Crystal data for $\beta$-Ga$_2$Se$_3$

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The structure of the ordered form of the partially ordered cubic $\alpha$-Ga$_2$Se$_3$ is based on a tetragonal, body-centred cell, with space group $I4_1/acd$, $a=23.235$ (5), $c=10.828$ (2) Å, $Z=48$, $D_m=4.91$ g cm$^{-3}$ at 30°C. Diffractometer data up to $\theta \sim 80^\circ$ from Cu Kα radiation are given for the $\beta$ phase with nominal composition Ga$_2$Se$_3.03$.

Origin of specimens

During the investigation of extended defects in $\alpha$-Ga$_2$Se$_3$, it was found that for ingots made from stoichiometric melts of spectroscopically pure components annealing at $\sim 600^\circ$C in vacuum for 30 d had no effect on the state of ordering. Following the work of Palatnik & Belova (1965), four compositions represented by the formulae Ga$_{2.05}$Se$_3$, Ga$_{2.005}$Se$_3$, Ga$_2$Se$_3.03$ and Ga$_2$Se$_3.05$ were made from spectroscopically pure elements, sealed in evacuated, fused-quartz capsules and heated in a rocking furnace at $\sim 1270^\circ$C for 6 h, followed by slow cooling to the solidus at $\sim 1020^\circ$C in 2 h and final cooling within the furnace to room temperature.

Visual inspection of these capsules was carried out to check for unusual features, if any, before the start of the annealing runs at $\sim 600^\circ$C for 34 d. The ingots thus obtained were polycrystalline, dark red materials with total mass the same as at the start of the synthesis except for traces of pure elements condensed on the inner walls of the capsules during cooling from the liquidus. The crystals from each of the two ingots with excess Se were mostly composite and varied in size and form, while those from the excess Ga compositions were darker in colour, without intergrowing or adhering crystallites. Powdering of lumps indicated that the former set, referred to as $\beta$-Ga$_2$Se$_3$, by Palatnik & Belova (1965), was harder and more brittle than both the excess Ga compositions and the $\alpha$ phase, similarly annealed as referred to above.

Crystal geometry

Powder photographs of the four compositions indicated that the Ga-rich compositions were similar to the $\alpha$ form which was found by Hahn & Klinger (1949) to have the zincblende structure with $a_0=5.418$ Å and statistical occupation of the metal-atom sites. These photographs also showed that lines with all indices even were sharp while those with all indices odd were diffuse, similar to the observation of Woolley & Keating (1961). Hence the state of partial ordering for these two compositions was taken to be similar to that of the $\alpha$ phase. These extended three-dimensional defects are under investigation.

In marked contrast with the $\alpha$ phase, the two Se-rich compositions gave powder patterns with a large number of sharp lines and high-angle reflexions showing good $\alpha_1, \alpha_2$ resolution. The diffractometer runs indicated an even larger number of lines, mainly in the regions corresponding to some broad lines of the X-ray photographs of the $\alpha$ phase. Many of these closely spaced peaks had superimpositions of the $\alpha_1, \alpha_2$ components of the neighbouring reflexions. The similarity of the diffractometer and powder film data for several specimens from the Se-rich compositions and the absence of free Se or Ga and of GaSe indicated the formation of the same phase with a Se solubility range of 60.2 to 60.4 at.%. This has been designated as $\beta$-Ga$_2$Se$_3$. X-ray fluorescence analysis of the $\alpha$ and $\beta$-phase powders has further confirmed that their composition is quite close.

Before an attempt was made to index the reflexions, single-crystal data for the unit cell and space group were obtained from those few crystals, out of the large number investigated, which were most free from adhering and intergrowing crystallites. The $a$-axis rotation films indicated that the high-intensity layer lines corresponded to a translation axis of $\sim 7.75$ Å. However, the presence of weak layer lines suitably interspersed between the main layers clearly indicated the crystals to have a superlattice cell with $a \sim 23.25$ Å. Indexing of the main levels (0.3,6,9 and 12) and the weaker 2nd and 4th-level equi-inclination Weissenberg films could be done on a tetragonal cell with the following conditions for reflexion: $h+k+l=2n$; $hk0$: $hk=2n$; $0kl$: $kl=2n$; $hhl$: $l=2mh+4n$. The space group fulfilling these conditions is $I4_1/acd$. After preliminary indexing of the X-ray films on this cell and calculation of more accurate $a$ and $c$ parameters, the spacings obtained from the diffractometer runs were indexed.

Least-squares analysis of about 30 high-angle spacings, obtained with Cu Kα radiation $[\theta(\alpha_1)=1.54051$, $\theta(\alpha_2)=1.54433$ Å] in the 20 Bragg angle range 87.88 to 156.50°, from the diffractometer data has been carried out on an IBM 360 computer with the following results: $a=23.235$ (5), $c=10.828$ (2) Å at 30°C, $U=5845.66$ Å$^3$, $Z=48$, $D_m=4.91$ g cm$^{-3}$ at 30°C, $D_a=5.129$ g cm$^{-3}$.

Powder data

Table 1 gives the powder data obtained with a Philips 1310 diffractometer and Cu Kα radiation. In order to measure the peak intensities of the weak reflexions in the high-angle region, the counting rate was suitably adjusted and the intensity range necessary to accommodate the full pattern was thus found to be $1000$ 1 as given in the table. The intensities up to $\theta=34.22^\circ$ corresponding to the 12.12.0 reflexion are for the unresolved $\alpha_1, \alpha_2$ components, while for the succeeding reflexions the peak intensity of the $\alpha_1$ component has been given in Table 1. However, the close bunching of reflexions in certain Bragg-angle regions (corresponding mainly to regions of strong $\alpha$-phase reflexions) and the resulting superimposition of the $\alpha_1$ component of one on the $\alpha_2$ component of the preceding reflexion did require careful analysis. In spite of this, listed intensities are not altogether free from this source of error.

Comparison with other results

Apart from the data of Palatnik & Belova (1965) no further information is available on the phases of Ga$_2$Se$_3$ with limited
variability of composition. From the presence of weak superstructural lines in the patterns of compositions Ga$_2$Se$_3$-0.3 and Ga$_2$Se$_3$-0.1 they indicated that a tetragonal cell with constants $a(tet.)$ = 6$a_o$ and $c(tet.)$ = 2$a_o$ could be chosen where $a_o$ is the lattice parameter of the $\alpha$ phase. By rotating the $XY$ axes through 45 $^\circ$, a body-centred orthorhombic cell with constants $3a_o/2$, $6a_o/2$ and $2a_o$ could again be chosen by them and further reducing this cell to one with constants $2a_o/2$, $3a_o/2$ and $2a_o$, their powder data in the range $2\theta$ = 60$^\circ$ could be satisfactorily indexed. The space group suggested by them is $Pcca$ ($D_{2h}^5$). The JCPDS card No. 40-437 gives the spacings and indices on this cell. Now, taking only the evidence of our diffractometer data, it can be seen that almost all the main lines of the $\beta$ phase can be indexed on this smaller orthorhombic cell but at least seven lines remain with $hk0$ indices such that $h \neq 3n$, $k \neq 2n$. These cannot be indexed on the smaller orthorhombic cell of Palatnik & Belova, and the larger body-centred tetragonal cell chosen by us on the basis of single-crystal results is thus necessary. This is related to the $\alpha$ phase cell with $a \geq 3|a_o|$, $c \geq 2a_o$.

The agreement between the measured and calculated densities is not as good as expected, probably because of the presence of closed pores and poor wettability of the $\beta$ phase grains by the water used in the measurements. It may be mentioned that similar behaviour was observed for $\alpha$-Ga$_2$Se$_3$ by Hahn & Klinger (1949) with $D_{2h}^5 = 4.92$ and $D_2 = 5.20$ g cm$^{-3}$. The reason for this discrepancy is under investigation.

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References

