PRESSURE-INDUCED PHASES OF In_2Te_3 AND Ga_2Te_3*

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Phase transitions were found with use of an "in situ" X-ray anviltype of apparatus with a boron annulus at pressures up to 12 GPa. The disordering of vacancies in the sub-structure, or $\alpha \rightarrow \beta$ transition, was found in In_2Te_3 at $p > 1.9$ GPa. The next transformation from β-form into the Bi_2Te_3 type of structure was observed in both sesquitellurides at 2.0 GPa and 5.0 Gpa for In_2Te_3 and Ga_2Te_3 respectively. The In_2Te_3 metastable phase of the Bi_2Ga_3-type resulted from heating up 200 °C at $p > 4.0$ Gpa and it remained in a normal condition on release of the pressure. The unit-cell parameters of pressure-induced phases, volume changes and bulk moduli of both sesquitellurides are given. The compressibility anisotropy of the layer pressure-induced phase was observed. The mechanism of the crystal structure transformation from the face-centered cubic structure into the Bi_2Te_3 type is proposed to be due to the displacement of atoms from the space diagonal of the cube [111] into [112]-cubic direction and the rhombohedral distortion of the angle between these directions.

Introduction. In_2Te_3 and Ga_2Te_3, or $A_2^{III}B_3^{VI}$ are crystallized in a defect zinc-blende structure in which one-third of sites of the metal substructure are vacant. The vacancies are random ($\beta-In_2Te_3$, Ga_2Te_3), or orderly ($\alpha-In_2Te_3$) [1].

Earlier in the system In-Te, the metastable phases were synthesized by high pressure high temperature quenching [2]. X-ray diffraction investigation of the quenched In_2Te_3 phase led to the assumption of the Bi_2Te_3 type of structure for the metastable In_2Te_3. However, In_2Te_3 quenched together with the In_3Te_4 and excess tellurium, or the decomposition reaction was observed [2]. Bose *et al.*, [3] found the sharp decrease of the Ga_2Te_3 and $\beta-In_2Te_3$ resistivity at the hydrostatic pressure between 1 and 7 GPa and the irreversible change of In_2Te_3 resistivity was explained by the decomposition reaction.

Direct X-ray diffraction investigation of In_2Te_3 and Ga_2Te_3 at high pressure is not known. The present paper seeks to elucidate the crystal structure of $A_2^{III}B_3^{VI}$ tellurides at high pressure up to ~ 12 Gpa *in situ*.

A high pressure diffraction investigation of the ordered $\alpha-In_2Te_3$ ($In_{40.1}Te_{59.9}$) and disordered stoichiometric Ga_2Te_3 was carried out in the X-ray apparatus of the anvil type [4]. Samples mixed with polyethylene were put in a cylindrical hole in the amorphous boron annulus. The pressure was calibrated from the solid state data of NaCl, used as an internal standard. MoK_α X-rays and the film technique were used.

Results

High pressure room temperature experiments. The crystal structure changes were observed from high pressure patterns, obtained at the increase and the

* This report is a shortcut text of the paper, published in "Powder Diffraction", v. 7, № 2, pp. 99–102, 1992.

decrease of pressure. The superstructure lines of ordered $\alpha-In_2Te_3$ disappear at $p < 1.9$ GPa, or when $\alpha \rightarrow \beta$ transition is observed. Upon further increase of the pressure, the behaviour of both β-sesquitellurides (pressure-induced $\beta-In_2Te_3$ and original $\beta-Ga_2Te_3$) become the same. Strong odd-order lines of the zinc-blende sublattice (111), (311) weakened appreciably at $p > 2.7$ GPa for In_2Te_3 and $p > 5.0$ GPa for Ga_2Te_3 and disappeared at 3.8 GPa and 8.7 GPa, respectively. Simultaneously, the even-order (200), (220)-lines are getting stronger and (222) and some weak extra lines appear. The phase transition for In_2Te_3 may begin at $p = 2.0$ GPa, because the precision of the cubic cell determination is decreasing at this pressure and it achieves the value ± 0.2 Å at $p > 2.7$ GPa. From following the high pressure patterns of In_2Te_3 and Ga_2Te_3, it is proposed that the structure of the high pressure phase is close to the NaCl-type (considering only strong reflections) with a slight cell distortion ($\Delta = 0.2$ Å).

There is a two-phase region, extending from 2.0 GPa to 3.8 GPa, in agreement with earlier reported data on the resistance measurement of In_2Te_3 [3] in the same pressure interval. The two-phase region for Ga_2Te_3 (5.0–8.7 GPa), disagrees with the data of Bose (1–7.0 GPa). X-ray data possibly lead to a more correct interpretation because the ratio of ionic radii for $r_{Ga}/r_{Te} = 0.294$ is less than for In_2Te_3 (0.44). Therefore the transition for Ga_2Te_3 must begin at a higher pressure.

A structure of Bi_2Te_3 type [5] is proposed for high pressure phases of both compounds. It is based on the rhombohedral distortion of the NaCl type structure. It is a cubic closest-packed structure in which every third layer of metal octahedrons is empty. The unit cell parameters of original and high pressure phases, defined by the least-squares method, are listed in Table 1.

The volume change is about 13% at the transition pressure for both compounds. This value is close to that the volume of change of NaCl-type pressure-induced phase for $A^{II}B^{VI}$ (16%) [6].

This study extends the room temperature pressure-volume equation-of-state up to 12 GPa. The bulk modulus B_0 at $p = 0$ is obtained by fitting the Murnaghan-Birch equation to the volume-pressure data, assuming B_0' (pressure derivative of B_0) is equal to 4. The original and pressure induced phase B_0 values, shown in Table 2, are about equal, but both pressure induced phases have the same or lesser compressibility than the original phases. This fact could indicate that the pressure induced phases are close to instability.

The layer character of Bi_2Te_3 type phases is confirmed with the anisotropy of the compressibility for different axes. It is shown in Fig. 1, where the compressibility of the *c*-axis is more than that of the *a*-axis, and the *a*-axis is compressed very little.

High pressure high temperature experiments. The high pressure In_2Te_3 was found to remain at normal conditions after heating the sample to 200 °C at $p > 4.0$ GPa. The diffraction pattern at $p > 4.0$ GPa and 200 °C *in situ* contained identical d's, just the same as the diffraction pattern at $p > 4.0$ GPa and room temperature, and as the pattern of the quenched phase (taking into account the lattice compressibility). The decomposition reaction possibly occured at the higher temperature. The picnometric density value of the retained phase

Table 1. The relations between unit-cell parameters of the original and high pressure phase structures for both sesquitellurides.

			Observed values			
	ZnS type		Bi_2Te_3 type			
			Hexagonal aspect		Rhombohedral aspect	
	p, GPa	a_c, Å	a_h, Å	c_h, Å	A_r, Å	α_r, °
In_2Te_3	0*	6.150(5)	4.257(7)	29.21(7)	10.04	24.27
Ga_2Te_3	5.5	5.672(5)	3.987(4)	26.45(7)	9.239	24.92
Ga_2Te_3	0**	5.895(5)				
			Calculated values			
			$a_h = a_c\sqrt{2}/2$	$c_h = 2a_c\sqrt{6}$	$A_r = \sqrt{3}$	$\alpha_{r,c}$ °
In_2Te_3	0*		4.349	30.13	10.652	19.47
Ga_2Te_3	5.5		4.01	27.79	9.824	19.47
Ga_2Te_3	0**		4.165	28.879	10.210	19.47

*quenched

**original

The quenched phase of In_2Te_3 is used, because it allows the possibility for comparison under normal conditions

Table 2. Compressibility data of In_2Te_3 and Ga_2Te_3.

	Defect ZnS type		Bi_2Te_3 type	
	In_2Te_3	Ga_2Te_3	In_2Te_3	Ga_2Te_3
B_0, GPa	34.8	37.04	31.7	33.9
V/V_0	1	1	0.875	0.878

B_0 (bulk modulus) values are calculated at $p = 0$, assuming bulk modulus pressure derivative $B_0' = 4$; V/V_0 values are also given at $p = 0$

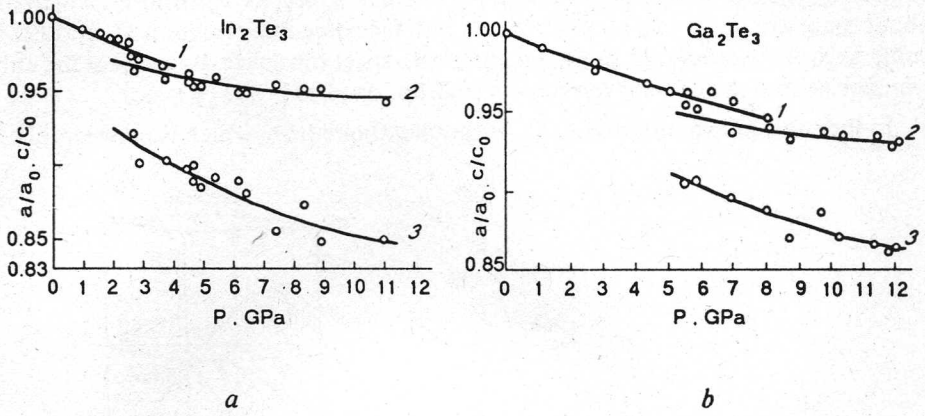

Fig. 1. Plots of the reduced lattice parameters vs. pressure for In_2Te_3 and Ga_2Te_3. Curve *1* shows the pressure dependence $a_{cub}/a_0(p)$; curve *2*, $a_{hex}/a_0(p)$; curve *3*, $c_{hex}/c_0(p)$. Hexagonals a_0 and c_0 are calculated from relations 1 and 2 (see text and Table 1). The form of the equation for axes compressibilities is polynomial: $(a/a_0, c/c_0) = a + bp + cp^2$

$\rho = 6.39$ g/cm^3 is in good agreement with the calculated value from X-ray data, $\rho = 6.57$ g/cm^3.

After heating the quenched In_2Te_3 to 120 °C at $p = 0$ for 3 hours, it reverted into β–In_2Te_3. After the *in situ* experiments at room temperature In_2Te_3 was obtained in the form of the β-phase also, and it did not revert to the α-form. The value of the cubic parameter a is equal to 6.15 ± 0.005 Å for both β-forms: the original disordered zinc-blende type [1] and the post-transition product. The pressure induced phase of Ga_2Te_3 is not retained after the apparatus unloading, either at room temperature or at heating to 250 °C under high pressure. The high temperature diffraction data were in agreement with the room temperature data of the pressure-induced Ga_2Te_3 phase.

Discussion. The mechanism of the transformation from the face-centered cubic structure (zinc-blende type) to the Bi_2Te_3 type for $A_2^{III}B_3^{VI}$ compounds under high pressure is proposed. Considering the lattice parameters of the investigated compounds of In_2Te_3 and Ga_2Te_3, these relations are proposed:

Hexagonal aspect

$$a_{hex} = a_{cub}\sqrt{2}/2 - \Delta_1 \qquad (1)$$

$$c_{hex} = 2a_{cub}\sqrt{6} - \Delta_2 \qquad (2)$$

Rhombohedral aspect

$$A_{rhomb} = a_{cub}\sqrt{3} - \Delta_3 \qquad (3)$$

Table 1 shows numerical values of parameters, calculated in this way. There is a good agreement with the values obtained by X-ray diffraction and those calculated by relations 1, 2, 3, parameters ($\Delta_{1,2,3}$ is a small value). Fig. 2 shows the proposed transformation of structures. At the hexagonal aspect Bi_2Te_3 type the face diagonal

of the cube [110] transforms into the hexagonal axis [10$\bar{1}$0], and the hexagonal axis [0001] lies along the [112] cubic direction in accordance with the relations (1,2). Fig. 2 and Table 1 show lengths of the hexagonal axes a and c, which are about equal to lengths [220] cubic axis, or half face diagonal (relation 1), and [224] cubic axis, respectively. In the rhombohedral aspect the space diagonal of the cube transforms into the edge of the rhombohedron, or $[100]_r \parallel [111]_c$ (3).

In the cubic phase, the angle $\alpha/2$ of the rhombohedron, which is between [111]

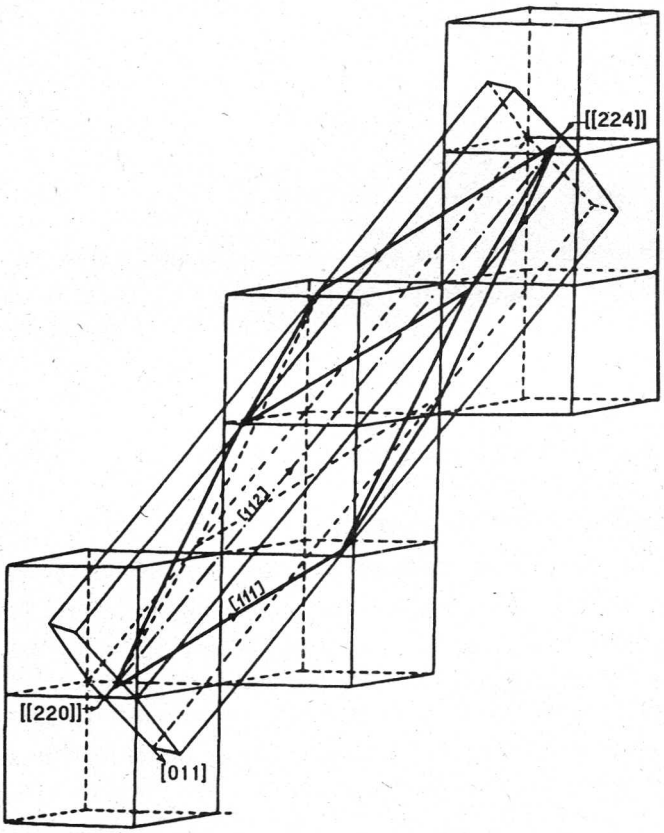

Fig. 2. The structural transformation at the high pressure transition from the face-centered cubic lattice to the rhombohedral Bi_2Te_3 type lattice. The cubic axes are signed. The rhombohedral unit cell is marked by bold lines

and [112] cubic directions, is equal to 19.47°, but at the phase transition this angle decreases to 12.5° (Table 1).

Therefore, the rhombohedral distortion of the face-centered cubic structure is probably about 7°, due to the decrease of value of the angle between [111] and [112] cubic directions at the transition, and the displacement of atoms from the space diagonal [111] into the [112] cubic direction.

The experimental results, described by this paper, and obtained at high pressures up to 12 GPa and high temperatures, up to 250 °C, are summarized in the tentative (P,T)-phase diagrams of Fig. 3. The data Geller et al., [2], on the decomposition of In_2Te_3 at 3.0 GPa and high temperature have been used.

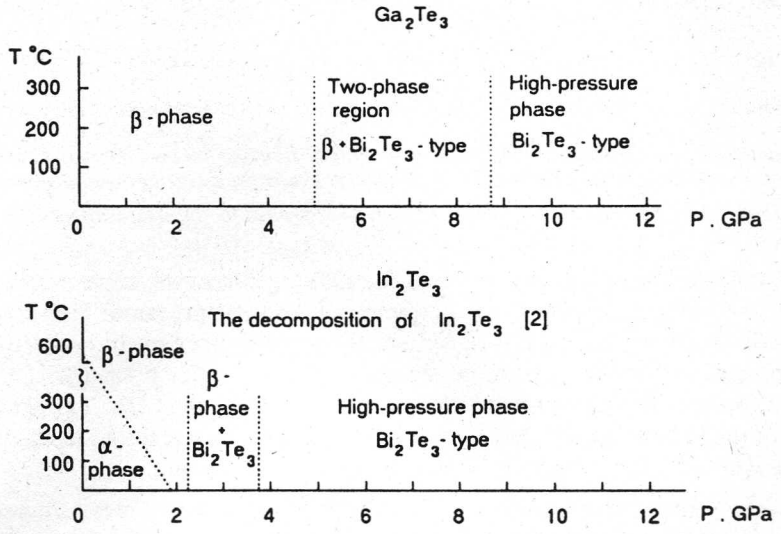

Fig. 3. Phase (P,T)-diagrams of Ga_2Te_3 and In_2Te_3. The proposal regions of the phase stability are drawn by dashed lines. α - and β-phases are crystallized in ordered and disordered defect zinc-blende types, respectively. The reaction of the In_2Te_3 decomposition is proposed, upper T = 340 °C, according to data [2]

Tentative phase boundaries, based on present results, are indicated with dashed lines. The high temperature region (T > 250 °C) were not studied at high pressures. The phase diagrams of both sesquitellurides are essentially identical, with the only difference consisting of the $\alpha \rightarrow \beta$ transition of In_2Te_3.

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