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X-ray study of the modulated structure in as-grown Ga_2Te_3 crystals with the defect zinc-blende lattice

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ABSTRACT

Ga_2Te_3 crystallizes in the zinc-blende structure, where one third of the cation sites are vacant. Single crystal X-ray diffraction studies were done on as-grown Ga_2Te_3 crystals. The diffraction measurements show, other than the zinc-blende type main reflections, satellite reflections at $q \approx 1/20(210)_c$, where the subscript c means the cubic sub-lattice. The analysis of the satellite reflections shows that the crystal contains a two-dimensional modulation with $q_1 \approx 1/20(210)_c$ and $q_{1'} \approx 1/20(2\bar{1}0)_c$. The modulated structure is composed of a coupled mode of the amplitude type modulation caused by Ga vacancies and the accompanying displacive modulation of surrounding Te atoms, which has the polarization vector along the $[001]_c$ direction. The nature of the atomic modulations is argued and the origin of the modulation is ascribed to the local distortion around a Ga vacancy.

1. Introduction

Metal sesqui-chalcogenides, $M_2^{III}X_3^{VI}$ (where M = Ga, or In and X = S, Se or Te) crystallize in the zinc-blende or wurtzite structure, where one-third of the cation sites is vacant in order to satisfy the chemical valencies. These vacancies noted as "structural vacancies" are inevitable to hold tetrahedral crystal structures. The orderings of the large amount of vacancies have received crystallo-chemical interest, and have been studied for a fairly long time. In earlier works on Ga_2S_3, Ga_2Se_3 and Ga_2Te_3, Hahn and Klinger [1] reported that Ga_2S_3 crystallizes in zinc-blende and wurtzite structures and that Ga_2Se_3 and Ga_2Te_3 crystallize only in the zinc-blende structure. The authors observed only main reflections and concluded that the crystals contain random distributions of cation vacancies. In subsequent works [2,3], it was recognized that, by annealing, Ga_2S_3 and In_2Se_3 crystallize into wurtzite based superlattice structures, while Ga_2Se_3 and Ga_2Te_3 crystallize into zinc-blende based superlattice structures. From powder X-ray diffractions, it was reported that Ga_2Te_3 has an orthorhombic structures with unit cells $a = 1/2[110]_c$, $b = 4[001]_c$ and $c = 3/2[1\bar{1}0]_c$ [2], and that Ga_2Se_3 has a monoclinic structure $a = 1/2[112]_c$, $b = 3/2[1\bar{1}0]_c$ and $c = 1/2[11\bar{2}]_c$ [3], where the subscript c means the cubic zinc-blende lattice.

In recent electron diffraction and electron microscopic studies done on Ga_2Te_3, by Hanada et al. [4] and Kienle et al. [5], observed satellite reflections at $1/10[111]_c$. These authors attributed the satellites to gatherings of the structural vacancies at every ten layer along the [111] axis. Hanada et al. [4] also reported that if the ordering of structural vacancies occurs at four $\langle 111 \rangle_c$ directions, equivalently, the total amount of vacancies becomes the nominal value 1/3; the vacancy ordering along a $\langle 111 \rangle_c$ direction causes 1/10 of the cation sites vacant, the ordering along another $\langle 111 \rangle_c$ direction causes 1/10 of the filled cation sites, $(1-1/10) \times 1/10$, further vacant. Therefore, the total amount of vacancies becomes $1/10 + (1 - 1/10) \times 1/10 + (1 - 1/10)^2 \times 1/10 + \cdots = 0.34$.

In order to investigate the nature of the vacancy orderings, we have been performing single crystal X-ray diffraction studies of Ga_2Te_3. In a recent study, we found that quenched Ga_2Te_3 crystals show satellites at $q \approx (0.06\,0.06\,0.0)_c$ [6]. In defect zinc-blende compounds, it is well known that the ordering of vacancies depends upon its thermal history. In this paper, we report on X-ray diffraction study of as-grown Ga_2Te_3 crystals.

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2. Experimentals

Single crystal samples of Ga_2Te_3 were grown by direct reaction of the elements. A mixture containing appropriate amounts of Ga and Te (99.999%), was sealed in an evacuated quartz ampoule and set in a furnace. The temperature of the furnace was raised above the melting temperature of Ga_2Te_3 (1065 K) held at 1133 K for 12 h, and was decreased at the rate of 6 K/h down to 853 K. Then the furnace was shut off and the sample was allowed to cool to room temperature over about three hours. The obtained samples were aggregations of small crystals. The crystals have metallic luster with most surfaces terminated by $\langle 111 \rangle_c$ planes.

Preliminary studies were done by taking powder X-ray scattering patterns and Buerger precession photographs in order to survey the diffraction pattern and check the crystal symmetry. The intensity data were collected by step scanning in reciprocal space using a Huber four-circle diffractometer with graphite monochromated Mo$K\alpha$ radiation. The resolution of the diffractometer is, about 0.06 (full width at half maximum, FWHM) in the longitudinal direction (toward the reciprocal origin), and about 0.02 (FWHM) in the transversal direction (both in unit of a^*, where we used the cubic lattice parameter of Ga_2Te_3, $a_0 = 5.895(5)$). Details of the used diffractometer are reported elsewhere [6].

3. Experimental results and discussion

3.1. General aspect of the diffraction pattern of as-grown Ga_2Te_3 crystals

The powder diffraction pattern of as-grown Ga_2Te_3 crystals, taken with graphite monochromated Cu$K\alpha$ radiation is shown in Fig. 1. The diffraction peaks can be indexed by the cubic zinc-blende lattice with $a_0 \approx 5.9$ Å. However, a close inspection of the data reveals the following two points. Firstly, small extra peaks are observed at 35° and 57° (denoted by asterisks in Fig. 1). Comparing the diffraction pattern with that of $CuGaTe_2$, these peaks are indexed as (211/2) and (321/2), corresponding to chalcopyrite structure which has the unit cell $a = b = a_0$ and $c = 2a_0$. These extra peaks are absent in quenched Ga_2Te_3 crystals, indicating the existence of chalcopyrite type orderings in as-grown Ga_2Te_3 crystals. Secondly, the width of the Bragg diffraction peak is abnormally wide, suggesting that the crystals contain large local strains. These points will be argued again in a later section. The precession photographs taken with Cu radiation are shown in Figs. 2(a)–(c). These photographs indicate main Bragg reflections ascribable to the cubic zinc-blende structure. Fig. 2(b) also reveals weak diffuse streaks along the $\langle 111 \rangle_c$ direction. The diffuse streaks have a broad maximum around $q \approx 1/2(111)_c$ indicating an anti-ferro type short range ordering of vacancies along the $\langle 111 \rangle_c$ direction. The result will be compare with those of recent electron diffraction studies of annealed Ga_2Te_3 crystals [4,5], where satellite reflections are observed at $1/10[111]_c$.

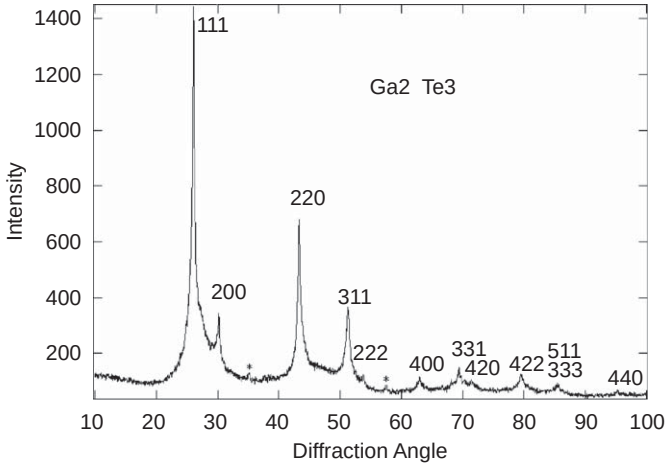

Fig. 1. Powder diffraction pattern of as-grown Ga_2Te_3 taken with Cu$K\alpha$ radiation. The diffraction pattern is indexed using the cubic zinc-blende lattice. The small peaks at 35° and 57°, marked by asterisks, are indexed as (211/2) and (321/2). These reflections correspond to the chalcopyrite ($CuFeS_2$) type structure.

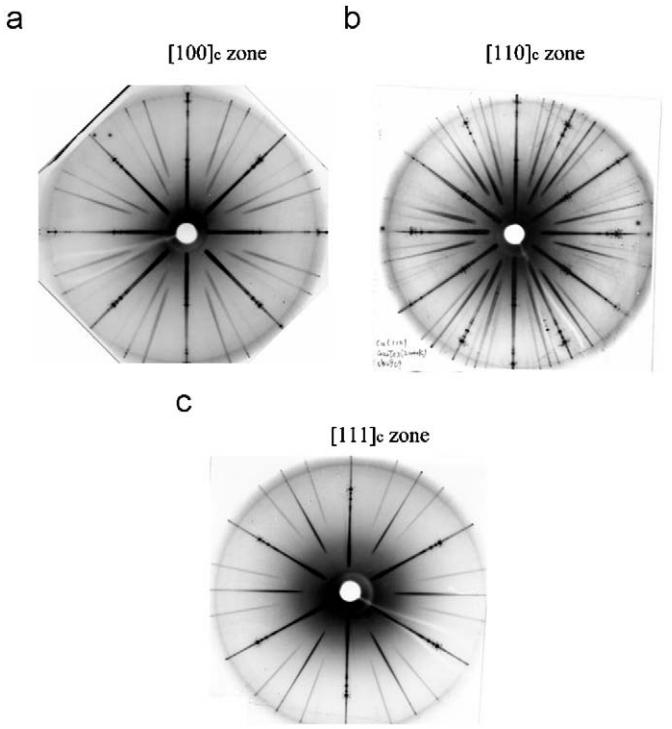

Fig. 2. (a) Precession photographs of as-grown Ga_2Te_3 crystals, taken with Cu radiation. (a) The $[100]_c$ zone, horizontal: $[010]_c$ axis, and vertical: $[001]_c$ axis. (b) The $[110]_c$ zone, horizontal: $[1\bar{1}0]_c$ axis, and vertical: $[001]_c$ axis. (c) The $[111]_c$ zone, horizontal: $[11\bar{2}]_c$ axis, and vertical $[1\bar{1}0]_c$ axis.

A close inspection of the precession photographs also disclosed fine satellite reflections around the main reflections, which are not resolved well in Figs. 2(a)–(c). In order to search for the satellite positions, detailed diffraction measurements were done step by step in the reciprocal space at points with spacing 0.01 along the a^* and b^* axes and 0.025 along the c^* axis. Figs. 3(a)–(k) show X-ray intensity maps of as-grown Ga_2Te_3 crystals taken around several main reflections. For comparison, the contour map taken in quenched Ga_2Te_3 crystal is shown in Fig. 3(l).

3.2. Analysis of the satellite diffraction

The contour maps show the followings.

(i) The satellite reflections appear at $q \approx (0.089(9)\, 0.050(7)\, 0.000(6))_c$ and equivalent positions, where the figure in the parentheses shows the standard deviation estimated using the positions of several equivalent satellite reflections. This shows that the as-grown Ga_2Te_3 crystals have a long period incommensurate structure, the modulation wave vector is