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Hexagonal (superlattice) form of Ga_2Te_3

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Gallium telluride (Ga_2Te_3) was synthesized at different temperatures (850 to 460° C) using different cooling rates. Materials synthesized at higher temperatures (including quenched materials from the melt) always yielded zinc-blende lattice with well resolved $\alpha_1\alpha_2$ doublet X-ray powder diffraction lines. In the material synthesized at lower temperature ($\sim$460° C), we obtained additional (superlattice) lines as reported by Newman and Cundall [4]. It was possible to index these reflections not only on an orthorhombic unit cell (a = 0.417, b = 2.360, c = 1.252 nm) but also on cubic (a = 1.7678 nm) and hexagonal (a = 0.832, c = 3.065 nm) unit cells. To us, the hexagonal cell appears to be more realistic. If sufficient time is given to reach equilibrium, the whole of the zinc-blende form of Ga_2Te_3 is transformed to the hexagonal form. It has been further observed that conversion of the hexagonal into the cubic form and vice versa can be brought about by heating the material at temperatures greater or less than 460° C, respectively. Lastly, the zinc-blende phase of Ga_2Te_3 is metastable and slowly transforms to hexagonal form at room temperature.

1. Introduction

Among the complex semiconductor materials with diamond-like structure that have been investigated in the past, the defect compounds and alloys of the $A_2^{III}B_3^{VI}$ type were found to be of particular interest. It is well known that structure of zinc-blende in normal non-defect compounds is associated with the existence of tetrahedral bonds involving electron pairs. These tetrahedral bonds may not be retained in defect compounds, like Ga_2Te_3, which crystallize in zinc-blende lattice with one-third of cation sites randomly vacant [1], and thus some of the bonds would have to start from vacant sites. For a general review of diamond-like defect semiconductors, as well as solid solutions and alloys based on these compounds, see Goryunova and Radautsan [2].

The crystal structure of gallium telluride was first determined by Hahn and Klinger [1] who reported the lattice as face-centred cubic with space group $F\bar{4}3m$ and lattice parameter $a_0 = 0.5886$ nm. Hahn [3] found that long-time annealing of Ga_2Te_3 revealed superstructure lines in addition to that of zinc-blende structure. Newman and Cundall [4] reported the superstructure formation in Ga_2Te_3 with an orthorhombic unit cell having dimensions 0.417 nm ($a_0/\sqrt{2}$), 2.360 nm ($4a_0$) and 1.252 nm ($3a_0/\sqrt{2}$). Contrary to this, Wooley and Pamplin [5] and Newman *et al.* [6] did not observe any superstructure lines which might point out to ordering of vacancies in Ga_2Te_3. These conflicting observations have increased interest in the study of Ga_2Te_3 superlattices. In this communication we describe our attempts to synthesize Ga_2Te_3 and the related X-ray diffraction study of the crystalline phases formed. Our study shows that the superlattice lines observed by Newman and Cundall [4] belong in fact to the transformed hexagonal phase of Ga_2Te_3 which is most stable at room temperature. The effect of quenching and annealing of the samples has also been studied, in order to explore the equilibrium state of the crystalline phases.

2. Experimental procedures

The materials used in the synthesis of Ga_2Te_3 were pure elements of gallium and tellurium obtained from the Nuclear Fuel Complex, Hyderabad, India. Stoichiometric amounts of these were reacted in a sealed evacuated quartz ampule for 2 h at 850° C, followed by furnace cooling. To ensure complete miscibility of elements in molten state, the melt was rocked for 1 h before switching off the furnace. The ingot thus prepared was poly-crystalline and greyish black in colour, with tiny mirror like faces imbedded in it. Different cooling rates and quenching methods were employed to arrive at eventually at the reported superlattice structure.

We have also attempted to synthesize the compound Ga_2Te_3 peritectically at a relatively lower temperature ($\simeq$ 460° C) as suggested by Newman and Cundall [4]. Annealing of synthesized samples was also carried out at different temperatures (450 and 660° C) over different time periods in order to observe any crystallographic changes in the synthesized material.

X-ray diffraction patterns of the synthesized materials (−200 BS mesh powders) were taken on Philips X-ray diffractometer PW 1310/01 using CuK_α radiation (35 kV, 12 mA) with pulse height discrimination and a scintillation counter. The alignment of the diffractometer was checked by using silicon (NBS 640a) as a standard.

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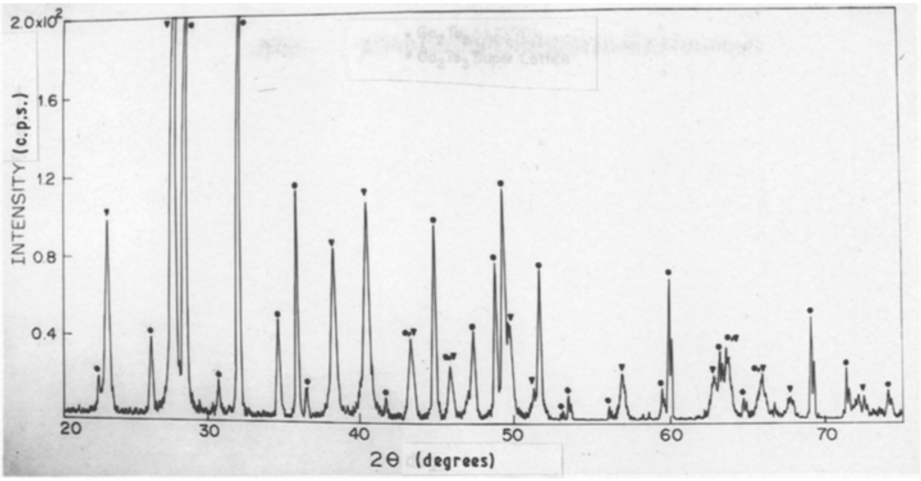

Figure 1 X-ray diffraction pattern of the material synthesized on heating a mixture of 77.5 at % Te and 22.5 at % Ga. ●, Ga_2Te_5; ▼, Ga_2Te_3 superlattice.

3. Results and discussion

The X-ray diffraction pattern of Ga_2Te_3, prepared by reacting stoichiometric elements at 850° C followed by furnace cooling, matches well with the standard JCPDS data. All lines were sharp with well resolved $\alpha_1\alpha_2$ doublets at higher 2θ values, and the complete diffraction pattern was indexible on a zinc-blende cell with a lattice parameter equal to 0.5887 nm. No superlattice lines, however weak, were found in the X-ray diffraction pattern of this preparation. Slower cooling rates ($\sim 1° \text{min}^{-1}$) or quenching of the melt in cold water yielded similar materials with same diffraction pattern of zinc-blende Ga_2Te_3. The only difference in slow-cooled samples was that one could find larger single crystals of a few millimetres in size, with mirror-like $\{1\,1\,1\}$ reflecting faces embedded in the polycrystalline ingot.

We repeated the experiment of Newman and Cundall [4] by heating a mixture of 77.5 at % Te and 22.5 at % Ga in an evacuated sealed quartz capsule of 1 cm diameter and about 6 to 7 cm in length, and obtained crystalline phases of Ga_2Te_5 and so-called

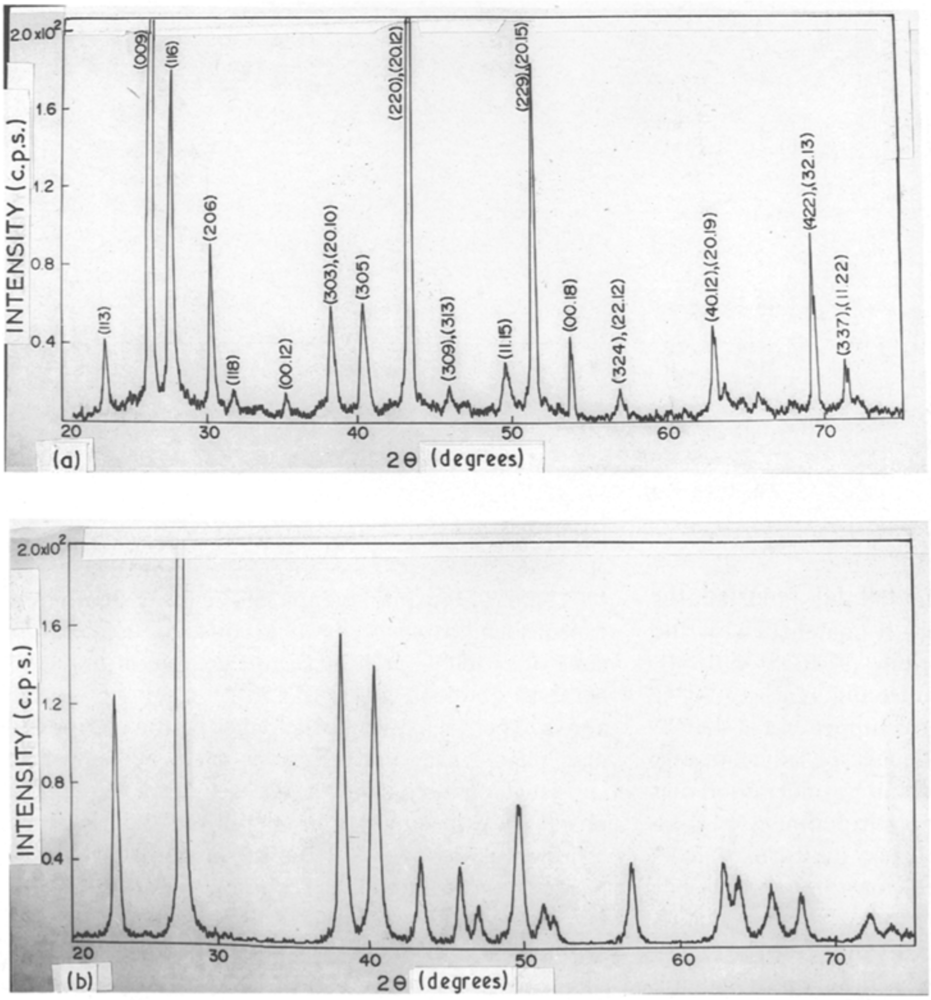

Figure 2 X-ray diffraction pattern of (a) hexagonal (superlattice) Ga_2Te_3; and (b) tellurium plus hexagonal (transformed) phase of Ga_2Te_3.

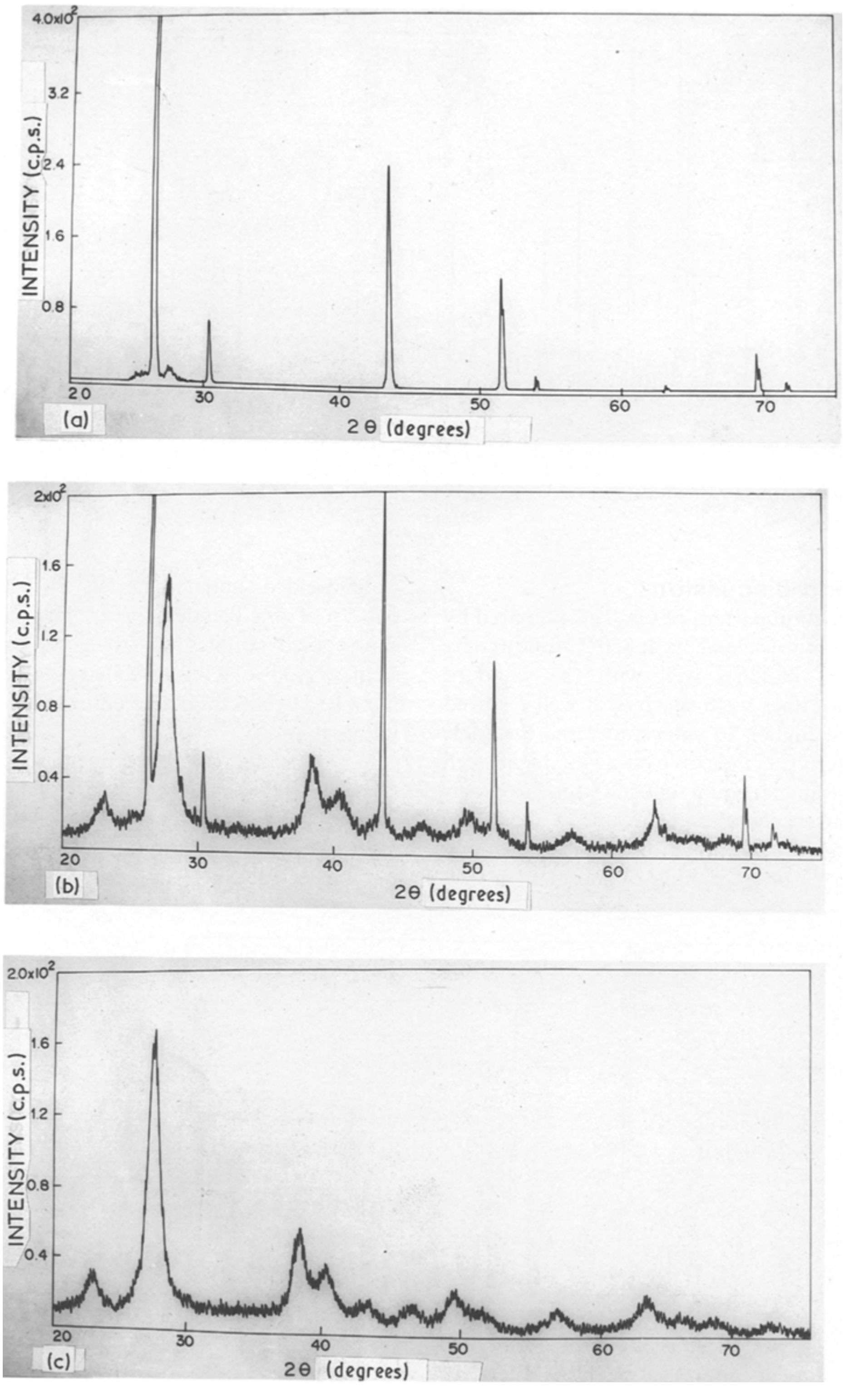

Figure 3 X-ray diffraction pattern of Ga_2Te_3 powder (a) as synthesized; (b) after 12 months storage; and (c) after 24 months' storage.

superlattice lines (Fig. 1). The d-values and relative intensity of the latter practically matched with the diffraction pattern of tellurium [JCPDS 4–0554]. Despite the planned temperature difference of 30° C between two ends of the ampule (upper end at 430° C and lower end at 460° C) no deposit of tellurium was found at the cooler end. This could be understood due to temperature fluctuations in our experiment. In spite of the use of a voltage stabilizer, the furnace temperature could be maintained constant only within ± 10° C during the worst periods of mains fluctuations. To overcome this difficulty, to make the excess tellurium evaporate, we selected larger lengths ($\simeq$ 15 cm) of the quartz ampule. The lower 5 cm of the capsule length was kept in a constant temperature zone of ~460° C and the rest of the length in a temperature gradient of 460 to 150° C. Carrying out the above experiment even for a longer period (10 instead of 5 days) gave similar results, that is, the residue consisted of a mixture of Ga_2Te_5 (as a prominent phase) and the superlattice phase; but this time, tellurium was deposited at the upper cooler end. The residue, consisting of Ga_2Te_5 and superlattice lines of Ga_2Te_3, was made to undergo the same process of synthesis for a longer period of 30 days. We then found the superlattice form of Ga_2Te_3 in the residue

TABLE I Indexing powder diffraction data of the fully transformed phase of Ga_2Te_3 on different unit cells

No.	d_{obs} (nm)	Orthorhombic cell (a = 0.4162 nm; b = 2.3544 nm; c = 1.2486 nm)		Cubic cell (a = 1.7678 nm)		Hexagonal cell (a = 0.832 nm; c = 3.065 nm)	
		h k l	d_{calc}(nm)	h k l	d_{calc} (nm)	h k l	d_{calc} (nm)
1	0.387	1 1 1	0.389	4 2 1	0.386	1 1 3	0.385
2	0.323	0 7 1	0.325	5 2 1	0.323	1 1 6	0.323
3	0.234	1 6 3	0.2356	5 4 4; 7 2 2	0.2342	3 0 3 20.10	0.2338 0.2335
4	0.223	1 8 2	0.2244	6 5 1; 7 3 2	0.2245	3 0 5	0.2236
5	0.2083	0 0 6; 1 8 3 2 0 0	0.2082 0.2081	6 6 0; 8 2 2	0.2083	20.12 2 2 0	0.2084 0.2080
6	0.1961	0 4 6; 0, 12, 0	0.1962	6 6 3; 7 4 4; 8 4 1; 9 0 0	0.1964	3 0 9 3 1 3	0.1963 0.1961
7	0.1836	1 2 6; 2 2 3 2 6 0	0.1838 0.1836	8 5 2	0.1833	11.15	0.1834
8	0.1776	1 4 6	0.1776	7 5 5; 7 7 1; 9 3 3	0.1777	20.15 2 2 9	0.1778 0.1775
9	0.1615	2 9 1	0.1615	10, 4, 2	0.1614	3 2 4 22.12	0.1616 0.1613
10	0.1471	2 0 6 2 1 6	0.1471 0.1469	8 8 4; 12, 0, 0	0.1473	40.12; 20.19	0.1472

(Fig. 2a) and the evaporated portion (Fig. 2b) at the cooler end of the quartz ampule, contained tellurium as the main phase, in addition to weak lines of the transformed hexagonal phase of Ga_2Te_3. The deposited material at the cooler end of the quartz ampule, when checked by the X-ray fluorescence method for elemental analysis, indicated mostly tellurium, along with a small quantity of gallium.

We have observed recently that the zinc-blende structure of Ga_2Te_3 is unstable at room temperature and changes on storage [7]. The X-ray diffraction patterns of as-synthesized Ga_2Te_3, and after 12 and 24 months of storage at room temperature, are shown in Fig. 3a to c. The final, transformed X-ray diffraction pattern (Fig. 3c) is indexible on the orthorhombic unit cell of the superlattice reported by Newman and Cundall [4]. The pattern also matches to first approximation with the diffraction pattern of tellurium, except that the lines are broad and diffuse. It was also possible to index these superlattice lines on cubic ($a = 3a_0$) and hexagonal unit cell (a = 0.832 nm, c = 3.065 nm) as shown in Table I. No comments can be made on the space group, particularly when the diffraction lines are few and can be indexed on three unit cells belonging to different systems. To us, the hexagonal unit cell appears to be more realistic because the zinc-blende structure is geometrically related to the wurtzite structure in the same way as the cubic to hexagonal close packing. Here the (1 1 1) planes of cubic structure lie parallel to (0 0 0 1) planes of hexagonal form, while lines of closest packing [1 1 0] of the cube lie parallel to $[1 0 \bar{1} 0]$ direction of the hexagonal structure. In this way, transforming a zinc-blende cubic unit cell of $a_0 = 0.5887$ nm into an equivalent hexagonal unit cell, we find that the hexagonal unit cell of the superlattice (a = 0.832 nm, c = 3.065 nm) consists of a nine-layer packet of (1 1 1) cubic planes. The a-axis and the c-axis of the hexagonal cell lie parallel to the $[\bar{1} 1 0]$ and [1 1 1] directions of the cubic cell, respectively. The a-parameter of the hexagonal unit cell is twice the distance between tellurium atoms in the (1 1 1) cubic planes of the zinc-blende lattice. The hexagonal unit cell thus contains nine cubic unit-cells; and on transformation from cubic to hexagonal (superlattice) form a small increase in cell volume of the order of 0.07% has been observed. The phase relation of Ga_2Te_3 appears to be somewhat similar to that of carbon and boron nitride, which exist in both wurtzite and zinc-blende forms. We can thus conclude, that at higher temperatures the equilibrium form of Ga_2Te_3 is cubic, and at lower temperatures the equilibrium form is hexagonal. Our recent work [8] has also shown that this phase transformation can be brought about speedily by excessive grinding.

The effect of annealing zinc-blende Ga_2Te_3 and superlattice of Ga_2Te_3 powders was also studied. There was practically no change in diffraction pattern when the zinc-blende gallium telluride was annealed at 660° C for 1 month, except that the satellite side bands [9] of the (1 1 1) reflection became somewhat prominent. However, annealing fine powder (−200 BS mesh) of zinc-blende Ga_2Te_3 at lower temperature (460° C) initiated transformation to the hexagonal form (superlattice) and the annealed powder was found to be mixture of two phases, the zinc-blende and hexagonal (superlattice) forms of Ga_2Te_3. If annealing is carried out at this temperature ($\simeq$ 440° C) over a prolonged period, the whole of zinc-blende is converted to the hexagonal (superlattice) form of Ga_2Te_3. The opposite is also true, that is, the superlattice form can be brought back to the zinc-blende form by annealing at 660° C for 72 h.

Our study has thus revealed that the equilibrium form of Ga_2Te_3 at temperatures less than 460° C is hexagonal (superlattice). This result was also confirmed by our single crystal observations on the zinc-blende Ga_2Te_3. Figure 4 shows Laue photographs using CuK radiation (35 kV) with an X-ray beam normal to (1 1 1) cubic face on as synthesized (from melt) and after two years of storage at room temperature. It can be seen clearly that the single crystal has

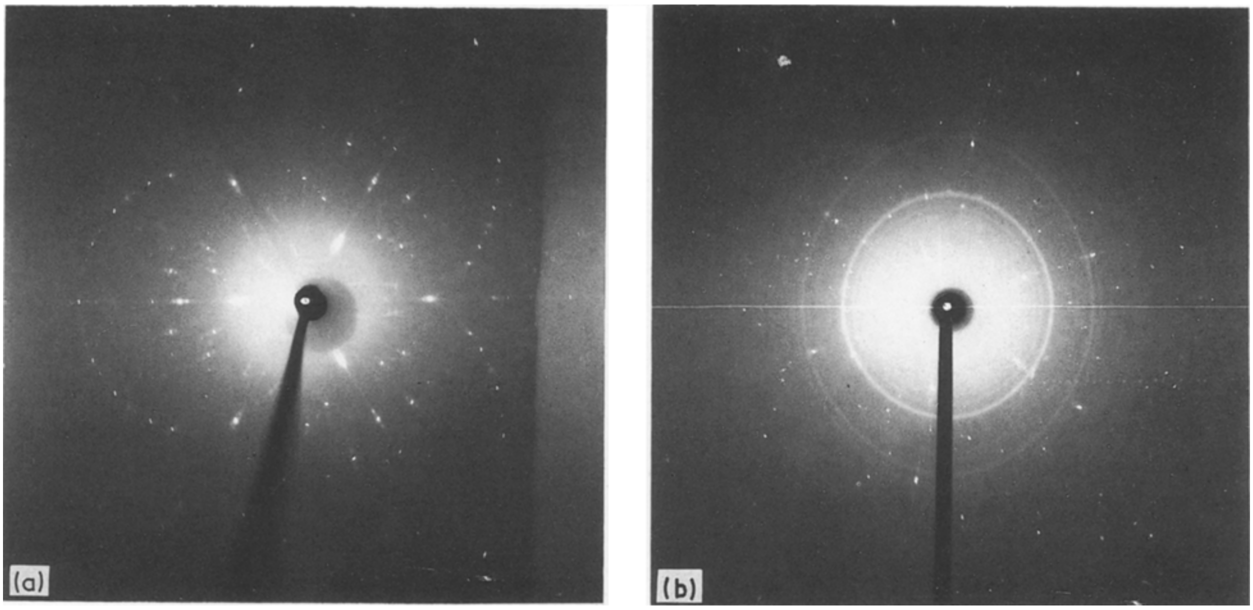

Figure 4 Laue photograph of Ga_2Te_3 with X-ray beam normal to (1 1 1) cubic face (a) as synthesized; (b) after 24 months' storage.

partly transformed into a polycrystalline form. The polycrystalline Debye–Scherrer rings were found to be due to the hexagonal (superlattice) phase of Ga_2Te_3. It can be further noted that the high-angle single-crystal reflections of the Laue photographs have practically vanished on storage, suggesting disintegration of the crystallized state of zinc-blende lattice of Ga_2Te_3.

4. Conclusions

In preparing Ga_2Te_3 from melt, the zinc-blende form of gallium telluride is always obtained. The diffusion rate is quite high and the quenched alloy was found to be close to equilibrium conditions. However another form of Ga_2Te_3, previously known as superlattice, can be synthesized at low temperatures around 460° C. The X-ray powder diffraction lines of this superlattice (in fact, the transformed phase of Ga_2Te_3, as no trace of zinc-blende form was present) were indexible on three different unit cells of cubic, orthorhombic and hexagonal systems. All these unit cells are related to the parent zinc-blende cell. The hexagonal form appears to be more realistic. It is concluded that the atoms form a zinc-blende lattice to attain equilibrium conditions at higher temperatures. At lower temperatures ($\leqslant 460°$ C) the hexagonal form is in equilibrium. The zinc-blende or hexagonal form of Ga_2Te_3 can be changed into either of these by annealing at low and high temperatures.

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