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AN X-RAY DIFFRACTION STUDY OF THE SYSTEM Al - In - S

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The most widely investigated semiconductor in the system In - S is β-In_2S_3, stable at room temperature. Its crystal structure was first studied, by means of X-ray diffraction, by Hahn and Kringler (1), who ascribed to it a cubic symmetry of disordered cation deficient spinel, with the unit cell dimension $a_0 = 10.7_7$ Å. From X-ray powder diffraction patterns Rooymans (2) concluded that β-In_2S_3 had a spinel type structure with ordered indium vacancies along the screw axis 4_1, this indicating a tetragonal symmetry. The crystal structure was solved by King (3) and Steigmann et al. (4) using single crystal diffraction patterns. They confirmed, that the symmetry was tetragonal, with space group $I4_1/amd$, and the unit cell, consisting of three spinel blocks, with dimensions $a_\beta = 7.61_8$ Å ($\approx a_0/\sqrt{2}$), $c_\beta = 32.33$ Å ($\approx 3a_0$) (5). The sulphur atoms are in cubic close-packed arrangement, with the indium atoms distributed over the octahedral and tetrahedral interstices. According to van Landuyt and Amelinckx (6), on the basis of electron microscopy and diffraction, the tetrahedrally coordinated indium atoms become mobile enough above 420°C, that a disordering of the tetrahedral vacancies takes place. The resulting structure is defined by the ordered octahedral vacancies, with the cubic unit cell, a_0 (6,7). Above 750°C the transformation to γ-phase takes place with a redistribution of the indium atoms (6,5,7). According to Kundra and Ali (5) and to Bartzokas et al. (7) γ-In_2S_3 is a hexagonal layered structure consisting of successive packets of layers S-In-S-In-S with the unit cell dimensions (at 800°C) $a_\gamma = 3.85$Å ($\approx a_0/(2\sqrt{2})$), $c_\gamma = 9.15$Å ($\approx a_0\sqrt{3}/2$) (5). Diehl and Nitsche (8) found that γ-In_2S_3 can be stabilized at room temperature with a few atomic percent of As or Sb.

A partial replacement of In with other metal atoms has not been widely investigated. The compounds obtained with partial replacement of In with Zn or Tl have the crystal structure resembling to that of γ-In_2S_3. For instance;

$ZnIn_2S_4$: a = 3.85 Å = a_γ, c = 37.0$_2$ Å ≈ $4c_\gamma$,

$Zn_2In_2S_5$: a = 3.85 Å = a_γ, c = 46.2$_7$ Å ≈ $5c_\gamma$,

$Zn_3In_2S_6$: a = 3.85 Å = a_γ, c = 18.50 Å ≈ $2c_\gamma$, (9-11);

$TlInS_2$: a = 3.81Å ≈ a_γ, c = 14.91 Å (≈(5/3)c_γ) (12,13).

By partial replacing of In with Cr a continuous series of cubic compounds was obtained, with the unit cell dimension in the range from $a_\beta\sqrt{2}$ = 10.77Å for β-In_2S_3 to a = 10.59 Å for $CrIn_2S_4$ (14).

The first data of investigation of partial replacement of In with Al were reported by Etlinger, who prepared $Al_2In_{12}S_{21}$ and studied some of its physical properties (15). Afterwards a systematic study of the system $(Al_xIn_{1-x})_2S_3$ has been undertaken, with x changing from 0 to 1/3. The first results are given in the present communication. Seven compounds with x = 0 (β-In_2S_3), 1/13, 1/11, 1/9, 1/7, 1/5 and 1/3 were prepared by a modified SSD (solid, solution, diffusion) method (16). The compounds were investigated by X-ray diffraction, using a counter diffractometer with a monochromatized CuKα radiation. Already for small values of x (x = 1/13) the intensities of diffraction lines, which are a consequence of ordering of cation vacancies along the screw axis 4_1 (Fig. 1, x = 0), decrease essentially. With further increase of concentration of Al (x = 1/11) these diffraction lines disappear completely. The X-ray diffraction powder pattern contains only diffraction lines which correspond to a face-centred cubic symmetry, with the unit cell dimension $a_{fcc} \approx a_\beta\sqrt{2}$ (Fig. 1, x = 1/9). Miller indices hkl given in Fig. 1 are in terms of this unit cell. The value of a_{fcc} continuously decreases with the increase of partial replacement of In with Al from 10.77$_2$ Å for

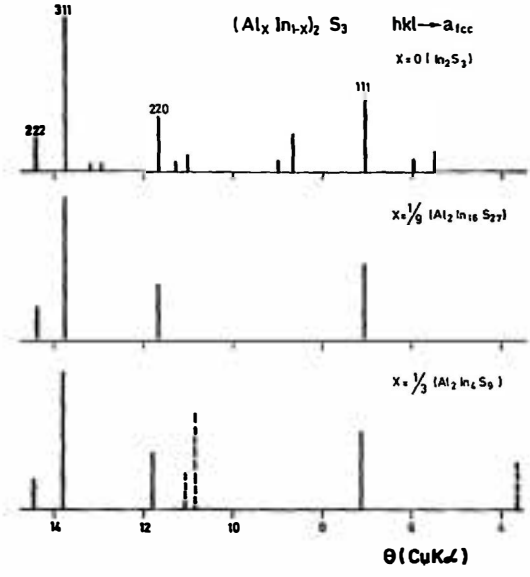
311
$(Al_x In_{1-x})_2 S_3$
hkl→a_{fcc}
X=0 (In_2S_3)
111
220
222
X=1/9 ($Al_2In_{16}S_{27}$)
X=1/3 ($Al_2In_4S_9$)
14
12
10
θ(CuKα)

Fig. 1.

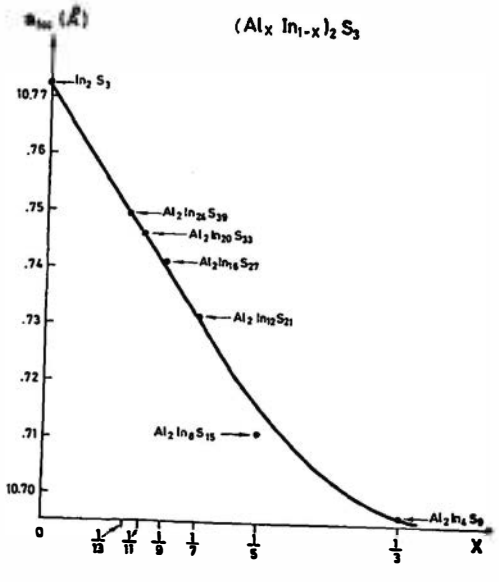
a_{fcc} (Å)
$(Al_x In_{1-x})_2 S_3$
$In_2 S_3$
10.77
.76
.75
$Al_2In_{24}S_{39}$
$Al_2In_{20}S_{33}$
.74
$Al_2In_{16}S_{27}$
.73
$Al_2In_{12}S_{21}$
.72
.71
$Al_2In_8S_{15}$
10.70
$Al_2In_4S_9$
0
1/13
1/11
1/9
1/7
1/5
1/3
X

Fig. 2.

$x = 0$ (β-In_2S_3) to 10.69_7 Å for $x = 1/3$, or for 0.70% (Fig. 2). At $x = 1/7$ faint diffraction lines of another phase appear in diffraction pattern. Their intensities increase with the increase of concentration of Al. The preparation with $x = 1/3$ contains, say, 10% of this phase. An attempt to identify this phase by means of the JCPDS powder diffraction file led to an assumption that this might be an aluminium sulphate.

Further investigation of the system is in the course.

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