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Synthesis, growth and investigation of the physical–chemical properties of single crystals of TmSb, TmTe and their solid solutions $TmSb_{1-x}Te_x$

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Abstract

A complete series of $TmSb_{1-x}Te_x$ single crystals has been prepared in order to enable a systematic investigation of the valence change of Tm between nearly +3 for semimetallic TmSb and +2 for semiconducting TmTe. A discontinuous semiconductor–metal transition is observed at $x = 0.8$–0.9.

1. Introduction

The valence of Tm ions fluctuates between the f^{12} and f^{13} configurations, both of which are magnetic for Tm. TmSb and TmTe crystallize in the cubic NaCl structure. In TmSb thulium has +3 valency ($r_{Tm^{3+}} = 0.087$ nm). In TmTe its valency is +2 ($r_{Tm^{2+}} = 0.104$ nm). In accordance with the electrical properties TmSb is a semimetal, and TmTe is a semiconductor [1–5].

The aim of the present work is to obtain solid solutions of the $TmSb_{1-x}Te_x$ type and to study their properties.

2. Samples and experimental details

Our samples were synthesized from 99.89% pure thulium metal and high purity antimony and tellurium.

First thulium metal turnings and tellurium and antimony in stoichiometric amounts were heated in evacuated ampoules of molybdenum glass at temperatures below 500 °C for 1 week. The products were obtained in powder form. They were examined by X-ray analysis that showed characteristic lines of the rock-salt structure.

The resulting powder was pressed into pellets and heated in closed tantalum tubes at 1500 °C. Single crystals of TmTe, TmSb and $TmSb_{1-x}Te_x$ have been grown by directional freezing of the melt in closed molybdenum tubes. Phase identification of the obtained specimens was carried out by X-ray, microstructural and chemical analyses. X-ray analysis showed that in the $TmSb_{1-x}Te_x$ system a continuous series of solid solutions is formed.

The density of the specimens was measured by using the picnometric technique with an accuracy of ±5%. The electrical properties were measured within the temperature range from liquid helium to room temperature. Heat conductivity was measured in the temperature range from liquid nitrogen to 400 °C. The magnetic properties of TmSb, TmTe and $TmSb_{1-x}Te_x$ have been investigated in a broad temperature range from 4.2 to 300 K.

3. Results and discussion

The results of the $TmSb_{1-x}Te_x$ system investigation are given in Table 1 and in Fig. 1. The lattice constants of TmSb and TmTe are the same as those found by other authors [1, 2]. Solid solutions of intermediate composition between TmSb and TmTe ($TmSb_{1-x}Te_x$) exist in the whole concentration range, and the compounds crystallized in the cubic NaCl-type structure. A sharp change of the lattice parameter was observed at $x \approx 0.85$, which corresponds to a change of the elementary cell volume of $\Delta v/v \approx 15\%$.

The beginning of the metal–semiconductor phase transition is seen in Fig. 2, showing the temperature dependence of ρ for $TmSb_{0.15}Te_{0.85}$. The data for $TmSb_{0.1}Te_{0.9}$ and TmTe suggest that these compounds have semiconducting properties (Fig. 3).

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TABLE 1. Some characteristics of thulium monoantimonide, thulium monotelluride and their solid solutions $TmSb_{1-x}Te_x$

x	Chemical composition	Lattice parameter, a (nm)	Density ($g\ cm^{-3}$)	
			d_{exp}	d_{calc}
0	TmSb	0.61054	8.61	8.576
0.1	$TmSb_{0.9}Te_{0.1}$	0.60565	8.93	8.756
0.2	$TmSb_{0.8}Te_{0.2}$	0.60443	8.83	8.827
0.3	$TmSb_{0.7}Te_{0.3}$	0.6091	8.25	8.68
0.4	$TmSb_{0.6}Te_{0.4}$	0.60505	8.77	8.807
0.5	$TmSb_{0.5}Te_{0.5}$	0.6023	8.36	8.97
0.6	$TmSb_{0.4}Te_{0.6}$	0.60255	8.47	8.98
0.7	$TmSb_{0.3}Te_{0.7}$	0.6098	8.50	8.64
0.8	$TmSb_{0.2}Te_{0.8}$	0.6052	–	8.98
0.9	$TmSb_{0.1}Te_{0.9}$	0.6276	7.98	7.99
1.0	TmTe	0.6338	7.79	7.778

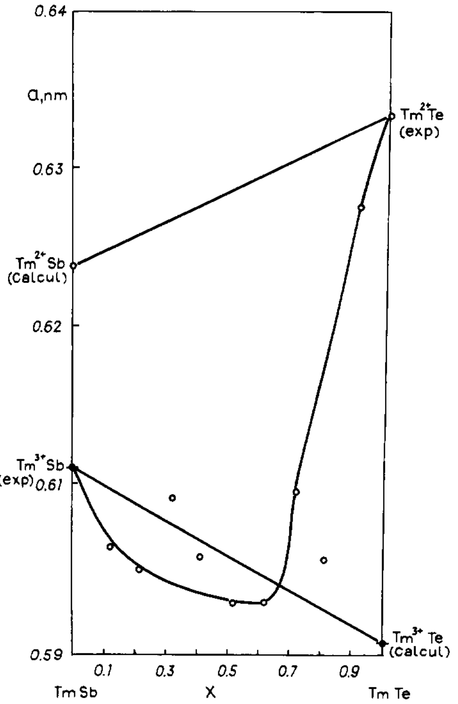

Fig. 1. Dependence of lattice parameters of $TmSb_{1-x}Te_x$ on the composition (x).

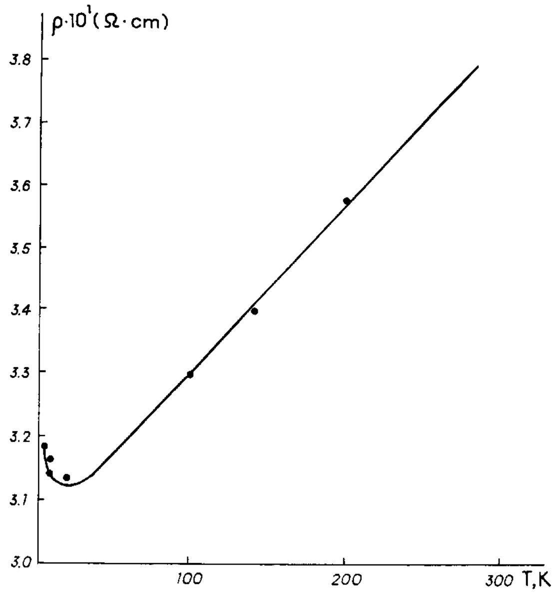

Fig. 2. Dependence of electrical resistance of $TmSb_{0.15}Te_{0.85}$ on the temperature.

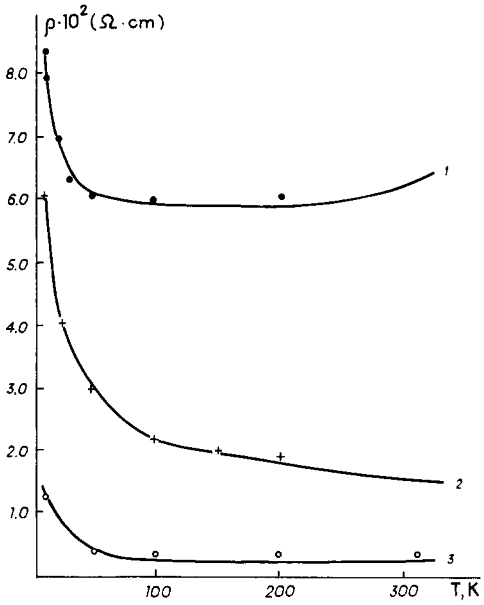

Fig. 3. Dependence of electrical resistance of TmTe (1), $TmSb_{0.05}Te_{0.95}$ (2) and $TmSb_{0.1}Te_{0.9}$ (3) on temperature.

The magnetic susceptibility for TmSb follows the Curie–Weiss law at high temperatures. The high-temperature slope of χ^{-1} (Γ) might be interpreted as Curie–Weiss behaviour with an effective moment $\mu_{eff}=7.20$ μ_B per Tm ion. The dependence of the magnetic susceptibility on temperature for $TmSb_{0.1}Te_{0.9}$ can be described by the Curie–Weiss law at temperatures higher than 30 K, and the effective magnetic moment is $\mu_{eff}=5.31$ μ_B per Tm ion.

The sharp change of lattice constant in the range $x=0.8$–0.9 indicates the occurrence of a semiconductor–metal phase transition along with the valency change of Tm. The dependence of the lattice parameter on composition is qualitatively similar with the dependence obtained for $TmSe_{1-x}Te_x$, but there is an essential difference, namely, the displacement of the sharp change from the range $x=0.2$–0.4 to the range $x=0.8$–0.9 for $TmSb_{1-x}Tm_x$. This change in transition region is possibly associated in $TmSe_{1-x}Te_x$ with the variation in ionic radii from Se^{2-} to Te^{2-} whereas in the case of $TmSb_{1-x}Te_x$, the variation is from Sb^{3-} to Te^{2-}. Apparently, in the range $x=0.15$ the semiconductor–metal transition is due to the change of Tm valency. The

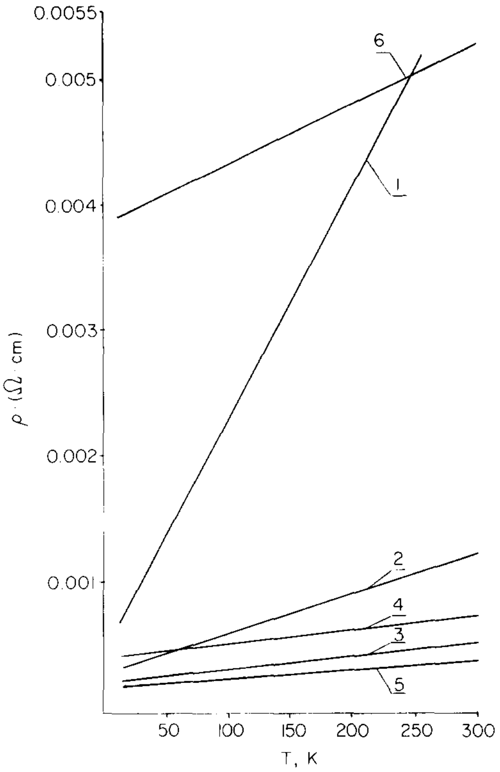

Fig. 4. Dependence of electrical resistance of TmSb (1), $TmSb_{0.9}Te_{0.1}$ (2), $TmSb_{0.8}Te_{0.2}$ (3), $TmSb_{0.7}Te_{0.3}$ (4), $TmSb_{0.6}Te_{0.4}$ (5) and $TmSb_{0.5}Te_{0.5}$ (6).

valency of Tm in $TmSb_{0.1}Te_{0.9}$ derived from the lattice parameter is ~2.28, and from magnetic measurements it is ~2.3.

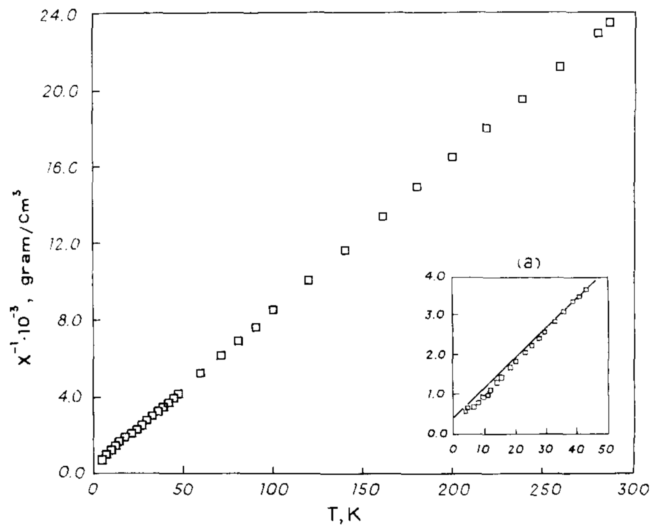

Fig. 5. Dependence of magnetic susceptibility of $TmSb_{0.1}Te_{0.9}$ on temperature.

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