

Synthesis and structure of Nb₃SiTe₆, a new layered ternary niobium telluride compound

Jing Li*, Michael E. Badding and F. J. DiSalvo

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853-1301 (USA)

(Received November 13, 1991)

Abstract

Nb₃SiTe₆, a new type of layered ternary telluride compound, has been synthesized. The structure is determined by single-crystal X-ray diffraction methods. The compound crystallizes in space group *Pnma* (No. 62) with $Z=4$, $a=6.353(2)$ Å, $b=13.938(5)$ Å, $c=11.507(4)$ Å, $V=1018.9(6)$ Å³, $R=4.77\%$ and $R_w=4.88\%$. The structure contains sheets of mixed niobium and silicon with tellurium atoms capping both sides. The layered framework has an unusual coordination environment.

1. Introduction

Early transition metals such as niobium and tantalum are well known for their ability to form low dimensional compounds with chalcogens. Among these are, for example, MX₂ (M≡Nb, Ta; X≡S, Se, Te) [1], MX₃ (M≡Nb, Ta; X≡S, Se) [2], MTe₄ (M≡Nb, Ta) [3], Nb₃X₄ (X≡S, Se, Te) [4], Ta₂X (X≡S, Se) [5] and Ta₃S₂ [6]. Upon addition of the third element, many of these compounds form intercalation products, because the bonding between the chains (one dimensional) or layers (two dimensional) is weak (van der Waals force) and this allows for insertion of a wide range of both atoms and molecules into the structure (see for example ref. 7). However, we have noticed that the MTe₂ (M≡Nb, Ta) series behave quite differently from the corresponding disulfides upon addition of the third element. The disulfides give almost exclusively intercalation products even with less electropositive elements, *e.g.* iron [8]. The parent structure remains unchanged during the intercalation process. Reaction of iron (or cobalt or nickel) with a stoichiometric ratio of M (M≡Nb, Ta) and Te, however, produces a new line phase MT'Te₂ (T'≡Fe, Co, Ni) which has a structure unrelated to the parent MTe₂ structure [9, 10]. During the investigations of ternary niobium and tantalum telluride systems we find another phase that exhibits similar structural properties and we report here briefly on the synthesis and structure of this compound, Nb₃SiTe₆.

*Present address: Department of Chemistry, Rutgers University, Camden College of Arts and Sciences, Camden, NJ 08102, USA.

2. Experimental details

The plate-like crystals of Nb_3SiTe_6 were initially obtained in a reaction of 1 g mixture of niobium, silicon and tellurium with a 2:1:4 molar ratio. A quartz tube 5 in long and of 10 mm inside diameter containing the three elements and the transport agent (TeCl_4 ; 10 mg) was sealed under vacuum and placed in a furnace. The tube was slowly heated to 850 °C and the reaction was kept at this temperature for 4 days before being cooled to room temperature. Better-quality single crystals used in the structure determination were grown in a reaction at a higher temperature (950 °C) for 14 days. The crystals of Nb_3SiTe_6 show metallic luster and are stable in air.

3. Results

The structure of Nb_3SiTe_6 was determined using a Syntex P2₁ diffractometer on a well-formed single crystal (0.1 mm × 0.2 mm × 0.005 mm). Rotational and axial photographs revealed *mmm* Laue symmetry and yielded approximate lattice constants. The final lattice parameters were obtained by centering on 26 reflections selected from a shell data collection ($2\theta = 15\text{--}23^\circ$). Four octants of data were collected and merged. An analytical absorption correction procedure was applied to the data after measuring the crystal faces. Systematic absences ($hk0$, $h = 2n + 1$, $0kl$, $k + 1 = 2n + 1$) reduced the possible space groups to the *Pnma* (No. 62) and *Pna2*₁ (No. 33). The structure was solved by direct methods in the centrosymmetric space group *Pnma* and refined using SHELXTL Plus programs [11] running on a Microvax computer. The final refinement generated an $R = 4.77\%$, $R_w = 4.88\%$ and a goodness of fit of 2.34. Important crystal data and unit cell dimensions are tabulated in Table 1. Table 2 lists atomic positions and isotropic thermal parameters. The atomic coordinates and R factors refined in the non-centrosymmetric space group were not significantly different from those in *Pnma*.

TABLE 1
Crystallographic data and unit-cell parameters for Nb_3SiTe_6

Chemical formula	Nb_3SiTe_6	T	25 °C
Space group	<i>Pnma</i> (No. 62)	λ	0.71073 Å
a	6.353(2) Å	Absorption coefficient μ	20.108 mm ⁻¹
b	13.938(5) Å	2θ range	0–55°
c	11.507(4) Å	Largest and mean Δ/σ	0.001/0.000
α	90°	Observed reflections	941 [$F > 3\sigma(F)$]
β	90°	ρ_{calc}	6.991 g cm ⁻³
γ	90°	R^a	4.77%
Formula weight	1072.4	R_w^b	4.88%
V	1018.9(6) Å ³		
Z	4		

$$^a R = \sum(|F_o| - |F_c|) / \sum(|F_o|).$$

$$^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum (w|F_o|^2)]^{1/2}, w = 1/[\sigma^2(F_o) + 0.0001F_o^2].$$

TABLE 2

Atomic (fractional) coordinates and equivalent isotropic displacement coefficients for Nb₃SiTe₆

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a (×10 ³ Å ²)
Nb(1)	4c	0.8309(1)	0.75	0.1650(1)	9(1)
Nb(2)	4c	0.3050(1)	0.75	0.0334(1)	7(1)
Nb(3)	4c	0.0302(1)	0.75	0.6883(1)	7(1)
Si	4c	0.9251(1)	0.75	0.9254(1)	8(1)
Te(1)	8d	0.1514(1)	0.6134(1)	0.1820(1)	9(1)
Te(2)	8d	0.2017(1)	0.6161(1)	0.8450(1)	9(1)
Te(3)	8d	0.6465(1)	0.6198(1)	0.0017(1)	9(1)

^aEquivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Nb₃SiTe₆ represents a new layered type of structure. As shown in Fig. 1, each layer consists of a sheet of bonded niobium and silicon atoms which is then capped on both sides by the tellurium atoms. The coordination of silicon to niobium is distorted square planar, giving four different Nb–Si bond lengths, 2.715 Å, 2.809 Å, 2.822 Å and 2.829 Å. These are close to the corresponding Nb–Si distance (2.76 Å) found in NbSi₂ [12]. Each silicon atom is also bonded to four tellurium atoms, two above and two below the plane (2.683 Å and 2.725 Å), forming also a distorted square planar geometry. Such a coordination environment for silicon is quite unusual. There are three structurally non-equivalent niobium atoms, Nb(1), Nb(2) and Nb(3). Nb(1) and Nb(2) bond to one silicon (2.822 Å and 2.715 Å respectively) whereas Nb(3) forms two bonds with the silicon atoms (2.809 Å and 2.829 Å). The only metal–metal bond found in this structure, 2.925 Å, is between Nb(2) and Nb(3) and is slightly longer than an Nb–Nb bond in a niobium metal (b.c.c., 2.86 Å) [13]. All niobium-to-tellurium coordination can be described as distorted trigonal prismatic, and the Nb–Te distances range from 2.683 to 2.936 Å. The local geometry of each atom is drawn in Fig. 2, and all important interatomic distances are summarized in Table 3. The interlayer Te–Te distances are of typical van der Waals type.

It is interesting to notice the stacking pattern of the anions, in this case the tellurium atoms. Unlike many of the known metal chalcogenide compounds, Nb₃SiTe₆ does not contain simple close-packed tellurium layers. The two adjacent, slightly puckered tellurium layers (approximately hexagonal arrangement of tellurium atoms in each layer) that sandwich the Nb–Si sheet are directly superposed to form an AbA three-layer unit (b representing the Nb–Si sheet). In fact, the tellurium layers form a four-layer repeat unit (AABB) similar to the sulfur atoms in the β-MoS₂ structure [14]. This is indeed quite different from the parent structure, NbTe₂ [15], in which the tellurium atoms are close packed to give an ...ACAC... sequence. A similar situation has been also observed in the NbMTe₂ structure [9], where the tellurium layers distort severely from close packing.

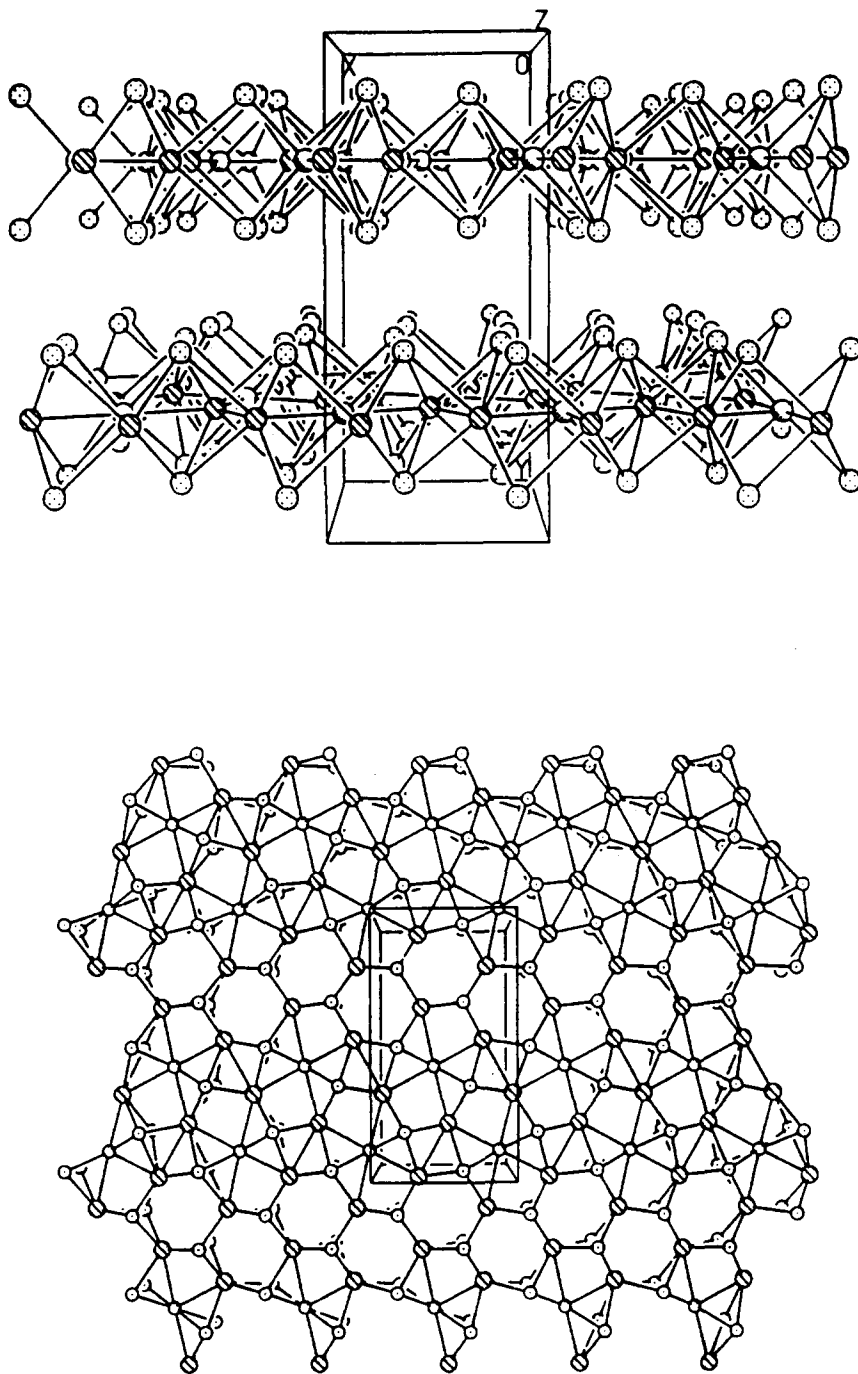


Fig. 1. Perspective views of the layered Nb_3SiTe_6 structure ((a) view along the c axis, (b) view along the b axis): \bullet , niobium atoms; \circ , silicon atoms; \odot , tellurium atoms.

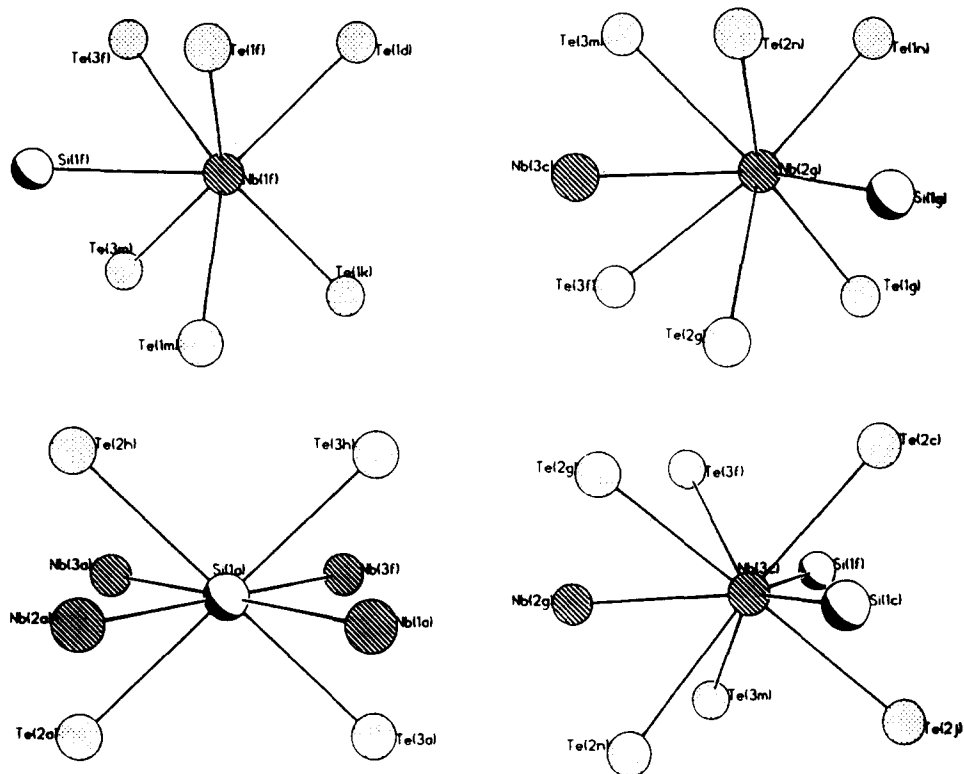


Fig. 2. Coordination environment of the atoms in Nb_3SiTe_6 : \odot , niobium atoms; \circ , silicon atoms; \oplus , tellurium atoms.

TABLE 3

Important interatomic distances in Nb_3SiTe_6

A-B	Distance (Å)	A-B	Distance (Å)
Nb(1)			
Nb(1)-Si	2.822(7)		
Nb(1)-Te(1)	$2 \times 2.833(2)$	Nb(1)-Te(1)	$2 \times 2.795(1)$
Nb(1)-Te(3)	$2 \times 2.683(2)$		
Nb(2)			
Nb(2)-Si	2.715(8)		
Nb(2)-Nb(3)	2.925(3)		
Nb(2)-Te(1)	$2 \times 2.739(2)$	Nb(2)-Te(2)	$2 \times 2.935(2)$
Nb(2)-Te(3)	$2 \times 2.853(2)$		

(continued)

TABLE 3 (continued)

A-B	Distance (Å)	A-B	Distance (Å)
Nb(3)			
Nb(3)-Si	2.809(7)	Nb(3)-Si	2.829(8)
Nb(3)-Nb(2)	2.925(3)		
Nb(3)-Te(2)	2 × 2.814(2)	Nb(3)-Te(2)	2 × 2.826(2)
Nb(3)-Te(3)	2 × 2.936(2)		
Si			
Si-Nb(1)	2.822(7)	Si-Nb(2)	2.715(8)
Si-Nb(3)	2.809(7)	Si-Nb(3)	2.829(8)
Si-Te(2)	2 × 2.725(6)	Si-Te(3)	2 × 2.683(6)

During the course of the investigations, we have also found an isostructural phase, Nb_3GeTe_6 . Structural characterization of this compound is currently in progress. Studies of the physical properties of both compounds are being conducted as well at the present time.

Acknowledgments

We are grateful to the US Department of Energy, Division of Basic Energy Sciences, for its generous support through Grant DE-FG02-87ER45298. J.L. is grateful for a Research Council grant and the Henry Rutgers Research Fellowship in completion of this work.

References

- 1 F. Jellinek, G. Brauer and H. Müller, *Nature*, **185** (1960) 376.
B. E. Brown and D. J. Beerntsen, *Acta Crystallogr.*, **18** (1965) 31.
L. H. Brixner, *J. Inorg. Nucl. Chem.*, **24** (1962) 257.
F. Jellinek, *Ark. Kem.*, **20** (1963) 447.
F. Kadijk, R. Huisman and F. Jellinek, *Recl. Trav. Chim. Pays-Bas*, **83** (1964) 768.
K. Selte, E. Bjerkelund and A. Kjekshus, *J. Less-Common Met.*, **11** (1966) 14.
- 2 T. Sambong, K. Tsutsumi, K. Shiozaki, M. Yamamoto, K. Yamaya and Y. Abe, *Solid State Commun.*, **22** (1977) 729.
J. Rijnsdorp and F. Jellinek, *J. Solid State Chem.*, **25** (1978) 325.
J. L. Hodeau, M. Marezio, C. Roncau, R. Ayroles, A. Meerschaut, J. Rouxel and P. Monceau, *J. Phys. C.*, **11** (1978) 4117.
E. Bjerkelund, J. H. Fermor and A. Kjekshus, *Acta Chem. Scand.*, **20** (1966) 1836.
- 3 E. Bjerkelund and A. Kjekshus, *J. Less-Common Met.*, **7** (1964) 231.
K. Selte and A. Kjekshus, *Acta Chem. Scand.*, **18** (1964) 690.
- 4 K. Selte and A. Kjekshus, *Acta Crystallogr.*, **17** (1964) 1568.
A. F. J. Ruysink, F. Kadijk, A. J. Wagner and F. Jellinek, *Acta Crystallogr., Sect. B*, **24** (1968) 1614.
- 5 H. F. Franzen and J. G. Smeggil, *Acta Crystallogr., Sect. B.*, **25** (1969) 1736.
B. Harbrecht, *Angew. Chem., Int. Edn. Engl.*, (1989) 1660.

- 6 S.-J. Kim, K. S. Nanjundaswamy and T. Hughbank, *Inorg. Chem.*, 30 (1991) 159.
- 7 F. R. Gamble and T. H. Geballe, in N. B. Hannay (ed.), *Solid State Chemistry*, Vol. 3, Plenum, New York, 1976.
G. Huan and M. Greenblatt, *Mater. Res. Bull.*, 22 (1987) 505, 943.
- 8 J. M. Van der Berg and P. Cossee, *Inorg. Chim. Acta*, 2 (1968) 143.
B. Van Laar, H. M. Rietveld and D. J. W. Ijdo, *J. Solid St. Chem.*, 3 (1971) 154.
- 9 J. Li, M. E. Badding and F. J. DiSalvo, *Inorg. Chem.*, in the press.
- 10 B. Huang, B. Shang and J. Huang, *Jiegou Huaxue (J. Struct. Chem.)*, 7 (1988) 133.
B. Huang, B. Shang and J. Huang, *Jiegou Huaxue (J. Struct. Chem.)*, 7 (1988) 214.
B. Huang, B. Shang and J. Huang, *Jiegou Huaxue (J. Struct. Chem.)*, 8 (1989) 145.
- 11 Release 4.11 of SHELXTL Plus Program for Nicolet Crystallographic Research Systems, 1990.
- 12 H. J. Wallbaum, *Z. Metallkd.*, 33 (1941) 378.
- 13 J. C. Slater, *Quantum Theory of Molecules and Solids: Symmetry and Energy Bands in Crystals*, Vol. 2, McGraw-Hill, New York, 1965.
- 14 P. P. Ewald and C. Hermann, *Strukturbericht*, 1 (1931) 164.
- 15 B. E. Brown, *Acta Crystallogr.*, 20 (1966) 264.