POLYMORPHISM OF BISMUTH TELLURIDE AT HIGH PRESSURES AND TEMPERATURES

É. Ya. Atabaeva, E. S. Itskevich, S. A. Mashkov, S. V. Popova, and L. F. Vereshchagin

Institute for High-Pressure Physics, Academy of Sciences of the USSR, Moscow

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A new metastable bismuth telluride phase, Bi_2Te_3 II, was found in polycrystalline samples at pressures of more than 40 kbars and temperatures higher than 400°C. Annealing in helium atmosphere for 20 h at 400°C produced a reverse transition back to the original phase. Bi_2Te_3 II has a rhombohedral cell belonging to the space group $R\bar{3}m$. The hexagonal cell parameters are: $a_H = 4.417$ Å, $c_H = 29.84$ Å. The hexagonal cell contains three molecules. All atoms occupy crystallographic positions 3(a): 00z; $\frac{1}{3}\frac{2}{3}\frac{1}{3} + z$; $\frac{2}{3}\frac{1}{3}\frac{2}{3} + z$. The following structural parameters were determined by the minimization of the R factors: $z_{Bi_1} = 0.188$, $z_{Bi_2} = 0.598$, $z_{Te_1} = 0.389$, $z_{Te_2} = 0.800$, $z_{Te_3} = 0$. The R factor was 0.19.

Earlier investigations [1, 2] of the pressure dependence of the electrical conductivity of bismuth telluride (Bi_2Te_3) and bismuth selenide (Bi_2Se_3) as well as a study of an irreversible polymorphic transition of bismuth selenide [3] have shown that the application of pressure alters considerably the properties of these layered semiconductors.

The present study should be regarded as a continuation of the earlier investigations of irreversible changes in bismuth telluride at high pressures and temperatures.

As reported in [3], Bi_2Se_3 undergoes an irreversible polymorphic transition to a bismuthite-type structure (Bi_2S_3), which has an orthorhombic cell and belongs to a space group Pbnm = D^{16}_{2h}. In spite of the great similarity of the crystal structures and electron energy spectra of bismuth selenide and telluride, it has been found that irreversible transitions of these compounds under high pressures are different.

Bi_2Te_3 crystallizes in a tetradymite-type structure: The cell is rhombohedral, the space group is $R\bar{3}m$, and the cell parameters in terms of the hexagonal axes are: $a_H = 4.383$ Å, $c_H = 30.487$ Å [4]. Bismuth and tellurium atoms form monatomic layers, perpendicular to the c axis and alternating in the following manner: –Te–Bi–Te–Bi–Te–Te–.

We used polycrystalline bismuth telluride samples of the stoichiometric composition, which were subjected to high pressures ranging from 40 to 120 kbars and temperatures from 400 to 700°C. The results are presented in Table 1. To prevent contamination of the investigated substance with graphite from the heater, the compacted samples were placed in a container made of platinum, nickel, or tantalum (the method is described in detail in [3]).

The Debye diffraction patterns of samples subjected to high pressures (P > 40 kbars) and temper-

TABLE 1. Results of Experiments at High Pressures and Temperatures

P, kbars	T, °C	Duration of exp., min	Structure
130	650	3	Bi_2Te_3 II
110	400	5	
110	500	15	
110	600	120	
100	280	15	Bi_2Te_3
100	400	8	Bi_2Te_3 II
100	500	20	
65	500	10	
60	800	2	
45	500	25	Bi_2Te_3
45	650	15	
20	650	30	