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Phase Diagram of the Tl_2Te_3–Bi_2Te_3 System and Properties of the Alloys Obtained

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In studying the phase diagram of the Tl–Te system, we discovered a new compound, Tl_2Te_3, possessing semiconducting properties. The compound Tl_2Te_3 is formed from a melt of the corresponding composition after annealing for no less than 200 hr at a temperature of 200°. It has a high thermoelectromotive force (+800 μV/deg) and a very low electrical conductivity 4 $\Omega^{-1} \cdot cm^{-1}$. Rabenau, Stegherr, and Eckerlin preceded us in publishing their results, which fully coincide with our data ([1]). Continuing our investigations of the compound Tl_2Te_3, we came to the conclusion that, despite its high thermoelectric power, Tl_2Te_3 is not very effective as a thermoelectric material because of its extremely low electrical conductivity and high thermal conductivity. In addition, it is brittle, and upon incongruent melting it transforms into the compound TlTe, which does not possess semiconducting properties. Since partial replacement of cations in the lattice of a p-type thermoelement leads to a decrease in thermal conductivity and an increase in electrical conductivity, we set ourselves the task of studying the properties of Tl_2Te_3 alloys with replacement of the thallium cation by bismuth. In order to study the nature of the interaction of thallium and bismuth tellurides, the phase diagram of the Tl_2Te_3–Bi_2Te_3 system and some properties of the alloys obtained were investigated.

Experimental Procedure

The starting materials used for preparing the alloys were: thallium, grade Tl-00, with impurities less than $1 \cdot 10^{-4}$%; bismuth, grade V-000, with impurities less than $3 \cdot 10^{-4}$%; imported tellurium, Johnston, Matthey and Co. grade, with impurities less than $1 \cdot 10^{-6}$%. The samples were prepared by melting the starting components in Pyrex ampoules evacuated to 10^{-2} mm Hg. Melting was carried out with thorough stirring for 2-3 hr, after which the alloys were cooled in air and subjected to prolonged annealing. The annealing temperature was gradually increased as the low-melting constituents disappeared. The annealing time was up to 2 months.

The attainment of equilibrium in the alloys was monitored by measurement of electrical conductivity and by X-ray phase analysis. Thermal analysis of the annealed alloys was carried out by recording heating curves on an N. S. Kurnakov

Fig. 1. Phase diagram of the system Tl_2Te_3–Bi_2Te_3

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Fig. 2. Dependence of electrical conductivity on alloy composition

Figure 2: Fig. 2. Dependence of electrical conductivity on alloy composition

pyrometer. Aluminum was used as the standard. Measurements of electrical conductivity and thermoelectric power were made on a PPTN-1 potentiometer using an M/17-2 galvanometer. Probes and thermocouples were attached to the specimen by spot welding. The thermoelectromotive force was measured relative to copper at a temperature difference of 10-15°. X-ray phase and structural analysis was carried out by the powder method using iron radiation.

Experimental Part

Although Tl_2Te_3 melts with decomposition, the Tl_2Te_3–Bi_2Te_3 system can be regarded as a quasibinary section of the ternary Tl–Bi–Te system, since in all the alloys studied it was precisely the compound Tl_2Te_3 that was detected by X-ray phase analysis, and not TlTe, which is formed upon its decomposition. Apparently, the presence of Bi_2Te_3 stabilizes the Tl_2Te_3 lattice.

The phase diagram of the system Tl_2Te_3–Bi_2Te_3, constructed from differential thermal analysis data (Fig. 1), makes it possible to infer the formation of a new compound, $TlBiTe_3$, in the system through the interaction of the initial bismuth and thallium tellurides in the melt. Its melting temperature is 600°. According to X-ray structural analysis data (powder method), this compound crystallizes in the trigonal system. The unit-cell dimensions are: $a_0 = 4.51 \pm 0.01$ kX, $c_0 = 57.45 \pm 0.02$ kX (or $a_{rh} = 19.33$ kX, $\alpha = 13°24'$).

Fig. 1. Phase diagram of the system Tl_2Te_3–Bi_2Te_3

Fig. 2. Dependence of electrical conductivity on alloy composition

The density of $TlBiTe_3$, calculated on the basis of the obtained cell dimensions, is 7.78 g/cm^3, which agrees well with the density measured pycnometrically, 7.75 g/cm^3. One elementary hexagonal cell contains 6 formula units of $TlBiTe_3$. In the dimensions of the unit cell and in the values of the intensities and interplanar spacings, the compound described differs from the known thallium and bismuth tellurides.

When the melt corresponding to this compound solidifies, the ingot is an aggregate of large rhombohedral crystals, sometimes reaching 5 mm and more, which indicates a high rate of crystallization and the ease of obtaining single crystals of $TlBiTe_3$. The region of primary crystallization of $TlBiTe_3$ from the melt is wide–from 20 to 75 at.% Bi_2Te_3. Joint crystallization of $TlBiTe_3$ with Tl_2Te_3 and Bi_2Te_3 occurs at 220 and 525°, respectively. In the region where melts are

saturated with bismuth telluride, solid solutions based on it with $TlBiTe_3$ are formed. According to thermal and X-ray phase analysis data, the region of solid solutions extends from 100 to 95 at.% Bi_2Te_3.

Studies of electrical conductivity and thermoelectromotive force were carried out for annealed alloys (Table 1). Prolonged annealing led to a sharp change in their properties. On the curves showing changes in alloy properties as a function of composition, the maximum values of electrical conductivity and thermoelectromotive force correspond in the system to the compound $TlBiTe_3$. In the homogeneous region of solid solutions based on bismuth telluride there is a smooth change in these properties (Figs. 2, 3). $TlBiTe_3$, the compound formed in the system, has an electronic type of conductivity, judging from the sign of the thermo-e.m.f. Its electrical conductivity at room temperature is

$\sigma = 673.4\ \Omega^{-1} \cdot \text{cm}^{-1}$.

The band gap, calculated from the temperature dependence of the electrical conductivity, is $E = 0.500$ eV. Calculated from the values

Table 1

Properties of alloys of the system

Composition, mol. %		Group, Cast alloys		Annealed		Composition, mol. %		Group, Cast alloys		Annealed	
Tl_2Te_3	Bi_2Te_3	σ, $\Omega^{-1} \cdot \text{cm}^{-1}$	α, μV/deg	σ, $\Omega^{-1} \cdot \text{cm}^{-1}$	α, μV/deg	Tl_2Te_3	Bi_2Te_3	σ, $\Omega^{-1} \cdot \text{cm}^{-1}$	α, μV/deg	σ, $\Omega^{-1} \cdot \text{cm}^{-1}$	α, μV/deg
100.00	–	–	–	5.0	+800.0	40.00	60.00	936.1	−70.2	500.3	−492.3
97.00	3.00	–	–	4.7	+468.0	35.00	65.00	561.7	−152.1	445.1	−370.6
95.00	5.00	–	–	4.3	+143.6	25.00	75.00	–	−85.8	298.5	−50.0
90.00	10.00	–	–	7.3	+100.2	15.00	85.00	–	−70.2	315.6	+50.3
80.00	20.00	–	–	77.61	−144.0	5.00	95.00	–	–	432.5	+70.1
70.00	30.00	–	–	241.80	−158.7	3.00	97.00	–	–	290.7	+78.6
60.00	40.00	459.1	−70.2	405.9	−234.5	1.50	98.50	–	–	74.2	+78.0
50.00	50.00	683.9	−58.5	673.4	−1482.0	–	100.00	–	–	585.7	+200.1
45.00	55.00	778.4	−128.7	583.3	−1000.1						

From the values of electrical conductivity and the Hall effect, the values of the mobility and concentration of current carriers are, respectively: $\mu = 385\ \text{V}^{-1} \cdot \text{sec}^{-1} \cdot \text{cm}^2$, $n = 0.7 \cdot 10^{19}\ \text{cm}^3$.

The starting components, thallium and bismuth tellurides, are compounds with hole-type conductivity, judging by the positive sign of the thermoelectric emf. $TlBiTe_3$ has a negative thermoelectric-emf coefficient and, consequently, electronic conductivity. Thus, alloys of the system have a very wide range of variation of the thermoelectric-emf coefficient, from +800 μV/deg for Tl_2Te_3 to

−1482 μV/deg for Tl_2Te_3−$TlBiTe_3$; and the combination of materials with the most extreme values (Tl_2Te_3−$TlBiTe_3$) makes it possible to obtain a thermoelement with $E = 2282$ μV/deg.

The approximately measured thermal conductivity of $TlBiTe_3$ is half an order of magnitude higher than that of Bi_2Te_3 and is equal to $\chi = 0.0273$ cal/g · cm · sec.

Fig. 3. Dependence of thermoelectric emf on the composition of alloys

Thus, in the Tl_2Te_3−Bi_2Te_3 system, a new semiconductor compound, $TlBiTe_3$, melting at 600°C, has been found, and the region of solid solutions based on Bi_2Te_3 has been determined within concentrations up to 95 at. % Bi_2Te_3.

The new compound $TlBiTe_3$ has high electrical conductivity and a high thermoelectric-emf coefficient, along with comparatively low thermal conductivity, which makes it possible to recommend it as a promising thermomaterial.

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CITED LITERATURE

1. A. Rabenau, A. Stegberr, P. Eckerlin, *Zs. Metallkunde*, **51**, 5, 295 (1960).

Note: Figure translations are in progress. See original paper for figures.