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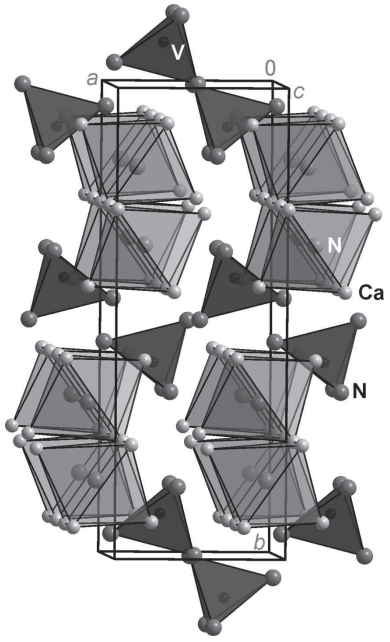
Alexander Ovchinnikov and Peter Höhn*

Crystal structure of pentacalcium tetranitridovanadate(V) mononitride based on a powder diffraction study, $Ca_5[VN_4]N$



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Abstract

Ca_5N_5V, orthorhombic, *Pbcm* (no. 57), $a = 6.0371(3)$ Å, $b = 16.6146(7)$ Å, $c = 6.7815(3)$ Å, $V = 680.21(5)$ Å^3, $Z = 4$, $R(P) = 0.0100$, $R_F(all) = 0.0348$, $T = 293$ K.

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Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

***Corresponding author: Peter Höhn,** Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187, Dresden, Germany, e-mail: hoehn@cpfs.mpg.de
Alexander Ovchinnikov: Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187, Dresden, Germany

Table 1: Data collection and handling.

Sample, setting:	Yellow powder, transmission geometry
Wavelength, μ:	Cu K_α radiation (1.54056 Å), 450.05 cm^{-1}
Diffractometer, scan mode:	Huber Guinier G670, step scan (0.005°)
2θ range / data points:	8.0-100.3°, 18461
Background funtion:	26 Legendre polynoms
Profile function:	Pseudo-Voigt
N(hkl), N(param.):	334, 61
Programs:	JANA2006 [6], Diamond [7]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
Ca(1)	8*e*	0.2914(9)	0.5750(3)	0.510(1)	0.018(2)
Ca(2)	4*d*	0.190(2)	0.4176(6)	0.25	0.018(3)
Ca(3)	4*d*	0.514(1)	0.2625(5)	0.25	0.009(3)
Ca(4)	4*c*	0.045(1)	0.25	0.00	0.017(3)
V(1)	4*d*	0.287(1)	0.0937(4)	0.25	0.011(2)
N(1)	8*e*	0.367(3)	0.153(1)	0.030(3)	0.007(3)
N(2)	4*d*	0.000(4)	0.050(1)	0.25	0.007(3)
N(3)	4*d*	0.488(5)	0.005(2)	0.25	0.007(3)
N(4)	4*d*	0.138(4)	0.829(2)	0.25	0.007(3)

Source of material

Calcium nitride, Ca_3N_2, was prepared from calcium lumps and nitrogen gas at 1023 K. The resulting red single phase material was mixed with vanadium powder in the ratio Ca:V = 5:1. The mixture was pelletized and annealed under nitrogen stream at 1000 K for 60 h and then at 1323 K for 48 h. The yellow microcrystalline product was identified as a new phase according to PXRD.

Discussion

Although isolated $[VN_4]^{7-}$ units were found in different crystal modifications of Li_7VN_4 [1], only crystal structures with one-dimensional anions represented by infinite chains of corner sharing $^1{}_\infty(VN_{2/2}N_2{}^{4-})$ tetrahedra have been reported

so far for nitridovanadates(V) of alkaline earth metals [2, 3]. Inspection of the PXRD pattern and further Rietveld refinement revealed that the title phase is isotypic with another group V element ternary nitride, Sr_5NbN_5 [4], and belongs to the Na_5OAsO_4 structure type [5]. The structure can be described as consisting of isolated $[VN_4]^{7-}$ tetrahedra and zigzag chains of corner-sharing ${}^1_\infty(NCa_4{Ca_{2/2}}^{7+})$ octahedra running along the *c* direction as shown in the figure. A distortion of the tetrahedra lowers the local symmetry down to C_s. Refined V—N distances lie in the range 1.85(2) Å – 1.91(3) Å, which is close to the values observed for other nitrides bearing tetrahedrally coordinated V(V) [1–3]. Band-structure calculations revealed an insulating ground state in accordance with the crystal structure.

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