

X-RAY INVESTIGATION OF SOME BISMUTH
AND ANTIMONY CHALCOGENIDES

(UDC 548.736)

M. M. Stasova

A. A. Baikov Metallurgy Institute

Translated from Zhurnal Strukturnoi Khimii, Vol. 5, No. 5,

pp. 793-794, September-October, 1964

Original article submitted January 31, 1964

We became interested in x-ray investigation of bismuth and antimony chalcogenides in connection with recently published papers [1-3] in which substantial changes were made in the phase diagrams of the binary systems Bi-Se, Bi-Te, and Sb-Te. In these studies the new compounds Bi_2Se , BiSe , Bi_2Te , BiTe , Sb_2Te , SbTe , and regions of solid solutions based on some of them were found by thermal analysis and microstructure investigation. The results were confirmed by measuring electrical conductivity and thermoelectromotive force.

Compound	a, Å	c, Å
Sb_2Te	4,26	17,8
BiSe	4,18	22,8
BiTe	4,40	24,0

The purpose of the present investigation was x-ray study of single crystals of some of the new compounds.

Samples for investigation were prepared by alloying stoichiometric quantities of the starting substances in vacuo. The alloys were stirred in the liquid state and then cooled to room temperature at a rate of 5° per h. The alloys were kept at their peritectic reaction temperatures for 4 h. The prepared samples were checked by microstructures for single-phase character and the absence of liquation. Only the alloys BiSe , BiTe , and Sb_2Te were obtained single-phase by slow cooling. The alloys Bi_2Se , Bi_2Te , and SbTe required subsequent prolonged annealing for homogenization. Owing to this, only the compounds BiSe , BiTe , and Sb_2Te were investigated further.

All alloys had a highly stratified, coarsely crystalline structure. For the x-ray work tablets ~ 0.1 mm thick, having the most even surfaces and the smallest number of cleavage steps, were selected from the samples. Small crystals having a cross section of $\sim 0.3 \times 0.3$ mm were pricked out from them. Laue photographs showed that all the compounds belong to Laue class D_{3d} . The threefold axis is perpendicular to the planes of the tablets. To determine the unit cell periods (see table) and space groups, we obtained scannings of the $h0l$ and $h1l$ planes of the reciprocal lattice in copper and molybdenum radiations, and scannings of the $h2l$ and $h3l$ planes in molybdenum radiation, using a reciprocal-lattice camera. Extinctions occur only in the $hk0$ plane: $h - k = 3n$. The periods a of the hexagonal unit cells are short; hence, the atoms can be located only in special positions on the verticals: $00z$, $\frac{1}{3} \frac{2}{3} z$, and $\frac{2}{3} \frac{1}{3} z$. These conditions, as well as the regular arrangement of reflections in the reciprocal-lattice planes, are consistent with the space groups D_{3d}^3 and C_{3v}^1 .

The x-ray photographs of all compounds under consideration are very similar to those of the known compounds Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 , which are isostructural with tetradymite [4-6]. The particularly intense reflections have l indices which are multiples of 3 for Sb_2Te , multiples of 4 for BiSe and BiTe , and multiples of 5 for tetradymite. These strong reflections form rhombohedral pseudocells, and for them the following condition is met: $h - k + l' = 3n$, where $l' = l/3$ for Sb_2Te , $l' = l/4$ for BiSe , and BiTe , and $l' = l/5$ for tetradymite. Presumably the structures under consideration, analogously to tetradymite, consist of atomic layers perpendicular to the z axis. However, if the hexagonal unit cell of tetradymite consists of 15 atomic layers, the hexagonal unit cell of Sb_2Te can contain only nine atomic layers, and the unit cells of BiSe and BiTe , 12 atomic layers.

We did not find the cubic modifications of BiSe and BiTe [6], which occur in thin films. Probably they appear when thin films are deposited by vacuum evaporation.

In connection with the results obtained, one cannot but mention two papers dealing with the phase diagrams of the binary systems under consideration. Brown and Lewis [7] deduce from powder patterns of alloys of the Bi-Te and Sb-Te systems that continuous regions of solid solutions exist in the Sb-Te system, based on Sb_2Te_3 , in the interval from 11 to 60 mole % Te, and in the Bi-Te system, based on Bi_2Te_3 , from 30 to 60 mole % Te. Godovikov [8], reasoning from the indexing of the powder pattern for the compound $\text{Bi}_{4.26}\text{Se}_3$, asserts that in the Bi-Se system a continuous region of solid solutions based on Bi_2Se_3 exists in the interval from 41.3 to 60 mole % Se. However, our x-ray determination of compounds found earlier by other methods in [1-3] confirms that in the binary systems Bi-Se, Bi-Te, and Sb-Te, several compounds exist which are very similar to the known compounds Bi_2Te_3 , Bi_2Se_3 , and Sb_2Te_3 . The new compounds cannot be regarded as solid solutions based on the corresponding tetradymite-type compounds.

The author thanks Professor N. Kh. Abrikosov for the proposed subject and his constant attention to the work.

LITERATURE CITED

1. N. Kh. Abrikosov and V. F. Bankina, *Zh. neorg. khim.*, 3, 3, 659 (1958).
2. N. Kh. Abrikosov, V. F. Bankina, and K. F. Kharitonovich, *Zh. neorg. khim.*, 5, 9, 2011 (1960).
3. N. Kh. Abrikosov, L. V. Poretskaya, and I. P. Ivanova, *Zh. neorg. khim.*, 4, 11, 2525 (1959).
4. E. Dönges, *Z. anorg. Chem.*, 265, 58 (1951).
5. M. H. Francombe, *Brit. J. Appl. Phys.*, 9, 415 (1958).
6. S. A. Semiletov, *Tr. Inst. Kristallografii, AN SSSR*, 10, 76 (1954).
7. A. Brown and B. Lewis, *J. Phys. Chem. Solids*, 23, 1597 (1962).
8. A. A. Godovikov, *Zh. strukt. khimii*, 3, 44 (1962).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.
