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Abstract

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A NEW SEMICONDUCTING PHASE IN THE ZINC-ANTIMONY SYSTEM

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The intermetallic compound Zn_4Sb_3 in the Zn—Sb system was first discovered by Taken (^{1}). Subsequently the existence of this compound was confirmed by other authors ($^{1-3}$).

At present it is known that the intermetallic Zn_4Sb_3, in contrast to ZnSb, crystallizes in a monoclinic cell (^{3}). More precisely, the β-modification of Zn_4Sb_3 possesses a monoclinic lattice; at about 485–491° it transforms into γ-Zn_4Sb_3. In the temperature interval from $-10°$ to $-20°$ β-Zn_4Sb_3 probably transforms into the α-modification (^{1}).

The physicochemical and electrical properties of the intermetallic compound Zn_4Sb_3 have not been studied. At the same time, another compound in the Zn—Sb system, namely ZnSb, is an intermetallic semiconductor that has already found practical application. A semiconductor in the same system is also the compound Cd_4Sb_3 (^{4,5}). Therefore it was natural to assume a semiconducting character for the compound Zn_4Sb_3. For this purpose we chose the β-modification of Zn_4Sb_3, which exists stably from $-10°$ to 485°.

The compound Zn_4Sb_3 was obtained by melting calculated amounts of the components in evacuated quartz ampoules. The melt was held somewhat above the melting temperature of Zn_4Sb_3 with continuous vibrational stirring. The starting zinc of grade TsO was subjected to double vacuum distillation by the method described in (^{6}). Antimony of grade SuOOO was used. Samples of stoichiometric composition were investigated; the accuracy of maintaining stoichiometry was $2 \cdot 10^{-3}\%$.

We obtained three series of samples of the compound Zn_4Sb_3. The samples of series A were obtained by quenching the melt in ice water. As microstructural and thermographic investigations showed, such "quenching" leads only to the formation of fine crystals of the β-modification of Zn_4Sb_3. Even at room temperature we never observed the high-temperature phase γ-Zn_4Sb_3 in the quenched samples. This is evidently explained by the fact that the rate of transformation of γ-Zn_4Sb_3 into β-Zn_4Sb_3 exceeds the cooling rate that was achieved in our experiments. In Fig. 1 (on the inset, see p. 1353) we present the microstructure of β-Zn_4Sb_3 obtained by rapid cooling of the melt.

The samples of series B were obtained by slow cooling of the melt according to a special schedule and had a coarse-crystalline structure. The homogeneity of the alloys was monitored microstructurally, with the aid of a thermoprobe, and also thermographically using a combined thermocouple. On the ordinary and differential records of the heating curves of samples of all series, only two endothermic effects are observed, corresponding to the polymorphic β—γ transformation and to the incongruent melting of Zn_4Sb_3. For illustration we give the thermogram of sample B3 (Fig. 2).

The samples of series V, obtained by zone recrystallization of alloys of series B, were single crystals (checked by taking Laue patterns). To prevent disturbance of stoichiometry, zone recrystalliza-

tion was carried out by the method of zone melting of decomposing compounds (^{7}), the rate of motion of the zone being 3 cm/hour. In this case the specimen for measurement was cut in the form of a rectangular parallelepiped from a single-crystal ingot in the longitudinal direction.

In appearance, the compound Zn_4Sb_3 is a gray substance with a metallic luster, rather brittle, with a slightly glassy, conchoidal fracture. Its microhardness is about 200 kg/mm^2. The pycnometric specific gravity of large crystals is 6.81. Zn_4Sb_3 is readily etched by a mixture of 2 parts 2.5% HF, 4 parts perhydrol, and 4 parts glycerin for 4-6 min.

Fig. 2. Thermogram of specimen B3

We measured the temperature dependence of the electrical conductivity and thermoe.m.f. of the compound Zn_4Sb_3 in the interval from 20° to 400°. The Hall constant was measured at room temperature; an electromagnet with a field strength in the gap of 2500 oersted served as the source of the magnetic field. Electrical measurements were carried out on the apparatus described in (^{8}), by a compensation circuit using the two-probe method.

All the specimens obtained had hole conductivity according to the sign of the thermoe.m.f. and the sign of the Hall effect. The results of electrical measurements carried out at room temperature are collected in Table 1. Measurements on specimens of the same series gave well-coinciding results.

As can be seen from the data of Table 1, zone recrystallization is effective also for purifying Zn_4Sb_3. In particular, for specimen B8 the table gives data after three passes. Although our task was only to obtain single crystals, it may be thought that by means of the method of zone purification of decomposing compounds it is possible to achieve deep purification of the compound Zn_4Sb_3, as occurs in the case of obtaining ultrapure single crystals of indium antimonide by zone recrystallization (^{9}).

In Figs. 3 and 4 are shown the temperature dependences of the conductivity and thermoe.m.f. of the same specimens. The curves of the temperature dependence

Fig. 4. Dependence of the differential thermoe.m.f. on reciprocal temperature. The designations are the same

Figure 1: Fig. 4. Dependence of the differential thermoe.m.f. on reciprocal temperature. The designations are the same

of electrical conductivity (Fig. 3), together with the data of Table 1, indicate that the compound Zn_4Sb_3 is a semiconductor. The width of the forbidden band, found from the temperature graph of the specific conductivity, is 1.20 eV. Comparatively high values of the differential thermoe.m.f. also indicate the semiconducting nature of the intermetallic compound Zn_4Sb_3.

Fig. 3. Dependence of the specific conductivity on inverse temperature. B8 –zone recrystallization, B3 –slow cooling, A10 –rapid cooling

The metallic behavior of the conductivity in specimen A10 in the impurity region is evidently caused by the fact that, during quenching of the specimen, additional acceptors appear, due to imperfections of the lattice of the Zn_4Sb_3 crystals. This is confirmed by the larger concentration of holes and, as a consequence, by the higher conductivity of specimen A10 in comparison with B3 (see Table 1). Meanwhile, the chemical purity of the alloys should have been the same. The appearance of acceptor levels due to lattice defects

during rapid cooling in the quenching process increases the concentration of majority carriers and the conductivity by an entire order of magnitude. Owing to the high carrier concentration, the hole gas enters the region of energetic degeneracy, as a result of which semimetallic properties are observed in sample A10.

The rather smooth change of the differential thermoe.m.f. with temperature (Fig. 4) indicates that the samples in the region of impurity conduction are partially degenerate[10], which is most noticeable for sample A10.

Attention is drawn to the relatively high value of the hole mobility in sample B8 (998 $cm^2/V \cdot s$), for which the impurity content is still fairly high and is equal to $8.52 \cdot 10^{17}$ cm^{-3} (see Table 1). This is all the more interesting because the compound Zn_4Sb_3 has, for an intermetallic compound, a rather considerable band-gap width, equal to 1.20 eV. Thus, in the Zn–Sb system there is a second semiconductor compound, Zn_4Sb_3, along with the semiconductor ZnSb[11], whose band-gap widths differ by at least a factor of two.

Fig. 4. Dependence of the differential thermoe.m.f. on reciprocal temperature. The designations are the same.

Thus, in the zinc–antimony system a new semiconductor intermetallic phase, β-Zn_4Sb_3, has been found and characterized; single crystals of this substance have been obtained for the first time, and the possibility of purifying it by zone recrystallization has been shown.

Table 1

Some electrical properties of Zn_4Sb_3

Experimental series	Sample No.	Thermoe.m.f., μV/deg	Conductivity, $ohm^{-1} \cdot cm^{-1}$	Carrier conc., cm^{-3}	Mobility, $cm^2/V \cdot s$
B	B8	+162	136	$8.52 \cdot 10^{17}$	998
	3	+136	173	$1.65 \cdot 10^{18}$	649
A	A10	+128	1498	$1.98 \cdot 10^{19}$	470

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CITED LITERATURE

1. M. Hansen, K. Anderko, *Structure of Binary Alloys*, 2, Moscow, 1962, p. 1249.
2. Ya. A. Ugai, ZhNKh, **3**, 678 (1958).
3. V. Tyudlitat, Czechoslovak Journal of Physics, **9**, 638 (1959).
4. Ya. A. Ugai, Yu. Ya. Dolgova, T. A. Zyubina, DAN, **138**, 856 (1961).
5. A. Ya. Ugai, E. M. Avrosakhidze et al., *Fiz. tverd. tela*, **4**, 615 (1962).
6. V. M. Amonenko, A. A. Kruglykh, I. I. Papirov, *Fiz. met. i metalloved.*, **11**, 633 (1961).
7. J. Van den Boomgaard, F. A. Kröger, H. J. Vink, *J. Electronics*, **1**, 212 (1955).
8. O. V. Emel' yanenko, N. V. Trishin, *Pribory i tekhn. eksp.*, No. 1, 98 (1960).
9. K. I. Vinogradova, V. V. Galavanov et al., *Fiz. tverd. tela*, **1**, 403 (1959).
10. A. G. Samoilovich, L. L. Korenblit, UFN, **57**, 577 (1955).
11. S. S. Shalyt, in the collection *Semiconductors in Science and Technology*, **1**, 1957, p. 82.

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