

# Synthesis and structure of a caesium niobium(V) nitride, CsNbN<sub>2</sub>

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## Abstract

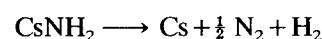
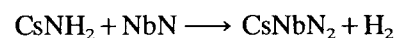
Deep red transparent single crystals of air-stable caesium niobium(V) nitride, CsNbN<sub>2</sub>, were obtained by the reaction of CsNH<sub>2</sub> with NbN (molar ratio 10:1) at 600 °C in high pressure autoclaves for 9 days. The structure was determined on the basis of X-ray single-crystal data: *Fd*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

## 1. Introduction

Unlike Li<sub>3</sub>N, the heavier alkali metals do not form thermodynamically stable nitrides. However, with tantalum we synthesized for the first time ternary compounds MTaN<sub>2</sub> 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<sub>2</sub> and their X-ray structure determination.

## 2. Experimental details

An excess of caesium amide reacts with NbN to give CsNbN<sub>2</sub>:



The compound was synthesized by heating a mixture of NbN and CsNH<sub>2</sub> (molar ratio 1:10) for 9 days to 600 °C in high pressure autoclaves [3]. Crystals of CsNbN<sub>2</sub> 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<sub>2</sub>

Crystal size (mm <sup>3</sup> )	0.05 × 0.05 × 0.05
Unit cell parameter <i>a</i> (Å)	8.740(5)
<i>V</i> (Å <sup>3</sup> )	667.6
Space group	<i>Fd</i> $\bar{3}$ <i>m</i>
<i>D<sub>x</sub></i> (g cm <sup>-3</sup> )	5.051
1/μ (Mo Kα) (mm)	0.071
Radiation	Mo Kα
Monochromator	Graphite
Scan mode	ω/2θ
θ <sub>max</sub> (°)	40
<i>h</i> , <i>k</i> , <i>l</i>	±15, 15, 15
<i>R<sub>int</sub></i> (%)	7.7
Absorption correction	None
Independent reflections	139
Reflections with <i>I</i> > 2σ( <i>I</i> )	37
Variables	5
Final <i>R/R<sub>w</sub></i> ( <i>w</i> = 1)	0.025/0.028
Largest peak in final difference map (e Å <sup>-3</sup> )	0.24

TABLE 2. Atomic coordinates and isotropic thermal parameters for CsNbN<sub>2</sub>

Site	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
8 <i>a</i>	8 Nb	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	0.86(1)
8 <i>b</i>	8 Cs	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$	2.80(1)
16 <i>c</i>	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<sub>2</sub> reveals that this

TABLE 3. Anisotropic thermal parameters (10<sup>-3</sup> Å<sup>2</sup>) for CsNbN<sub>2</sub>

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<sub>2</sub> and CsTa<sub>2</sub>N<sub>2</sub>

CsNbN <sub>2</sub>		CsTa <sub>2</sub> N <sub>2</sub> [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 CsTa<sub>2</sub>N<sub>2</sub> [1], both having the filled-up β-cristobalite-type structure [5].

The distance  $d(\text{Nb-N}) = 1.89 \text{ \AA}$  is nearly the same as the distance  $d(\text{Ta-N}) = 1.90 \text{ \AA}$  in CsTa<sub>2</sub>N<sub>2</sub>, while the

caesium-nitrogen distances are  $d(\text{Cs-N}) = 3.62$  and  $3.64 \text{ \AA}$  respectively.

The preparation of single crystals of ternary nitrides MNbN<sub>2</sub> with M ≡ K and Rb is in progress.

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