

PHYSICOCHEMICAL ANALYSIS
OF INORGANIC SYSTEMS

Physicochemical Study of SmTe–In₂Te₃ and SmTe–InTe Systems

N. R. Akhmedova, S. M. Agapashaeva, and O. M. Aliev

Institute of Chemical Problems, National Academy of Sciences of Azerbaijan, Baku, Azerbaijan

Received March 1, 2008

Abstract—SmTe–In₂Te₃ and SmTe–InTe quasi-binary joins were studied using physicochemical methods. The SmTe–In₂Te₃ system forms two compounds, SmIn₂Te₄ and SmIn₄Te₇, which melt incongruently at 1075 and 960 K, respectively. An In₂Te₃-base solid solution at 400 K extends to 3 mol % SmTe. The SmTe–InTe system at the component ratio 3 : 2 (mol/mol) forms the ternary compound Sm₃In₂Te₅, which melts with decomposition at 970 K. The InTe-based solubility range is 10 mol % SmTe.

DOI: 10.1134/S0036023609100258

The compound SmTe melts congruently at 2100 K and has a NaCl-type cubic structure ($a = 6.594 \text{ \AA}$) [1]. Semiconductors InTe and In₂Te₃ also melt congruently at 969 and 940 K [2, 3], respectively. InTe has a layered TlSe-type structure; its unit cell is tetragonal with the parameters $a = 8.437$, $c = 7.13 \text{ \AA}$ [4]. In₂Te₃ is a defect semiconductor with the bandgap width $\Delta E = 1.02 \text{ eV}$ in α -In₂Te₃ and 1.026 eV in β -In₂Te₃ [5].

In this work, we study phase equilibrium in the Sm–In–Te system along SmTe–In₂Te₃ and SmTe–InTe joins.

EXPERIMENTAL

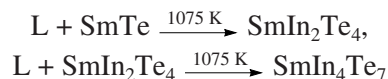
Alloys were synthesized from SmTe, InTe, and In₂Te₃ alloyages that had been prepared from the constituent elements at 950–1100 K. The alloys with compositions lying along SmTe–In₂Te₃ and SmTe–InTe joins were annealed at 700–750 K for 80 h for homogenization.

Phase equilibria in the SmTe–In₂Te₃ and SmTe–InTe systems were studied using differential thermal analysis, X-ray powder diffraction, and microstructure observations as in [6].

RESULTS AND DISCUSSION

Figure 1 depicts the T - x diagram of the SmTe–In₂Te₃ condensed system.

SmTe–In₂Te₃ is a quasi-binary join of the Sm–In–Te ternary system. Compounds formed by the peritectic reaction



were found on this join. The SmIn₄Te₇ and β -In₂Te₃ primary separation lines meet at 15 mol % SmTe and 850 K.

SmIn₂Te₄ single crystals were prepared by chemical transport ($T = 900 \text{ K}$, $T_2 = 785 \text{ K}$, $c_{T_2} = 5 \text{ mg/cm}^3$, $\tau = 75 \text{ h}$). X-ray diffraction analysis of these crystals showed that SmIn₂Te₄ crystallizes in orthorhombic structure with the unit cell parameters $a = 11.80 \text{ \AA}$, $b = 11.42 \text{ \AA}$, $c = 6.94 \text{ \AA}$, space group $Bmbm$. The SmIn₂Te₄ phase is isostructural to EuGa₂Se₄ [6]. SmIn₂Te₄ microhardness is 1600 MPa; $\Delta E = 1.10 \text{ eV}$.

Microhardness measurements for intermediate phases of the SmTe–In₂Te₃ system gave four sets of values: one corresponds to In₂Te₃-base α -solid solutions (1660–1700 MPa), second to YbIn₄Te₇ (1250 MPa), third to YbIn₂Te₄, and fourth to samarium monotelluride (3250 MPa).

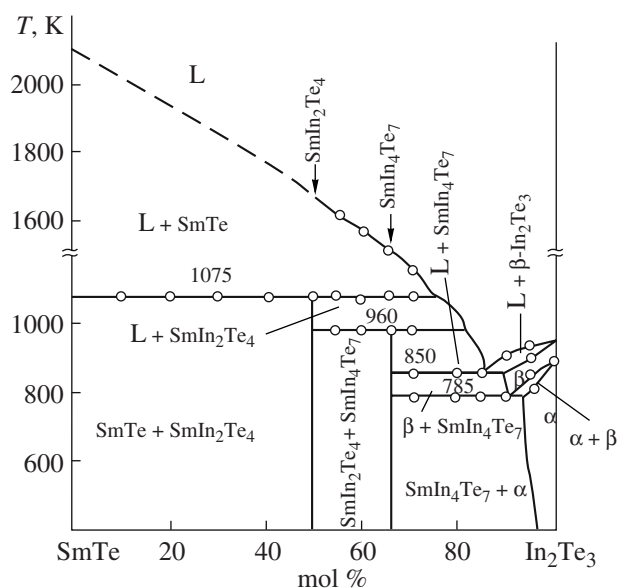


Fig. 1. Phase diagram for the SmTe–In₂Te₃ join.

Medvedeva said [2] that In_2Te_3 has three polymorphs: $\alpha\text{-In}_2\text{Te}_3$, $\beta\text{-In}_2\text{Te}_3$, and $\gamma\text{-In}_2\text{Te}_3$. However, Yatsenko [3] mentioned only two In_2Te_3 phases: high-temperature $\beta\text{-In}_2\text{Te}_3$ and low-temperature $\alpha\text{-In}_2\text{Te}_3$. Figure 1 makes it clear that the $\alpha\text{-In}_2\text{Te}_3 \rightleftharpoons \beta\text{-In}_2\text{Te}_3$ phase transition occurs at 785 K and has a eutectoid character. Primary crystals of $\beta\text{-In}_2\text{Te}_3$ -base solid solution are separated from a cooled liquid in the In_2Te_3 crystallization region (70–90 mol % In_2Te_3).

Addition of SmTe to indium sesquitelluride depresses the polymorphic transition temperatures. The change in the $\alpha\text{-In}_2\text{Te}_3 \rightleftharpoons \beta\text{-In}_2\text{Te}_3$ transition temperature is especially serious. Regions in which $\alpha + \beta$ solid solutions coexist are insignificant (Fig. 1).

The extent of In_2Te_3 -base solid solution is 10 mol % at 850 K and ~ 3 mol % SmTe at room temperature.

The SmTe–InTe phase diagram (Fig. 2) shows that this a quasi-binary join and one incongruently melting compound ($\text{Sm}_3\text{In}_2\text{Te}_5$) is formed by the peritectic reaction $L + \text{SmTe} \rightleftharpoons \text{Sm}_3\text{In}_2\text{Te}_5$ at 970 K.

The liquidus consists of the primary separation curves of SmTe, $\text{Sm}_3\text{In}_2\text{Te}_5$, and α InTe-base solid solutions. The eutectic coordinates are 23 mol % SmTe and 800 K. The InTe-base solubility at room temperature is 9 mol % SmTe. In measuring microhardness of alloys of the SmTe–InTe system, we obtained three sets of values corresponding to the dark SmTe phase (3250 MPa), gray $\text{Sm}_3\text{In}_2\text{Te}_5$ phase (1450 MPa), and light InTe phase (400–450 MPa).

Figures 1 and 2 make it clear that the SmTe solubility in In_2Te_3 and InTe depends substantially on the phase to which samarium telluride is added. The largest homogeneity region exists along the SmTe–InTe join. Indium is known to tend, under certain conditions, to form octahedral structures; an InTe phase existing at high pressures crystallizes in a NaCl-type structure, as SmTe. This is responsible for the considerable solubility of SmTe in InTe. The dimensional factor is also favorable: the relative difference between the Sm^{2+} and In^{2+} ionic radii is 10%.

Solubility along the SmTe– In_2Te_3 join is far lower than along the SmTe–InTe join. This is likely because of a dimensional factor. Along the SmTe– In_2Te_3 join, there are stoichiometric vacancies in the cationic sublattice, along with indium atoms; the crystal-chemical radius of these vacancies (in In_2Te_3) is smaller than the In^{2+} radius. As a result, the relative difference between the Sm^{2+} ionic radius and the mean ionic radius of the substituent complex ($3\text{Sm} \rightarrow 2\text{In} + a^0$, where a^0 stands for a neutral vacancy) increases.

The unit cell parameters of $\text{In}_{1-x}\text{Sm}_x\text{Te}$ solid solutions linearly increase with composition (for $\text{In}_{0.09}\text{Sm}_{0.01}\text{Te}$, $a = 8.48 \text{ \AA}$, $c = 7.16 \text{ \AA}$; for $\text{In}_{0.91}\text{Sm}_{0.09}\text{Te}$,

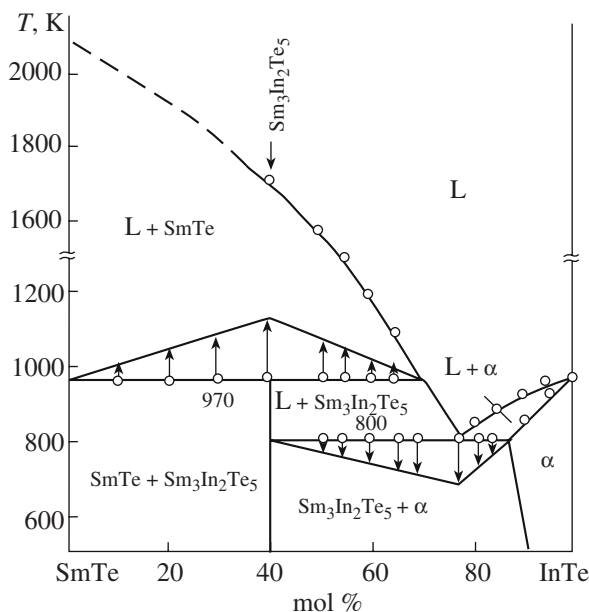


Fig. 2. Phase diagram for the SmTe–InTe join.

$a = 8.56 \text{ \AA}$, $c = 7.24 \text{ \AA}$) because In^{2+} has a smaller ion radius than Sm^{2+} (~ 1.13 against 1.09 \AA [7]). Addition of SmTe to InTe leads to the formation of substitutional solid solutions with vacancies in the cationic sublattice.

In summary, we have studied the Sm–In–Te system along SmTe– In_2Te_3 and SmTe–InTe joins using physicochemical methods and constructed phase diagrams of these joins.

We have found ternary tellurides SmIn_2Te_4 , SmIn_4Te_7 , and $\text{Sm}_3\text{In}_2\text{Te}_5$ and indium telluride-base incomplete solid solutions.

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