X-ray study of the air-oxidised $\alpha$-Ga$_2$Se$_3$ and Ga$_2$Te$_3$ powders

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MS received 5 November 1979

Abstract. X-ray studies of the stoichiometrically prepared $\alpha$-Ga$_2$Se$_3$ and Ga$_2$Te$_3$ 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 Ga$_2$Te$_3$ are also reported over the complete 2$\theta$ range with remarkable difference in the relative intensities of the (444) and (642) reflections. In $\alpha$-Ga$_2$Se$_3$ the oxidation proceeds by formation of the most stable phase, beta-gallium sesquioxide, complete oxidation occurring at 650°C. For Ga$_2$Te$_3$ a mixture of Ga$_2$TeO$_6$ and TeO$_2$ 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 Ga$_2$Te$_3$, along with Te and unchanged Ga$_2$Te$_3$ lines, are observed. Oxidation at the higher temperature of 650°C led to the disappearance of TeO$_2$ lines leaving Ga$_2$TeO$_6$ as the final well-crystallised phase.

Keywords. X-ray study; $\alpha$-Ga$_2$Se$_3$, Ga$_2$Te$_3$; air-oxidised powders.

1. Introduction

$\alpha$-Ga$_2$Se$_3$ and Ga$_2$Te$_3$ are the $A_2^{\text{III}}B_3^{\text{VII}}$ 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 Ga$_2$Se$_3$ and Ga$_2$Te$_3$ were originally reported by Hahn and Klingler (1949) as 5.418 kX and 5.879 kX respectively. In the case of Ga$_2$Se$_3$, 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 $\alpha$-Ga$_2$Se$_3$, 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 $\alpha$-Ga$_2$Se$_3$ and Ga$_2$Te$_3$ 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

$\alpha$-Ga$_2$Se$_3$ and Ga$_2$Te$_3$ 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 \( \alpha \)-Ga Ses and black for Ga Te . Powder photographs
of \( \alpha \)-Ga Ses 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 20 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 Ga Te . Complete powder
data for Ga Te have been obtained with a Philips 1310 diffractometer and CuK \( \alpha \)
radiation with pulse height discrimination in conjunction with NaI(Tl) scintillation
counter.

Preliminary experiments on air-oxidation of \( \alpha \)-Ga Ses and Ga Te 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 Ga Te 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 Ga Te 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 \( \pm 10^\circ C \) from the set temperature. X-ray powder photo-
graphs were taken in 11·46 cm diameter Philips camera using CuK \( \alpha \) radiation.

3. Results and discussion

The lattice parameter of Ga Te extrapolated from the high angle reflections in the
powder film using Taylor and Sinclair (1945) function was found to be \( 5.898 \pm 0.001 \) Å. Table 1 gives the powder data of Ga Te obtained with a Philips 1310
diffractometer and CuK \( \alpha \) 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 2θ =
30·3° corresponding to the 200 reflections are for the unresolved \( a_1a_2 \) components,
while for the succeeding reflections the peak intensity of the \( a_4 \) 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
Ga Te (table 1) shows that the (111) reflection is actually the strongest peak in the
diffractograms in contrast to the (311) peak. The \( d_{ab1} \) values computed for the
extrapolated \( a_4 = 5.898 \) 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 \( a_4 \) for the Hahn and Klingler data show a systematic decrease with
increase in \( \theta \) in the high \( \theta \) region which is quite the reverse of the trend expected