Journal of Alloys and Compounds, 191 (1993) 51–52
JALCOM 449

Synthesis and structure of a sodium niobium(V) nitride, $NaNbN_2$

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(Received July 25, 1992)

Abstract

Red single crystals of air-stable sodium niobium(V) nitride, $NaNbN_2$, were obtained by the reaction of $NaNH_2$ 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, $Z=3$, $R/R_w=0.038/0.043$, $N(F_0^2)\geqslant 3\sigma(F_0^2)=156$, $N(\text{var.})=9$. The compound has the α-$NaFeO_2$-type structure.

1. Introduction

Apart from Li_3N, the heavier alkali metals do not form thermodynamically stable nitrides. However, with tantalum we synthesized for the first time ternary compounds $MTaN_2$ with M ≡ 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 $NaNbN_2$.

2. Experimental

An excess of sodium amide reacts with NbN to give $NaNbN_2$:

$$NaNH_2 + NbN \longrightarrow NaNbN_2 + H_2$$

and

$$NaNH_2 \longrightarrow Na + \tfrac{1}{2}N_2 + H_2$$

The compound was synthesized by heating a mixture of NbN and $NaNH_2$ (molar ratio 1:10) for 5 days to 800 °C in high pressure autoclaves [2]. $NaNbN_2$ 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 Kα) led to the trigonal crystal system and to the possible types of space groups $R3$, $R\bar{3}$, $R32$, $R3m$ and $R\bar{3}m$. 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 $NaNbN_2$ and $NaTaN_2$ [1]

Crystal size (mm^3)	$0.025\times0.1\times0.1$
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 Kα) (mm)	0.168
Absorption correction	Empirical method [4]
Transmission (%)	65.1 (min. rel.)
Radiation	Mo Kα
Monochromator	Graphite
Scan mode	$\omega/2\Theta$
Θ_{max} (deg)	60
h, k, l	$7, \pm7, \pm40$
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 $NaNbN_2$

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)

0925-8388/93/$6.00

TABLE 3. Anisotropic thermal parameters for $NaNbN_2$

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 $NaNbN_2$ and $NaTaN_2$ [1]

	$NaNbN_2$		$NaTaN_2$ [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 $NaNbN_2$ reveals that this compound crystallizes isotypically to $NaTaN_2$ [1], both with the α-$NaFeO_2$-type structure [5]. In a cubic close-packed arrangement of nitrogen octahedral holes are occupied by sodium and tantalum in the following sequence:

$\cdots|$A Na B Ta C Na A Ta B Na C Ta$|\cdots$

The distance d(Nb–N) = 2.123 Å is nearly the same as in $NaTaN_2$ with d(Ta–N) = 2.114 Å and for sodium–nitrogen d(Na–N) = 2.502 Å and 2.509 Å respectively.

We hope that we can prepare single-crystals of ternary nitrides $MNbN_2$ even with the heavier alkali metals M ≡ K, Rb, Cs and determine exact crystal structure data.

Acknowledgments

Financial support was given by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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