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Investigation of Phase Equilibrium in Systems Formed by Antimony Chalcogenides

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Chalcogenides of elements of group V of D. I. Mendeleev' s periodic system, and especially solid solutions based on them, have long attracted the attention of researchers. A large number of works have been devoted to a detailed study of bismuth chalcogenides, as well as of complex systems based on them.

Earlier investigations of bismuth chalcogenides made it possible to gain a deeper understanding of the nature of conductivity in these substances, to establish the relation between their crystal-chemical nature and the physical properties of the phases formed, and also to find a whole series of new materials for use in photo- and thermoelements.

Phase equilibria in systems formed by antimony chalcogenides have not been investigated up to the present time. Only the properties and crystal structure of individual compounds have been studied.

In the present work the phase equilibria and certain physical properties in the systems $Sb_2S_3-Sb_2Se_3$ and $Sb_2Se_3-Sb_2Te_3$ have been investigated. The compound Sb_2S_3 melts with an open maximum at 555° (^{1}). This compound crystallizes in an orthorhombic lattice, structural type D_5^8, with constants $a = 11.22$ Å, $b = 11.30$ Å, and $c = 3.84$ Å (^{2}). The compound Sb_2Se_3 melts with an open maximum. The melting temperature of Sb_2Se_3, according to data of various authors, differs and lies in the range 575–617° (^{1}). This compound is isomorphous with Sb_2S_3; lattice constants: $a = 11.62$ Å, $b = 11.77$ Å, and $c = 3.962$ Å (^{3}). The compound Sb_2Te_3, like the two preceding compounds, melts with an open maximum at 622° (^{1}). According to the data of work (^{4}), this compound at room temperature deviates from stoichiometry and corresponds to a composition of 59.17 mole % Te.

In contrast to the two preceding compounds, Sb_2Te_3 crystallizes in the tetradymite structure, structural type C33 (^{5}). Lattice constants: $a = 4.26$ Å and $c = 30.42$ Å.

The starting materials used were: antimony SU-000 with contents of Te, As, Pb, Al, Cu (about $1 \cdot 10^{-4}$%); sulfur, twice sublimed in vacuum, with contents of Mg < 0.001, As < 0.01, Fe and Al $< 1 \cdot 10^{-4}$%; reactive selenium with contents

Figure 3

Figure 1: Figure 3

Fig. 1. Phase diagram of the Sb_2S_3–Sb_2Se_3 system

Figure 2: Fig. 1. Phase diagram of the Sb_2S_3–Sb_2Se_3 system

of Pb, Fe, Cu < 0.01, Te < 0.1%; tellurium, remelted from powder and twice sublimed in vacuum, with contents of Mg, Pb, Cu, Bi, Ca, Fe, Al–traces. The content of impurities in the starting materials was determined by qualitative spectral analysis. The alloys were prepared from charges corresponding to the composition of the binary compounds. The Sb_2Te_3 charge was prepared taking into account the deviation of the compound from stoichiometry, according to work (^{4}). Charges and alloys were prepared in evacuated sealed quartz ampoules. After melting of the charge, the ampoules with alloys of the Sb_2Se_3–Sb_2Te_3 system were removed from the furnace and rapidly cooled in air. Alloys of the Sb_2S_3–Sb_2Se_3 system, after melting, were cooled together with the furnace. To bring them to the equilibrium state, the alloys were annealed for a long time over the course of several months in sealed ampoules filled with argon, at a temperature of 500° for alloys of the Sb_2S_3–Sb_2Se_3 system and 520–560° for the Sb_2Se_3–Sb_2Te_3 system. Greater tem-

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Fig. 3. Microstructure of alloys, \$$\times 200. **a** — alloy 90 mol. \{2\}S\{3\}, 10 mol. \{2\}Se\{3\}, annealed; ** b ** — alloy 75 mol. \{2\}S\{3\}, 25 mol. \{2\}Se\{3\}, annealed; **c** — alloy 58.5 mol. \{2\}Te\{3\}, 41.5 mol. \{2\}Se\{3\}, as-cast; * * d * * — alloy 58.5 mol. \{2\}Te\{3\}, 41.5 mol. \{2\}Se\{3\}, annealed; * * e * * — alloy 16 mol. \{2\}Te\{3\}, 84 mol. \{2\}Se\{3\}, as-cast; **f** — alloy 20.2 mol. \{2\}Te\{3\}, 79.8 mol. \{2\}Se\{3\}$\$, as-cast.

Alloys lying in the region of the solid solution based on Sb_2Te_3 were subjected to annealing.

The alloys of the Sb_2Se_3–Sb_2Te_3 system reached equilibrium more rapidly when vibrational stirring of the melt was used, followed by holding for 8 h in the liquid-solid state and subsequent cooling together with the furnace in which the melts were prepared. Attainment of equilibrium in the systems under study was monitored by examination of the microstructure. In the Sb_2S_3–Sb_2Se_3 system the polished sections were etched with a 5% solution of $FeCl_3$ in HCl, while alloys rich in antimony selenide were etched with a 5% solution of NaOH in water. In the Sb_2Se_3–Sb_2Te_3 system, the polished sections of cast alloys were etched with a solution of aqua regia in alcohol (1 : 1/2), and those of annealed alloys–in the region of solid solution–with a 5% solution of $FeCl_3$ in HCl.

Fig. 1. Phase diagram of the Sb_2S_3–Sb_2Se_3 system

Differential thermal analysis was carried out by recording heating curves of equilibrium alloys on an N. S. Kurnakov pyrometer in Stepanov quartz vessels.

Fig. 2. Phase diagram of the Sb_2Se_3–Sb_2Te_3 system

Figure 3: Fig. 2. Phase diagram of the Sb_2Se_3–Sb_2Te_3 system

The chemical compound SnTe served as the standard in the thermal analysis.

Because of the large supercooling of the alloys of the Sb_2S_3–Sb_2Se_3 system observed during crystallization, the liquidus and solidus lines for this system were constructed from heating curves of equilibrium alloys.

Fig. 2. Phase diagram of the Sb_2Se_3–Sb_2Te_3 system.
a –single-phase alloys, *b* –two-phase alloys

For alloys of the Sb_2Se_3–Sb_2Te_3 system, the liquidus was constructed from cooling curves, and the solidus from heating curves.

The phase diagram of the Sb_2S_3–Sb_2Se_3 system, constructed from thermal-analysis data and microstructural study, is shown in Fig. 1. A continuous series of solid solutions with a minimum is formed in this system. The minimum lies at a concentration of 27 mol.% Sb_2Se_3 and 545°. Annealed alloys over the entire concentration range had a single-phase polyhedral structure with uniform grain coloration (Fig. 3 *a*, *b*). X-ray analysis confirmed that all the alloys studied had the structure of antimony sulfide.

Measurements of the microhardness and thermal conductivity of alloys annealed at 500° showed a continuous variation of these properties as a function of alloy composition. The microhardness has a shallow maximum lying somewhat closer to the Sb_2S_3 compound and corresponding to a value of the order of 140 kg/mm^2. The thermal conductivity has a shallow minimum lying closer to the Sb_2Se_3 compound and corresponding to a value of about 2 cal/cm · sec °C.

The phase diagram of the Sb_2Se_3–Sb_2Te_3 system, of eutectic type with limited regions of solid solutions, is shown in Fig. 2. The eutectic is formed at a concentration of 18 mol.% Sb_2Te_3 and a temperature of 560°. At the eutectic temperature, about 5 mol.% Sb_2Te_3 dissolves in solid Sb_2Se_3. On the Sb_2Te_3 side there extends a broad region of solid-

solid solutions, lying within the concentration range 34–100 mol.% Sb_2Te_3.

The phase diagram of the Sb_2Se_3–Sb_2Te_3 system, constructed from thermal-analysis data, is well confirmed by the study of the microstructure. Figure 3b shows the microstructure of a cast nonequilibrium alloy containing 58.5 mol.% Sb_2Te_3. This alloy lies in the region of the solid solution based on Sb_2Te_3. A zonal solid solution, formed because of slow diffusion in solid alloys, is clearly visible. The darker central part of the crystals is enriched in Sb_2Te_3; these regions of the crystals crystallize first. As crystallization proceeds, the alloy becomes enriched in Sb_2Se_3; in the photograph these regions of the crystals appear light in color. After annealing, the alloy has a polyhedral, single-phase structure (Fig. 3c). Figures 3d, e show the microstructure of two alloys lying in the two-phase region. The first of these alloys, containing 16 mol.% Sb_2Te_3, lies in the region of primary crystallization of the solid solution based on Sb_2Se_3; the crystals of the solid solution are white. The second figure shows the microstructure of an alloy with 20.2 mol.% Sb_2Te_3, lying in the field of primary crystallization of the solid solution based on Sb_2Te_3. The crystals of the solid solution separate in the form of needle-like crystals. In both figures the eutectic is clearly visible.

On cooling below the eutectic temperature, the limiting concentration of both solid solutions decreases. The boundaries of the solid-solution regions were determined by studying the microstructure of alloys brought to an equilibrium state at a given temperature and quenched from that temperature. Four series of alloys were prepared, their compositions differing by 1 mol.%. These alloys were annealed at 500 and 300° and then quenched in ice water.

Study of the microstructure of an alloy of composition 2 mol.% Sb_2Te_3, quenched from 500 and 300°, showed that the alloy has a single-phase polyhedral structure and, consequently, lies in the region of the solid solution based on the compound Sb_2Se_3. In an alloy of composition 4 mol.% Sb_2Te_3, quenched from 500°, precipitates of a second phase are clearly visible: the solid solution based on the compound Sb_2Te_3. In an alloy of the same composition quenched from 300°, no significant increase in the amount of the second phase was observed. This study made it possible to place the boundary of the limiting solubility of the solid solution based on Sb_2Se_3 between the compositions 2 mol.% Sb_2Te_3 and 4 mol.% Sb_2Te_3. Study of the microstructure of an alloy of composition 34 mol.% Sb_2Te_3, quenched from 500°, showed that a small amount of the second phase —the solid solution based on the compound Sb_2Se_3—separates along the boundary of the solid solution based on Sb_2Te_3. In an alloy of the same composition quenched from 300°, the amount of the second phase increased considerably. An alloy of composition 35 mol.% Sb_2Te_3, quenched from 500°, has a single-phase structure; consequently, the boundary of the solid solution based on Sb_2Te_3 at 500° lies between the compositions 34 mol.% Sb_2Te_3 and 35 mol.% Sb_2Te_3.

In the microstructure of an alloy of composition 38 mol.% Sb_2Te_3, quenched from 300°, slight precipitates of the second phase are visible, whereas an alloy of composition 39 mol.% Sb_2Te_3, quenched from 300°, has a single-phase structure; consequently, the boundary of the solid solution based on Sb_2Te_3 at 300° lies between the compositions 38 mol.% Sb_2Te_3 and 39 mol.% Sb_2Te_3. The properties of alloys lying in the region of solid solutions based on Sb_2Te_3 were measured.

The microhardness has a shallow minimum at a composition close to 55 mol.% Sb_2Te_3. The microhardness of an alloy of this composition corresponds to a value on the order of 50 kg/mm^2. The lattice thermal conductivity decreases as the concentration of Sb_2Se_3 increases.

Similar changes in microhardness and thermal conductivity were observed by some authors (^{6}) in a large group of compounds with the chalcopyrite structure, in the halide compounds of alkali metals.

The electrical conductivity decreases continuously as the content of Sb_2Se_3 increases.

The curves of the changes in properties in the investigated part of the system have no singular points indicating the presence of ordered structures in alloys annealed at 560°.

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[1] M. Hansen, *Constitution of Binary Alloys*; N. Y.—Toronto—London, 1958.
[2] W. Hoffmann, *Zs. Krystallogr.*, **86**, 225 (1933).
[3] N. W. Tideswell, F. H. Kruse, G. D. McCullough, *Acta Crystallogr.*, **10**, 99 (1957).
[4] H. Kh. Abrikosov, L. V. Poretskaya, I. P. Ivanova, *ZhNKh*, **4**, 2525 (1959).
[5] W. R. Beke-brede, O. G. Guentert, *J. Phys. Chem. Solids*, **23**, 1023 (1962).
[6] V. P. Zhuze, T. A. Kontorova, *ZhTF*, **28**, 1727 (1958).

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