

Synthesis and structure of a sodium niobium(V) nitride, NaNbN₂

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Abstract

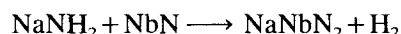
Red single crystals of air-stable sodium niobium(V) nitride, NaNbN₂, were obtained by the reaction of NaNH₂ with NbN (molar ratio 10:1) at 800 °C in high pressure autoclaves for 5 days. The structure was determined on the basis of single-crystal data: $R\bar{3}m$, $a=3.144(1)$ Å, $c=16.942(3)$ Å, $Z=3$, $R/R_w=0.038/0.043$, $N(F_o^2) \geq 3\sigma(F_o^2)=156$, $N(\text{var.})=9$. The compound has the α -NaFeO₂-type structure.

1. Introduction

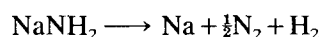
Apart from Li₃N, the heavier alkali metals do not form thermodynamically stable nitrides. However, with tantalum we synthesized for the first time ternary compounds MTaN₂ with $M \equiv \text{Na, K, Rb, Cs}$. Their structures were characterized by powder methods on the basis of X-ray and neutron diffraction data [1]. Here we report about the synthesis of single crystals and structure determination of NaNbN₂.

2. Experimental

An excess of sodium amide reacts with NbN to give NaNbN₂:



and



The compound was synthesized by heating a mixture of NbN and NaNH₂ (molar ratio 1:10) for 5 days to 800 °C in high pressure autoclaves [2]. NaNbN₂ is resistant against moisture and air. The pure compound was isolated as red hexagonal platelets by washing the reaction product with water. The 1:1 composition of Na:Nb was proved by energy-dispersive X-ray analysis.

Precession photographs (Mo K α) led to the trigonal crystal system and to the possible types of space groups $R\bar{3}$, $R\bar{3}$, $R32$, $R3m$ and $R3m$. Intensity data were collected on an Enraf–Nonius CAD 4 diffractometer. The structure was calculated with the SDP system of programs [3]. Experimental details and positional and

thermal parameters are summarized in Tables 1, 2 and 3. Some interatomic distances are given in Table 4.

TABLE 1. Crystal data for NaNbN₂ and NaTaN₂ [1]

Crystal size (mm ³)	0.025 × 0.1 × 0.1
Unit cell parameters (Å)	$a = 3.144(1)$ $c = 16.942(3)$
V (Å ³)	145.0
Space group	$R\bar{3}m$
D_x (g cm ⁻³)	4.943
$1/\mu$ (Mo K α) (mm)	0.168
Absorption correction	Empirical method [4]
Transmission (%)	65.1 (min. rel.)
Radiation	Mo K α
Monochromator	Graphite
Scan mode	$\omega/2\theta$
Θ_{max} (deg)	60
h, k, l	$7, \pm 7, \pm 40$
R_{int} (%)	7.5
Independent reflections	320
Reflections with $I > 3\sigma(I)$	156
Variables	9
Final R/R_w ($w=1$)	0.038/0.043
Largest peak in the final difference map (electrons Å ⁻³)	2.9

TABLE 2. Atomic coordinates and isotropic thermal parameters for NaNbN₂

Site	Occupancy	x	y	z	B (Å ²)
3a	3Nb	0	0	0	0.926(9)
3b	3Na	0	0	1/2	0.56(4)
6c	6N	0	0	0.2683(3)	0.29(4)

TABLE 3. Anisotropic thermal parameters for NaNbN₂

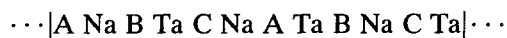
Atom	U_{11} ($\times 10^3$ Å ²)	U_{22} ($\times 10^3$ Å ²)	U_{33} ($\times 10^3$ Å ²)	U_{12} ($\times 10^3$ Å ²)	U_{13} ($\times 10^3$ Å ²)	U_{23} ($\times 10^3$ Å ²)
Nb	10.2(2)	U_{11}	14.7(3)	U_{11}	0	0
Na	5.2(8)	U_{11}	11(1)	U_{11}	0	0
N	1.2(9)	U_{11}	8(1)	U_{11}	0	0

TABLE 4. Interatomic distances (Å) for NaNbN₂ and NaTa₂N₂ [1]

	NaNbN ₂		NaTa ₂ N ₂ [1]
Nb–N	6 × 2.123(2)	Ta–	2.114(1)
–Na	6 × 3.357(0)		3.359(0)
–Nb	6 × 3.144(0)	–Ta	3.134(1)
Na–N	6 × 2.502(3)		2.509(2)
–Na	6 × 3.144(0)		3.134(1)
N–N	3 × 2.855(5)		2.837(4)
	6 × 3.144(0)		3.134(0)
	3 × 3.894(6)		3.918(4)

3. Discussion

For the first time we were able to grow single crystals of a ternary niobium nitride with sodium. The structure determination on NaNbN₂ reveals that this compound crystallizes isotypically to NaTa₂N₂ [1], both with the α -NaFeO₂-type structure [5]. In a cubic close-packed arrangement of nitrogen octahedral holes are occupied by sodium and tantalum in the following sequence:



The distance $d(\text{Nb–N}) = 2.123$ Å is nearly the same as in NaTa₂N₂ with $d(\text{Ta–N}) = 2.114$ Å and for sodium–nitrogen $d(\text{Na–N}) = 2.502$ Å and 2.509 Å respectively.

We hope that we can prepare single-crystals of ternary nitrides MNbN₂ even with the heavier alkali metals $M \equiv K, Rb, Cs$ and determine exact crystal structure data.

Acknowledgments

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