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The Intermetallic Compound Cd_4Sb_3

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In connection with a systematic study of semiconductor compounds of antimony with elements of the second group of the periodic system, the Cd–Sb system was subjected to careful examination. According to the literature data (ˆ1), cadmium and antimony form only two compounds: CdSb and Cd_3Sb_2. The first compound is considered stable, and the second metastable.

We studied the Cd–Sb system by methods of thermal analysis and X-ray diffraction, microstructure and microhardness, electrical conductivity, and thermoelectric emf. The alloys for measuring electrical conductivity and thermoelectric emf were prepared from cadmium containing not more than $5 \cdot 10^{-3}\%$ impurities and antimony of the Su000 grade. For the other studies, cadmium of the Kd0 grade and antimony of the Su00 grade were used. The accuracy of weighing was 10^{-4} g.

In all, three series of alloys were studied, prepared by melting the components in Pyrex ampoules evacuated to $7 \cdot 10^{-3}$ mm Hg. The ampoules were heated to 650°, and the melt was thoroughly mixed for 5 hours by turning over and shaking the ampoules at a temperature of 500–550°. The first series of alloys was cooled in air, the second—together with the furnace at a rate of 1–1.5° per 1 min. The alloys of the third series were subjected to a week-long anneal at various temperatures (from 250 to 420°), depending on composition. Control chemical analysis showed that, under the conditions we adopted for preparation and heat treatment of the alloys, their composition corresponded to the synthesized composition. The accuracy of determination of antimony and cadmium was of the order of 0.05%. More than 20 different compositions were investigated (over 60 alloy specimens), especially in detail near the compounds Cd_3Sb_2 and CdSb.

Thermograms were recorded on a Kurnakov FPK-55 pyrometer using a circuit for programmed temperature control. The conditions of thermal analysis were the same for all alloys: an evacuated Stepanov vessel, the mass of the sample and standard, the furnace heating rate, the resistances to the simple and differential thermocouples, etc. For compositions in the crystallization region of CdSb and Cd_3Sb_2, cooling curves were recorded in an atmosphere of dry carbon dioxide with the use of appropriate seed crystals.

X-ray studies were carried out by the Debye–Scherrer method. X-ray diffraction patterns were taken in a standard camera with a diameter of 57.3 mm.

Figure 3

Figure 1: Figure 3

Figure 1

Figure 2: Figure 1

On the basis of analysis of the heating and cooling curves of alloys of all series, as well as the results of interpretation of X-ray diffraction patterns, studies of microhardness and microstructure, electrical conductivity, and thermoelectric emf, a phase diagram of the Cd—Sb system was constructed (Fig. 1). Without discussing the phase diagram as a whole, we wish only to draw attention to the presence of a new compound, Cd_4Sb_3 (44.9 wt.% Sb). The compound Cd_4Sb_3 melts congruently at a temperature of 460°.

The microstructure of the compound Cd_4Sb_3 (Fig. 2) confirms its complete homogeneity; it differs from the microstructure of the other phases of the system. For comparison, in the same Fig. 2 we give the microstructure of an alloy 30% Sb + 70% Cd, where large crystals of the Cd_3Sb_2 compound, closest in composition to the compound Cd_4Sb_3 under discussion, are visible against the dark background of the eutectic. The microhardness of Cd_4Sb_3 proved to be 180 kg/mm^2; it does not coincide with the microhardness of the compounds CdSb and Cd_3Sb_2.

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Fig. 3. Debyegrams of the compounds: a —CdSb; b —Cd_3Sb_2; c —Cd_4Sb_3

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Fig. 1. Electrophoregrams of blood plasma: upper —rabbit, lower —cat

In contrast to the other compounds of the Cd—Sb system, the compound Cd_4Sb_3 is obtained upon rapid cooling (alloys of the first series). In general, among all Cd—Sb systems, the compound Cd_4Sb_3 is obtained most simply and easily. In this connection it is interesting to note that on the "composition—height of the differential-recording peak" diagram ([2]), the compound Cd_4Sb_3 corresponds to a sharp maximum. To construct this diagram we took the height of the exothermic peak of the differential record corresponding to crystallization on the cooling curves of various compositions.

Figure 3 gives Debyegrams for three compounds: CdSb, Cd_3Sb_2, and Cd_4Sb_3. The sharp difference in the position and intensity of the diffraction lines for Cd_4Sb_3 is noteworthy. Consequently, X-ray analysis also confirms the existence of the compound Cd_4Sb_3 as an independent chemical individual.

Measurement of the X-ray lines, as well as analysis of the character of the variation of $\sin^2 \vartheta$, shows that the compound Cd_4Sb_3 has a tetragonal lattice, presumably of the rutile structural type, with parameters $a = 8.1$ Å, $c = 13.0$

Fig. 1. Phase diagram of the Cd–Sb system (according to the authors' data)

Figure 3: Fig. 1. Phase diagram of the Cd–Sb system (according to the authors' data)

Å, $c/a = 1.6$. The compound CdSb crystallizes in the rhombic system, and Cd_3Sb_2 in the monoclinic system (^{3}).

Fig. 1. Phase diagram of the Cd–Sb system (according to the authors' data)

In pure form, the compound Cd_4Sb_3 consists of silvery-gray, lustrous, very brittle crystals. Its fracture is conchoidal, similar to the fracture of germanium. Even in appearance Cd_4Sb_3 differs strongly from the other compounds of the Cd–Sb system. Cd_4Sb_3 crystals are readily etched in a mixture of nitric acid and hydrogen peroxide. When heated in air, the compound Cd_4Sb_3 oxidizes less than the other phases of the Cd–Sb system. Its specific conductivity at room temperature is $20\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$. The largest value of the thermoelectric emf that we observed for it is 420 μV/deg. At elevated temperatures the thermoelectric emf decreases strongly. The temperature dependence of the electrical conductivity of the compound Cd_4Sb_3 is typically semiconducting.

By the Bridgman method (^{4}), single crystals (checked by Lauegrams) of the new compound Cd_4Sb_3 were obtained. Examining the surface of Cd_4Sb_3 single crystals, one can observe spiral-type steps (Fig. 4), the formation of which is interpreted by a number of authors as the result of growth along a screw dislocation with a large Burgers vector. We note that the formation of spiral steps is also observed during the growth of crystals with a layered structure. Almost all compounds on which such steps are observed yield, upon rapid cooling, larger crystals. We have established experimentally that with increasing cooling rate the size of Cd_4Sb_3 crystals increases greatly.

Finally, the ability of the compound Cd_4Sb_3 to dissolve excess amounts of antimony relative to stoichiometry is of some interest. With decreasing temperature, the homogeneity range based on Cd_4Sb_3 narrows, and an excess phase separates out. At room temperature Cd_4Sb_3 dissolves up to 2% antimony. At the same time, this compound practically does not dissolve excess cadmium. Both the pure compound Cd_4Sb_3 and solid solutions of antimony in it have hole conductivity (according to the sign of the thermo-

Fig. 2. *a* –microstructure of a composition corresponding to the compound Cd_4Sb_3; *b* –microstructure of a composition 70% Cd + 30% Sb

Fig. 4. Spiral-type steps on a Cd_4Sb_3 single crystal

etc.). In contrast, the compound CdSb with an excess of antimony has electronic conductivity (^{5}).

Thus, on the basis of the experimental material set forth above, one can draw the unambiguous conclusion that the compound Cd_4Sb_3 objectively exists, analogously to the compound Zn_4Sb_3 in the Zn—Sb system (1).

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