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Ya. A. Ugai, Yu. P. Zavalskii, V. A. Ugai,

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Abstract

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**Ya. A. Ugai, Yu. P. Zavalskii, V. A. Ugai,
S. A. Mostovaya, L. A. Bitutskaya**

Tin Arsenide—a New Intermetallic Semiconductor

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In the Sn—As system there is the compound Sn_3As_2 (tin arsenide), which crystallizes in a rhombohedral cell (^{1}). There are grounds for assuming that tin arsenide is a semiconductor. First, this substance is formed according to the rules of valence; in its ionic formula tin is positively divalent, and arsenic is negatively trivalent. Second, in the macrodiagram of the state of the Sn—As system (^{1}), near the ordinate of tin arsenide there are no visible regions of homogeneity. Finally, similarly constructed zinc and cadmium arsenides (Zn_3As_2 and Cd_3As_2) are typical semiconductors (^{2}).

Moreover, as far as we know, tin arsenide has not been obtained as an independent physicochemical individual, and its properties have not been investigated, apart from an attempt to measure the electrical conductivity of an alloy corresponding to the composition Sn_3As_2 (^{3}).

The synthesis of tin arsenide was carried out by us by two methods: direct fusion of the components (the metallurgical method) and precipitation of it from a solution of a soluble tin salt (the preparative chemical method).

To obtain Sn_3As_2 by the first method, calculated amounts of metallic tin and arsenic were fused in evacuated quartz ampoules with continuous vibrational stirring (frequency 100 Hz, amplitude 1.5 mm). In calculating the starting components, the high volatility of arsenic was taken into account; the vapor pressure of arsenic at 600° is 7 times greater than the vapor pressure of tin. Therefore, in order to obtain Sn_3As_2 as close as possible to the stoichiometric composition, it is necessary to maintain above the melt an equilibrium vapor pressure of the more volatile component. In our experiments this was achieved by taking a weight excess of arsenic relative to stoichiometry. In the calculations, the free volume of the ampoule and the synthesis temperature were taken into account, as well as the atomicity of the arsenic molecules under these conditions. According to our calculations, to obtain tin arsenide of stoichiometric composition with the optimal dimensions of the ampoules used by us, an arsenic excess of 4.4 wt.% is required. Figure 1 shows the microstructure of a polycrystal of arsenic arsenide obtained with an excess of 4.0 wt.% arsenic. If an excess of As of 5

Fig. 2. Plot of the dependence of the logarithm of the electrical conductivity on reciprocal temperature for a metallurgical sample of Sn_3As_2

Figure 1: Fig. 2. Plot of the dependence of the logarithm of the electrical conductivity on reciprocal temperature for a metallurgical sample of Sn_3As_2

wt.% relative to stoichiometry is taken, then segregation of elemental arsenic is observed along the grain boundaries. With an excess amount of arsenic of 4.4 wt.%, the microstructure of Sn_3As_2 is the same as in Fig. 1, only the dark boundaries of the individual grains are still narrower.

The compound Sn_3As_2 is silver-gray in color, brittle, with a clearly pronounced layered structure on fracture. Its melting point according to our data is 598°, its pycnometric specific gravity is 6.44 g/cm^3, and its microhardness is 114.5 kg/mm^2. In air under room conditions tin arsenide does not change; when heated it oxidizes. Sn_3As_2 does not react with water. Under the action of hydrochloric acid it does not change, while nitric acid gives

white precipitate of metastannic acid. In alkalis, tin arsenide does not dissolve.

According to the sign of the thermo-emf, the conductivity type of the compound Sn_3As_2 proved to be hole-type. The differential thermo-emf at room temperature is 10 and decreases to 6 μV/deg at 200°. The Hall constant is $7.2 \cdot 10^{-3}$ cm^3/C, and the carrier concentration is $8.7 \cdot 10^{20}$ cm^{-3} at room temperature. The Hall mobility of the holes under these conditions is 270 cm^2/V $\cdot$ s, and the specific electrical conductivity is $3.7 \cdot 10^4\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$.

In Fig. 2 we give a plot of the temperature behavior of the conductivity for one of the polycrystalline samples of the compound Sn_3As_2.

Fig. 2. Plot of the dependence of the logarithm of the electrical conductivity on reciprocal temperature for a metallurgical sample of Sn_3As_2

A similar dependence of electrical conductivity on temperature is exhibited by all the investigated samples of tin arsenide obtained with an excess arsenic content relative to the stoichiometric one, from 4 to 5 wt.% in steps of 0.1%. Heating to 400° does not reveal a semiconducting course of electrical conductivity. The curves of the temperature dependence of conductivity were taken under conditions excluding oxidation of the samples.

Thus, the data from the study of the electrical properties of tin arsenide obtained by the metallurgical method indicate its metallic nature: a small thermo-emf, a large value of specific conductivity, a high concentration of current carriers, and a negative temperature coefficient of electrical conductivity. If one takes into account that starting substances of high purity were used for the synthesis of tin arsenide (arsenic grade V5 and tin OVCh-000), then the reason for this may be a strong violation of the stoichiometric composition in the metallurgical method of obtaining Sn_3As_2. In addition, X-ray spectral analysis of tin in Sn_3As_2 showed that in it there is no overlap of the bands of valence electrons not participating in chemical bonds. Therefore the metallic character of the conductivity of tin arsenide cannot be explained by overlap of the bands of these electrons.

Since, in our opinion, the main reason for the metallicity of tin arsenide obtained by fusing the components is a violation of stoichiometry, we decided to obtain this substance chemically by precipitation from solution. For this purpose a stream of dry arsine was passed into a saturated solution of stannous chloride in absolute alcohol. It is well known, for example, that when even the less stable stibine is passed through a solution of silver nitrate, a precipitate of Ag_3Sb is formed ([4]). To avoid decomposition of arsine during the experiment, the entire system was cooled with ice water. Arsine was obtained by reducing an alkaline solution of sodium arsenite with hydrogen at the moment of evolution. As arsine was passed through, the solution became opaque. The color of the solution changed from light yellow through brown to black. The precipitation reaction was carried out for 6-7 h. The precipitate was separated from the mother liquor by centrifugation and washed first with alcohol and then with water until chloride ions disappeared. The well-washed precipitate was dried at 60–70° in an argon atmosphere.

The powder of precipitated Sn_3As_2 is quite stable in air. It begins to oxidize noticeably at temperatures above 250°. It does not dissolve in sulfuric or hydrochloric acids, nor in alkalis. It is slowly decomposed by concentrated nitric acid. In this process arsine and metastannic acid are evolved.

Quantitative analysis of Sn_3As_2 obtained chemically, pro—

To the article by Ya. A. Ugai, Yu. P. Zaval' skii et al., p. 663

Fig. 1. Microstructure of a polycrystal of Sn_3As_2 obtained by the metallurgical method with an excess of 4.0 wt.% arsenic relative to stoichiometry. 200×, etchant $FeCl_3 + HCl$

Fig. 3. X-ray diffraction patterns of various Sn_3As_2 samples: *a* —precipitated and annealed; *b* —obtained by the metallurgical method

was converted into tin, and arsenic was found by difference. Tin was determined colorimetrically by the phosphomolybdate method (^5). The advantage of this method is that admixtures of arsenic, antimony, bismuth, cadmium, zinc, and iron do not interfere with the quantitative determination of tin in solution. The sample was dissolved in aqua regia. The average value of the tin content in the weighed sample, found from three separate determinations, was 70.34 wt.%, which confirms the formula of tin arsenide.

An X-ray diffraction analysis was carried out on metallurgical and deposited samples of tin arsenide. X-ray films of the deposited and unannealed samples, after prolonged exposure, revealed barely noticeable X-ray lines against a strong general background. In other words, freshly deposited Sn_3As_2 has a very finely dispersed structure. The Debye patterns of the annealed and metallurgical samples of tin arsenide are completely analogous (Fig. 3a, b). Annealing of

Fig. 4. Graph of the temperature dependence of the specific conductivity of deposited and annealed tin arsenide

Figure 2: Fig. 4. Graph of the temperature dependence of the specific conductivity of deposited and annealed tin arsenide

Sn_3As_2 obtained chemically was carried out in evacuated and argon-filled glass ampoules at a temperature of 300° for 3 hours.

Fig. 4. Graph of the temperature dependence of the specific conductivity of deposited and annealed tin arsenide

To measure the temperature dependence of electrical conductivity, the deposited powdery Sn_3As_2 was pressed under a pressure of 2500 kg/cm^2. The specific conductivity of the pressed tin arsenide samples was of the order of $10^{-6}\ \Omega^{-1}\cdot\text{cm}^{-1}$. Annealing increases the electrical conductivity by 3–4 orders of magnitude. In Fig. 4 we give one of the typical curves of the temperature dependence of the electrical conductivity of tin arsenide obtained chemically and annealed. The reproducibility of such graphs is satisfactory. As can be seen from Fig. 4, deposited Sn_3As_2, in contrast to metallurgical Sn_3As_2, is a typical impurity semiconductor. Its thermal band gap is 0.47 eV. Intrinsic conductivity begins at a temperature of about 100°.

Thus, using tin arsenide as an example, we are convinced that, in order to decide unambiguously whether an intermetallic compound belongs to metals or semiconductors, it is not sufficient to study only "metallurgical" samples of this substance obtained by fusing the initial components. In the case of a significant violation of stoichiometric composition during the preparation of the intermetallic compound, impurity levels of superstoichiometric atoms (when their solubility in the host lattice is sufficiently large) may split and form an impurity band. If the latter overlaps with the conduction band or the valence band, then the potential semiconductor turns into a metal. Obviously, when Sn_3As_2 is obtained by the metallurgical method, one of the components dissolves in it in sufficient amounts to form an impurity band overlapping with the valence band, as a result of which a metallic type of conduction is observed. In addition, because of the high concentration of charge carriers, degeneration of the hole gas takes place.

We studied the temperature dependence of the electrical conductivity of a metallurgical sample of tin arsenide up to 400°. This is a rather high temperature for a substance melting at 598°. In any case, intrinsic conductivity should set in well below 400° for a substance with a band gap of 0.47 eV. Hence it is quite clear that Sn_3As_2 obtained by the metallurgical method has metallic conductivity up to melting. It is possible that, upon the onset of intrinsic conductivity, the concentration of charge carriers in Sn_3As_2 increases, but this

the increase is compensated by a simultaneous decrease in their mobility, as a result of which the metallic character of the conductivity is preserved.

When tin arsenide is obtained by the preparative chemical method, conditions for a strong disturbance of the stoichiometric composition are excluded, and consequently impurity levels do not degenerate into an impurity band. According to the reaction, when three molecules of stannous chloride and two molecules of arsine interact, only one formula unit of tin arsenide is always formed, in accordance with the equation: $3SnCl_2 + 2AsH_3 = Sn_3As_2 + 6HCl$. Therefore there can be no question here of a disturbance of the stoichiometric composition. Moreover, the reaction is carried out at a temperature below room temperature. Hence the tin arsenide precipitated from solution incorporates only impurities of foreign atoms, the total content of which is many times smaller than that of the superstoichiometric atoms in the case of the metallurgical method of obtaining Sn_3As_2. For this reason, tin arsenide precipitated from solution is a typical impurity semiconductor. Thus, in reality the compound Sn_3As_2 is a new semiconducting intermetallic compound.

Voronezh State University
Voronezh Technological Institute

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REFERENCES

[1] M. Hansen, K. Anderko, *Structures of Binary Alloys*, 1, Moscow, 1962. [2] *Semiconductors in Science and Technology*, 1, Publishing House of the USSR Academy of Sciences, 1957. [3] M. Padoa, *Gazz. Chim. Ital.*, **55**, 975 (1925). [4] B. V. Nekrasov, *Course of General Chemistry*, Moscow, 1952. [5] N. A. Suvorovskaya, V. I. Titov et al., *Technical Analysis in Nonferrous Metallurgy*, Moscow, 1957.

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