Full Articles

New mixed tellurides of nickel and Group 13—14 metals $Ni_{3-\delta}MTe_2$ (M = Sn, In, Ga)

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Three new mixed tellurides of nickel and group 13—14 metals $Ni_{3-\delta}MTe_2$ (M = Sn, In, Ga) were prepared by high-temperature ampoule synthesis and studied by powder X-ray diffraction analysis. The compound $Ni_{3-\delta}SnTe_2$ was also studied by single crystal X-ray diffraction analysis. The structural model of this phase and two analogs was described as consisting of layers with nickel—main group metal bonds confined from the above by tellurium atoms. The van der Waals gap formed through contacts between the tellurium atoms of neighboring layers is partially occupied by nickel atoms.

Keywords: low-dimensional phases, layered phases, nickel—main group metal bonds, nickel subvalent tellurides.

Nickel is known to form two types of quasi-two-dimensional compounds (*i.e.*, those containing infinite two-dimensional fragments) with heterometallic nickel—main group metal bonds, namely, block and layered type compounds. The first type includes chalcogenides like $Ni_{6-\delta}MQ_2$ and $Ni_{9-\delta}M_2Q_2$ (M = Sn, Sb, Q=S, Se, Te).[1—3] The tellurides Ni_2SbTe_2 (see Ref. 4) and $Ni_{3-\delta}GeTe_2$ (see Ref. 5) belong to the second type. In all of these phases, layers of heterometallic nickel—main group element bonds alternate with layers of nickel—nonmetal bonds; phases of the second type involve also chalcogen—chalcogen van der Waals contacts.

In this study, we synthesized three mixed tellurides corresponding to quasi-two-dimensional layered phases: $Ni_{3-\delta}SnTe_2$, $Ni_{3-\delta}InTe_2$ and $Ni_{3-\delta}GaTe_2$. Powder X-ray diffraction patterns of all these compounds were successfully indexed with the assumption that the structure of these phases resembles that of Ni_2SbTe_2 (hexagonal system, $P6_3/mmc$, a = 3.903(1) Å, c = 15.634(3) Å).[4] The crystals of new phases grown by slow cooling of a stoichiometric mixture of the initial compounds were analyzed by energy dispersive X-ray (EDX) spectroscopy. The data on unit cell parameters and elemental composition of new tellurides are summarized in Table 1.

It can be seen from the Table that, with allowance for the error of the method, which is estimated as 1—2 at.%, the element ratio in nickel—indium and nickel—gallium tellurides is very close to 3 : 1 : 2, like this ratio found in

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Table 1. Unit cell parameters and averaged elemental composition of phases of the type $Ni_{3-\delta}MTe_2$ (M = Sn, In, Ga)

Composition of the nitial mixture	Hexagonal cell parameters/Å		Ni	M	Te	Formula from EDX data
	a	*c*	at.%			
2Ni : Sn : 2Te	3.9310(9)	15.777(4)	43.6	18.4	37.9	$Ni_{2.37}SnTe_{2.06}$
3Ni : In : 2Te	4.0033(5)	15.738(2)	47.3	16.5	33.6	$Ni_{2.87}InTe_{2.04}$
3Ni : Ga : 2Te	3.9378(2)	15.775(1)	47.9	16.2	32.9	$Ni_{2.96}GaTe_{2.03}$

another study,[5] whereas the tin-containing phase synthesized at an initial element ratio of 2 : 1 : 2 contains a somewhat lower amount of nickel (with respect to the indium and gallium phases synthesized at an initial stoichiometry of 3 : 1 : 2). Nevertheless, similar X-ray diffraction patterns and the results of indexing indicate that all compounds belong to layered quasi-two-dimensional heterometallic phases of the type $Ni_{3-\delta}MTe_2$. It is important that for group 13 metals, indium and gallium, low-dimensional tellurides with infinite systems of heterometallic bonds were prepared for the first time.

A single crystal suitable for X-ray diffraction experiment was obtained only for compound $Ni_{3-\delta}SnTe_2$. The X-ray diffraction data confirm the assumed structure of this compound: like the structure of Ni_2SbTe_2, the obtained crystal structure model (Fig. 1) is based on layers of heterometallic bonds formed by the fragments ${}^2_\infty[Ni_2Sn]$ (the Ni—Sn distance is ~2.62 Å). The heterometallic layers are confined on the the *c* axis by tellurium atoms (the Ni—Te distance is ~2.61 Å); however, the van der Waals gap between them accommodates the partially occupied sites of the nickel atom (Ni(2)); the same situation was observed for the $Ni_{3-\delta}GeTe_2$ phase, whereas in compound Ni_2SbTe_2, no nickel atoms were detected in the van der Waals gap. The refinement of the occupancy of the Ni(2) site using X-ray diffraction data gives a value of 0.58; hence the ultimate formula of the compound is $Ni_{2.58}SnTe_2$. In view of the final R-factor equal to 0.065, this value cannot be regarded as absolutely accurate. Nevertheless, this formula is generally consistent with EDX data, although it implies a somewhat higher amount for nickel. Apart from the error of structural experiment, this may be due to a inhomogeneity of samples subjected to EDX and the presence of crystals with different contents of nickel; in particular, the nickel content can be lower than that in the single crystal studied by X-ray diffraction. Note also that $Ni_{3-\delta}GeTe_2$ contains an additional partially occupied site of nickel atoms at the same crystallographic height as the germanium atom sites. Analysis of the difference Fourier map shows that in our case, this site is characterized by electron density of $<0.5\ e \cdot Å^{-3}$, which does not give grounds for placing there a nickel atom, even with partial occupancy. From this standpoint, the structure of the heterometallic layer in $Ni_{3-\delta}SnTe_2$ is similar to that in Ni_2SbTe_2. Thus, it can be considered that the structure of $Ni_{3-\delta}SnTe_2$ is a sort of intermediate link between nickel antimony and nickel germanium tellurides. With a high probability, phases of this type can be regarded as members of the homologous series $Ni_{3-\delta}SnTe_2$ where δ ranges from 0 to 1.

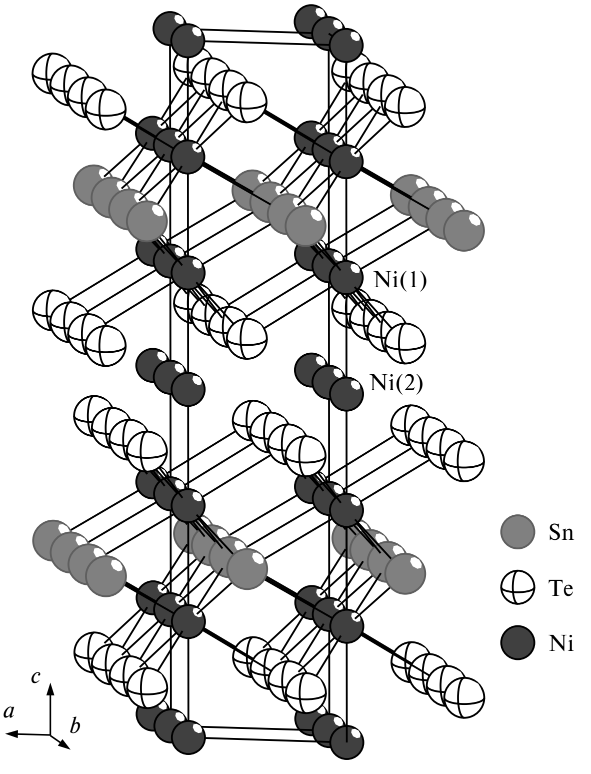

Fig. 1. Fragment of the $Ni_{3-\delta}SnTe_2$ structure (Ni(2) site occupancy is 58%).

Thorough analysis of the reciprocal space indicates that $Ni_{3-\delta}SnTe_2$ shows weak satellites between the major reflections. We have grounds for believing that they arise due to ordering of the nickel site occupancy caused by structure modulations. However, due to low intensity of these reflections, a special precision X-ray diffraction experiment aimed at the search and study of the superstructure is required. Thus, the description of the structure of $Ni_{3-\delta}SnTe_2$ that we presented in an averaged model of atom arrangement in the cell, which allows the presence of ordering in the nickel site occupancy in the van der Waals gap.

Experimental

Commercially available elemental nickel (99.99%), indium, gallium, tin, and tellurium (all 99.999%) were used as the starting substances. The samples of $Ni_{3-\delta}MTe_2$ were prepared by high-temperature ampoule synthesis. The stoichiometric mixtures of elements Ni : M : Te = 3 : 1 : 2 (M = In, Ga) and Ni : Sn : Te = 2 : 1 : 2 were placed into quartz ampoules, evacuated to a residual pressure of $\sim 5 \cdot 10^{-2}$ Torr, and sealed off. The samples were annealed in a furnace with programmed heating mode: heating to 750 °C over a period of 5 h, maintenance at this temperature for 10 days, and cooling in the switched-off furnace. The samples after annealing were air stable gray-colored polycrystalline cakes. The crystals were grown under the same heating conditions but with subsequent slow (2 °C h^{-1}) cooling.

Quantitative energy dispersive X-ray spectroscopic analysis was carried out using a JEOL JSM-820 scanning electron microscope equipped with an X-ray dispersion microanalyzer with a LINK AN-10000 semiconductor detector (accelerating voltage 20 kV, scanning time 120 s, ZAF correction). The chemical composition of the crystal was determined by averaging the values obtained for several points.

X-Ray diffraction analysis was carried out on a Nonuis CAD 4F four-circle automated diffractometer (T = 293 K, Mo-Kα radiation, graphite monochromator, ω-2θ scan mode), the absorption correction was applied by application of ψ curves on the initial array. A total of 404 reflections were collected; of these 131 reflections were independent, 110 reflections had an intensity of $2\sigma(I)$, the θ range was 2.58—24.83°. The X-ray experiment data for $Ni_{3-\delta}SnTe_2$ were interpreted using the SHELX-97 program package (see Ref. 6) in the hexagonal system with space group P-31c chosen on the basis of intensity statistics analysis. The Ni(1), Sn, and Te atoms were located by the direct method. The sites of Ni(2) atoms were identified by a combination of difference Fourier syntheses and least-squares refinement. The site occupancy was refined using X-ray diffraction experiment data as an independent parameter. All positions and thermal parameters were refined by the least-squares method in anisotropic approximation, the Ni(2) site occupancy was set to be equal to the value obtained in the isotropic approximation. The final structural parameters for $Ni_{2.58}SnTe_2$ were as follows: space group P-31c, a = 3.9310(6) Å, c = 15.795(3) Å, Z = 2, V = 211.3(1) $Å^3$, $R_1 = 0.065$, $R_{all} = 0.071$, $wR_1 = 0.177$, $wR_{all} = 0.182$, GOOF = 1.218. Selected interatomic distances and bond angles are summarized in Table 2. Note that although the statistics of intensities was favorable for the selection of P-31c group, solution of this structure with space group $P6_3/mmc$ is also possible. Since the known analogs of this phase were characterized exactly in the $P6_3/mmc$ group,[4,5] we attempted to solve the structure also in this group. However, with retention of qualitatively the same description as in the P-31c group, the resulting solution had a much higher R-factor (R_1 = 0.112), and this dictated the final choice of the space group for description of the structure of $Ni_{2.58}SnTe_2$.

Table 2. Selected interatomic distances (d) and bond angles (ω) for the crystal structure $Ni_{2.58}SnTe_2$

Bond	d/Å	Angle	ω/deg
Ni(1)—Sn	2.620(1)	Ni(1)—Sn—Ni(1)	59.9(1)
Ni(1)—Te	2.606(2)	Ni(1)—Te—Ni(1)	97.9(1)
Ni(2)—Te	2.645(1)	Ni(1)—Te—Ni(2)	60.4(1)

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