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Abstract

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CHEMISTRY

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INVESTIGATION OF THE SnTe–GeTe SYSTEM

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In previous works (^{1,2}) pseudobinary systems formed by semiconductor compounds with the NaCl-type structure were investigated: PbSe–PbTe and SnTe–PbTe; it was shown that continuous solid solutions are formed in both systems.

In the present work the ternary system Sn–Ge–Te has been investigated along the SnTe–GeTe section. In both compounds metallic properties are manifested to a considerable degree.

The phase diagram of the Sn–Te system was studied by Pelabon (^{3}), Feem (^{4}), Biltz and Mecklenburg (^{5}), and Kobayasi (^{6}). In this system there is one chemical compound, SnTe, which melts with an open maximum at 790°. The heat of formation of the compound SnTe is equal to 14.65 kcal/mole (^{7}). On the isotherms of the magnetic susceptibility of liquid alloys a sharp minimum is observed, corresponding to the composition of the compound SnTe, which indicates a very slight degree of its dissociation (^{8}). No region of solid solutions based on the compound SnTe has been found. The compound SnTe has the NaCl-type structure with a constant of 6.285 Å (^{9}). According to our investigation (^{2}), the electrical conductivity of SnTe is 8350 $\Omega^{-1} \cdot \mathrm{cm}^{-1}$, and the thermoelectromotive force relative to copper is 21 μV/deg.

The phase diagram of the Ge–Te system was developed by Klemm and Frischmuth (^{10}). In this system there is one chemical compound, GeTe, melting by a peritectic reaction at 725°. Schubert and Fricke (^{11}) determined the crystal structure of the compound GeTe. At room temperature this compound has a rhombohedral face-centered lattice with parameters $a = 5.962$ Å and $\alpha = 88°21'$. With increasing temperature this lattice transforms into a cubic face-centered lattice of the NaCl type, with a constant equal to 5.986 Å at 460° on the germanium side and 5.97 Å at 390° on the tellurium side. This transition occurs gradually as the temperature increases. The difference in transition temperatures as a function of the composition of the alloys may be explained by the solubility of the components in the solid compound. In the opinion of

Fig. 1. Phase diagram of the SnTe–GeTe system

Figure 1: Fig. 1. Phase diagram of the SnTe–GeTe system

Fig. 2. Microhardness of the alloys

Figure 2: Fig. 2. Microhardness of the alloys

the authors of work (^{11}), the boundary of the region of solid solutions based on the compound GeTe on the tellurium side lies at a concentration of 50 at.% Te.

The phase diagram of the Sn–Ge system is of the eutectic type, with the eutectic lying very close to pure tin. The melting temperature of the eutectic is 232° (^{12}).

The starting materials for carrying out the present investigation were germanium with a resistivity of 10 $\Omega \cdot$cm, tin of grade 01, and tellurium of the second grade, purified by double distillation in vacuum, with contents of iron, silicon, aluminum, and magnesium of less than 0.01%. The specimens for the investigation were melted in evacuated quartz ampoules. The liquid alloys were mixed by repeated shaking of the ampoules and were then cooled in air. Annealing of the alloys for the investigation of properties was carried out at 450° for 320 hours, and annealing for X-ray analysis at 500°. After

After annealing, the ampoules with the alloys sealed in them were removed from the furnace and cooled in air. The equilibrium state of the alloys was checked by examining the microstructure. The specimens were etched with diluted (1 : 1) nitric acid. This etchant colors SnTe dark and GeTe lighter. Thermal analysis was carried out by recording cooling curves of cast alloys and heating curves of annealed alloys on an N. S. Kurnakov pyrometer using a differential thermocouple. The reference standard was an alloy of 75% PbSe and 25% PbTe, brought to equilibrium by prolonged annealing.

Fig. 1. Phase diagram of the SnTe–GeTe system

Fig. 2. Microhardness of the alloys

X-ray patterns were taken in Debye cameras using iron radiation. Microhardness was measured on a PMT-2 instrument under a load of 20 g. The electrical conductivity and thermoelectromotive force were studied with a PPTV-1 potentiometer. The thermoelectromotive force was measured relative to copper.

Table 1

Lattice constants of the alloys

SnTe, wt. %	GeTe, wt. %	a, Å	α
100	0	6.29	90°
80	20	6.24	89°40′

SnTe, wt. %	GeTe, wt. %	a, Å	α
60	40	6.16	89°26′
40	60	6.10	88°58′
20	80	6.04	88°35′
1	100	5.94	88°22′

The results of the thermal analysis are shown in Fig. 1. The liquidus and solidus lines pass through a minimum at a concentration of about 80% GeTe and a temperature of 700°. All curves on the thermograms had the form typical for the crystallization of solid solutions. Examination of the microstructure of the alloys showed the formation of a continuous series of solid solutions: after annealing, the alloys were single-phase and had a polyhedral coarse-crystalline structure. In cast, rapidly cooled alloys, the crystals, after etching of the specimens, were colored nonuniformly as a result of dendritic segregation.

The results of thermal analysis and examination of the microstructure are confirmed by X-ray analysis and by the study of the properties of the alloys: X-ray patterns of the annealed alloys showed a gradual transition from the cubic face-centered lattice of the SnTe compound to the rhombohedral face-centered lattice of the GeTe compound.

Table 1 gives the values of the lattice constants of the alloys studied.

The microhardness of the alloys varies with composition along a curve with a maximum (Fig. 2). The electrical conductivity of the cast alloys varies along a curve with a minimum (Fig. 3), while the thermoelectromotive force of the cast and annealed alloys follows a curve with a maximum (Fig. 4). (The electrical conductivity of the annealed alloys was not measured because of the great brittleness of the alloys lying in the middle part of the system.) The change in the properties of the alloys is

characteristic of systems in which a continuous series of solid solutions is formed.

The investigation carried out on the Sn—Ge—Te system showed that, in this system, along the section between the two nonisostructural compounds

Fig. 3. Electrical conductivity of alloys

Fig. 4. Thermoelectromotive force of alloys

SnTe and GeTe, a continuous series of solid solutions with a minimum on the melting diagram is formed; the face-centered cubic lattice of the SnTe compound gradually changes into the face-centered rhombohedral lattice of the GeTe compound.

Fig. 3. Electrical conductivity of alloys

Figure 3: Fig. 3. Electrical conductivity of alloys

Fig. 4. Thermoelectromotive force of alloys

Figure 4: Fig. 4. Thermoelectromotive force of alloys

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