

The Structure of β -Vanadium Nitride

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(Received 3 July 1979; accepted 25 July 1979)

Abstract. β -V₂N, $a = 4.917$ (3), $c = 4.568$ (3) Å, $Z = 3$, $P\bar{3}1m$, was prepared by melting vanadium nitride in nitrogen at 1 MPa. The structure was determined from neutron diffraction data by the powder profile-refinement technique.

Introduction. β -Nb₂N (Christensen, 1976) and β -Ta₂N (Conroy & Christensen, 1977) have the ϵ -Fe₂N-type structure (Burdese, 1957) with the space group $P\bar{3}1m$. Superstructure lines have been observed in X-ray powder patterns of β -V₂N (Hahn, 1949), indicating that this compound also could have the ϵ -Fe₂N-type structure. To verify this hypothesis an investigation of the crystal structure of β -V₂N has been made from a neutron diffraction powder pattern.

Single crystals of the cubic phase δ -VN_{0.74} were made by zone melting of stoichiometric polycrystalline rods of the compound in a 2 MPa ambient nitrogen atmosphere (Christensen & Roedhammer, 1977). In the growth experiment it was observed that when the melt was formed the molten zone expanded or boiled and N₂ gas was released from the melt. X-ray powder patterns of the frozen zones obtained with a Guinier camera and Cu $K\alpha_1$ radiation (1.54051 Å) indicated that the centre of the zone was almost pure β -V₂N and that the surface contained a minor fraction of δ -VN. The sample of β -V₂N used in the present investigation was made from three batches of melt that were frozen immediately after melting of the polycrystalline specimens of VN in ambient nitrogen at a gas pressure of 1.0 MPa. The central parts of the frozen zones were cut from the bulk specimens by the spark-erosion technique and then crushed to a fine powder in a boron carbide mortar.

The measurements were made at the DR3 reactor at Risø with incident neutrons of wavelength 1.41 Å. The diffraction pattern was obtained at room temperature for scattering angles 2θ in the interval 14.0–89.9° in steps of 0.1°. The sample was housed in a 10 mm thin-walled Al container of cylindrical shape. The pattern of the empty container was also measured so that correction could be made for the scattering from the container. After this correction was made, the pattern showed nine resolved and four unresolved peaks corresponding to 34 reflections. In addition to the reflections from β -V₂N, the pattern contained scattering from the 111, 200, 220, and 311 reflections of δ -VN. Corrections could be made for the first three of these reflections as they only overlapped with two of the resolved reflections from β -V₂N. The 311 reflection, however, overlapped with the four unresolved reflections 203, 220, 302 and 221 of β -V₂N forming one of the broad peaks in the region $67 < 2\theta < 73^\circ$. Therefore, this section of the pattern was excluded in the refinement which was made by the profile-analysis technique (Rietveld, 1969). The scattering lengths for V and N were (Bacon, 1972) -0.052 and 0.940 ($\times 10^{-14}$ m), respectively. The results of the refinements are listed in Table 1.*

Discussion. The ϵ -Fe₂N structure has the metal atoms in hexagonal close packing and the N atoms in octa-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34639 (1 p.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Results of the refinement of the structure of β -V₂N

Scale factor = 0.0015 (1), $R(F) = 7.22\%$.

Atom site	x	y	z	B (Å ²)	Multiplicity	
					Theoretical	Calculated
V	6(k)	0.323 (5)	0	0.272 (5)	0.4 (7)	0.5
N(1)	2(d)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{2}$	0.3 (1)	0.16667
N(2)	1(a)	0	0	0	1.3 (2)	0.08333

hedral holes. Despite the low scattering power of V for neutrons, neutron diffraction was used because N has a large scattering power. Hence, in this experiment the structure was determined solely by the N atom positions. The investigation confirmed that β -V₂N has the ϵ -Fe₂N structure, similar to β -Nb₂N and β -Ta₂N.

Acknowledgement is made to the Carlsberg Fondet for supplying a spark-erosion machine for the crystal-growth project.

Acta Cryst. (1979). B35, 2678–2680

Structure of Dilithium Zinc Silicate γ_{11} -Li₂ZnSiO₄

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(Received 8 June 1979; accepted 25 July 1979)

Abstract. Li₂ZnSiO₄, monoclinic, $P2_1/n$, $a = 6.262$ (3), $b = 10.602$ (4), $c = 5.021$ (4) Å, $\beta = 90.51$ (5)°, $Z = 4$, $D_x = 3.41$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 7.65$ mm⁻¹. Crystals were twinned on (001) with a as the twin axis. The structure of the γ_{11} modification has been solved by the heavy-atom method and refined by the least-squares method to $R = 0.060$ for 772 observed reflections with the twin ratio 0.65:0.35. All cations are coordinated tetrahedrally by O atoms.

Introduction. Setoguchi & Sakamoto (1974) and Setoguchi (1979) have synthesized the compounds Li₂M²⁺SiO₄ ($M = \text{Zn, Mg}$) by a flux method. In this paper we deal with the structure determination of γ_{11} -Li₂ZnSiO₄ as part of a systematic study of these compounds.

Crystals of γ_{11} -Li₂ZnSiO₄ were grown from a Li₂MoO₄ solvent by a slow-cooling flux method. They were granular in shape with diameters ranging from 0.1 to 0.5 mm. Weissenberg photographs about \mathbf{b} of all crystals examined showed a double-lattice character, indicating that the crystals were twinned on (001). Further visual intensity estimations of the double spots gave twin ratios approximately equal to 0.6:0.4 for all the crystals. The photographs also showed monoclinic symmetry with systematic absences $0k0$ for k odd and $h0l$ for $h + l$ odd, indicating the space group $P2_1/n$. A roughly spherical crystal of diameter 0.2 mm was

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selected for the data collection. Cell dimensions and intensity data were measured on a Rigaku four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The cell dimensions were determined by a least-squares fit to the setting angles of 25 reflections from the larger of the twin components. Intensities were collected using the ω - 2θ scan technique with a scan range of $(1.2 + 0.5 \tan \theta)^\circ$. By using a receiving slit with a large aperture (5.5×5.5 mm), the intensities of pairs of reflections, hkl and $h\bar{k}l$, from the two twin components could be collected at the same time. The measured intensities of 1635 reflections ($2\theta < 55^\circ$) were averaged to yield a set of 772 symmetrically independent values, $I_o(hkl)$, after L_p corrections. No correction was made for absorption.

The intensities $I(hkl)$ and $I(h\bar{k}l)$ were separated from the observed intensities $I_o(hkl)$ and $I_o(h\bar{k}l)$ according to the following equations (Nes & Vos, 1978):

$$I_o(hkl) = w_1 I(hkl) + w_2 I(h\bar{k}l)$$

$$I_o(h\bar{k}l) = w_2 I(hkl) + w_1 I(h\bar{k}l),$$

where hkl refer to the larger of the twin components, and w_1/w_2 ($w_1 + w_2 = 1$) is the twin ratio. The initial set of intensity data was obtained for $w_1 = 0.6$.

A three-dimensional Patterson map revealed positions of the Zn atoms, and the Si and O atoms were located from subsequent Fourier maps. Refinements of