

X-ray study of the air-oxidised α -Ga₂Se₃ and Ga₂Te₃ powders

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Abstract. X-ray studies of the stoichiometrically prepared α -Ga₂Se₃ and Ga₂Te₃ are reported after various stages of air-oxidation in the temperature ranges 250 to 825° C and 250 to 650° C respectively. Diffractometric powder data of Ga₂Te₃ are also reported over the complete 2θ range with remarkable difference in the relative intensities of the (444) and (642) reflections. In α -Ga₂Se₃ the oxidation proceeds by formation of the most stable phase, beta-gallium sesquioxide, complete oxidation occurring at 650° C. For Ga₂Te₃ a mixture of Ga₂TeO₆ and TeO₂ is obtained as the intermediate oxidation products in the range 500 to 600° C, while at 450° C some extra lines which could be indexed on the super-lattice cell of Ga₂Te₃, along with Te and unchanged Ga₂Te₃ lines, are observed. Oxidation at the higher temperature of 650° C led to the disappearance of TeO₂ lines leaving Ga₂TeO₆ as the final well-crystallised phase.

Keywords. X-ray study; α -Ga₂Se₃, Ga₂Te₃; air-oxidised powders.

1. Introduction

α -Ga₂Se₃ and Ga₂Te₃ are the A₂ ^{III}B₃^{VI} type tetrahedral semi-conducting compounds having the defect zinc blende structure, with one-third of the metal sub-lattice positions unoccupied. The lattice parameters of Ga₂Se₃ and Ga₂Te₃ were originally reported by Hahn and Klingler (1949) as 5.418 kX and 5.879 kX respectively. In the case of Ga₂Se₃, Woolley and Keating (1961) found that the odd order lines in the powder photograph were blurred, while the even order lines were sharp. Later, Khan and Ali (1978) reported the lattice parameter of α -Ga₂Se₃, based on the sharp high angle lines, as 5.433 ± 0.001 Å. But no work has yet been reported on air-oxidation and concomitant phase transitions, if any, of the two compounds. We have carried out x-ray studies of the stoichiometrically prepared α -Ga₂Se₃ and Ga₂Te₃ along with their air-oxidation products in the temperature range 250° C-825° C and 250° C-650° C respectively. Mass change data are also reported.

2. Experimental

α -Ga₂Se₃ and Ga₂Te₃ were prepared from the stoichiometric melts of spectroscopically pure components sealed in evacuated fused quartz capsules and heated in a rocking furnace above the respective melting points (1020° C; 790° C) for

about 6 hr, followed by slow cooling to the solidus in 2 hr and final cooling within the furnace to room temperature. The ingots thus obtained were polycrystalline, colours being dark red for α -Ga₂Se₃ and black for Ga₂Te₃. Powder photographs of α -Ga₂Se₃ showed that lines with even indices and $h + k + l = 4n$ were sharp while those with all indices odd were diffuse, similar to the observation of Woolley and Keating (1961). Apart from the limited 2θ range of the powder data of Hahn and Klingler (1949) and absence of relative intensity information by Newman *et al* (1961), no further x-ray information is available on Ga₂Te₃. Complete powder data for Ga₂Te₃ have been obtained with a Philips 1310 diffractometer and CuK _{α} radiation with pulse height discrimination in conjunction with NaI (Tl) scintillation counter.

Preliminary experiments on air-oxidation of α -Ga₂Se₃ and Ga₂Te₃ indicated no further change in the powder patterns of each compound after 8–10 hr of air-oxidation at the given temperature and conditions of experiment. Hard sticking of the oxidised materials with fused-quartz or platinum crucibles in Ga₂Te₃ restricted their use as suitable containers for the oxidation experiment. Finally a charge of approximately 250 mgm of –200 B.S. mesh powder of each compound was thinly spread in a gold crucible and placed in a muffle furnace previously heated to a predetermined temperature and kept overnight. The sticking of the air-oxidised Ga₂Te₃ powders was somewhat less when the gold crucible was used. During the oxidation period, the muffle was kept slightly ajar to allow easy access of air and it was on this account as well as due to mains fluctuations that furnace temperature varied $\pm 10^\circ\text{C}$ from the set temperature. X-ray powder photographs were taken in 11.46 cm diameter Philips camera using CuK _{α} radiation.

3. Results and discussion

The lattice parameter of Ga₂Te₃ extrapolated from the high angle reflections in the powder film using Taylor and Sinclair (1945) function was found to be 5.898 ± 0.001 Å. Table 1 gives the powder data of Ga₂Te₃ obtained with a Philips 1310 diffractometer and CuK _{α} radiation along with the previously reported data of Hahn and Klingler (1949). To measure the peak intensities of the weak reflections in the high angle region, the divergence slit and the counting rate were suitably adjusted and the intensity range necessary to accommodate the full pattern was thus found to be 1000 – 1 as given in table 1. The peak intensities up to $2\theta = 30.3^\circ$ corresponding to the 200 reflections are for the unresolved a_1a_2 components, while for the succeeding reflections the peak intensity of the a_1 component has been given in table 1, the background having been smoothly drawn and allowed for.

A comparison of the present observations with the published powder data of Ga₂Te₃ (table 1) shows that the (111) reflection is actually the strongest peak in the diffractograms in contrast to the (311) peak. The d_{hkl} values computed for the extrapolated $a_0 = 5.898$ Å naturally agree well with the experimental values since the diffractometer values are not affected by the absorption correction in an angular-dependent manner as in the cylindrical specimen case. However, the computed values of a_0 for the Hahn and Klingler data show a systematic decrease with increase in θ in the high θ region which is quite the reverse of the trend expected

Table 1. Comparison of the present observations with JCPDS† data on Ga₂Te₃.

| $d_{\text{cal.}}$ (Å) using $a_0 = 5.898$ Å | Present investigation | | hkl | JCPDS data (card No. 5-734) $a_0 = 5.886$ Å | | |
|--|-----------------------|-----------|----------|--|-----------------------|----------------|
| | $d_{\text{obs.}}$ (Å) | I/I_0^* | | I/I_0 | $d_{\text{obs.}}$ (Å) | a_0 (cal.) Å |
| 3.405 | 3.403 | 1000 | 111 | 60 | 3.393 | 5.877 |
| 2.949 | 2.949 | 138 | 200 | 20 | 2.938 | 5.876 |
| 2.085 | 2.085 | 766 | 220 | 90 | 2.081 | 5.886 |
| 1.778 | 1.777 | 237 | 311 | 100 | 1.771 | 5.874 |
| 1.703 | 1.702 | 37 | 222 | 20 | 1.699 | 5.886 |
| 1.475 | 1.474 | 43 | 400 | 40 | 1.472 | 5.888 |
| 1.353 | 1.353 | 102 | 331 | 69 | 1.351 | 5.889 |
| 1.319 | 1.318 | 33 | 420 | 40 | 1.317 | 5.890 |
| 1.204 | 1.204 | 89 | 422 | 80 | 1.202 | 5.889 |
| 1.135 | 1.135 | 40 | 333, 115 | 60 | 1.131 | 5.877 |
| 1.043 | 1.042 | 20 | 440 | 45 | 1.040 | 5.883 |
| 0.9969 | 0.9968 | 23 | 531 | 80 | 0.9939 | 5.880 |
| 0.9830 | 0.9827 | 8 | 600, 442 | 20 | 0.9801 | 5.880 |
| 0.9326 | 0.9326 | 14 | 620 | 80 | 0.9296 | 5.879 |
| 0.8994 | 0.8995 | 11 | 533 | .. | .. | .. |
| 0.8891 | 0.8890 | 5 | 622 | .. | .. | .. |
| 0.8513 | 0.8512 | 6 | 444 | .. | .. | .. |
| 0.8259 | 0.8259 | 12 | 551, 117 | .. | .. | .. |
| 0.8179 | 0.8180 | 3 | 640 | .. | .. | .. |
| 0.7882 | 0.7882 | 22 | 642 | .. | .. | .. |

* Peak intensities of the unresolved a_1a_2 doublet on the diffractometer charts for (111) and (200), and for the a_1 component of the subsequent reflections, above background.

† Joint Committee on Powder Diffraction Standards.

for cylindrical specimens if absorption is the main factor affecting θ . Our powder films also indicate the same intensity relation between the 111 and 311 reflections as the diffractometer data which are in contrast to the Hahn and Klingler findings given in the card. The observed unusually low intensity of (444) reflection compared to that of (642) could not be explained in terms of the random distribution of vacant metal sub-lattice sites in the defect zinc-blende structure where all the reflections having $h + k + l = 4n$ should be strong, since for these $|F|^2 = (f_{\text{Te}} + 2/3f_{\text{Ga}})^2$ and the atomic structure factors of Te and Ga decrease almost in the same ratio in the θ region corresponding to 444 and 642. The reason for this discrepancy is under investigation using single crystal methods.

The mass changes recorded on air-oxidation of α -Ga₂Se₃ and Ga₂Te₃ at different temperatures are given in table 2. For α -Ga₂Se₃ a steady loss in mass was recorded until it became practically constant in the temperature range 650° C–825° C, where x-ray powder patterns showed only the β -Ga₂O₃ phase. With Ga₂Te₃ gain in mass was observed at 550° C and above, a temperature where Ga₂TeO₆ and TeO₂ were identified. A study of the x-ray patterns of α -Ga₂Se₃ along with the oxidised phases at different temperatures revealed the presence of a weak and broad line at the

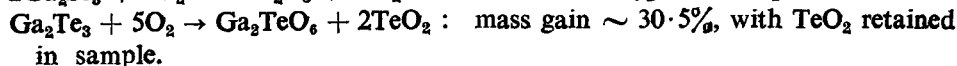
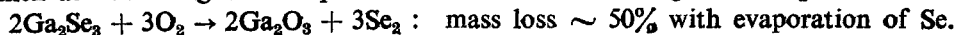
Table 2. Per cent changes in mass recorded in the air-oxidation of α -Ga₂Se₃ and Ga₂Te₃

+, - indicate gain/loss in mass.

| | Temperature of oxidation | | | | | | Calculated mass gain/loss due to oxidation |
|---|--------------------------|--------|--------|--------|--------|--------|--|
| | 250° C | 350° C | 450° C | 550° C | 650° C | 825° C | |
| α -Ga ₂ Se ₃ | -6% | -16% | -25% | -39% | -50% | -49% | ~ 50% loss |
| Ga ₂ Te ₃ | Nil | Nil | Nil | +14% | +25% | .. | ~ 30% gain |

position of the strongest line of β -Ga₂O₃ in the powder pattern of the oxidised α -Ga₂Se₃ material at 350° C, thus indicating the presence of large enough crystallites of the oxide even though the loss in mass had started at 250° C. The crystalline phase analysis of the oxidised samples in the range 350° C–600° C showed a mixture of β -Ga₂O₃ and the starting material, α -Ga₂Se₃. The diffuse character of the α -Ga₂Se₃ lines with *h, k, l*, all odd, appeared to be unaffected by heating in air at these temperatures. Finally, at 650° C the oxidation of α -Ga₂Se₃ was found to be complete with the formation of β -Ga₂O₃ as the x-ray powder patterns of the sample oxidised at higher temperatures of 750° C, 825° C did not change except that the high angle lines became progressively sharper indicating larger and well-crystallised grains.

For Ga₂Te₃, powder photographs of air-oxidised materials in the range 250° C–450° C showed Te lines along with the starting phase. It was interesting to note that the x-ray pattern of the material oxidised at 450° C exhibited several weak extra lines which could be indexed on the super-lattice cell of Ga₂Te₃ with lattice parameters: $a = 4.17$, $b = 23.60$, $c = 12.52$ Å, as reported by Newman and Cundall (1963), in addition to the Te and Ga₂Te₃ phases. Table 3 gives the x-ray powder data of Ga₂Te₃ air-oxidised at 450° C containing these lines. Subsequently a mixture of Ga₂TeO₆ and TeO₂, former being the predominant phase, was observed in the range 500° C–600° C. With increase of temperature of oxidation at 650° C, TeO₂ (m.p. 733° C) lines disappeared from the x-ray powder pattern leaving Ga₂TeO₆ as the final well-crystallised stable phase. The attainment of the constant mass in the case of α -Ga₂Se₃ and of near theoretical gain in the case of Ga₂Te₃ can be taken as indicating the completion of oxidation according to the equations:



The x-ray patterns of the final oxidised products in both the cases, at 825° C for α -Ga₂Se₃ and at 650° C for Ga₂Te₃, were found to be in good agreement with the published data for β -Ga₂O₃ and Ga₂TeO₆ respectively.

The process of air-oxidation of solid materials is principally controlled by the diffusion of oxygen atoms in the lattice. In α -Ga₂Se₃ the Se atoms are eliminated from the lattice creating vacant sites for relatively easy diffusion of oxygen atoms.

This results in the formation of β -Ga₂O₃, the most stable form of gallium sesquioxide.

For Ga₂Te₃ air-oxidised at 450° C, the presence of super-lattice lines can be explained as due to a volume fraction of the initial material which transforms to the larger cell structure under the action of heat and restricted supply of oxygen, while the outer layers of the grains suffer Te dissociation which is present on the grains in the elemental form. However, the width of the Ga₂Te₃ cubic (111) reflection at $d = 3.405 \text{ \AA}$ is such as to rule out the presence of another line close by at $d = 3.37 \text{ \AA}$, indexible as (070) of the super-lattice cell. This absence of (070)

Table 3. Powder data for air-oxidised Ga₂Te₃ at 450° C (upto $2\theta \sim 82^\circ$).

| Air-oxidised Ga ₂ Te ₃ at 450° C | | Te (JCPDS No. 4-554) | | | Ga ₂ Te ₃ (Present film data) | | | Ga ₂ Te ₃ super cell $a = 4.17 \text{ \AA}$ $b = 23.60 \text{ \AA}$ $c = 12.52 \text{ \AA}$ | |
|--|--------------------|-----------------------|---------|----------|---|--------------------|-------|--|----------|
| $d_{\text{obs.}}$ (Å) | Relative intensity | $d_{\text{obs.}}$ (Å) | I/I_0 | hkl | $d_{\text{obs.}}$ (Å) | Relative Intensity | hkl | $d_{\text{cal.}}$ (Å) | hkl |
| 4.26 | vw | | | | | | | 4.28 | 042 |
| 3.85 | w | 3.86 | 20 | 100 | | | | | |
| 3.405 | m | | | | 3.408 | s | 111 | 3.404 | 043 |
| 3.243 | s | 3.23 | 100 | 01 | | | | | |
| 3.077 | vw | | | | | | | 3.09 | 014 |
| 2.943 | m | | | | 2.949 | w | 200 | 2.947 | 103 |
| 2.757 | vw | | | | | | | 2.761 | 044 |
| 2.557 | w | | | | | | | 2.564 | 171 |
| 2.355 | m | 2.351 | 37 | 102 | | | | 2.357 | 163 |
| 2.232 | m | 2.228 | 31 | 110 | | | | | |
| 2.092 | m | 2.087 | 11 | 111 | 2.085 | m | 220 | 2.084 | 183 |
| 1.974 | w | 1.980 | 8 | 003 | | | | | |
| 1.929 | vw | 1.930 | 4 | 200 | | | | | |
| 1.901 | vw | | | | | | | 1.905 | 056, 250 |
| 1.840 | w | 1.835 | 20 | 201 | | | | | |
| 1.784 | m | 1.781 | 7 | 112 | 1.777 | m | 311 | 1.777 | 146 |
| 1.702 | vw | | | | 1.702 | vw | 222 | 1.701 | 086 |
| 1.623 | w | 1.616 | 12 | 202 | | | | | |
| 1.478 | m | 1.479 | 13 | 113 | 1.474 | w | 400 | 1.474 | 206 |
| 1.456 | w | 1.459 | 8 | 210 | | | | | |
| 1.422 | w | 1.417 | 8 | 211 | | | | | |
| 1.382 | w | 1.383 | 7 | 104, 203 | | | | | |
| 1.357 | w | | | | 1.353 | w | 331 | 1.352 | 1, 12, 6 |
| 1.314 | w | 1.309 | 6 | 212 | 1.318 | vw | 420 | 1.318 | 286 |
| 1.262 | vw | 1.257 | 4 | 301 | | | | | |
| 1.207 | w | | | | 1.204 | w | 422 | 1.203 | 189 |
| 1.178 | vw | 1.180 | 3 | 302 | | | | | |

vw = very weak, w = weak, m = medium, s = strong.

is at variance with that of Newman and Cundall (1963), who did not report the spacings and relative intensities of Ga_2Te_3 super-lattice lines but only the lattice parameters of the super-cell. The agglomeration of the oxidised mass and its sticking to the container in the case of Ga_2Te_3 at 550°C , and at 650°C , temperatures well below the melting point of TeO_2 is most probably due to the formation of its glassy phase, Dutton and Cooper (1966), which also explains the disappearance of the TeO_2 lines in the powder patterns.

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