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Thermal behaviour of titanium seleno-telluride Ti_5Ch_8 in Ar and N_2 atmospheres

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Abstract

A series of $TiSe_{1.60-x}Te_x$, where $0 \leq x \leq 1.60$, was prepared. The samples were characterized by powder X-ray diffraction and thermo-gravimetric analysis in Ar and N_2 atmospheres. The XRD measurements showed that the titanium seleno-tellurides form a continuous solid solution of a hexagonal structure. Thermal behaviour of the compounds was studied by thermogravimetric analysis for samples $x = 0$, 0.16, 0.80, 1.44, 1.60 in the temperature interval from 25 to 1273 K. After heating in Ar, no mass loss was observed in selenide ($x = 0$). In contrast, for telluride ($x = 1.60$) mass loss took place due to a formation of ditelluride. For seleno-tellurides in nitrogen atmosphere both disproportion reaction and a reaction of ditelluride with N_2 occurred simultaneously.
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Series of nonstoichiometric compounds Ti_2Ch_3, Ti_5Ch_8 and $TiCh_2$ with a hexagonal structure of the CdI_2-type have been observed in binary systems of titanium–selenium and titanium–tellurium from sesqui- to dichalcogenide. Broadness of homogeneity ranges in solid solutions, discreteness of different phases, and structures of the compounds determined by powder X-ray diffraction vary in different chalcogenides. The literature on these topics is contradictory. Therefore it is expedient to obtain single crystal of the phases in order to establish reliably their symmetries and structures. Chemical vapor transport (CVT) is a unique technique for preparing single crystal chalcogenides of specific stoichiometry. Rimmington and Balchin [1] were the first to succeed in growing single crystal series of composition $Ti(Se,Te)_2$ by the iodine vapor transport technique.

In the titanium–tellurium system, the Ti_5Te_8 ($TiTe_{1.60}$) phase is formed. Brunie and Chevreton [2] considered this

telluride as an individual compound but we found [3] that it was the last member of hexagonal structures in series Ti_2Te_3–Ti_5Te_8. In the titanium–selenium system, Gronvold and Langmyhr [4] and Bernusset [5] observed formation of the monoclinic Ti_5Se_8 ($TiSe_{1.60}$). In our previous study [6], we revealed a continuous solid solution of selenides Ti_2Se_3–Ti_5Se_8 of a hexagonal structure. Among the hexagonal selenides, Ti_5Se_8 has the shortest lattice parameters. We synthesized $TiSe_{1.60}$ single crystal by two variants of CVT that differ by the choice of selenium source, namely Se or $TiSe_2$. Unlike other selenides studied, $TiSe_{1.60}$ has the Laue group $\bar{3}m$ with a superstructure 2a, 2c [7].

The goal of this study was to determine the homogeneity range of the solid solution Ti_5Ch_8 ($TiSe_{1.60-x}Te_x$) and examine the thermal behaviour of the titanium seleno-tellurides in Ar and N_2 atmospheres. These mixed chalcogenides have not been investigated earlier. In addition, thermogravimetric analysis (TGA) is very important for choosing optimal conditions for CVT to obtain single crystal of nonstoichiometric chalcogenides [8].

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1. Experimental

In this work, a continuous series of $TiSe_{1.60-x}Te_x$, where $0 \leq x \leq 1.60$ with $\Delta x = 0.16$ was prepared via the direct synthesis in an ampoule. The starting materials were selenium (99.9%), tellurium (99.99%) and metallic titanium obtained from the titanium hydride TiH_2 (with a purity of more than 99%) by dehydrogenation in vacuum at 1153 K. The stoichiometric amounts of the initial elements were put in quartz ampoules, which were evacuated to a residual pressure of 0.13 Pa and sealed. To obtain homogenous chalcogenides [6], the synthesis was carried out in a furnace using two heating steps: 170 h at 823 K for primary reaction and 720 h at 1123 K in the final step. After that, the ampoules were quenched in cold water at 273 K. The fast cooling was performed in order to retain the structure adopted at a given annealing temperature.

The phase purity and composition, homogeneity and lattice parameters were determined by powder X-ray diffraction at room temperature using DRON-3 diffractometer (Cu Kα, external standard α-Al_2O_3). Lattice parameters were obtained by least squares calculation for an interval of reflection angles, $40° < 2\theta < 104°$. The uncertainity in lattice parameters value was ±0.005 Å.

Thermal behaviour of titanium seleno-telluride Ti_5Ch_8 was studied by thermogravimetric analysis. A Mettler Toledo TA8000 system equipped with TGA850 thermobalance was used. Sample amounts were about 10 mg. Dynamic experiments (5 K/min) from 298 to 1273 K and back to 373 K were performed under flowing argon (99.99%) and nitrogen (99.999%) atmospheres. The phases of samples decomposed after TGA measurements were determined using Philips Analytical PW1710/00 (Cu Kα, $1.5° < 2\theta < 154°$, internal standard CaF_2) and DRON-3 diffractometers. All reflections were indexed using Param and TREOR softwares.

2. Results and discussion

2.1. Solid solution $TiSe_{1.60-x}Te_x$

X-ray diffraction patterns showed that all samples are single phases. The titanium seleno-tellurides adopt the structure of CdI_2-type. $TiSe_{1.60-x}Te_x$ forms a continuous series of hexagonal solid solutions. Fig. 1 shows typical XRD patterns of the samples $x = 0.16, 0.80, 1.44$.

Lattice parameters $a = 3.845$ Å, $c = 6.388$ Å for $TiTe_{1.60}$ agree with the data of the previous work [2]. Table 1 shows powder XRD data for hexagonal $TiSe_{1.60}$ with the lattice parameters $a = 3.574$ Å and $c = 5.984$ Å. It is worth noticing that previously [4,5] only monoclinic structure was determined for the selenide.

The hexagonal lattice parameters and the unit cell volume are shown as function of composition in Fig. 2. There is only a small negative and positive deviation from the Vegard's law for the a- and c-axis, respectively.
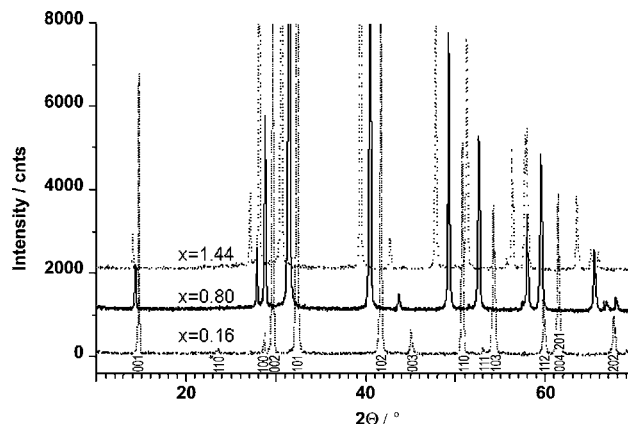

Fig. 1. Powder XRD patterns for $TiSe_{1.60-x}Te_x$ ($x = 0.16, 0.80, 1.44$). Asterisks denote a reflection of the superstructure 2a, 2c (according to single crystal data [7]).

Table 1
Powder XRD pattern of $TiSe_{1.60}$

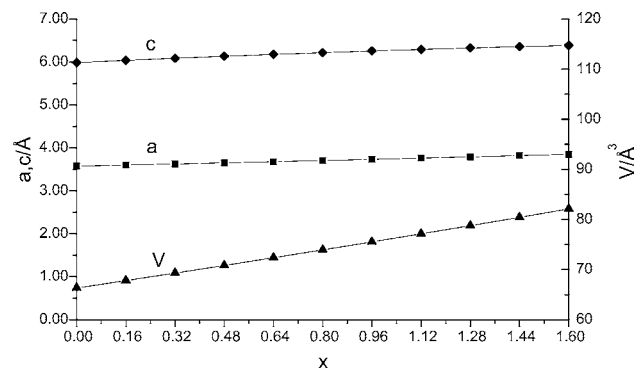| N	I/I_0 (%)	Θ (°)	$h\,k\,l$
1	57	7.45	0 0 1
2	2	14.42	1 0 0
3	86	14.95	0 0 2
4	77	16.25	1 0 1
5	66	21.00	1 0 2
6	27	22.72	0 0 3
7	17	25.58	1 1 0
8	33	27.35	1 0 3
9	6	30.15	1 1 2
10	100	31.00	2 0 1
11	100	31.00	0 0 4
12	5	34.10	2 0 2
13	<1	34.90	1 0 4
14	<1	35.40	1 1 3
15	5	39.05	2 0 3
16	19	42.12	2 1 1
17	<1	42.25	1 1 4
18	13	43.60	1 0 5
19	4	44.95	2 1 2
20	2	48.30	3 0 0
21	6	49.70	2 1 3
22	5	50.55	0 0 6
23	1	52.15	3 0 2

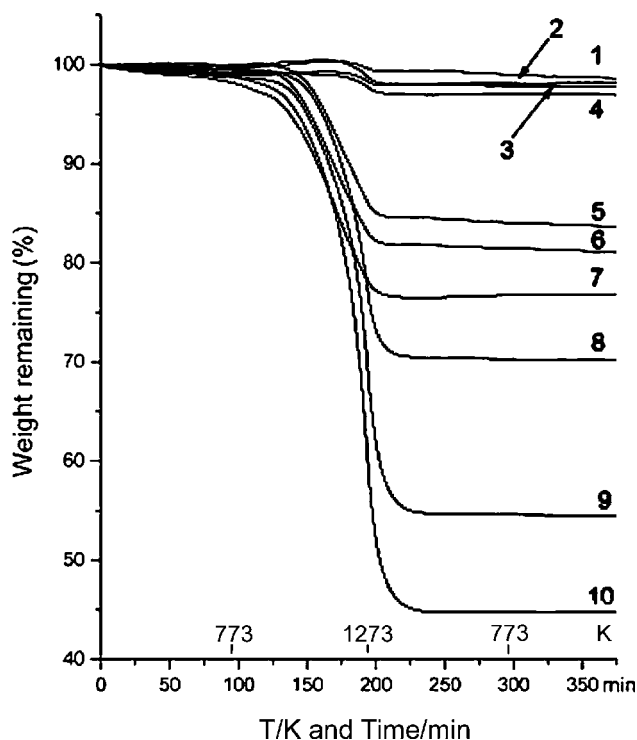Fig. 2. Lattice parameters and unit cell volume of hexagonal titanium chalcogenides $TiSe_{1.60-x}Te_x$.

Fig. 3. TG curves of $TiSe_{1.60-x}Te_x$ in Ar and N_2 atmospheres: (1) $TiSe_{1.44}Te_{0.16}/Ar$; (2) $TiSe_{1.6}/N_2$; (3) $TiSe_{1.44}Te_{0.16}/N_2$; (4) $TiSe_{1.6}/Ar$; (5) $TiSe_{0.80}Te_{0.80}/Ar$; (6) $TiSe_{0.16}Te_{1.44}/Ar$; (7) $TiTe_{1.6}/Ar$; (8) $TiSe_{0.80}Te_{0.80}/N_2$; (9) $TiSe_{0.16}Te_{1.44}/N_2$; (10) $TiTe_{1.60}/N_2$.

2.2. TGA measurements

Fig. 3 shows the TG curves for 10 experiments.

Earlier data about thermal decomposition of the titanium selenides and tellurides have only been reported for stoichiometric compounds $TiCh_y$, where $y \geq 2$. Suzuki and Wahlbeck [9] investigated Ti–Te system by evaporation in the temperature range from 573 to 1523 K and determined that evaporation of tellurides is incongruent and elemental tellurium is released. For the Ti–Se system, the same investigation has not been carried out. Only a few authors [10] used thermal dissociation of sesqui- and diselenide to prepare selenides with lower Se content.

2.3. Argon atmosphere

In argon atmosphere only thermal dissociation took place. TGA of $TiSe_{1.60}$ ($x = 0$) are performed in Ar revealed that the sample is the most stable one in the studied series of chalcogenides. It practically does not show any mass loss. This observation is in good agreement with XRD patterns that are very similar for $TiSe_{1.60}$ before and after heating in Ar. In contrast, the mass loss of $TiTe_{1.60}$ ($x = 1$) after heating in argon atmosphere is the biggest among the five chalcogenides, and the telluride compositions before and after heating differ.

The thermal dissociation of the telluride could be described in two different ways. First, the telluride dissociates to
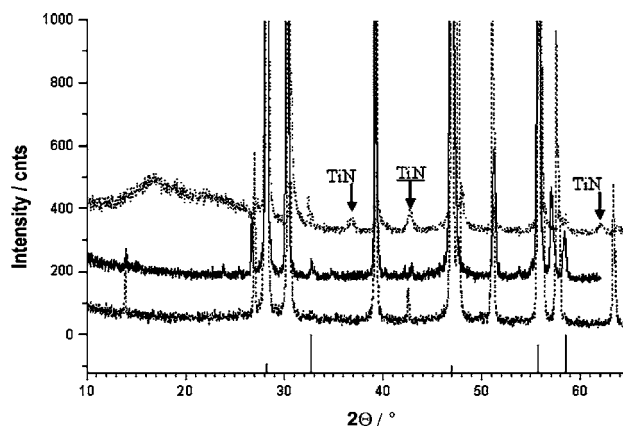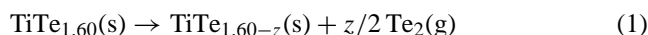

Fig. 4. Powder XRD patterns for $TiSe_{0.16}Te_{1.44}$. Dashed line: sample before heating, solid line: sample after heating in TGA to 1273 K under Ar; dotted line: sample after heating in TGA to 1273 K under N_2. The bars mark: CaF_2 internal standard.

pure gaseous tellurium and other tellurides, which are richer in metal than the initial compound:

$$TiTe_{1.60}(s) \rightarrow TiTe_{1.60-z}(s) + z/2\,Te_2(g) \qquad (1)$$

According to the mass loss in TGA, the composition of the telluride after heating should be about $TiTe_{1.14}$. However, this composition disagrees with XRD data that give $TiTe_{1.5}$. Second possibility for the thermal dissociation is that, disproportion reaction takes place and two tellurides are formed: one is richer in chalcogen and the other is richer in metal than the initial telluride. We propose that in argon atmosphere at temperature about 1173–1273 K, the following reaction may take place:

$$TiTe_{1.60}(s) \rightarrow 0.8\,TiTe_{1.50}(s) + 0.2\,TiTe_2(g) \qquad (2)$$
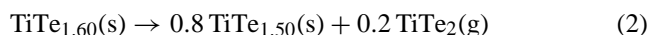
This hypothesis is in good accordance with our quantitative data. According to TGA (Fig. 3), the mass loss in the experiment was 23.14%; our calculation with reaction (2) gives about 24%. The literature data also supports this proposal because $TiTe_2$ is evaporating easier than the other tellurides [9].

2.4. Nitrogen atmosphere

Nitrogen atmosphere is not inert for the $TiSe_{1.60-x}Te_x$ compounds, the pure selenide ($x = 0$) being an exception. TGA experiment showed that the composition of $TiSe_{1.60}$ did not change and the results were similar in both nitrogen and argon atmospheres.

For seleno-tellurides in N_2 atmosphere, the disproportion reaction (2) and a reaction of ditelluride with nitrogen (3) take place simultaneously:

$$TiTe_2(g) + (1/2)N_2(g) \rightarrow TiN(s) + Te_2(g) \qquad (3)$$

Formation of titanium nitride is observed by XRD measurements for seleno-tellurides where $x \geq 0.8$ (Fig. 4).

The $TiTe_{1.60}$ shows a mass loss about 55% after TGA heating in nitrogen atmosphere but both XRD patterns before and after TGA measurement are very similar. The result again supports that reaction (2) is taking place instead of reaction (1). The evaluation of TG curve shows that the mass ratio $TiN:TiTe_{1.50}$ in the final mixture is about 2:3. In other words, 3/4 of $TiTe_{1.60}$ mass had time to decay and the $TiTe_2$ reacted during the TGA experiment. The diffuse reflections at small angle in XRD patterns (Fig. 4) show that the sample contains amorphous material. It is partly because the reaction is not complete after TG measurement. It may well be, that part of TiN is amorphous. The incompleteness of the reaction is additionally supported by supplementary TGA experiments made in nitrogen atmosphere with low heating rate or interval annealing at 1223 K, the mass loss increased.

For intermediate titanium seleno-tellurides for $x = 0.16$, 0.80, 1.44, TGA data shows the same general tendency in both atmospheres. When the tellurium content increases, the mass loss at 1023–1273 K becomes more significant. The bigger is the tellurium content the larger is the difference between the mass loss after heating in N_2 and Ar. It is directly related to processes (2) and (3). For $x = 0.16$ only reaction (2) takes place in N_2 atmosphere. For $x = 1.44$, reaction (3) is probably dominant one and nitrogen substitutes tellurium. This is supported by XRD patterns shown in Fig. 4 for $TiSe_{0.16}Te_{1.44}$ ($x = 1.44$) before and after heating in Ar and N_2.

3. Conclusions

The $TiSe_{1.60-x}Te_x$ compounds studied formed a continuous solid solution of CdI_2-type structure. However, the selenide $TiSe_{1.60}$ and the telluride $TiTe_{1.60}$ behaved very differently under heating in argon, and nitrogen atmospheres. On the whole, the selenide is much more stable than the telluride. Thermal behaviour of titanium tellurides differs from the thermal dissociation described by Suzuki and Wahlbeck [9]. In Ar atmosphere only the dissociation of chalcogenides with an evaporation of ditelluride took place. In N_2 atmosphere, the dissociation of titanium tellurides and reaction with nitrogen took place simultaneously. The reaction of tellurides with residue of nitrogen has been observed [11] in preparation of titanium ditelluride single crystals by chemical vapor transport method. All the intermediate titanium seleno-tellurides showed the same tendency in both atmospheres: selenide is more stable; telluride dissociates and reacts with nitrogen.

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