K, the TEC variation with temperature is nearly linear, reaching the value 3.16×10^{-6} K^{-1} at 300 K. This value is comparable with those of III-V nitrides.[40]

(2) The $\alpha(T)$ curve deduced from the first-principles calculations shows excellent agreement with the experimental curve up to ~ 800 K. Above this temperature, the experimental TEC data[27] match the theoretical values of Ref. 32 but the present calculated values are slightly lower. This discrepancy should be related to the shortcomings of the Debye model at temperatures above Θ_D, which is computed to be 1150 K in this system.

(3) Small discrepancies in the experimental data of Refs. 27 and 31 might be partially due to different synthesis techniques and specific assumptions concerning the fitting function of the lattice parameter as well as a difference in the number and scatter of experimental points studied. Crystallite size dependence of TEC has been reported for other silicon nitride based materials—e.g., $MoSi_2$-Si_3N_4 composites.[41] The average crystallite size of the sample used here and in Ref. 27 is about 140 nm, while using a shock-compression method as in Ref. 31, smaller c-Si_3N_4 crystallites could be formed.[6] What concerns the fitting procedure, we are convinced, in particular, that use of the $1/T$ term allows for improvement of the fitting in the HT region.

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