

On the phase diagram of the Ga-Te system in the composition range 55 at % Te

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Monoclinic Ga-Te was heated in the electron microscope. At about 800° C decomposition was observed and after cooling down to room temperature, two compounds were identified: the fcc Ga₂Te₃ and the Ga₃Te₄, for which a trigonal structure was identified. A relation between the three structures of Ga-Te, Ga₃Te₄ and Ga₂Te₃ is put forward.

1. Introduction

The phase diagram of the Ga-Te system was established by Klemm and Vogel [1] by means of thermal analysis and later by Newman *et al.* [2] by thermal analysis and direct observations of melting points under controlled Te pressures. Recently Alapini *et al.* [3] published results in good agreement with those of Klemm and Vogel [1].

All authors agree on the existence of two compounds (Fig. 1): (a) Ga-Te (64.65 wt % Te), with two structural modifications, a monoclinic [3-8] and an hexagonal structure [4] and (b) Ga₂Te₃ (73.30 wt % Te), with an fcc zinc blende structure [1-4, 9, 10]. An orthorhombic superstructure is also reported [11].

There are also some other compounds reported by various investigators. Thus, Newman *et al.* [2] proposed Ga₃Te₂ (54.96 wt % Te), the compound Ga_{2+x}Te₃ is proposed by Semiletov and Vlasov [12], with a cubic cell of $a = 10.32 \text{ \AA}$, Lissauskas and Yasutis [13] working on thin films proposed the compound Ga₃Te₄ (70.93 wt % Te), with a rhombohedral unit cell of $a = 10.10 \text{ \AA}$ and $\alpha = 89^\circ 35'$, Newman *et al.* [2] also reported the compound GaTe₃ (84.59 wt % Te), with an hexagonal cell of $a = 6.43 \text{ \AA}$ and $c = 14.20 \text{ \AA}$ and finally Alapini *et al.* [3] presented the compound Ga₂Te₅ (82.06 wt % Te) with an hexagonal cell of $a = 7.913 \text{ \AA}$ and $c = 6.848 \text{ \AA}$. All these compounds, except the Ga₃Te₄ proposed by Lissauskas and Yasutis [13], are outside the region of the compositions GaTe-Ga₂Te₃.

It is worth noting that, in all the phase diagrams

[1-3], a common feature is the eutectic for GaTe-Ga₂Te₃ at the composition 56.5 at % Te.

As part of a wider programme studying structural, electrical and optical properties of III-VI compounds, an examination of the Ga-Te system was undertaken. The room temperature monoclinic structure of Ga-Te was confirmed [8] before studies on the decomposition of the phase within the electron microscope at elevated temperatures. The results are presented in this paper together with the structure of the compound Ga₃Te₄ and also some evidence for the formation of com-

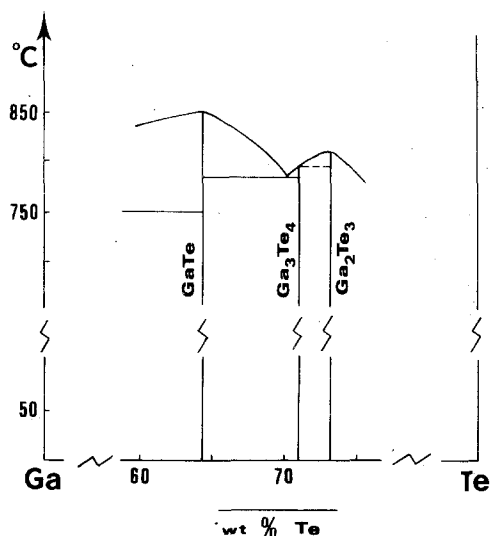


Figure 1 The region 60 to 75 wt % Te of the phase diagram of the GaTe system [3]. The new compound Ga₃Te₄ at the composition 70.93 wt % Te has been added (see text for details).

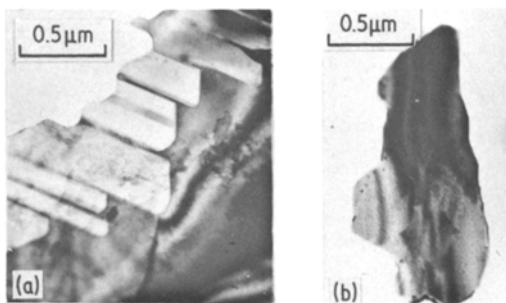


Figure 2 *In situ* decomposition of Ga–Te (a) at 750° C instability starts to appear and (b) by heating to 800° C and cooling to room temperature, island-like particles are formed.

pounds in the range 64 wt% Te to 74 wt% Te. This is based on the distortion of the original Te lattice, when Ga atoms are added.

2. Experimental procedure

GaTe was grown using the Bridgman technique. The correct proportion of the component materials was placed in quartz ampoules and sealed off under vacuum. These were put into a vertical furnace with a linear temperature gradient between 850 and 400° C. The samples obtained were single crystals of good quality; they were brittle, showing a layer structure. Chemical analysis, using atomic absorption, was used to establish the composition.

Specimens for transmission electron microscopy (TEM) were prepared by cleavage in the usual way. A JEOL 120CX electron microscope, with a $\pm 60^\circ$ tilt–rotation goniometer stage and a $\pm 45^\circ$ heating stage, was used in the experiments.

3. Results

The GaTe compound was identified by X-ray analysis [8]. Heating experiments were then carried out within the microscope. The temperature of the monoclinic GaTe was increased slowly. During this procedure no phase transformation was observed. At about 750° C an instability was observed, which indicated that the material was slowly decomposing (Fig. 2a). Heating was continued up to 800° C, where the instability ceased and was followed by recrystallization. At this point the cooling procedure was started and trial experiments produced island shaped particles (Fig. 2b). These areas showed two types of diffraction patterns. One (Fig. 3a, b) can easily be identified as belonging to fcc Ga_2Te_3 and the

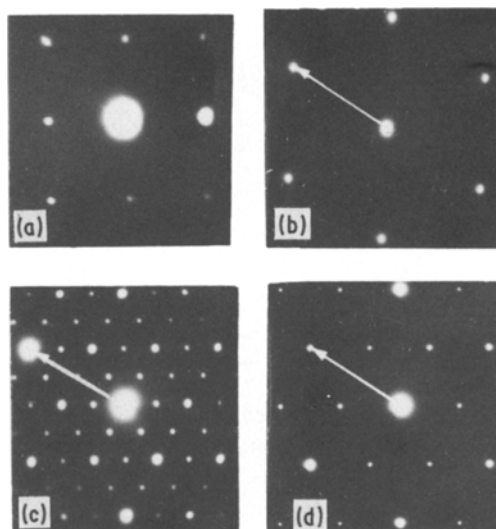


Figure 3 (a) and (b) 100 and 111 diffraction patterns of fcc Ga_2Te_3 , (c) the basic diffraction pattern of the Ga_3Te_4 compound and (d) the diffraction pattern of the cleavage plane of monoclinic GaTe. Notice the same orientation and the equality of the length of the g.

calculated lattice parameter was found to be $a = 5.89 \text{ \AA}$. The diffraction pattern of the second type, at zero tilt, is shown in Fig. 3c (Fig. 3d belongs to the monoclinic structure). In order to construct the reciprocal lattice of this second structure, tilt experiments around the direction marked, were performed. This direction proved to be a diad axis. There was no evidence of any four-fold axis. The results (referred to one direction of the tilt, since it was proved symmetrical about the orientation of zero tilt) are shown in Fig. 4. Only spots which were aligned parallel to the lines of the drawing are on the plane of the figure. The tilt axis should be considered vertical to it. No structure compatible with these patterns was found in the literature for any Ga–Te compound. The angles between the different sections were read from the goniometer and then calculated using the method proposed by Delavignette [14].

Fig. 5 shows lattice fringes, taken with the objective aperture in symmetrical position. From this image it may be deduced that the new periodicity is formed homogeneously in the matrix and this confirms the argument that we are dealing with a single phase structure and not with a superposition of two or more variants along every $(2\ 2\ 0)$ direction. The zone axis should be either a third or a sixth-fold one. It is easily

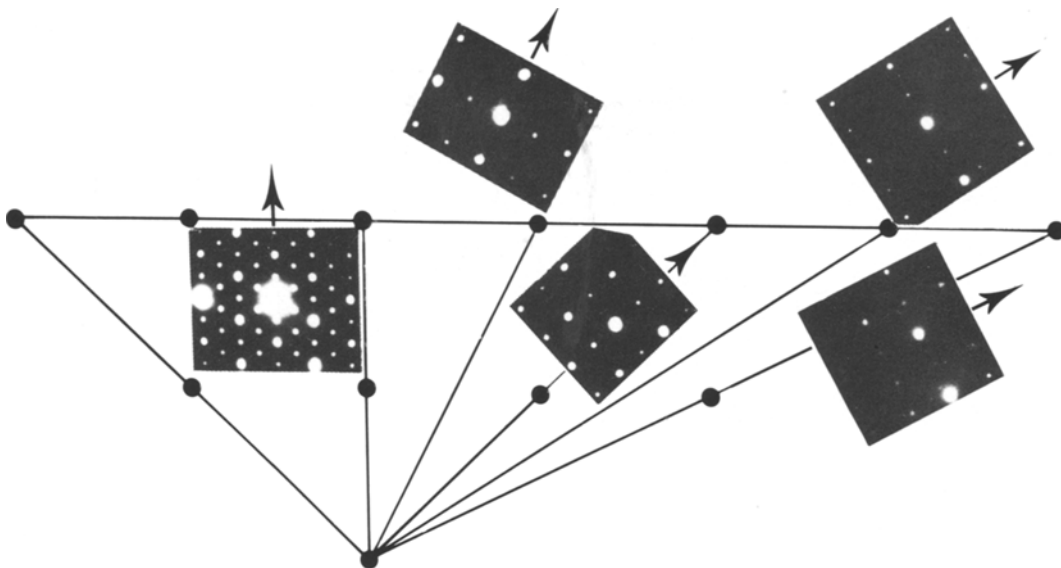


Figure 4 A drawing of a section of the reciprocal space of Ga_3Te_4 , constructed by rotation around the two-fold axis. The axis should be considered as perpendicular to the plane of the drawing. The superimposed patterns are also perpendicular to the drawing with the arrowed directions on it. (The two patterns to the right are at 120 kV).

proved that it is a third order screw axis. Therefore, the material has a trigonal structure, with one fourth of the Ga sites unoccupied. Such an assumption leads to the structure indicated in Fig. 6, which is the projection of the atomic positions of Ga, where the positions of the screw triads involved are shown. This arrangement corresponds to the $P3_121$ space group, where the three atoms in each unit occupy the special position $3a$ [15]. The length of the 220-type diffraction vectors of the fcc Ga_2Te_3 are preserved in this new structure, and it can be seen from Fig. 3b and c. Besides, 110-type reflections appear in Fig.

3c, whilst the 422-type reflection has been divided into six. These observations can be explained on the basis of new periodicities introduced because of the presence of the Ga vacancies (Fig. 6). The unit cell is indicated on the projection and from it, the material is characterized as Ga_3Te_4 . The calculated crystal constants are $a = a_{\text{fcc}}2^{1/2} = 8.29 \text{ \AA}$ and $c = 6.89 \text{ \AA}$.

Once formed, Ga_3Te_4 appears to be stable down to room temperature and can therefore be shown on the T-X phase diagram at 70.93 wt% Te (Fig. 1). This point is to the right of the eutectic point, which has been observed by all investigators,

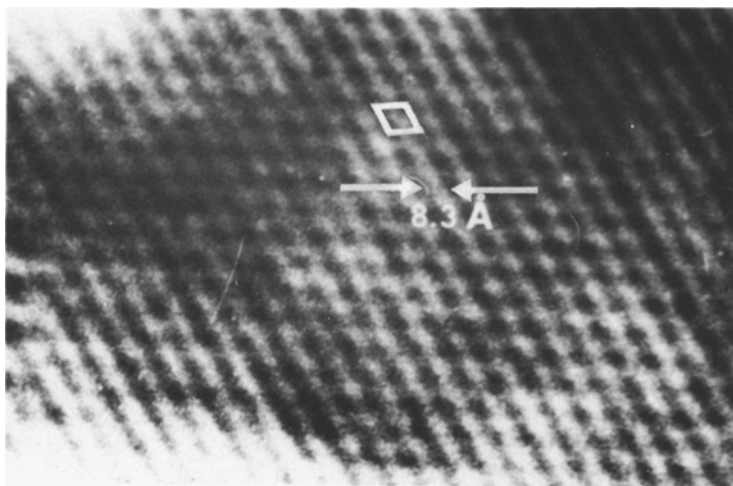


Figure 5 8.3 Å lattice fringes of the trigonal Ga_3Te_4 . The basal plane of the unit cell is also indicated.

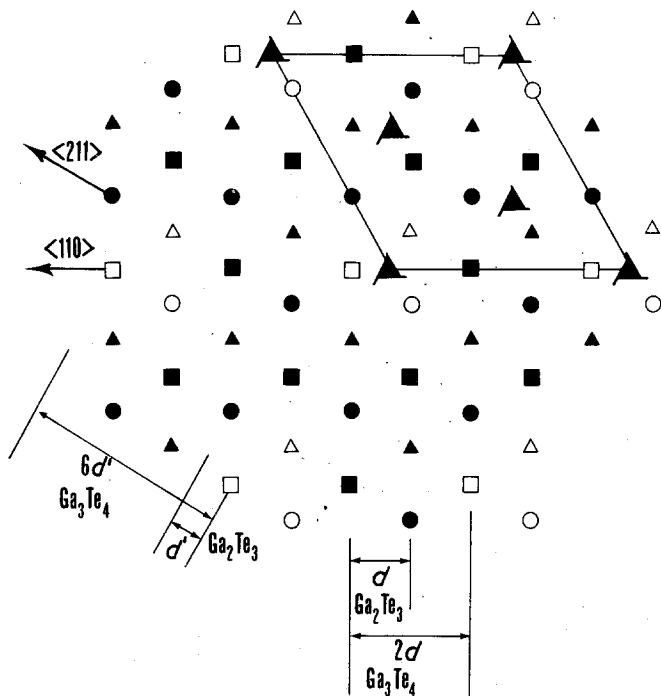


Figure 6 A c -axis projection of the Ga atoms of the Ga_3Te_4 compound. \blacksquare atoms at 0 and 1, \bullet atoms at $1/3$, \blacktriangle atoms at $2/3$. Open symbols represent vacant sites. The basal plane, the position of the screw-triads and the new periodicities are also shown.

i.e. in the region of the zinc-blende Ga_2Te_3 . Such a compound also appears at the same composition in the case of In-Te [16].

4. Discussion and conclusions

The main findings are summarized in Fig. 3b to d which present a series of reflection patterns obtained in the *in situ* heating experiment. From these patterns it is evident that in the transformation from the monoclinic Ga-Te state to the fcc Ga_2Te_3 and trigonal Ga_3Te_4 state the g vector (which is indicated on the pictures) preserves its length and its direction (within 1° or 2°). This direction of the g vector is a two-fold axis in all states.

The Te lattice is an hexagonal one with the Te atoms forming infinite parallel chains along the c -axis [17]. The Te atoms are placed at the corners of a tetrahedron with one corner vacant. The lattice constants are $a = 4.457 \text{ \AA}$ and $c = 5.929 \text{ \AA}$.

If we consider that all the Ga-Te compounds, in the range centred at 55 at% Te, are superstructures of the Te lattice, so that the Te anions play a stabilizing role, then the three compounds Ga_2Te_3 , Ga_3Te_4 and GaTe should be related. This view is in agreement with previous findings concerning the related In-Te system in the same range of compositions [16, 18].

4.1. The Ga_2Te_3 structure

In this case we may consider the Ga atoms as forming an intermediate layer between the Te atom layers. This leads to the fcc structure of the disordered Ga_2Te_3 with $a = 5.89 \text{ \AA}$. In this structure the distance among the Te chains is almost preserved, since we have $5.89/2^{1/2} = 4.16 \text{ \AA}$ against 4.457 \AA , while in the direction of the c -axis the constant is $5.89 \times 3^{1/2} = 10.20 \text{ \AA}$ against 11.858 \AA (2×5.929). This indicates that the hexagonal Te lattice shrinks to form the fcc structure.

4.2. The Ga_3Te_4 structure

In this structure the Ga vacancies are arranged in tetrahedral chains as in the Te structure. This arrangement preserves the length of the two-fold axis (in Fig. 6 the distance between the chains is $a/2 = 4.15 \text{ \AA}$) while the lattice constant in the direction of the three-fold axis becomes 6.89 \AA , forming the trigonal structure.

4.3. The GaTe structure

In this case the length of the two-fold axis is preserved, but the Ga atom layers are inserted between the Te atom layers. This insertion causes a shear in the $[\bar{1}10]$ direction of the fcc structure leading to the monoclinic structure; Fig. 7

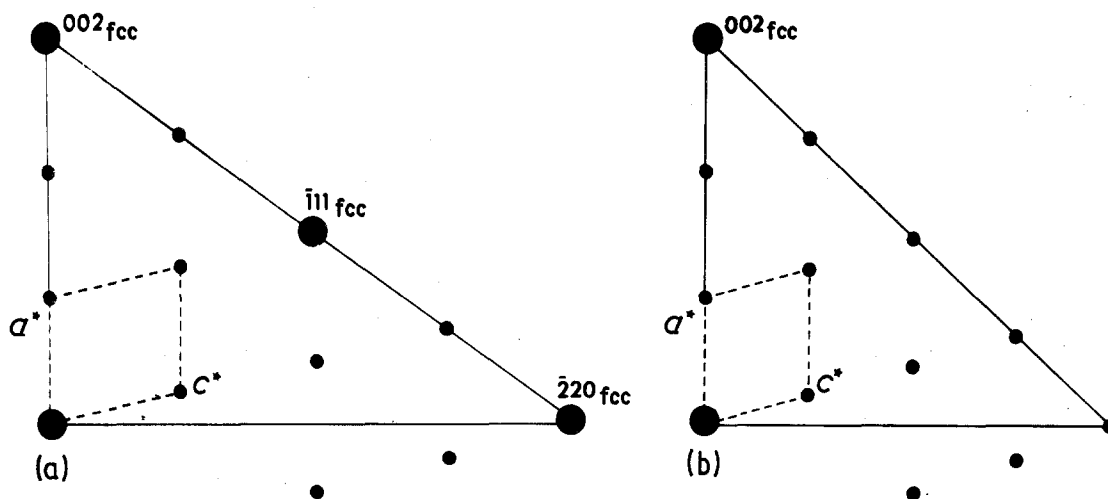


Figure 7 (a) Formation of a monoclinic basal plane within a $(1\ 1\ 0)$ fcc reciprocal plane and (b) same formation after a shear along the $[\bar{1}\ 1\ 0]$ direction of the fcc structure.

explains this mechanism. In Fig. 7a the formation of a monoclinic structure within the reciprocal space of the fcc lattice is presented. If a similar shear is considered in the $[\bar{1}\ 1\ 0]_{\text{fcc}}$ direction then the reciprocal lattice of the monoclinic cell of GaTe results, with the exact relation for the a^* and c^* parameters [8]. The two-fold axis which is preserved, is perpendicular to the plane of the drawing. It is observed that a^* is one third of $g = 0\ 0\ 2_{\text{fcc}}$. Observing that a^* is in the centred side of the monoclinic structure, then $3 \times (5.89/2) = (17.31/2) = 8.65\ \text{\AA}$.

Thus it may therefore be concluded that there is an intimate relation between the three structures, the final structure depending on the number of vacant sites in the cation sublattice and on the actual valence of the Ga atoms. The Ga-Te system (around 55 at % Te) may be considered as a single phase material with all structures arising from the same metastable high temperature arrangement, where the actual assembly of clusters depends on the Ga atom to vacancy ratio. It may be considered that the Te atom is tetrahedrally co-ordinated in all structures. In Ga_2Te_3 the validity of the rule $e/a = 4$ is obvious by counting the vacancies per formula unit and assigning zero valence to them. The deviation from this rule in the case of Ga_3Te_4 is due to a resonance between GaII-GaIII states, a phenomenon used previously to explain the stability of analogous structures. Finally in the case of GaTe each Te atom is co-ordinated with three Ga atoms at the corners of a tetrahedron while the fourth corner is occupied by an electron s^2 pair which leads to 2 per point electron atom ratio

with complete saturation. It was well established that lattice parameter changes may be associated with changes in the electronic state of the elements in chalcogenides and that this can lead to the formation of different crystal structures.

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