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Thermal Decomposition of $Ti_5(Se,Te)_8$ in Argon and Nitrogen Atmospheres

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Abstract—Chalcogenides $TiSe_{1.60-x}Te_x$ ($0 \leq x \leq 1.60$), forming a continuous series of hexagonal solid solutions, were prepared by the direct ampule procedure. The thermal decomposition of $TiSe_{1.60-x}Te_x$ was studied for the samples with x = 0, 0.16, 0.80, 1.44, and 1.60 in Ar and N_2 atmospheres in the course of heating from 25 to 1000°C. The selenide undergoes no weight loss under Ar, in contrast to the telluride which disproportionates and loses weight owing to the formation of volatile $TiTe_2$. At high temperatures, tellurides are more sensitive than selenides to the presence of nitrogen: The disproportionation is accompanied by the reaction of $TiTe_2$ with N_2, yielding low-volatile titanium nitride and free tellurium. Titanium selenide and telluride as components of the solid solutions behave similarly to the corresponding individual chalcogenides.

In the binary systems Ti–Se and Ti–Te, in the interval from sesqui- to dichalcogenides, a series of nonstoichiometric phases of the CdI_2 structure are formed: Ti_2Ch_3, Ti_5Ch_8, and $TiCh_2$. Data on the boundaries of the homogeneity, continuity, and discreteness areas and on the structures of these phases, mostly obtained by powder X-ray diffraction, are still ambiguous and sometimes contradictory. The best method for crystallization of nonstoichiometric chalcogenides is chemical gas transport. In particular, Rimmington and Balchin [1] have grown series of $Ti(S,Se)_2$, $Ti(S,Te)2$, and $Ti(Se,Te)_2$ single crystals by iodide gas transport.

In the Ti–Te system, in the examined composition range, formation of Ti_5Te_8 ($TiTe_{1.60}$) was observed; this compound was considered either as an individual compound [2] or as the extreme member of the series Ti_2Te_3–Ti_5Te_8 [3]. In the Ti–Se system, Gronvold and Langmyhr [4] and Bernusset [5] revealed monoclinic Ti_5Se_8 ($TiSe_{1.60}$). Previously [6] we proved the existence of a continuous hexagonal series of selenides Ti_2Se_3–Ti_5Se_8, in which the hexagonal unit cell parameters were the smallest for Ti_5Se_8 ($TiSe_{1.60}$). The fact that Ti_5Se_8 is an individual compound is also supported by formation of its crystals (Laue class $\bar{3}m$, superstructure $2a$, $2c$) in various versions of the gas transport reaction, including that with $TiSe_2$ as selenium source [7].

The goal of this study was to determine the homogeneity area of the $Ti_5(Se,Te)_8$ ($TiSe_{1.60-x}Te_x$) solid solution and to evaluate its thermal stability in Ar and N_2 atmospheres, which is particularly important when performing chemical transport reactions for growing nonstoichiometric transition metal chalcogenides [8].

According to X-ray phase analysis, $TiSe_{1.60-x}Te_x$ forms a continuous series of hexagonal solid solutions from $TiSe_{1.60}$ to $TiTe_{1.60}$. Typical diffraction patterns of the samples with x = 0.16, 0.80, and 1.44 are shown in Fig. 1.

The unit cell parameters a 3.845 and c 6.388 Å for $TiTe_{1.60}$ are consistent with those reported in [2]. The powder X-ray diffraction data and unit cell parameters for $TiSe_{1.60}$ are given in the table. Only the monoclin-

Powder X-ray diffraction data for $TiSe_{1.60}$ (a 3.754, c 5.984 Å)

I/I_0, %	θ, deg	*hkl*	I/I_0, %	θ, deg	*hkl*
57	7.45	001	<1	34.90	104
2	14.42	100	<1	35.40	113
86	14.95	002	5	39.05	203
77	16.25	101	19	42.12	211
66	21.00	102	<1	42.25	114
27	22.72	003	13	43.60	105
17	25.58	110	4	44.95	212
33	27.35	103	2	48.30	300
6	30.15	112	6	49.70	213
100	31.00	201	5	50.55	006
100	31.00	004	1	52.15	302
5	34.10	202			

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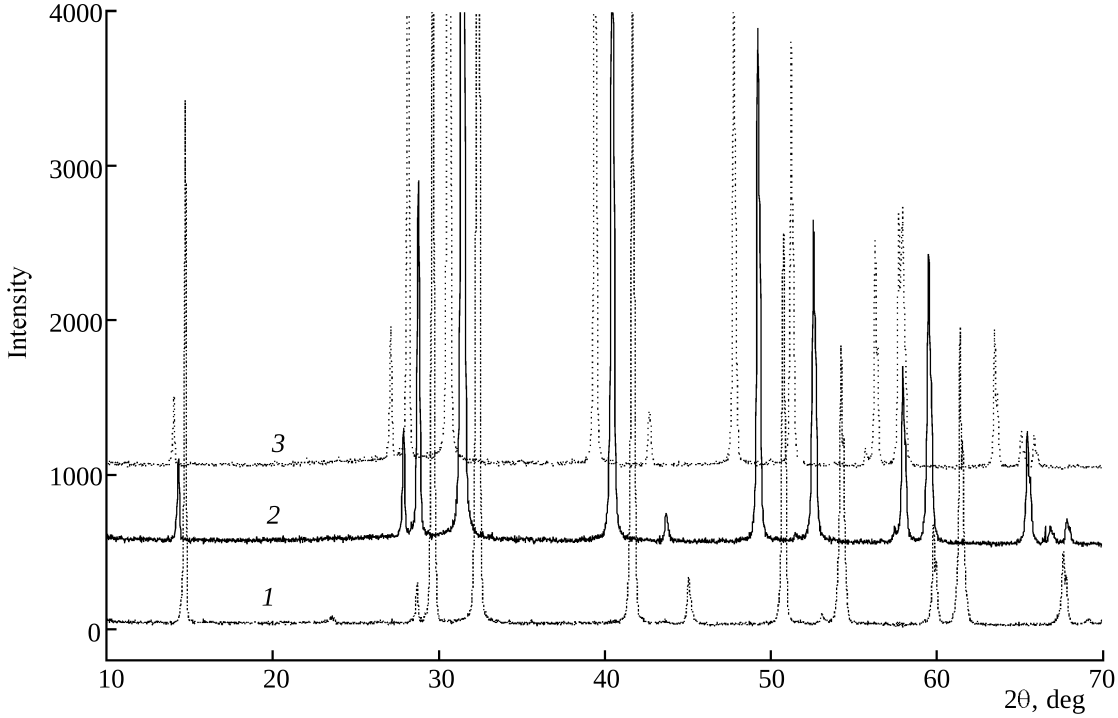

Fig. 1. Powder X-ray diffraction patterns of $TiSe_{1.60-x}Te_x$. x: (*1*) 0.16, (*2*) 0.80, and (*3*) 1.44.

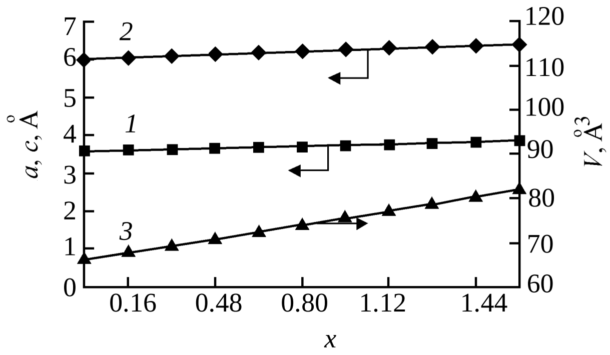

Fig. 2. Hexagonal cell parameters (*1*) a and (*2*) c, and (*3*) unit cell volume V of chalcogenides $TiSe_{1.60-x}Te_x$ as functions of x.

ic structure was reported for this compound previously [4, 5].

Figure 2 shows how the hexagonal cell parameters and unit cell volume of chalcogenides $TiSe_{1.60-x}Te_x$ depend on the composition. The parameter a shows a small negative deviation, and the parameter c, positive deviation from the linearity.

The thermal decomposition of $TiSe_{1.60-x}Te_x$ was studied systematically in Ar and N_2 atmospheres. Chalcogenides with $x = 0$, 0.16, 0.80, 1.44, and 1.60 were heated in an Ar or N_2 atmosphere from 25 to 1000°C and then cooled to 100°C. The TG curves for all the ten runs are shown in Fig. 3.

Data on the thermal dissociation of titanium selenides and tellurides are mainly limited to higher compounds $TiCh_y$ with $y \geq 2$. Suzuki and Waldbeck [9] studied the Ti–Te system by the Knudsen method and found that titanium tellurides vaporize incongruently, with the release of tellurium as the only gaseous product. No such studies were made for the Ti–Se system. There are only indications [10] that thermal dissociation of higher titanium selenides (from sesqui- to diselenide) is a route to lower selenides.

Since the Ar atmosphere is inert, the weight loss of the chalcogenide during the experiment can be assumed to be exclusively due to its thermal dissociation.

The selenide $TiSe_{1.60}$ shows virtually no weight loss in an Ar atmosphere, and the composition of the selenide remains unchanged. The powder patterns of the selenide before and after heating in an Ar atmosphere are identical.

On the contrary, $TiTe_{1.60}$ shows significant weight loss, and its powder pattern changes. The thermal dissociation of the chalcogenide can be described by one of the two reactions. The first alternative is the dissociation into the gaseous chalcogen and chalcogenide enriched in the metal relative to the starting compound:

$$TiTe_{1.60}(solid) \longrightarrow TiTe_{1.60-z}(solid) + z/2Te_2(gas). \quad (1)$$

In this case, the composition of the chalcogenide should approach $TiTe_{1.14}$, which contradicts the results of X-ray phase analysis, according to which the composition of the chalcogenide formed is close to $TiTe_{1.50}$.

Another alternative is the disproportionation into a higher chalcogenide and a chalcogenide with a lower chalcogen content than that in the starting compound. Then, taking into account the composition of the resulting chalcogenide determined by X-ray diffraction, the following reaction can be assumed to occur in an Ar atmosphere at 900–1000°C:

$$TiTe_{1.60}(solid) \rightarrow 0.8TiTe_{1.5}0(solid) + 0.2TiTe_2(gas). \quad (2)$$

Such a hypothesis is well consistent with the quantitative data. The weight loss in the course of this TG run was 23.14%, and Eq. (2) implies 24%.

Thus, the thermal decomposition of the tellurides under the conditions of our experiment cardinally differs from that observed in [9] under the effusion conditions.

Our preliminary experiments showed that the nitrogen atmosphere is not inert toward the solid solutions under consideration. Only the selenide $TiSe_{1.60}$ did not change its composition, as in the experiment under Ar. For the compounds containing Te, thermal dissociation (2) can be accompanied by the successive reaction of the gaseous titanium dichalcogenide with nitrogen, with the formation of low-volatile titanium nitride and free tellurium:

$$TiTe_2(gas) + 1/2N_2(gas) \longrightarrow TiN(solid) + Te_2(gas). \quad (3)$$

The formation of TiN could be clearly seen in the powder patterns of the selenotellurides with $x \geq 0.8$ (Fig. 4).

The powder patterns of $TiTe_{1.60}$ before and after heating under N_2 differ insignificantly, whereas the weight loss in the course of the experiment is as large as 55%. This fact additionally counts in favor of the occurrence of reaction (2) rather than (1). The calculations show that the $TiN : TiTe_{1.50}$ weight ratio in the final mixture should be 2 : 3. Hence, 3/4 of the $TiTe_{1.60}$ decomposed under the conditions of the TG experiment, and the resulting $TiTe_2$ fully reacted with N_2. The diffuse reflections at small angles of the powder pattern (Fig. 4) indicate that the sample contains an amorphous phase. This result indicates that the reaction could be incomplete and that TiN could also be amorphous. In the experiments involving longer heating of $TiTe_{1.60}$ under N_2 (additional heating for 15 min at 950°C), the weight loss increased.

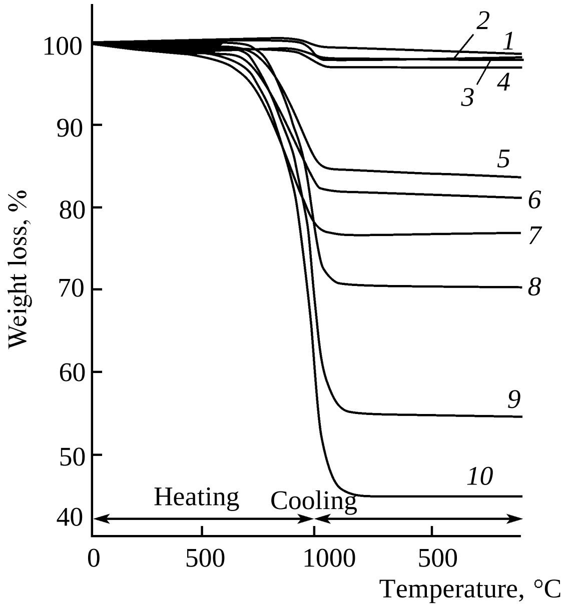

Fig. 3. TG curves of $TiSe_{1.60-x}Te_x$ in Ar and N_2 atmospheres: (*1*) $TiSe_{1.44}Te_{0.16}$/Ar, (*2*) $TiSe_{1.6}/N_2$, (*3*) $TiSe_{1.44}Te_{0.16}/N_2$, (*4*) $TiSe_{1.6}$/Ar, (*5*) $TiSe_{0.80} \cdot Te_{0.80}$/Ar, (*6*) $TiSe_{0.16}Te_{1.44}$/Ar, (*7*) $TiTe_{1.6}$/Ar, (*8*) $TiSe_{0.80}Te_{0.80}/N_2$,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

Titanium selenide and telluride as components of the solid solutions (x = 0.16, 0.80, 1.44) behave similarly to the corresponding individual chalcogenides (Fig. 3). For chalcogenides of the same composition, the difference in the weight loss in different atmospheres, determined by the occurrence of reactions (2) and (3), grows with an increase in the tellurium content. In a nitrogen atmosphere, at a low Te content (x = 0.16), reaction (2) is the major process, i.e., only the thermal dissociation of the chalcogenide occurs. At a higher Te content (x = 1.44), replacement of nitrogen for tellurium [reaction (3)] becomes the major process. The diffraction patterns of $TiSe_{0.16}Te_{1.44}$ before and after heating under Ar and N_2 are shown as examples in Fig. 4.

Thus, $TiSe_{1.60-x}Te_x$ forms a continuous series of hexagonal solid solutions with a CdI_2 structure. Nevertheless, titanium selenides and tellurides cardinally differ in the thermal behavior in Ar and N_2 atmospheres. On the whole, the selenides are considera-

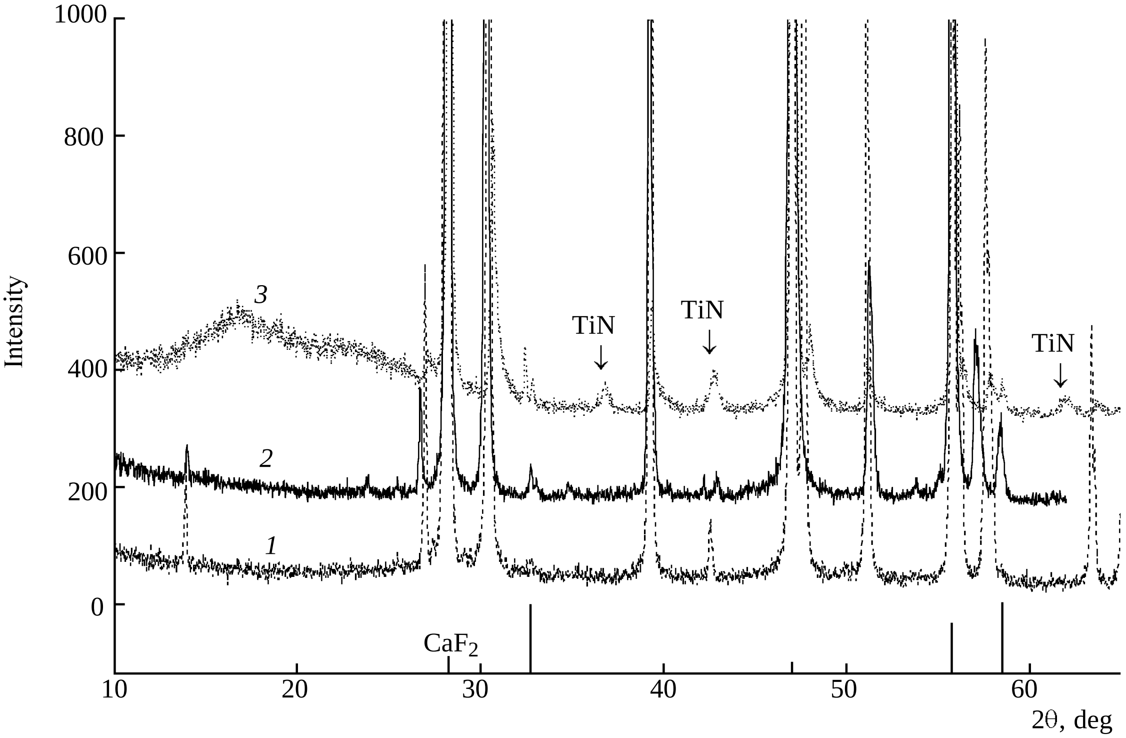

Fig. 4. Powder diffraction patterns of $TiSe_{0.16}Te_{1.44}$: (*1*) before TGA, (*2*) after TGA under Ar, and (*3*) after TGA under N_2.

bly more stable than the tellurides. We found that the thermal behavior of titanium tellurides differs from the thermal dissociation described previously [9]. On the one hand, at temperatures of up to 1000°C, in an inert atmosphere, tellurides show a much stronger tendency for thermal dissociation than selenides. This fact may be responsible for the faster growth of titanium telluride crystals, compared to selenides. On the other hand, titanium tellurides, compared to selenides, appeared to be more reactive toward nitrogen. Therefore, when performing gas transport reactions involving titanium tellurides, it is necessary to provide as high vacuum as possible, to avoid side reactions. We observed previously the binding of residual nitrogen [11] when growing single crystals of titanium diselenide by a chemical gas transport reaction in the diffusion mode. Similar trends are shown by intermediate titanium selenotellurides in both atmospheres.

EXPERIMENTAL

Polycrystalline samples of $TiSe_{1.60-x}Te_x$ ($0 \le x \le 1.60$, $\Delta x = 0.16$) were prepared by a direct ampule procedure. The starting substances were selenium (ultrapure V grade), tellurium (ultrapure T-A_1 grade), and titanium prepared from titanium hydride by vacuum dehydrogenation at 850°C. The content of impurities (wt %) in this titanium sample, as determined by spectral analysis, was as follows: Fe 0.03, Si 0.01, Al 0.01, and Cr 0.001. To avoid oxidation, the metal was stored in evacuated ampules. Stoichiometric amounts of the starting substances were placed in ampules made from vacuum compression quartz; the ampules were evacuated to 0.13 Pa and sealed. The syntheses were performed in a muffle furnace in the stepwise heating mode: 550°C, 170 h (primary reaction) and then 850°C, 720 h, followed by quenching in water at 0°C. Two samples of each composition were prepared.

The composition of titanium selenide was determined by gravimetric analysis (calcination to TiO_2 in an oxygen flow at 900°C [6]). The phase composition of the synthesis products and the unit cell parameters were determined by X-ray phase analysis (DRON-3, graphite, CuK_α radiation, external reference α-Al_2O_3). The unit cell parameters were determined by the least-squares method from the peaks at $20° \le \theta \le 52°$, Δ 0.005 Å. After the thermogravimetric analysis (TGA), the phase composition of titanium selenotellurides was determined with a Philips Analytical PW-1710/00 diffractometer from the peaks at $1.5° \le 2\theta \le 154°$. Samples after TGA (10 mg) were mixed with CaF_2 (internal reference, 40 mg).

The thermal behavior of $TiSe_{1.60-x}Te_x$ was studied for five compositions: x = 0, 0.16, 0.80, 1.44, and 1.60, by TGA on a Mettler-Toledo Ta-8000 device equipped with a TGA-850 thermal balance. The experiments were performed in an Ar or N_2 flow; the sample weight was ~10 mg, and the heating rate, 5 deg min^{-1}. The samples were heated from 25 to 1000°C and then cooled to 100°C.

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REFERENCES

1. Rimmington, H.P.B. and Balchin, A.A., *J. Cryst. Growth*, 1974, vol. 21, no. 2, p. 171.
2. Brunie, S. and Chevreton, M., *Mater. Res. Bull.*, 1968, vol. 3, no. 4, p. 309.
3. Pankratova, O.Yu., Grigor'eva, L.I., Zvinchuk, R.A., and Suvorov, A.V., *Zh. Neorg. Khim.*, 1993, vol. 38, no. 3, p. 410.
4. Gronvold, F. and Langmyhr, F.J., *Acta Chem. Scand.*, 1961, vol. 15, no. 10, p. 1949.
5. Bernusset, P., *C. R. Acad. Sci. Paris*, 1963, vol. 257, no. 19, p. 2840.
6. Pankratova, O.Yu., Vladimirova, V.A., and Zvinchuk, R.A., *Zh. Neorg. Khim.*, 1991, vol. 36, no. 4, p. 1050.
7. Pavlova, G.V., Pankratova, O.Yu., Zvinchuk, R.A., and Suvorov, A.V., *Vestn. S.-Peterb. Gos. Univ., Ser. 4: Fiz., Khim.*, 2000, issue 2, no. 11, p. 117.
8. Pankratova, O.Yu., Grigor'eva, L.I., Zvinchuk, R.A., and Suvorov, A.V., *Vestn. S.-Peterb. Gos. Univ., Ser. 4: Fiz., Khim.*, 1997, issue 1, no. 4, p. 119.
9. Suzuki, A. and Wahlbeck, P.G., *J. Phys. Chem.*, 1966, vol. 70, no. 6, p. 1914.
10. McTaggart, F.K. and Wadsley, A.D., *Aust. J. Chem.*, 1958, vol. 11, no. 4, p. 445.
11. Pankratova, O.Yu., Grigor'eva, L.I., Zvinchuk, R.A., and Suvorov, A.V., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 10, p. 1598.