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Synthesis and structure of a caesium niobium(V) nitride, $CsNbN_2$

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Abstract

Deep red transparent single crystals of air-stable caesium niobium(V) nitride, $CsNbN_2$, were obtained by the reaction of $CsNH_2$ with NbN (molar ratio 10:1) at 600 °C in high pressure autoclaves for 9 days. The structure was determined on the basis of X-ray single-crystal data: $Fd\bar{3}m$, $a = 8.740(5)$ Å, $Z = 8$, $R/R_w = 0.025/0.028$, $N(F_o^2) \geq 2\sigma(F_o^2) = 37$, N(variables) = 5. The compound has a filled-up β-cristobalite-type structure.

1. Introduction

Unlike 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 and Cs. Their structures were characterized by powder methods on the basis of X-ray and neutron diffraction data [1]. We also reported the synthesis and structure of a sodium niobium(V) nitride [2]. Now we have been successful in the synthesis of single crystals of $CsNbN_2$ and their X-ray structure determination.

2. Experimental details

An excess of caesium amide reacts with NbN to give $CsNbN_2$:

$$CsNH_2 + NbN \longrightarrow CsNbN_2 + H_2$$

$$CsNH_2 \longrightarrow Cs + \tfrac{1}{2} N_2 + H_2$$

The compound was synthesized by heating a mixture of NbN and $CsNH_2$ (molar ratio 1:10) for 9 days to 600 °C in high pressure autoclaves [3]. Crystals of $CsNbN_2$ are resistant against moisture and air. The pure compound was isolated as deep red, transparent regular octahedra by washing the reaction product with water. The 1:1 composition of Cs:Nb was proved by energy-dispersive X-ray analysis.

Intensity data were collected on an Enraf–Nonius CAD 4 diffractometer. The structure was calculated with the SDP system of programmes [4]. Experimental details and positional and thermal parameters are summarized in Tables 1–3. Some interatomic distances are given in Table 4.

TABLE 1. Crystal data for $CsNbN_2$

Crystal size (mm^3)	$0.05 \times 0.05 \times 0.05$
Unit cell parameter a (Å)	8.740(5)
V (Å^3)	667.6
Space group	$Fd\bar{3}m$
D_x (g cm^{-3})	5.051
$1/\mu$ (Mo Kα) (mm)	0.071
Radiation	Mo Kα
Monochromator	Graphite
Scan mode	$\omega/2\Theta$
Θ_{max} (°)	40
h, k, l	±15, 15, 15
R_{int} (%)	7.7
Absorption correction	None
Independent reflections	139
Reflections with $I > 2\sigma(I)$	37
Variables	5
Final R/R_w ($w = 1$)	0.025/0.028
Largest peak in final difference map (e Å^{-3})	0.24

TABLE 2. Atomic coordinates and isotropic thermal parameters for $CsNbN_2$

Site	Occupancy	x	y	z	B (Å^2)
8*a*	8 Nb	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	0.86(1)
8*b*	8 Cs	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$	2.80(1)
16*c*	16 N	0	0	0	3.4(2)

3. Discussion

For the first time we have succeeded in growing single crystals of a ternary nitride with caesium. The structure determination on $CsNbN_2$ reveals that this

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TABLE 3. Anisotropic thermal parameters (10^{-3} Å^2) for $CsNbN_2$

Atom	$U(11)$	$U(22)$	$U(33)$	$U(12)$	$U(13)$	$U(23)$
Cs	35.4(6)	$U(11)$	$U(11)$	0	0	0
Nb	10.9(4)	$U(11)$	$U(11)$	0	0	0
N	44(8)	$U(11)$	$U(11)$	−10(10)	$U(12)$	$U(12)$

TABLE 4. Interatomic distances (Å) for $CsNbN_2$ and $CsTaN_2$

$CsNbN_2$		$CsTaN_2$ [1]	
Cs–N	12×3.622	Cs–N	12×3.637
–Cs	4×3.783	–Cs	4×3.799
–Nb	4×3.783	–Ta	4×3.799
	6×4.368		6×4.386
Nb–N	4×1.892	Ta–N	4×1.899
–Nb	4×3.783	–Ta	4×3.799
N–N	6×3.089	N–N	6×3.102

compound crystallizes isotypically to $CsTaN_2$ [1], both having the filled-up β-cristobalite-type structure [5].

The distance d(Nb–N) = 1.89 Å is nearly the same as the distance d(Ta–N) = 1.90 Å in $CsTaN_2$, while the caesium–nitrogen distances are d(Cs–N) = 3.62 and 3.64 Å respectively.

The preparation of single crystals of ternary nitrides $MNbN_2$ with M ≡ K and Rb is in progress.

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