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Preparation and crystal structures of the new channel compounds $Tl_{0.5}Nb_6Te_{8-y}As_y$ ($y=0$, 0.5 and 2.0) and Nb_3Te_3As

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Abstract

The new quaternary compounds $Tl_{0.48}Nb_6Te_6As_2$, $Tl_{0.49}Nb_6Te_{7.5}As_{0.5}$ as well as Nb_3Te_3As and $Tl_{0.45}Nb_6Te_8$ crystallize in the hexagonal Nb_3S_4 structure type. The As atoms are exclusively located on one of the two possible crystallographic sites. The preferential substitution of Te by As as well as the change of the valence electron concentration (VEC) per Nb atom drastically change the different interatomic interactions. In the As-rich samples the Nb-Nb distances within the zig-zag chains parallel to the crystallographic *c*-axis are significantly enlarged whereas the separation between the chains is reduced. The intercalation of Tl into the hexagonal channels only slightly affects the interatomic interactions. The results strongly suggest that the Nb–Nb bond distances within the zig-zag chains is determined mainly by the VEC (electronic effect) whereas the inter-chain separation as well as the Nb–(Te/As) distances are mainly influenced by the size of the anions (size effect). The one-dimensional character of the As-containing compounds is less pronounced than in the pure tellurides. The As-containing samples show no transition into the superconducting state down to about 2 K.

Keywords: Channel compounds; Crystal structure

1. Introduction

Binary and ternary compounds with the Nb_3Se_4 structure type have attracted considerable interest due to their quasi-one-dimensional metallic properties [1–6]. A number of different compounds with this structure type have been synthesized, e.g. $Tl_xTi_6Se_8$ [7], $K_xTi_3S_4$ [8], $Tl_xV_6S_8$ [9], $A_xV_6S_8$ [10,11], $A_xNb_6X_8$ [12,13] (A = K,In,Rb; X = S,Se,Te). Especially the members of the series Nb_3X_4 (X = S,Se,Te) have been investigated extensively with respect to their anisotropic conductivity [1,3,4,14], superconductivity [1,2], CDW transition and microdomain formation [15,16]. The observed physical behaviour reflects the quasi-one-dimensionality within the series and can be rationalized with electronic band structure calculations [17,18]. It is noteworthy that the Nb–Nb distances within the metal zig-zag chains parallel to the crystallographic *c*-axis are nearly identical in Nb_3S_4 (2.881 Å) [19] and Nb_3Se_4 (2.885 Å) [20] despite the larger size of Se, and are comparable with the Nb–Nb separation in metallic Nb (2.858 Å). In Nb_3Te_4 this distance amounts to 2.973 Å [21]. The distance between Nb atoms of neighbouring chains increases significantly with increasing size of the chalcogen. As a consequence the isolation of the Nb–Nb zig-zag chains increases in the order Te > Se > S.

Recently we have demonstrated that in $Tl_xV_6S_8$ and $Tl_xV_6Se_8$ the chalcogen atoms can partially be substituted by phosphorus [22,23]. This substitution leads to significant changes of the metal-to-metal distances, a less pronounced one-dimensional character and, as a consequence, to drastic changes of the electrical properties [22,23]. These interesting results encouraged us to try to substitute Te partially by As in Nb_3Te_4 to “manipulate” the Nb–Nb interatomic distances and to study the effect of the substitution on the different interatomic interactions. At least two different effects must be taken into account to try to explain the changes. The substitution of the Te by the smaller As and the introduction of the large Tl into the hexagonal channels may be regarded as a geometrical effect. The change of the valence electron concentration introduced by the substitution as well as by the intercalation of Tl may be regarded as an electronic effect. To separate the geometrical from the electronic contributions to the alterations a number of different compounds have been prepared and were investigated by single crystal X-ray experiments.

The present contribution reports the preparation and crystal structures of the novel compounds $Tl_{0.48}Nb_6Te_6As_2$, $Tl_{0.49}Nb_6Te_{7.5}As_{0.5}$, Nb_3Te_3As and $Tl_{0.45}Nb_6Te_8$.

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2. Experimental details

The different samples were prepared in the following ways.

For $Tl_{0.49}Nb_6Te_6As_2$ the quasi-binary compound Nb_3Te_3As was prepared by reacting weighed amounts of the elements in sealed and evacuated silica ampoules at 1273 K for 10 days. The product consists of black and very thin whisker-like needles. The most intense reflections of the X-ray powder diffraction pattern could be indexed on the basis of the hexagonal Nb_3Te_4 type structure. Minute amounts of a second phase could not be identified. Single crystals suitable for crystal structure determination were obtained after reacting the educt with Tl metal at 1223 K for 14 days. The composition of a number of crystals was semi-quantitatively determined by means of energy dispersive analysis of X-ray (EDX) and yields $Tl_{0.48(3)}Nb_6Te_{6.1(1)}As_{1.9(1)}$ in good agreement with the composition finally determined during the crystal structure determination.

$Tl_{0.49}Nb_6Te_{7.5}As_{0.5}$ was obtained after prolonged annealing of the As-rich sample at 1273 K for 3 weeks. The composition of selected single crystals was confirmed by EDX analysis.

For Nb_3Te_3As a stoichiometric mixture of the three elements was placed in sealed and evacuated silica ampoules. The ampoules were heated gradually at 100 K h^{-1} to 1273 K and were held at this temperature for 7 days. Finally the ampoules were quenched in ice water. The X-ray powder pattern showed only reflections of the Nb_3X_4 phase.

Single crystals of $Tl_{0.45}Nb_6Te_8$ were formed as a minority phase during an attempt to prepare $TlNb_5Te_8$. The elements in the ratio 0.8:5:8 (Tl:Nb:Te) were placed in a quartz ampoule and sealed under vacuum. The mixture was first fired to 775 K for 1 day, then heated at 1075 K for 1 day and further annealed at 1273 K for 4 days. Finally the ampoule was cooled to room temperature by turning the furnace off.

Attempts to prepare Tl-free crystals of the As-containing samples with a topotactic redox reaction using iodine in acetonitrile (1 mg I_2/ml CH_3CN) were unsuccessful. After 2 days only minute amounts of the Tl were removed. Longer reaction times result in a destruction of the crystals. Further work is in progress to remove the Tl by an electrochemical redox reaction.

Single crystal X-ray work was performed on a STOE AED II diffractometer using monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Technical details of the data acquisition as well as some refinement results are summarized in Table 1. The observed intensities were reduced to F_o. Lorentz, polarization and a numerical absorption correction were applied. The final weighting scheme was varied until no significant dependence on F/F_{max} or sin Θ/λ was observed. All calculations were done with the software package SHELX TL plus. Atomic coordinates are listed in Table 2 and selected interatomic separations are given in Table 3.

3. Results and discussion

The fundamental structural unit composed of three face-sharing NbX_6 octahedra is displayed in Fig. 1. These triple units are connected via their common edges to each other and the resulting three-dimensional network exhibits large hexagonal channels parallel to the crystallographic *c*-axis. The Tl atoms are confined within these channels.

The Tl content of the single crystals was determined in the following way. It is well known that the site occupation factor (*sof*) and the displacement parameter U_{iso} are strongly correlated. Hence, in the early stages of the refinements the U_{iso} of the Tl was fixed and the *sof* refined. The resulting *sofs* correspond to about 0.48(2), 0.49(2) and 0.45(2) Tl atoms per $Nb_6Te_6As_2$, $Nb_6Te_{7.5}As_{0.5}$ and Nb_6Te_8 unit respectively. These values are in excellent agreement with the results of the EDX analyses. During the final refinement cycle the Tl atom was refined with anisotropic displacement parameters.

As in a large number of ternary compounds with the formal composition $A_xM_6X_8$ (A = K, In, Tl, Ag; M = Ti, V, Nb; X = S, Se, Te (S,P), (Se,P), (Te,As)), the electropositive Tl atom of the title compounds exhibits an unusual large anisotropic displacement component U_{33} which is of no physical meaning. The difference Fourier synthesis and the thermal parameters of Tl indicate that the positions of the Tl atoms oscillate strongly about the average value $z = 0.25$. We therefore assume that this is due to a displacive modulation as reported for $K_{0.7}V_5S_8$ [24]. A diffuse streak parallel and somewhat below the first layer line was observed on strongly exposed rotation photographs of $Tl_{0.76}Ti_6Se_8$ [7] and $Tl_{0.8}V_6S_8$ [25]. For the average structure of the Tl-containing compounds space group $P6_3/m$ was adopted.

Assuming the coordinate $z = 0.25$ as the center of gravity, the Tl atoms are in a quite irregular environment. Three Te atoms are at the same height with Tl–Te distances of 3.203 Å, 3.239 Å and 3.300 Å and six other Te atoms are at distances of 3.669 Å, 3.712 Å and 3.774 Å in $Tl_{0.48}Nb_6Te_6As_2$, $Tl_{0.49}Nb_6Te_{7.5}As_{0.5}$ and $Tl_{0.45}Nb_6Te_8$ respectively.

In TlTe the interatomic separations range from 3.40 to 3.67 (CN = 7) [26] with an average ⟨Tl–Te⟩ distance of 3.516, which is near the sum of the ionic radii of Tl^+ and Te^{2-} ($Tl^+ = 1.50$ Å, $Te^{2-} = 2.11$ Å). In the title compounds the three short separations are significantly smaller than the sum of the ionic radii whereas the six other Tl–Te contacts are larger. It is noted that distances up to about 4.3 Å were treated as weak Tl–Te

Table 1
Technical details of data collection and some refinement results for (A) $Tl_{0.48}Nb_6Te_6As_2$, (B) $Tl_{0.49}Nb_6Te_{7.5}As_{0.5}$, (C) Nb_3Te_3As and (D) $Tl_{0.45}Nb_6Te_8$

	A	B	C	D
S.G.	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$
a (Å)	10.4322(8)	10.5107(6)	10.4058(3)	10.6767(6)
c (Å)	3.5773(3)	3.6236(5)	3.5684(1)	3.6621(4)
V (Å^3)	337.16(7)	346.68(6)	334.62(4)	361.52(8)
Z	1	1	2	1
ρ_{calc} (Mg m^{-3})	7.737	7.922	7.322	7.672
μ (mm^{-1})	28.185	27.146	22.685	25.367
ΣI	754	2167	2237	1706
Unique	374	384	407	402
$N_o[F_o > 4\sigma(F_o)]$	358	337	380	370
T_{min}/T_{max}	0.7584/0.8369	0.742/0.839	0.61/0.837	0.866/0.929
x [a]	0.0021(1)	0.000 30(6)	0.0029(1)	0.001 06(5)
y [b]	0.000 05	0.000 005	0.000 024	0.000 007
N_p	18	19	16	18
R (%)	1.39	1.98	1.12	1.20
R_w (%)	1.38	1.58	1.16	1.19
GOF	1.29	1.31	1.18	1.48
δF (e Å^{-3})	0.77	1.79	0.84	0.95
	−0.91	−1.49	0.97	−0.70

[a] $F^* = F[1 + 0.002xF^2/\sin(2\Theta)]^{-1/4}$.
[b] $w = 1/(\sigma^2(F) + yF^2)$.

Table 2
Atomic coordinates (10^4) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$)

	x	y	z	U_{eq} [a]
$Tl_{0.48}Nb_6Te_6As_2$				
Tl	0	0	2500	131(3)
Nb	1265(1)	5035(1)	2500	7(1)
Te	521(1)	7224(1)	2500	7(1)
As	6667	3333	2500	5(1)
$Tl_{0.49}Nb_6Te_{7.5}As_{0.5}$				
Tl	0	0	2500	109(3)
Nb	1072(1)	4909(1)	2500	11(1)
Te(1)	603(1)	7265(1)	2500	12(1)
Te(2)	6667	3333	2500	8(1)
As	6667	3333	2500	8(1)
Nb_3Te_3As				
Nb	1262(1)	5035(1)	2500	6(1)
Te	526(1)	7235(1)	2500	7(1)
As	6667	3333	2500	8(1)
$Tl_{0.45}Nb_6Te_8$				
Tl	0	0	2500	224(14)
Nb	1034(1)	4888(1)	2500	8(1)
Te(1)	636(1)	7276(1)	2500	9(1)
Te(2)	6667	3333	2500	7(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected interatomic bond lengths (Å) for (A) $Tl_{0.48}Nb_6Te_6As_2$, (B) $Tl_{0.49}Nb_6Te_{7.5}As_{0.5}$, (C) Nb_3Te_3As, (D) $Tl_{0.45}Nb_6Te_8$ and (E) Nb_3Te_4

	A	B	C	D	E
Tl–Te 3×	3.203(1)	3.239(1)	–	3.300(1)	–
Tl–Te 6×	3.669(1)	3.712(1)	–	3.774(1)	–
Nb–Te	2.754(1)	2.755(1)	2.753(1)	2.786(1)	2.768
Nb–Te 2×	2.798(1)	2.753(1)	2.798(1)	2.784(2)	2.781
Nb–Te	2.938(1)	2.945(1)	2.929(1)	2.978(1)	2.950
Nb–As/Te2 2×	2.661(1)	2.820(1)	2.655(1)	2.885(1)	2.877
⟨Nb–Te/As⟩	2.768	2.8075	2.765	2.850	2.839
δ	0.277	0.191	0.274	0.194	0.182
$Nb–Nb_{intra}$	3.158(1)	2.971(1)	3.145(1)	2.968(1)	2.973
$Nb–Nb_{inter}$	3.412(1)	3.743(1)	3.407(1)	3.862(1)	3.854
I (%)	8.0	26	8.3	30.1	29.6
VEC/Nb	2.083	2.333	2.00	2.42	2.333

$\delta = (Nb–Te_{max} – Nb–Te_{min})$.
$I = [(Nb–Nb_{inter})/(Nb–Nb_{intra})] \times 100$ in %.

interactions [27]. Hence it can be assumed that the coordination number of Tl in the title compounds is 9 rather than 3.

Compared with the pure binary telluride Nb_3Te_4 the introduction of the smaller As for Te results in a significant reduction of the *a*- as well as of the *c*-axis. A comparison of the lattice parameters of Nb_3Te_3As and of $Tl_{0.48}Nb_6Te_6As_2$ as well as of Nb_3Te_4 and $Tl_{0.45}Nb_6Te_8$ reveals that the intercalation of Tl into the hexagonal channels results in a small expansion of both the *a*- and *c*-axis (compare Table 1). It is noted that the lattice parameters of $Tl_{0.45}Nb_6Te_8$ are significantly larger than those reported for $TlNb_6Te_8$ [13].

In principle two different crystallographic sites are available for the As atom. On site 1 the anion is irregularly coordinated by four Nb and one Tl atom in $Tl_{0.48}Nb_6Te_6As_2$, $Tl_{0.49}Nb_6Te_{7.5}As_{0.5}$ and $Tl_{0.45}Nb_6Te_8$

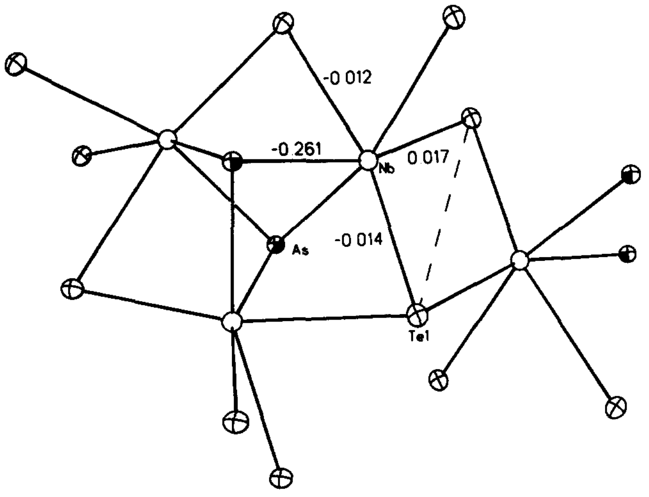

Fig. 1. One triple unit of face-sharing NbX_6 octahedra in $Tl_{0.48}Nb_6Te_6As_2$. The connection to the next unit via a common edge is schematically shown by the broken line between Te atoms. The numbers give the change of the interatomic distances in Å compared to Nb_3Te_4. The probability ellipsoids are drawn at the 70% level.

and only by four Nb atoms in Nb_3Te_3As. On site 2 the anion is coordinated by six Nb atoms in a trigonal prismatic polyhedron. The refinement of the As-rich samples with Te on site 2 yields always a low isotropic displacement factor. The refinement of $Tl_{0.48}Nb_6Te_6As_2$ and Nb_3Te_3As with As on this site gives an U_{iso} that is comparable with that obtained for Te on site 1. Hence, the crystal structures were finally refined with As on site 2. Attempts to place As and Te on site 2 and to refine the individual *sof* (the U_{iso} of As and Te were tied) always yield a *sof* value for the Te with an esd significantly larger than the refined *sof*. For the As-poorer sample the *sofs* of Te and As were refined with a tied U_{iso}. The *sofs* obtained in this way correspond to 7.50(3) Te and 0.50(3) As per formula unit. In binary niobium phosphides and arsenides the P or As atoms are in a trigonal prismatic environment [28–31]. This fact further supports the experimental results.

In the binary telluride Nb_3Te_4 the Nb–Te2 distance amounts to 2.877 Å. The substitution of Te2 by the smaller As leads to a shortening of the Nb–X2 separation and may be regarded as a further evidence that the As atoms are located on site 2. On the other hand the Nb–Te1 distances change in a different way. These changes of the individual Nb–X bond distances result in a different distortion of the $Nb(Te/As)_6$ octahedron (compare also Fig. 1). This is demonstrated by the parameter δ, which is defined as the difference between the largest and shortest Nb–Te/As separation. The obtained values of 0.277 Å and 0.274 Å for the As-rich samples suggest a significant stronger distortion compared with the pure telluride ($\delta = 0.182$ Å). In the As-poorer compound as well as in $Tl_{0.45}Nb_6Te_8$ the distortion of the NbX_6 octahedron is less pronounced (compare Table 3). It is also noted that the introduction of the As in the Nb_3Te_4 host lattice leads to markedly reduced average ⟨Nb–X⟩ separations of 2.768 Å, 2.765 Å and 2.808 Å for $Tl_{0.48}Nb_6Te_6As_2$, $Tl_{0.49}Nb_6Te_{7.5}As_{0.5}$ and Nb_3Te_3As respectively (Nb_3Te_4: 2.839 Å). A small increase of ⟨Nb–Te⟩ compared with the binary telluride is observed for $Tl_{0.45}Nb_6Te_8$.

The introduction of the As atoms also strongly affects the Nb–Nb separations. In the two As-rich samples the Nb–Nb distances within the zig-zag chains parallel to the *c*-axis of 3.158 Å and 3.145 Å ($Tl_{0.48}Nb_6Te_6As_2$ and Nb_3Te_3As) are about 6% larger than in Nb_3Te_4 whereas the inter-chain separations of 3.412 Å and 3.407 Å are about 13% smaller than in the binary telluride. It is of high interest that in the As-poorer sample the Nb–Nb distance within the zig-zag chain is nearly identical with the values found for Nb_3Te_4 and $Tl_{0.45}Nb_6Te_8$, whereas the inter-chain separation is significantly shorter than in the two tellurides. It is also noteworthy that the intercalation of Tl into the channels of Nb_3Te_4 only slightly affects the interatomic Nb–Nb separations (see Table 3).

Two different factors must be taken into account to explain these findings. First, the intercalation of Tl (as Tl^+) as well as the substitution of Te by the smaller As produce geometrical alterations (size effect). But, despite the large radius of Tl^+ ($r(Tl^+) = 1.50$ Å) the axes of $Tl_{0.45}Nb_6Te_8$ and of $Tl_{0.49}Nb_6Te_6As_2$ are only slightly larger than that of the non-intercalated samples (compare Table 1). As discussed above, the interatomic separations of Nb_3Te_3As or Nb_3Te_4 are only little affected by the intercalation of Tl into the channels.

On the other hand, the substitution of Te by As results in a significant reduction of the lattice parameters and in pronounced changes of the interatomic separations (see above). Within a formal ionic picture Te^{II-} anions are substituted by As^{III-} anions. The radius of As^{III-} is roughly 10.5% smaller than that of Te^{II-} (1.91 Å vs. 2.11 Å). The average radius of the anions decreases from 2.11 Å (pure telluride) to 2.06 Å (for Nb_3Te_3As), i.e. a decrease of about 2.5%. The observed contractions of the lattice parameters caused by the substitution of Te by As are of this order.

The second factor affecting the interatomic distances as well as the lattice parameters is the valence electron concentration (VEC) per Nb atom (electronic effect). The total number of valence electrons in the pure binary telluride amounts to 39. With the assumption of Te^{II-} ions 7 electrons are left for the 3 Nb atoms. Hence, the VEC per Nb amounts to 2.333. If Tl is in the monovalent state and if the charge is totally transferred to the Nb_3Te_4 host lattice the VEC per Nb increases from 2.333 to about 2.42 for $Tl_{0.45}Nb_6Te_8$, affecting both the Nb–Te and Nb–Nb interatomic bonding interactions (see discussion above). The substitution of one Te by As in the binary telluride decreases the VEC per Nb to 2.0. Here it is interesting to note that the average ⟨Nb–X⟩ distance decreases by about 2.7%, a value expected from the decrease of the average radius of the anions (size effect). On the other hand the Nb–Nb intra-chain distance increase by about 6% and the inter-chain separation decreases by about 13%. These contradicting alterations of the interatomic Nb–Nb separations cannot be explained on the basis of the lowered average radius of the anions. In this context the most interesting cases are Nb_3Te_4 and $Tl_{0.48}Nb_{7.5}As_{0.5}$. The VEC of 2.333 per Nb is identical for these two samples. The analysis of the Nb–Nb interatomic distances clearly reveals that the Nb–Nb intra-chain distance is identical whereas the inter-chain separation is significantly smaller in the As-containing sample.

This detailed analysis demonstrates that the ⟨Nb–X⟩ distances as well as the Nb–Nb inter-chain separations are mainly affected by the size of the anions whereas the intra-chain separation is mainly determined by the VEC per Nb atom. This conclusion is further supported by the following observations. In the series Nb_3X_4 (X = S, Se and Te) the VEC per Nb is constant and the size of the anion increases from S to Te. The Nb–Nb intra-chain distance increases only slightly with increasing size of X but the inter-chain separation as well as the average ⟨Nb–X⟩ distances show a strong increase as a function of $r(X^{II-})$.

At the end we want to discuss the possible physical properties of the new compounds. The difference I between the inter- and intra-chain distance expressed in percent can be regarded as an indication for the isolation of the metal atom chains. It is also a hint for the dimensionality of the metallic character of the material. Compared to the pure telluride the introduction of As results in a pronounced decrease of I and hence a less good isolation of the metal atom zig-zag chains (see Table 3). Therefore, it is expected that the one-dimensional character of the As-substituted compounds is less pronounced than in Nb_3Te_4. In addition, the decrease of the VEC may also reduce the density of states at the Fermi level. Preliminary measurements of the electrical properties performed on powders of the As-containing samples showed no transition into the supraconducting state down to about 2 K. For Nb_3Te_4 the transition into the supraconducting state starts at about 3.5 K and was not finished at about 2 K. For Nb_3Te_4 single crystals a T_c of about 1.8 K was reported in [1]. Further experiments are under way to prepare single crystals large enough for electrical resistivity measurements. The calculated electronic band structure of Nb_3Te_4 and Nb_3Te_3As will be published in the near future.

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