# Brief Communications

## Thermodynamic properties of titanium selenides with variable composition $TiSe_2$—$TiSe_{1.80}$

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The thermodynamic investigation of the system $TiSe_2$—$TiSe_{1.80}$ was carried out by the static method of vapor pressure measurements using the quartz membrane-zero manometers in the temperature range from 713 to 1395 K. The analysis of the $p_{Se}$—$T$—$x$ dependences obtained showed that titanium diselenide formed a continuous solid solution. The enthalpies and entropies of dissociation processes of $TiSe_x$ were derived from the experimental data. The standard enthalpies of formation, the absolute entropies, and the free Gibbs energies of formation of selenides belonging to the homogeneity region of $TiSe_2$ were estimated using literature data. The obtained set of thermodynamic characteristics may be used for the calculation of phase equilibria and for thermodynamic modeling in the system Ti—Se.

**Key words:** titanium selenides, enthalpies and entropies of dissociation, static method of pressure measurement.

Titanium diselenide is the initial compound for the synthesis of intercalated materials with the polaron type of charge carriers. Such materials possess a series of very unusual properties, for instance, metal—semiconductor transition with dielectrization on heating,[1] reversible disordering of an impurity on cooling,[2] and equilibrium heterogeneities of electron concentration.[3] The behavior of multicomponent systems should be analyzed in order to develop the technology of preparation of intercalated materials. This analysis can be performed using thermodynamic modeling based on the comparative analysis of the behavior of the free Gibbs energy of components of the system ($\Delta_f G°$) as a function of the external parameters. A basic drawback of the existing approaches is that they ignore nonstoichiometry of individual compounds in the systems considered. It is known for many materials that the change in the free energy within the homogeneity region is comparable with the energy of formation. Thus, consideration

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of the dependence of $\Delta_f G°$ on the degree of nonstoichiometry can result in a quite different pattern of stability of phases in a multicomponent system.

Titanium diselenide is a compound of variable composition $TiSe_x$ with $1.45 \le x \le 2.0$ with a discontinuity in the homogeneity region between $x = 1.85$ and $x = 1.92$.[4] The enthalpies of formation of phases with a low selenium content ($1.45 \le x \le 1.85$) were obtained by the calorimetric method,[4] and the enthalpies of formation of phases with the composition $1.92 \le x \le 2.0$ were not found because of a high volatility of selenium.

The purpose of the present work is to obtain these values by measuring selenium volatility upon the thermal dissociation of $TiSe_2$ and to determine the dependence of the free Gibbs energy of formation of titanium selenides on their composition.

## Experimental

The samples under study were prepared at $T = 800$ °C by the ampoule synthesis method from the initial elements (titanium with purity 99.99 and selenium (trade mark special purity 19—5). According to the X-ray diffraction data, the samples were individual phases $TiSe_2$.[1]

The temperature dependence of the saturation vapor pressure over $TiSe_2$ was measured by the static method using quartz membrane-zero manometers in the isothermal[5] and nonisothermal variants.[6] In the latter case, the sensitive element of the membrane was at a constant temperature (~920 K) during the whole experiment. Similar design made it possible to completely eliminate effects of "reversible" and "irreversible" deformations (plastic deformation of quartz glass at temperatures above 1100 K) and to simultaneously exclude the possibility of diffusion of the compensating gas (air) and gaseous selenium through the membrane. The dissociation pressure was determined at a specified temperature of the furnace, approaching the equilibrium state on both heating and cooling. Coincidence of pressures determined at the same temperatures was a criterion of the equilibrium state of the system which the measured values refer to. The equilibration time varied from 40 h at the minimum temperature of experiment to 60 min at the maximum temperature. The measurement accuracy was 1 Torr, 0.5 K, and 0.01 formula units for the pressure, temperature, and composition of the solid phase, respectively.[7] The studies were carried out in wide ranges of pressures ($1 \le p$/Torr $\le 760$), temperatures ($713 \le T$/K $\le 1395$), and compositions ($0.7 \le m/V$/g dm$^{-3} \le 30$).

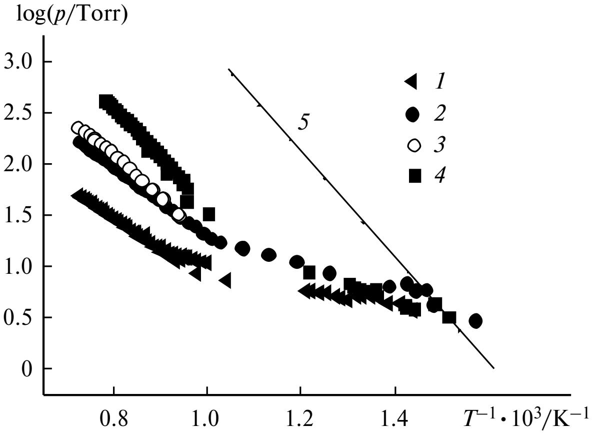

**Fig. 1.** Data of four experiments with different ratios of weighed samples to the volume of the membrane-zero manometer ($0.7 \le m/V$/g dm$^{-3} \le 30$) in the coordinates log*p*—1/*T*. Here and in Fig. 2, $m/V = 0.7$ (*1*), 4 (*2*), 7 (*3*), and 30 g dm$^{-3}$ (*4*). Line (*5*) corresponds to Se (l) = Se (g), where l and g are the liquid and gas phase, respectively.

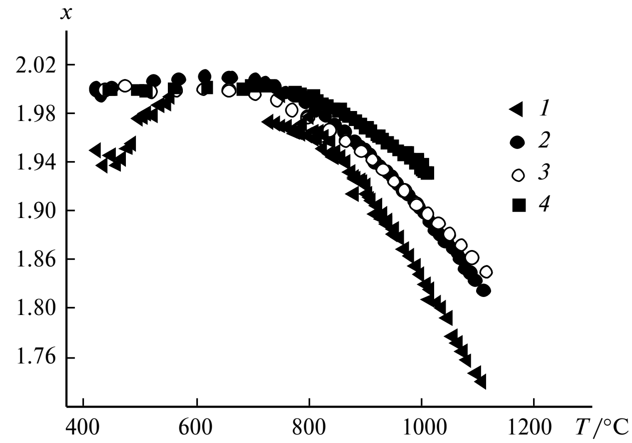

**Fig. 2.** Composition ($x$) of the condensed $TiSe_x$ phase *vs* temperature.

The composition of the condensed phase in each experimental point was calculated from the experimental temperature dependence of pressure using the ideal gas law and the equilibrium constant of selenium polymerization in the gas phase $Se_n \rightleftarrows n\, Se$.[8] The experimental data for the $p_{Se}$—$T$—$x$ diagram are presented in Figs 1 and 2.

## Results and Discussion

The properties under study change continuously and monotonically and no discontinuity in the homogeneity region is observed at $x = 1.92$—$1.85$ (see Fig. 2). An analysis of the obtained dependences $p_{Se}$—$T$—$x$ (see Figs 1 and 2) suggested that titanium diselenide forms a continuous solid solution in the range of compositions $TiSe_2$—$TiSe_{1.80}$.

The enthalpies and entropies ($\Delta_r H_{298}$ and $\Delta_r S°_{298}$) of the dissociation process were determined for these compositions

$$TiSe_2\,(s) \longrightarrow TiSe_{2-\delta}\,(s) + \delta/2\ Se_2\,(g),$$

where $\delta \to 0$; and s and g designate the solid and gaseous states, respectively.

The experimental data were processed using the second and third laws of thermodynamics. In the first case, the heat capacities were considered to be known and the enthalpies and entropies of the reactions referred to 298.15 K were considered unknown. When processing by the third

**Table 1.** Enthalpies ($\Delta_r H_{298}$) and entropies ($\Delta_r S^\circ_{298}$) of dissociation processes in the system $TiSe_2$—$TiSe_{1.80}$ calculated by application of the second (II) and the third (III) laws of thermodynamics

| Process | $\Delta_r H_{298}$/kJ mol$^{-1}$ | | $\Delta_r S^\circ_{298}$/J mol$^{-1}$ K$^{-1}$ | |
|---|---|---|---|---|
| | II | III | II | III |
| $100\ TiSe_2\ (s) \rightleftharpoons 100\ TiSe_{1.98}\ (s) + Se_2\ (g)$ | 196.6±4.2 | 197.1±4.2 | 163.2±3.8 | 163.6±5.0 |
| $100\ TiSe_{1.98}\ (s) \rightleftharpoons 100\ TiSe_{1.96}\ (s) + Se_2\ (g)$ | 204.6±3.3 | 201.3±3.3 | 166.5±2.9 | 163.6±5.0 |
| $100\ TiSe_{1.96}\ (s) \rightleftharpoons 100\ TiSe_{1.94}\ (s) + Se_2\ (g)$ | 209.2±2.8 | 206.8±2.8 | 165.7±2.3 | 163.6±5.0 |
| $100\ TiSe_{1.94}\ (s) \rightleftharpoons 100\ TiSe_{1.92}\ (s) + Se_2\ (g)$ | 217.9±2.6 | 218.6±2.6 | 162.9±2.0 | 163.6±5.0 |
| $100\ TiSe_{1.92}\ (s) \rightleftharpoons 100\ TiSe_{1.90}\ (s) + Se_2\ (g)$ | 222.7±4.1 | 224.2±4.1 | 162.4±3.2 | 163.6±5.0 |
| $100\ TiSe_{1.90}\ (s) \rightleftharpoons 100\ TiSe_{1.88}\ (s) + Se_2\ (g)$ | 222.3±3.3 | 224.2±3.3 | 162.3±2.9 | 163.6±5.0 |
| $100\ TiSe_{1.88}\ (s) \rightleftharpoons 100\ TiSe_{1.86}\ (s) + Se_2\ (g)$ | 233.6±5.0 | 231.6±5.0 | 165.1±3.8 | 163.6±5.0 |
| $100\ TiSe_{1.86}\ (s) \rightleftharpoons 100\ TiSe_{1.84}\ (s) + Se_2\ (g)$ | 231.4±3.3 | 230.9±3.3 | 164.0±2.5 | 163.6±5.0 |
| $100\ TiSe_{1.84}\ (s) \rightleftharpoons 100\ TiSe_{1.82}\ (s) + Se_2\ (g)$ | 240.4±2.7 | 240.8±2.7 | 163.3±2.0 | 163.6±5.0 |
| $100\ TiSe_{1.82}\ (s) \rightleftharpoons 100\ TiSe_{1.80}\ (s) + Se_2\ (g)$ | 229±7.0 | 243±7.0 | 153.5±5.0 | 163.6±5.0 |

law, heat capacities and entropies were considered known. The temperature dependences of the heat capacity and entropy for $Se_2$ (g), which are necessary for calculations, were taken from the manual,[8] and the data for $TiSe_2$ (s) were taken from the literature.[9] For other compositions of $TiSe_x$, the heat capacities and entropies were calculated by the additive method using the data for $TiSe_2$ (s)[9] and Se (s).[8] As can be seen from Table 1, the results of calculations by two independent methods coincide within the indicated inaccuracies.

The standard enthalpies of formation and absolute entropies of titanium selenides $TiSe_x$ (s) with $1.80 \le x \le 2.0$ were calculated using the literature[4,9] and estimated data. Their values are given in Table 2.

Based on the data of Table 1 obtained using the second law, we calculated the free Gibbs energy of formation ($\Delta_f G^\circ = \Delta_f H_{298} - T\Delta_f S^\circ_{298}$) of titanium selenides $TiSe_2$—$TiSe_{1.80}$. As can be seen from Fig. 3, the free Gibbs energy increases monotonically with $x$. Slight breaks in the curve of the dependence $\Delta_f G^\circ = f(x)$ are observed in the composition regions $x \approx 1.93$ and $x \approx 1.85$. Note that it is the composition range where the discontinuity in the homogeneity region was earlier reported.[4] According to our data, no discontinuity in the homogeneity region is observed but, probably, the structure of the solutions changes. Since it is well known that structure imperfection in materials of this type is related to the presence of excessive metal atoms located in the interlayer space of the main lattice,[10] it can easily be calculated that the breaks in Fig. 3 correspond to systems with ~4 and 8 mol.% of excess titanium. In the case of ordering, such a small concentration should result in long-period structures, which were not observed experimentally.

**Table 2.** Standard enthalpies ($\Delta_f H_{298}$) of formation and absolute entropies ($S^\circ_{298}$) of titanium selenides

| Solid phase | $-\Delta_f H_{298}$ /kJ mol$^{-1}$ | $S^\circ_{298}$ /J mol$^{-1}$ K$^{-1}$ |
|---|---|---|
| $TiSe_2$ | 352.7±7.0 | 94.1±1.0[a] |
| $TiSe_{1.98}$ | 352.1±7.0 | 93.3±3.5 |
| $TiSe_{1.96}$ | 351.5±7.0 | 92.5±3.5 |
| $TiSe_{1.94}$ | 350.9±7.0 | 91.8±3.5 |
| $TiSe_{1.92}$ | 350.1±7.0 | 91.0±3.5 |
| $TiSe_{1.90}$ | 349.4±7.0 | 90.1±3.5 |
| $TiSe_{1.88}$ | 348.6±7.0 | 89.25±3.5 |
| $TiSe_{1.86}$ | 347.7±7.0 | 88.4±3.5 |
| $TiSe_{1.84}$ | 346.8±7.0 | 87.6±3.5 |
| $TiSe_{1.82}$ | 345.8±7.0 | 86.5±3.5 |
| $TiSe_{1.80}$ | 345.0±2.0[b] | 85.6±5.0 |

[a] See Ref. 8.
[b] See Ref. 4.

At the same time, a similar effect related to a change in the degree of overlapping of the wave functions of electrons of intercalated atoms due to the achievement of the leakage thresholds was observed for iron-intercalated $TiSe_2$.[11] Deviations of critical concentrations from the exact fit (5 and 7.5 mol.% in Ref. 11 versus 4 and 8 mol.%

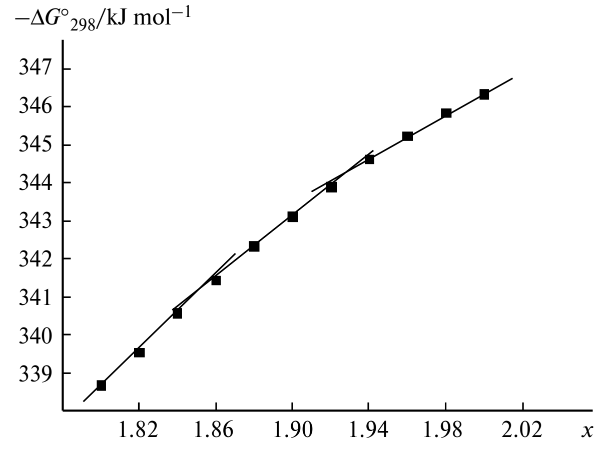

**Fig. 3.** Free Gibbs energy of formation ($\Delta_f G^\circ$) of $TiSe_x$ *vs* composition ($x$).

in the present work) can be explained by the presence of excess titanium in the $Fe_xTiSe_2$ samples, which slightly distorts the pattern.

The information obtained can be used for the calculation of phase equilibria and for thermodynamic modeling in the Ti—Se system.

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