



ESRF

Experiment title:

Powder diffraction investigation of α -P₃N₅

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CH- 192

Beamline:

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Report:

Within a systematic investigation of ternary and multinary non-metal nitrides we are interested in the class of phosphorus nitrides. Test measurements with synchrotron radiation clearly showed that the diffraction peaks of the originally proposed compound Mg₂PN₃ were too broad in spite of the high resolution of the instrument. In contrast a test measurement of a sample of α -P₃N₅ showed a splitting of some peaks due to a reduction of the primary supposed orthorhombic cell to a monoclinic one which was not visible with conventional X-ray diffractometers. As no structural model of α -P₃N₅ has yet been available in spite of many intensive efforts, we decided to use this compound which shows chemical similarities to Mg₂PN₃ for our experiment.

The diffraction investigations were carried out in Debye-Scherrer geometry. The sample was enclosed in a glass capillary (diameter 0.3 mm). A wavelength of 99.963(4) pm was selected by a Si(III) double crystal monochromator, and also a Si(111) crystal was used as analyzer. The FWHM at low 2 θ angles was smaller than $\Delta 2\theta = 0.03^\circ$.

We could index the obtained powder pattern unambiguously (Fig. 1) and the structure was determined by direct methods and refined by the Rietveld method (α -P₃N₅: Cc, a = 812.077(4), b = 583.433(4), c = 916.005(5) pm, $\beta = 115.809(1)^\circ$, Z = 4, F(000) = 320, $\mu = 5.283 \text{ mm}^{-1}$, measured range $10^\circ \leq 2\theta \leq 97.4^\circ$, 17203 data points, 699 observed reflections, 22 positional parameter refined, wR_p = 0.113, R_p = 0.091, R_F = 0.060).

in the solid state α - P_3N_5 has a three-dimensional network structure of connected PN_4 tetrahedra (Fig. 2). In consequence of the molar ratio $P : N = 3 : 5$ two fifths of the nitrogen atoms ($N^{[3]}$) are bound to three neighboring P and the remaining nitrogen atoms ($N^{[2]}$) to two P according to $\frac{3}{5}[P_3^{[4]}N_3^{[2]}N_2^{[3]}]$. In α - P_3N_5 zweier single chains occur parallel to $[110]$ and $[\bar{1}\bar{1}0]$ in which the PN_4 tetrahedra are connected alternately through edge- and corner-sharing. These zweier single chains are linked together through additional vertex-sharing PN_4 tetrahedra. In contrast to α - P_3N_5 in almost all other known condensed phosphorus(V) nitrides the PN_4 tetrahedra are connected exclusively through common corners. According to nitridosilicates the distances $P-N^{[2]}$ (151 - 160 pm) are significantly shorter than the values $P-N^{[3]}$ (164 - 174 pm). α - P_3N_5 crystallizes in a new and unprecedented structure type. Among the hitherto known binary compounds of the formula type A_3X_5 (e.g. Ti_3O_5 , V_3O_5 , Ta_3N_5 , Si_3Mn_5 , Si_3W_5) there are no examples which are isotypic to α - P_3N_5 . Here higher coordination numbers of either 6 (Ti_3O_5 , V_3O_5 , Ta_3N_5 , Si_3Mn_5) or 8 (Si_3W_5) are found for the A-atoms.

This work is published in:

[1] S. Horstmann, E. Irran, W. Schnick, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 1873.

[2] S. Horstmann, E. Irran, W. Schnick, *Z. Anorg. Allg. Chem.* 624 (1998) (in press).

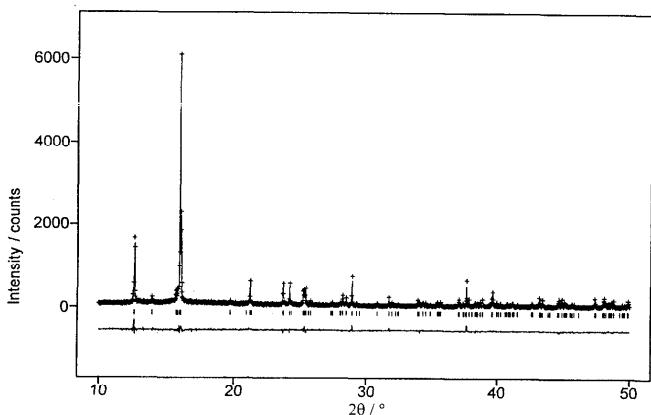


Fig. 1

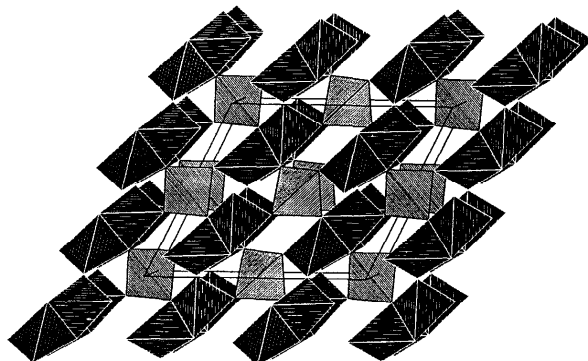


Fig. 2