

Supporting Information

High Pressure Synthesis and the Valence State of Vanadium Ions for the
Novel Transition Metal Pernitride, CuAl₂-type VN₂

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Experimental details

We have chosen the laser-heated diamond anvil cell (LHDAC) to generate the desired pressures. It can generate high pressures by placing a sample between a pair of diamonds, which are slowly mechanically compressed. The CuAl₂-type VN₂ was synthesized up to approximately 85 GPa by using LHDAC. Vanadium foil (The Nilaco Corporation, purity of 99.7 %) or δ -VN powder (Japan Metal Service Co., Ltd., purity of 99 %) were shaped into a square with the dimensions of 50×50 μm and a thickness of 10 μm . In the experiments using metal foil as the starting material, δ -VN was synthesized by nitridation at a pressure of approximately 20-30 GPa, and then CuAl₂-type VN₂ was synthesized by nitridation again at a higher pressure of approximately 73-85 GPa. The shaped square was placed at the center of the sample chamber together with a small ruby chip and NaCl plate which work as the pressure marker.¹⁻³ NaCl also worked as a thermal insulator. Pressure determination was also conducted by using pressure dependence of Raman spectrum for diamond.⁴ The sample chamber was filled with liquid nitrogen as a pressure medium and nitrogen source. The samples were heated by the irradiation of an infrared laser from both or one side after compression to the aimed pressure at room temperature.

Synchrotron XRD measurements were carried out at the BL2S1 at the Aichi Synchrotron Radiation Center of Aichi Science & Technology Foundation, Aichi, Japan⁵ and at the BL10XU at the SPring-8.⁶ For BL2S1 at the Aichi Synchrotron Radiation Center, the wavelength of X-rays was $\lambda = 0.75 \text{ \AA}$ and XRD measurements of ambient recovered samples and high-pressure *in-situ* XRD measurements were conducted. For BL10XU at the SPring-8, the wavelength of X-rays was $\lambda = 0.41 \text{ \AA}$ and *in-situ* XRD measurements at high-pressure, as well as high-temperature and high-pressure were carried out. In addition, the radiant thermometer was used to obtain synthetic temperature in the experiments at the BL10XU at the SPring-8. The recorded 2D diffraction patterns were integrated to the conventional 1D profile by using IPanalyzer.⁷ The phase identification and calculation of the lattice parameters were carried out using PDindexer.⁷ The determination of unit cell, space group, and atomic positions was conducted by using DICVOL06⁸ and *SUPERFLIP*, which is based on a charge flipping algorithm.⁹ The intensity data for structure determination by *SUPERFLIP* were given by Le Bail analysis with JANA2006 program.¹⁰ The structural refinement by Rietveld refinement was performed using RIETAN-FP.¹¹ VESTA¹² was used for drawing the crystal structure and electronic density obtained by *SUPERFLIP* and DFT calculation (the details of DFT calculation are mentioned below).

X-ray adsorption fine structure (XAFS) spectra on the K-edge of vanadium were measured at the BL5S1¹³ and BL11S2 at the Aichi Synchrotron Radiation Center of Aichi Science & Technology Foundation, Aichi, Japan. XAFS spectra were obtained under setup for transmission mode XAFS. The X-ray absorption near-edge structure (XANES) region of the obtained data was analyzed by using Athena in the Demeter software package.¹⁴

The crystal structure optimization and calculation for the electronic density, electronic band structure,

and density of states (DOS) were done via density functional theory (DFT) calculations performed using the CASTEP *ab initio* program.¹⁵ The generalized gradient approximation (GGA) of Perdew, Bruke, and Ernzerhof (PBE)¹⁶ was applied, and wave functions were characterized by a plane-wave basis set, and ultrasoft pseudopotentials were employed with a cutoff energy of 280 eV. *k*-point grids of $8 \times 8 \times 8$ were used for geometry optimizations and electronic structure calculations. The energy convergence criteria were set to 1×10^{-6} eV/atom.

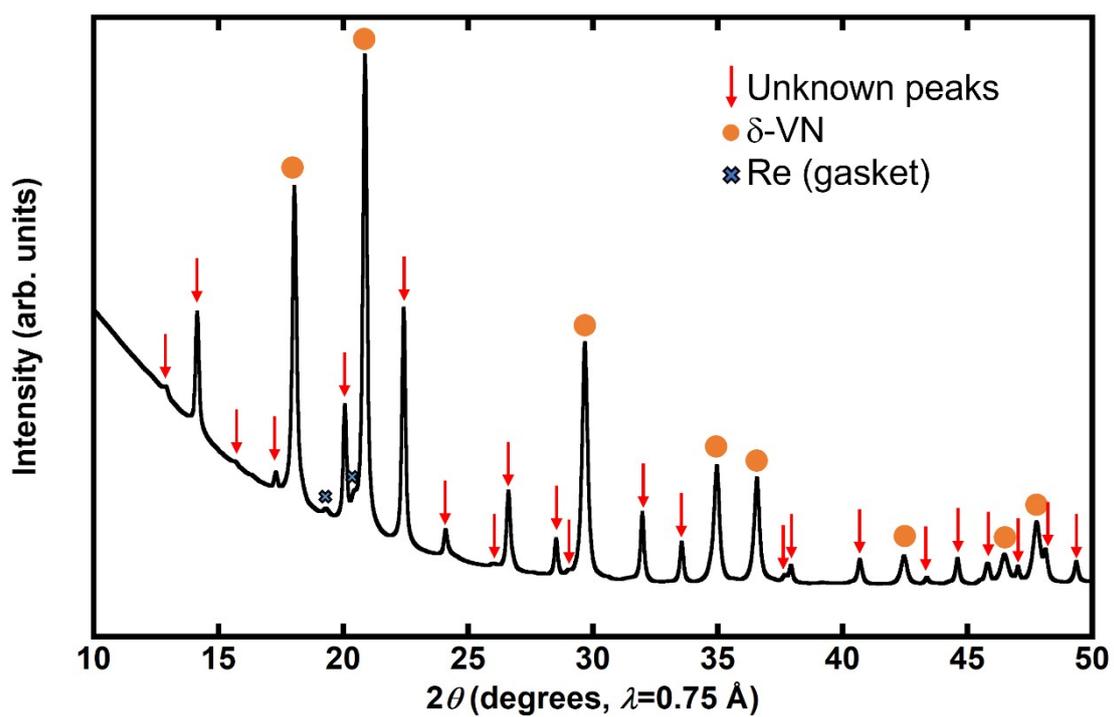


Figure S1 XRD profile of the ambient recovered sample synthesized at 84.2 GPa.

The orange circles and blue cross marks correspond to δ -VN and rhenium from starting material and gasket, respectively. The red arrows could not be explained by the known vanadium nitrides.

Table S1 Refined parameters and reliability factors for CuAl₂-type VN₂

Chemical formula	VN ₂
Formula weight /g mol ⁻¹	78.955
Space group	<i>I4/mcm</i> (No.140)
<i>a</i> / Å	4.30149(12)
<i>c</i> / Å	4.98273(16)
<i>V</i> / Å ³	92.195(5)
<i>Z</i>	4
<i>D</i> _{calc.} / g cm ⁻³	5.688
<i>2θ</i> range / deg.	13.21-52.99
<i>2θ</i> step / deg.	0.01
No. of refined parameters	53
<i>S</i> (goodness of fit)	0.3570
<i>R</i> _{wp} / %	1.211
<i>R</i> _p / %	0.855
<i>R</i> _B / %	0.561
<i>R</i> _F / %	0.315

Table S2 Atomic positions and the isotropic atomic displacement parameters B in the unit cell of CuAl₂-type VN₂ obtained from Rietveld refinement.

Atom	Wyckoff position	x	y	z	B (Å ²)
V	$4a$	0	0	1/4	0.31(4)
N	$8h$	0.1151(3)	0.6151	0	1.0 (fixed)

B of nitrogen were fixed. Wyckoff position of $8h$ is represents by $(x, x+1/2, 0)$. The occupancies of all atoms are fixed with 1.0.

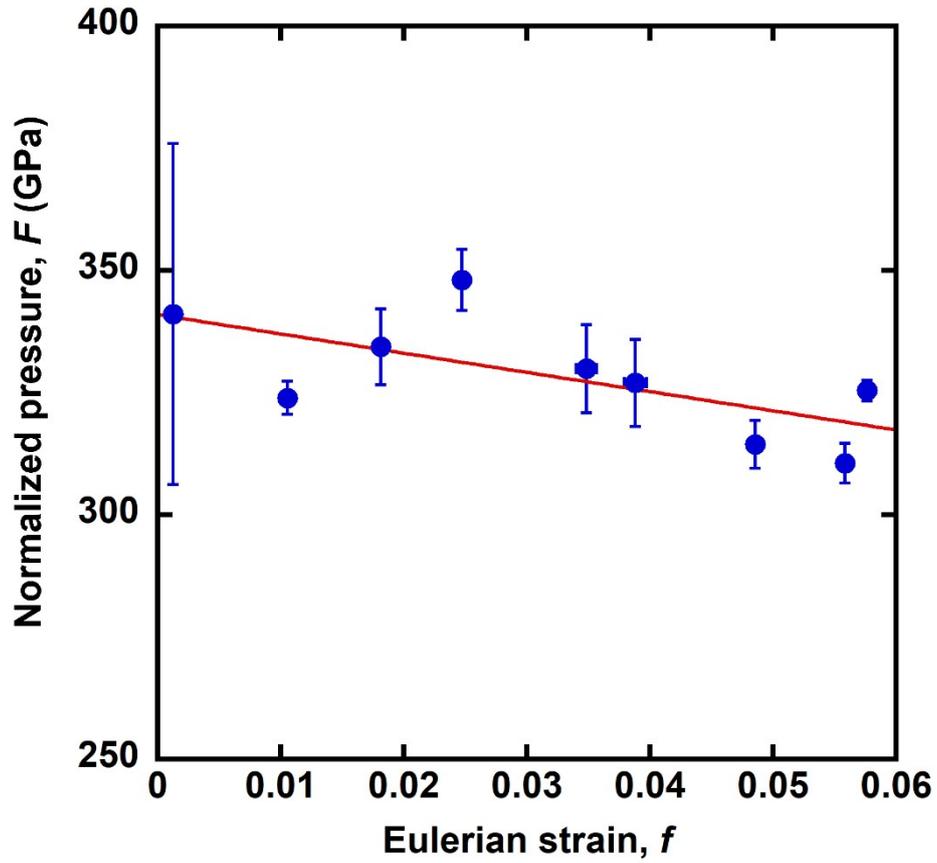


Figure S2 Normalized pressure F as a function of Eulerian strain f

The definitions of the Eulerian strain (f), normalized pressure (F) and 3rd-order Birch-Murnaghan equation of state are shown below ((S1)-(S3), respectively).

The red line represents the results fitted by equation (S1) which gives a value corresponding to $K_0=341(6)$ GPa and $K_0'=3.2(3)$. Therefore, the pressure-volume data were fitted to the 3rd-order Birch-Murnaghan equation of state.

$$f = \frac{\left(\frac{V}{V_0}\right)^{-2/3} - 1}{2} \#(S1)$$

$$F = \frac{P}{3f(2f+1)^{5/2}} = K_0 \left[1 + \frac{3}{2}(K_0' - 4)f \right] \#(S2)$$

$$P = \frac{3K_0}{2} \left(\frac{V}{V_0}\right)^{-5/3} \left[\left(\frac{V}{V_0}\right)^{-2/3} - 1 \right] \left\{ 1 + \frac{3}{4}(K_0' - 4) \left[\left(\frac{V}{V_0}\right)^{-2/3} - 1 \right] \right\} \#(S3)$$

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