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A COMPARATIVE RIETVELD REFINEMENT STUDY OF SPINEL-TYPE Si_3N_4

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After the recent discovery that the spinel-type Si_3N_4 phase (c-Si_3N_4) can be prepared under extreme high-pressure high-temperature conditions [1], the structural, physical and chemical properties of c-X_3N_4 nitrides (X = Si, Ge, Sn) have been extensively studied. In the present study, a comparative investigation is carried out aiming to precisely determine the structural parameters of the compound and to compare the capabilities of powder diffractometers of different construction, installed at synchrotron rings in MaxLab and in Hasylab,

A multi-anvil octahedral pressure assembly was employed in the synthesis of the spinel-type Si_3N_4 phase. A mixture of α- and β-Si_3N_4 powders was compressed at 17±0.5 GPa and 2100 K for 1 hour. The temperature of the experiment was monitored using a W3%Re-W25%Re thermocouple. Details of the sample preparation can be found in Ref. [2]. The recovered sample (about 10 mg in weight) was composed of light-yellow transparent sintered crystals with average grain size of approximately 140 nm determined by optical and scanning electron microscopy and X-ray powder diffraction. The X–ray diffraction studies were carried out using the Debye–Scherrer geometry, with a powder diffractometer at the B2 (Hasylab/DESY) bending–magnet beamline, and a Huber diffractometer (MaxLab, Lund, Sweden) at the I711 beamline, both equipped with readable-imaging-plate detectors. The structural model was based on the single-phase spinel structure (space group Fd3m). The Rietveld-refinement program Fullprof ([3]) was used for the structural analysis. A Pearson VII profile-shape function was assumed. Figure 1 shows an exemplary Rietveld refinement result of the c–Si_3N_4 phase for data at the B2 beamline (Hasylab, DESY). In particular, the obtained structural data for the free positional parameter of nitrogen atom were analyzed. Its value is found to slightly depend on the refinement assumptions. For example, if one assumes full occupancy of the silicon and nitrogen sites in the spinel cell, than the positional parameter is around 0.2559: this value is slightly lower than those given by previous determinations (theoretical 0.2604 [4], 0.2594 [5] and experimental 0.2583 [2, 6]). The obtained results show that satisfactory structural data can be obtained for this material using the synchrotron beam as a source of X-rays. Difficulties connected with small sample size and with nonlinearities of image-plate detectors will be addressed.

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References

[1] A. Zerr, G. Miehe, G. Serghiou, M. Schwarz, E. Kroke, R. Riedel, H. Fuess, P. Kroll, R. Boehler, *Nature* **400** (1999) 340

[2] J.Z. Jiang, K. Ståhl, R.W. Berg, D.J. Frost, T.J. Zhou, and P.X. Shi, *Europhys. Lett*. **51**, 62 (2000).

[3] J. Rodriguez-Carvajal, *Newslett. IUCr Commission Powd. Diffr*. **26** (2001) 12-19.

[4] P. Mori-Sánchez, R. Franco, A Martín Pendás, V. Luaña. J.M. Recio, *Phys. Rev. B* **65**, 161202 (2002).

[5] S.D. Mo, L. Ouyang, W.Y. Ching, I. Tanaka, Y. Koyama, R. Riedel, *Phys. Rev. Lett*. **83** (1999) 5046

[6] J.Z. Jiang, F. Kragh, D.J. Frost, K. Ståhl, H. Lindelov, *J. Phys.: Condens. Matter* **13** (2001) L515

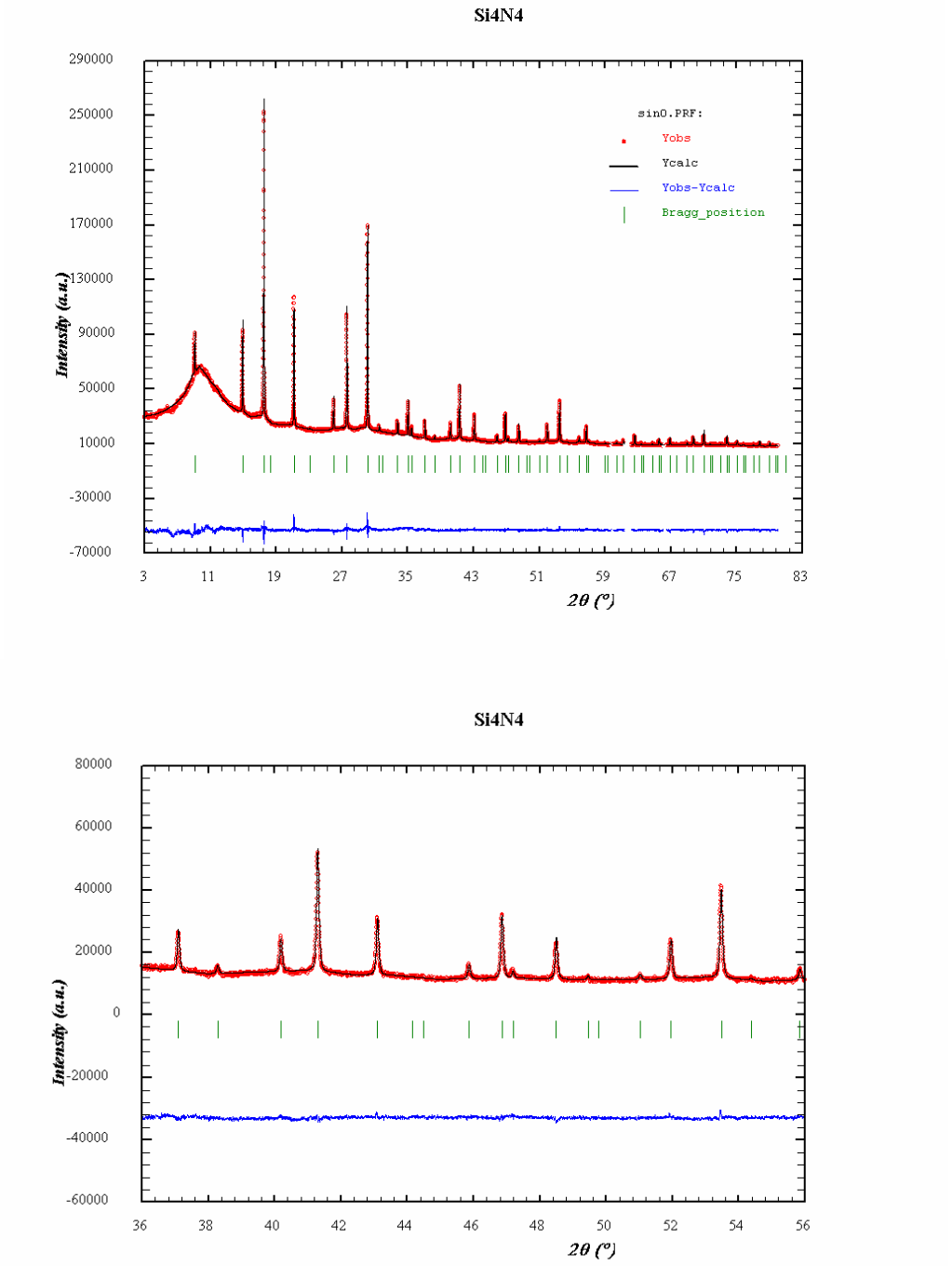

Figure 1. Rietveld refinement result in a broad angular range for the c-Si3N4 ceramics (upper panel). Experimental - crosses, calculated - solid line. The difference pattern is shown below the powder pattern. The lower panel (a magnified part of the upper one) illustrates the high quality of the fit.