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Synthesis and Crystal Structure of a New Metal-rich Layered Ternary Tantalum Telluride $TaNi_2Te_2$

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Abstract The title compound has been synthesized by high-temperature solid state reaction. The crystal structure was determined by single crystal X-ray diffraction method. The crystal belongs to orthorhombic system with space group *Pnma*, Z=4, a=6.480(1), b=3.5639(6), c=16.994(4) Å, V=392.5(1) Å^3, D_c=9.37g·cm^{-3}, $\lambda(MoK_\alpha)$=0.71069Å, $\mu(MoK_\alpha)$=514.43cm^{-1} and $F(000)$=932. The final R is 0.051 for 706 observations. $TaNi_2Te_2$ is a new metal-rich layered ternary telluride. In the structure two metal sheets are sandwiched below and above by Te layers, leading to planar trigonal coordination for Ta and trigonal pyramidic coordination for Ni by Te atoms. An important structural character of this compound is that all planar five-member $TeNi_4$ rings are fused together to form an extended structure, and each Ta atom is sandwiched by two $TeNi_4$ rings.

Keywords: Ternary layered telluride, Crystal structure, Synthesis

1 Introduction

Layered niobium and tantalum chalcogenides have attracted considerable attention in recent years because of their interesting properties such as superconductivity, charge density waves, anisotropic electrical and magnetic properties[1,2]. Many layered ternary niobium/tantalum sulfides/selenides have been reported[3,4], and much attension has been payed also to corresponding tellurides[5-11]. However, most layered ternary tellurides are not metal-rich. With the metal-rich atomic ratio of reactants in preparation, we have got several metal-rich layered compounds. Here we report the synthesis and crystal structure of $TaNi_2Te_2$.

2 Experiments

The title compound was synthesized from powders of the elements. A stoichiometric amount of elements, Ta(99.98%, 185mg, 1.02mmol, Zhuzhou Hard Alloy Plant), Ni(99.8%, 118mg, 2.01mmol, Shanghai Chemicals Supply Service Station), and Te(99.999%, 257mg,

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2.01mmol, Shanghai Chemicals Supply Service Station) was mixed, ground, and pressed into a pellet at pressure of 20 MPa. The pellet then was sealed in an evacuated SiO_2 tube (1.333×10^{-2}Pa) with a small amount of I_2 (about 5% of wt.) as transport agent. The tube was placed in a tubetype furnace with the pellet at the hot end, and subjected to 973 K for 7 days, then quenched to room temperature. Rectangle plate crystals were formed at the charge end. The crystal exhibits a shiny black luster. It is easy to be cleaved along the flat face, and is stable in air. Standless analysis result with the microprobe of JEOL scanning electron microscope on the fresh cleaved surface of several crystals shows the component of Ta 33.98%, Ni 18.11%, Te 47.53%, and other elements 0.38%. This is approximately confirmed in that calculated for $TaNi_2Te_2$ (Ta 32.69%, Ni 21.21% , and Te 46.10%).

The X-ray diffraction work for the single crystal was done on a RIGAKU AFC5R diffractometer. The 25 reflections searched in range of $20° < 2\theta < 25°$ were used to determine the unit cell and Laue symmetry. Four octants of diffraction data were collected and three standard reflections monitored at intervals of every 150 reflections showed no significant change in intensity during the course of data collection. Crystal data and data collection conditions are given in Table 1.

Calculations were carried out on a Micro VAX II computer with TEXSAN program system. The intensity data were corrected for Lp factors and DIFABS empirical absorption, and the equivalent reflections were averaged. The systematic absence (0kl: $k+l=2n+1$, hk0: $h=2n+1$) is consistent with the space group $Pnma$ or $Pn2_1a$. The structure was solved by direct methods in $Pnma$, and refined anisotropicly for all atoms by full-matrix least-squares, leading to final $R=0.051$ and $R_w=0.056$. In the final difference electron density map the largest residual peak is 10.85(-12.62) e·Å^{-3}, and no chemical features exist. Table 2 and 3 give the atomic parameters and the selected interatomic distances and bond angles, respectively.

3 Results and Discussion

$TaNi_2Te_2$ is a new metal-rich layered telluride with metal: non-metal ratio of 1.5. As shown in Figure 1, each TeMTe layer contains two sheets of metal atoms (Ta and Ni) which are puckered along [100] and sandwiched above and below by Te atoms. In each layer, two closest-packed Te sheets are stacked in AD fashion[12], producing two types of sites, trigonal and trigonal-antiprismatic (not octahedral), for the location of metal atoms. The trigonal-antiprismatic sites are occupied by Ni_2 pairs, and a half of planar trigonal sites by Ta atoms. Two adjacent closest-packed Te sheets of two neighbouring TeMTe layers are arranged in AB or AC type.

Figure 2a and 2b illustrate the coordination environments of metal atoms. Each Ta atom is surrounded in a trigonal fashion by Te atoms and is also bonded to eight Ni atoms.

Figure 2a and 2b illustrate the coordination environments of metal atoms. Each Ta atom is surrounded in a trigonal fashion by Te atoms and is also bonded to eight Ni atoms. So as a whole the coordination environment of Ta atom can be described as a mono-caped pentagonal prism. On the other hand, each Ni atom is coordinated by three Te atoms, Ni atom being the vertex of $NiTe_3$ triangular pyramid. This unusual coordination fashion for Ni atom is discovered firstly in layered ternary chalcogenides[3-11]. In addition, each Ni atom is also bonded to four Ta atoms and two Ni atoms, hence the total coordination environment of Ni atom is a distorted tri-capped trigonal prism, with two Ta and one Te atoms composing the trigonal base, and two Ni and one Te atoms acting as the capping atoms. In this structure Te atoms are μ_4-(Te(1)) and μ_5-(Te(2)) bridging atoms, being similar to that found in some layered tellurides such as Ta_2FeTe_4, $TaFeTe_2$, $TaNiTe_2$[11], and $TaNi_2Te_3$[13].

Table 1 Crystallographic data and data collection conditions

Formula	$TaNi_2Te_2$	Temperature	23 ℃
Formula weight	553.55	Scan mode	ω-2θ
Crystal size	0.30×0.20×0.08mm	Scan width	1.155+tgθ
Lattice parameters	a=6.480(1) Å	2θ(max)	74.1°
	b=3.5639(6)Å	No. data collected	4273(h 0 ~ 11, k-6 ~ 6,
	c=16.994(4)Å		l-29 ~ 29)
	V=392.5(1)Å^3	No. unique data	1228
Space group	$Pnma$		
Z value	4	Absorption Correction	transmission
D_{calc}	9.37g·cm^{-3}		(0.5239-1.6449)
F(000)	932	Second extinction	1.02×10^{-6}
μ(Mo K_α)	514.44cm^{-1}	No. observations	706
Radiation	Mo K_α(λ=0.71069Å)		
	Graphite-monochromated	($I>3\sigma(I)$)	
		No. variables	32
		Residuals: R; R_w	0.051; 0.056
		Goodness of fit indicator	1.24
		Maximum shift in final cycle	0.0007
		Largest peak in final diff. map	10.85(-12.62)e·Å^{-3}
		p Factor	0.05

Table 2 Positional parameters and B (eq)

atom	x	y	z	B(eq)
Ta(1)	0.4049(1)	1/4	0.72320(4)	0.54(2)
Ni(1)	0.6007(3)	3/4	0.8164(1)	0.72(7)
Ni(2)	0.7113(3)	3/4	0.6811(1)	0.72(7)
Te(1)	0.4041(2)	3/4	0.59134(7)	0.66(3)
Te(2)	0.4086(2)	1/4	0.89535(7)	0.73(3)

Table 3 Selected interatomic distances (Å) and bond angles(°)

Ta(1)-Ni(1)	2.701(2)	Ta(1)-Te(2)	2.926(2)
Ta(1)-Ni(1a)	2.701(2)	Ni(1)-Ni(2)	2.408(3)
Ta(1)-Ni(2b)	2.719(2)	Ni(1)-Te(1d)	2.515(2)
Ta(1)-Ni(2c)	2.719(2)	Ni(1)-Ni(2b)	2.524(3)
Ta(1)-Ni(1b)	2.741(2)	Ni(1)-Te(2e)	2.554(2)
Ta(1)-Ni(1c)	2.741(2)	Ni(1)-Te(2)	2.554(2)
Ta(1)-Ni(2)	2.762(2)	Ni(2)-Te(1)	2.508(2)
Ta(1)-Ni(2a)	2.762(2)	Ni(2)-Te(2d)	2.549(2)
Ta(1)-Te(1)	2.863(1)	Ni(2)-Te(2f)	2.549(2)
Ta(1)-Te(1a)	2.863(1)		
Ni(1)-Ta(1)-Ni(1a)	82.56(7)	Ni(2)-Ni(1)-Ni(2b)	108.3(1)
Ni(2)-Ta(1)-Ni(2a)	80.35(6)	Ni(2)-Ni(1)-Te(1d)	111.25(9)
Te(1)-Ta(1)- Te(1a)	76.98(4)	Te(1d)-Ni(1)-Ni(2b)	140.5(1)
Ni(1b)-Ta(1)-Ni(1c)	81.10(6)	Ta(1e)-Ni(1)-Ta(1)	82.56(7)
Ni(2b)-Ta(1)-Ni(2c)	81.91(7)	Ta(1d)-Ni(1)-Ta(1f)	81.10(6)
Te(1)-Ta(1)-Te(2)	141.51(2)	Te(2e)-Ni(1)-Te(2)	88.47(8)
Ni(1)-Ta(1)-Ni(2b)	55.51(6)	Ta(1f)-Ni(2)-Ta(1)	75.76(4)
Ni(1)-Ta(1)-Ni(2)	52.29(7)	Te(2f)-Ni(2)-Ta(1f)	67.38(4)
Ni(2b)-Ta(1)-Ni(1b)	52.34(7)	Te(2f)-Ni(2)-Ta(1)	92.38(3)
Ni(1b)-Ta(1)-Te(1)	53.27(5)	Ni(1)-Ni(2)-Ni(1d)	106.4(1)
Te(1)-Ta(1)-Ni(2)	52.92(5)	Ni(1)-Ni(2)-Te(1)	110.2(1)
Ni(2)-Ni(1)-Ni(2b)	108.3(1)	Te(1)-Ni(2)-Ni(1d)	143.5(1)
Ni(1)-Ni(2b)-Ni(1b)	106.4(1)	Ta(1d)-Ni(2)-Ta(1f)	81.91(7)
Ni(2b)-Ni(1b)-Te(1)	111.25(9)	Ta(1e)-Ni(2)-Ta(1)	80.35(6)
Ni(1b)-Te(1)-Ni(2)	103.96(8)	Te(2d)-Ni(2)-Te(2f)	88.69(8)
Te(1)-Ni(2)-Ni(1)	110.2(1)	Ni(2)-Te(1)-Ta(1)	61.48(5)
Ni(1)-Ta(1)-Te(2)	53.82(5)	Ta(1e)-Te(1)-Ta(1)	76.98(4)
Ni(2b)-Ta(1)-Te(2)	53.55(5)	Ni(1b)-Te(1)-Ta(1)	60.88(5)
Ta(1)-Ni(1)-Ta(1f)	76.40(4)	Ni(1)-Te(2)-Ta(1)	58.60(6)
Te(2)-Ni(1)-Ta(1)	67.58(4)	Ni(2b)-Te(2)-Ta(1)	59.07(6)
Te(2)-Ni(1)-Ta(1f)	91.49(3)	Ni(2b)-Te(2)-Ni(1)	59.27(6)

Symmetry codes: a. x, $-1+y$, z; b. $-1/2+x$, $3/2-y$, $3/2-z$; c.$-1/2+x$, $1/2-y$, $3/2-z$; d. $1/2+x$, $3/2-y$, $3/2-z$; e. x, $1+y$, z; f. $1/2+x$, $1/2-y$, $3/2-z$;

Ta-Ni distances, from 2.701 to 2.762 Å, are comparable with those in $Ta_2Ni_3Te_5$[10], $TaNiTe_2$[11] and $TaNi_2Te_3$[13], but vary in a small range. There are two kinds of Ni-Ni distances, 2.408Åand 2.524Å. The former is unusually short, and not found in other Ta/Nb-Ni-Te phases, (similar Ni-Ni distances have been found in some binuclear Ni complexes[14]); the latter is ordinary. Ta-Ta distances, 3.3656Å and 3.5639Å, are just between that in $TaFeTe_2$ and $TaNiTe_2$ (about 3.2Å) [11], and that in $Ta_2Ni_3Te_5$[10] and $TaNi_2Te_3$[13](about 3.7Å). The shortest interlayer Te-Te contact of 3.789Å is typical van der Waals type.

It is worthwhile to note that each Ta atom is sandwiched by two planar five-member rings $TeNi_4$, this is an important character of this structure. Also the structure of TeMTe layer can be described conveniently as the building of Ta centered mono-capped pentagonal prism units(see Fig.2a) . These units share their pentagonal base faces($TeNi_4$) along [010] and the rectangle side faces (Ni_4) along [100], forming a layer.

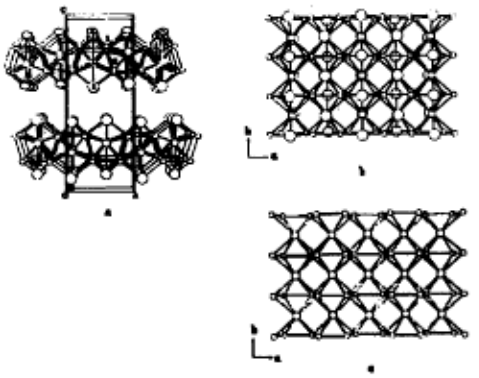

Fig.1 Structure of $TaNi_2Te_2$
(a) Perspective view along [010], showing the labeling scheme (large circles, Te; middle circles, Ta; small circles, Ni). (b) An individual layer viewed along [001] (large circles, Te; middle circles, Ta; small circles, Ni). (c) Projection of the metal cluster along [001] (large circles, Ta; small circles, Ni)

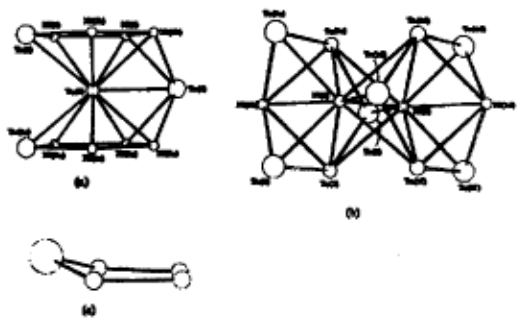

Fig.2 (a) Local coordination of Ta atoms in $TaNi_2Te_2$, (b) Local coordination of Ni atoms in $TaNi_2Te_2$, (c) Noplanar five-member ring $TaCo_4$ in $TeCo_2Te_2$.

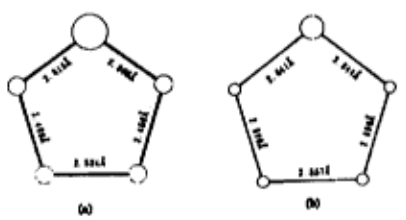

Fig.3 Interatomic distances in five-member rings
(a) $TaNi_4$ ring in compound $TaNi_2Te_2$ (b) $TaCo_4$ ring in compound $TaCo_2Te_2$

We have got an analogous compound, $TaCo_2Te_2$, from the reaction of the powder of the corresponding elements at 873K or 1073K, and determined its crystal structure[13]. $TaNi_2Te_2$ and $TaCo_2Te_2$ have a similar structure except that the five-member $TeCo_4$ ring in $TaCo_2Te_2$ (see Fig.2c) is nonplanar while the $TeNi_4$ ring in $TaNi_2Te_2$ is strictly planar, and that the corresponding interatomic distances are quite different, for instance[13], in $TaCo_2Te_2$ the Ta-Co distances vary from 2.571 to 2.837Å for one type of Ta atom band from 2.633 to 2.717Å for another type of Ta atom, and the bond lengths in $TeCo_4$ ring are different from that in $TeNi_4$ as shown in Figure 3.By the way, we have recently known that Tremel had published the crystal structure about $TaCo_2Te_2$[15], which

is only a little different from that we got.

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新的富金属三组元层状碲化物 $TaNi_2Te_2$ 的合成和晶体结构

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摘要 通过高温固相反应合成了标题化合物并测定了其晶体结构. 结晶学参数：正交晶系，空间群 *Pnma*, Z=4, a=6.480(1), b=3.5639(6), c=16.994(4)Å, V=392.5(1)Å^3, D_c=9.37g·cm^{-3}, $\lambda(MoK_\alpha)$=0.71069Å, $\mu(MoK_\alpha)$=514.43cm^{-1}, $F(000)$=932, 最终偏离因子 R=0.051.$TaNi_2Te_2$ 是一新的富金属三组元层状碲化物，在结构中两层金属原子夹于碲原子层之间，形成对 Ta 原子的平面三角形碲配位和对 Ni 原子的三角锥碲配位. 该化合物的一个重要结构特征是平面形的五元环 $TeNi_4$ 孪合形成扩展结构而每个 Ta 原子夹于两个 $TeNi_4$ 五元环之间.

关键词：三组元层状碲化物，　晶体结构，　合成