JOURNAL OF MATERIALS SCIENCE 12 (1977) 2441–2446

Crystallographic studies of some mixed thiogallate semiconductors

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A crystallographic study has been made of solid solutions of the tetragonal defect chalcopyrites ($I\bar{4}$), $CdGa_2S_4$ and $CdGa_2Se_4$. The compositions may be represented by $CdGa_2S_{4(1-x)}Se_{4x}$ where $x = 0.0, 0.25, 0.50, 0.75$ and 1.0. A complete solid solubility was observed between these two compounds. The *a*-axis values varied linearly with composition, whilst *c*-axis values initially showed a slower rise for $x < 0.5$ and then a marked rapid rise with increasing selenium content. Single crystals were grown of these compositions by the chemical transport method. Optimum conditions required for the growth of the crystals have been established. The crystals of $CdGa_2S_4$ and $CdGa_2S_3Se$ had the biggest face parallel to (0 0 1) plane whereas crystals of compounds $CdGa_2S_2Se_2$, $CdGa_2SSe_3$ and $CdGa_2Se_4$ were triangular prisms with a face parallel to (1 1 2) plane and ⟨1 1 0⟩ as the growth axis. The parameters x, y and z for selenium position in $CdGa_2Se_4$ were obtained by comparing the calculated values of F^2 factors with those obtained from observed intensities. The best match was found for $x = y = 0.25$ and $z = 0.15$.

1. Introduction

Compounds of the series AB_2C_4 (A = Zn, Cd, B = Ga, C = S, Se, Te) are ternary analogoues of the familiar II–VI compounds. Very little is known of either the electrical or optical properties of this class of materials. They are tetrahedrally co-ordinated semiconductors which crystallize in the uniaxial defect chalcopyrite structure ($I\bar{4}$) [1]. $CdGa_2S_4$ displays large birefringence and is potentially interesting as non-linear optical material [2–4]. Another compound $CdGa_2Se_4$ exhibits large photoconductivity in the visible range and is a promising photoconductor [5].

Crystal structure of these compounds was studied by Hahn *et al.* [1]. Crystal growth by chemical transport reaction (CTR) was reported by Nische *et al.* [6]. The CTR method has been successfully applied to grow homogeneous single crystals of pseudobinary systems such as $GaAs_{1-x}P_x$ [7] and of pseudoternary systems such as $CuGaS_{2-x}Se_x$ [8] and $ZnSiAs_xP_{2-x}$ [9]. We have applied this method to the growth of single crystal of pseudoternary system $CdGa_2S_{4(1-x)}Se_{4(x)}$. In this paper we have reported the crystal growth and structural studies of the system $CdGa_2S_{4(1-x)}Se_{4(x)}$, where $x = 0$, 0.25, 0.50, 0.75, 1.00.

2. Preparation

The samples were prepared from the elements S, Se, Cd, Ga (Koch-Light Co., USA) which were reacted in a carbon-coated vacuum sealed quartz ampoules. In order to avoid the dissociation of the compounds at their melting point, a slight excess of the volatile component (usually 0.1 mol %) was used. Heating was carried out in the following steps:

$$25^\circ \xrightarrow{2\,h} 250^\circ \xrightarrow{4\,h} 600^\circ \xrightarrow{24\,h} 600^\circ \xrightarrow{16\,h} 1050^\circ \xrightarrow[\text{rocking}]{12\,h} 1100^\circ \xrightarrow{24\,h} 500^\circ\,C$$

and then quenched in air. The quartz ampoules containing the material were found to crack at 500° C while cooling after the reaction was complete. In order to prevent the ingots from oxidation the ampoule containing the material was always enclosed in another quartz ampoule and vacuum sealed.

TABLE I

Composition Parameter	$CdGa_2S_4$	$CdGa_2S_3Se$	$CdGa_2S_2Se_2$	$CdGa_2SSe_3$	$CdGa_2Se_4$
Colour	Colourless	Yellow	Brown	Dark brown	Dark brown
Shape	Polyhedral	Polyhedral	Triangular prisms	Triangular prisms	Triangular prisms
Size (mm^3)	5 × 3 × 3	5 × 3 × 2	7 × 2 × 2	10 × 2 × 1.5	5 × 2 × 1
Hot end (° C)	625	675	725	767	775
Cold end (° C)	605	630	680	720	730
Iodine ($mg\,cm^{-3}$)	4	4	5	5	5
a (Å)	5.536	5.572	5.620	5.682	5.74
c (Å)	10.16	10.25	10.38	10.55	10.74
c/a	1.835	1.840	1.847	1.857	1.872
Growth direction	001	001	110	110	110

The polycrystalline ingots were removed and crushed to powder in an agate mortar and pestle. The finely powdered mass was analysed by X-ray powder diffraction at room temperature using a 14 cm Debye–Scherrer camera and Cu$K\alpha$ radiation filtered through a Ni-foil. The patterns were carefully checked for the formation of an homogeneous single-phase solid solution and the presence of extra lines due to unreacted materials.

3. Crystal growth

Single crystals of these compositions were grown by employing the chemical transport reaction [6] using iodine as a transport agent. Approximately 10 g of the charge (in the form of polycrystalline material prepared as above) was introduced along with 5 $mg\,cm^{-3}$ of iodine into the quartz tube (12 mm diameter × 150 mm long). The quartz tube was vacuum sealed maintaining the material at liquid air temperature and free from moisture etc. The ampoule was then placed in a tube furnace with a known preset temperature gradient. Various growth conditions and temperature gradients were used till uniform homogeneously coloured crystals were obtained. The optimum conditions used for the growth of crystals are given in Table I.

The literature shows that conventional methods [12] of growing single crystals of $CdGa_2S_4$ have failed to give colourless crystals. The yellowish colour of the crystals has been attributed to the nonstoichiometric composition of the crystal. Nische *et al.* [6] obtained colourless single crystals by the CTR method. They used a hot zone 50° C hgiher than the cold zone (600° C). We tried the same conditions but our trials failed to give colourless crystals. We therefore tried lower gradients and found that a difference of 20 to 25° C with the cold end at 600° C gave colourless crystals.

$CdGa_2Se_4$ crystals were grown by Nisch *et al.* [6] giving orange-red single crystals with a columnar a shape using a hot zone at 900° C and a cold zone at 700° C. Agaev *et al.* [13] used a higher concentration of iodine (8 $mg\,cm^{-3}$) than that of Nische *et al.* (5 $mg\,cm^{-3}$), and a hot zone of 780° C and a cold zone of 680° C. Though bigger crystals were produced by Agaev *et al.* these crystals probably contained a high concentration of iodine as impurity which is known to affect the forbidden band gaps. We therefore used lower temperature differences and low iodine concentrations, and these conditions gave brown triangular prisms (Table I).

The composition of the crystals was determined by taking their powder X-ray diffraction photographs and measuring their lattice parameters. The plots of lattice parameters as obtained from initial polycrystalline data versus composition (Figs. 1 and 3) were then compared to obtain the composition. Table II gives the comparison of the lattice parameters obtained from crushed single-crystals and initial polycrystalline data. It is rather an approximate method of deducing the composition of the crystals, but is still indicative of the fact that the composition of the crystals is nearly the same as expected in the chemical formulae; $CdGa_2S_4$, $CdGa_2S_3Se$, $CdGa_2S_2Se_2$, $CdGa_2SSe_3$ and $CdGa_2Se_4$.

The chemical analysis was made for the volatile components, mainly selenium, which indicated a deficiency of a selenium of approximately 1 wt %. The composition of the crystal has therefore been assumed to be the same as that of the starting polycrystalline material.

TABLE II Comparison of lattice parameters of the crushed single-crystals with those of the initial polycrystalline materials

Apparent composition	Initial polycrystalline data			Single-crystal crushed data		
	a(Å)	c(Å)	c/a	a(Å)	c(Å)	c/a
$CdGa_2S_4$	5.548	10.170	1.832	5.536	10.16	1.835
$CdGa_2S_3Se$	5.577	10.275	1.842	5.572	10.25	1.840
$CdGa_2S_2Se_2$	5.610	10.370	1.848	5.620	10.38	1.847
$CdGa_2S_1Se_3$	5.670	10.530	1.857	5.682	10.55	1.857
$CdGa_2Se_4$	5.738	10.738	1.872	5.74	10.74	1.872

Laue-back reflection photographs from the well-developed faces revealed that these faces were developed parallel to a (0 0 1) plane in the case of $CdGa_2S_4$ and $CdGa_2S_3Se$, whereas parallel to a (1 1 2) plane for the other compositions. The compositions $CdGa_2S_2Se_2$, $CdGa_2SSe_3$ and $CdGa_2Se_4$ crystallized with a triangular prism shape with a prism edge parallel to the ⟨1 1 0⟩ axis.

4. Results and discussion

Hahn *et al.* [1] named the compound $CdGa_2S_4$ as thiogallate which was found to have a structure very similar to chalcopyrite ($I\bar{4}2d$) and a space group S_4^2 (or $I\bar{4}$). Formally the thiogallate structure can be derived from the chalcopyrite structure by omitting the copper atoms at $\frac{1}{4}$ and $\frac{3}{4}$ heights. The atomic positions for $CdGa_2X_4$ then may be written with origin at $\bar{4}$ (0, 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) +

2Cd at 2*a* position: (0, 0, 0)
2Ga at 2*b* position: $(0, 0, \frac{1}{2})$
2Ga at 2*d* position: $(0, \frac{1}{2}, \frac{1}{4})$
8(S) at 8(g) position: $(x, y, z)(\bar{x}, \bar{y}, z)(y, \bar{x}, \bar{z})(\bar{y}, x, \bar{z})$

and condition limiting possible reflections is $h + k + l = 2n$. The ideal values of x, y and z for the chalcopyrite structure are $\frac{1}{4}$, $\frac{1}{4}$ and $\frac{1}{8}$ respectively. The unit cell of $CdGa_2X_4$ (X = S, Se, Te) is shown in Fig. 1.

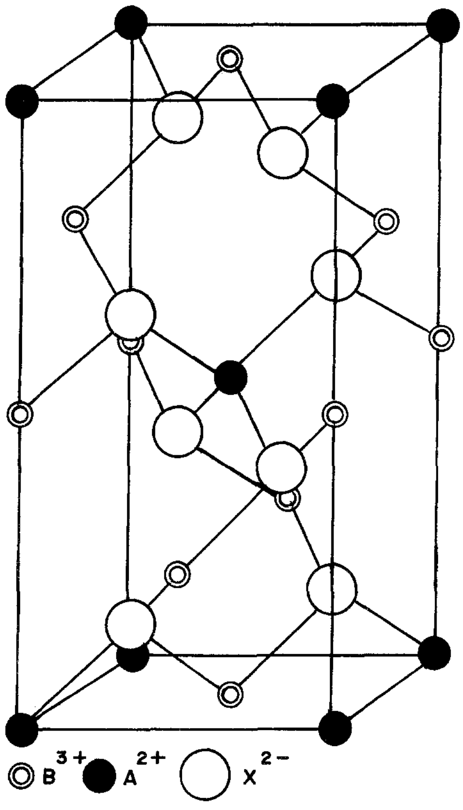

Figure 1 Unit cell of thiogallate structure ($I\bar{4}$)

Hahn *et al.* [1] first prepared these compounds and investigated the complete structure of $CdGa_2S_4$. They reported the lattice parameters to have values $a = 5.577$ Å, and $c = 10.08$ Å and $c/a = 1.808$ and the x, y, z parameters for sulphur in $CdGa_2S_4$ as 0.26, 0.27 and 0.14 respectively. Subseqently Antonov *et al.* [10] reported the lattice parameters to have values $a = 7.78$ Å, $c = 10.43$ Å. Hobden [3] analysed crushed powder of single-crystals grown by a slow cooling method and obtained $a = 5.54(6)$ Å, $c = 10.16$ Å. Mamedov [11] recently reported that the compound has $a = 5.57$ Å and $c = 10.01$ Å.

We have also examined carefully the structure of $CdGa_2S_4$. The lattice parameters as calculated from powder (polycrystalline ingot) and crushed single-crystals are: polycrystalline powder $a = 5.548$ Å, $c = 10.170$ Å, $c/a = 1.832$, single crystal powder $a = 5.536$ Å, $c = 10.16$ Å, $c/a = 1.835$.

There is only one structure reported for $CdGa_2Se_4$ [1], it is isomorphous to that of $CdGa_2S_4$. The lattice parameters for $CdGa_2Se_4$ were $a = 5.742$ Å, $c = 10.73$ Å with $c/a = 1.87$ whereas those obtained in the present investigation are $a = 5.738$ Å, $c = 10.738$ Å and $c/a = 1.872$.

Our X-ray powder diffraction measurements on $CdGa_2Se_4$ revealed an absence of the reflections

TABLE III

hkl	I_{app}	I_{true}	F^2_{true} (normalized)	F^2_{cal}	d^{-2}_{obs} (Å^{-2})	d^{-2}_{cal} (Å^{-2})
0 0 2	–	–	–	0.6	–	0.0347
1 0 1	12	27	3	4	0.0390	0.0390
1 1 0	14	28	10	8	0.0609	0.0607
1 1 2	97	161	50	54	0.0955	0.0954
1 0 3	21	33	11	5	0.1086	0.1084
2 0 0	–	–	–	1.7	0.1216	0.1214
0 0 4	–	–	–	0.1	–	0.1387
2 0 2	25	33	17	20	0.1563	0.1562
$2 1 1 + 2 \bar{1} 1$	15	20	10	7	0.1604	0.1605
1 1 4	21	24	17	20	0.2002	0.1994
$2 1 3 + 2 \bar{1} 3$	11	11	8	6	0.2305	0.2299
2 2 0	72	75	132	130	0.2436	0.2430
1 0 5	–	–	–	2	–	0.2472
2 0 4	100	100	96	100	0.2603	0.2602
2 2 2	2	2	2	0.1	0.2826	0.2776
$3 1 0 + 3 \bar{1} 0$	12	12	13	10	0.3052	0.3037
0 0 6	10	10	47	47	0.3111	0.3121
$3 1 2 + 3 \bar{1} 2$	89	76	100	107	0.3384	0.3384
3 0 3	–	–	–	2	–	0.3513
$2 1 5 + 2 \bar{1} 5$	–	–	–	4	–	0.3686
1 1 6	20	17	23	16	0.3723	0.3728
$3 2 1 + 3 \bar{2} 1$	8	6	9	5	0.4026	0.3980
2 0 6	–	–	–	5	–	0.4335
$3 1 4 + 3 \bar{1} 4$	17	16	29	29	0.4421	0.4424
$3 2 3 + 3 \bar{2} 3$	11	7	13	4	0.4730	0.4728
4 0 0	38	25	101	94	0.4844	0.4859

(0 0 2), (0 0 4), (1 0 5), (2 0 6) etc. These reflections were present with appreciable intensities in $CdGa_2S_4$. The intensities of these reflections decreased with increasing content of selenium in the solid solutions and were absent when the selenium content was more than 50 mol %. Such absences may be correlated to two factors: (1) increase in mass absorption coefficient in going from sulphur to selenium, and (2) a change in the values of parameters x, y and z from sulphur to selenium. (Hahn *et al.* deduced the values 0.26, 0.27 and 0.14 for sulphur). Assuming these values of x, y, z for selenium and changing mass absorption coefficient alone did not give a satisfactory explanation for the absence of the reflections. We have therefore calculated the intensities of several reflections by giving a set of values to x, y, z following the procedure described in the Appendix.

For the reflections 0 0 2, 0 0 4, 0 0 6, 0 0 8 etc. the values of A and B depend only on z parameters. The calculations for the absence of 0 0 2, 0 0 4 etc. indicated that the best value for $z = 0.15$.

The reflections 2 0 0, 4 0 0, 1 1 0, 2 2 0, 6 0 0, 3 1 0, 8 0 0 depend only on x and y. The reflections 2 0 0, 4 0 0, 2 2 0, 3 1 2, 1 0 3 were found to be sensitive to variation in values of x and y. Various values of x and y e.g. 0.2, 0.225, 0.25, 0.275, 0.300 were substituted in Equations 5 and 6 (see Appendix) for each reflection. The best match observed for $x = y = 0.25$, with $\mu R = 4.0$ and $z = 0.15$. The intensity measurements were made on a LIREPHO-2 Photomicrograph recorder. The observed and calculated values of F^2 are compared in Table III. The values of F^2 were normalized further by multiplying by a normalization factor

$$\frac{\Sigma |F^2_{\text{cal}}|}{\Sigma |F^2_{\text{true}}|}.$$

The factor

$$R = \frac{\Sigma |F^2_{\text{cal}} - F^2_{\text{true, nor}}|}{\Sigma |F^2_{\text{cal}}}$$

was found to be 12% when the absent reflections were included. If the absent reflections were omitted, R reduces to 10%.

The dependence of lattice parameters on compositions has been plotted in Fig. 2 and variation of c/a versus composition is given in Fig. 3 The continuous variation of the lattice parameters indicates that a complete range of solid solutions

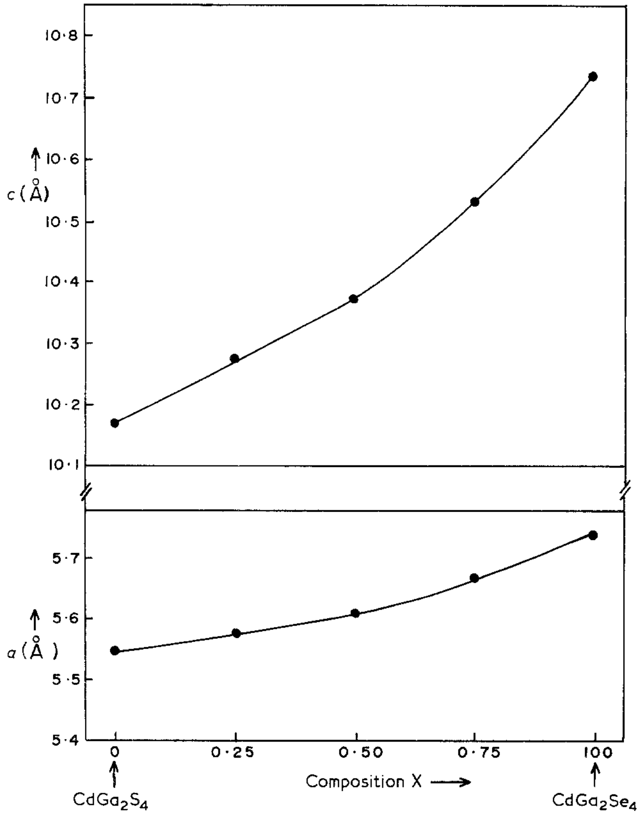

Figure 2 Variation of lattice parameters versus composition

form between sulphide and selenide chalcopyrites obeying Vegard's law with slight negative deviations Fig. 4 that the *a*-spacing varies linearly as a function of composition while the *c*-spacing shows a marked rapid rise with increasing selenium content. The overall rise in lattice parameters is obviously due to the larger ionic size of selenium, but the reason for a nonlinear rise in *c* value is not clear.

The various interatomic distances calculated are:

$$\text{Cd–Se} = 2.59\,\text{Å},\ \text{Ga–Se} = 2.59\,\text{Å},$$

$$\text{Ga–Cd} = 4.058\,\text{Å}$$

and the three

$$\text{Se–Se} = 4.058,\ 3.93 \quad \text{and} \quad 4.058\,\text{Å}.$$

5. Appendix

The following procedure was adopted for the structure factor calculations. The intensities of the observed reflections were assumed to be proportional to the height of the peaks in the photomicrograph and taking the intensity of 2 0 4 reflection to be 100, apparent intensity ($I_{\text{app}(h\,k\,l)}$ was obtained by using

$$I_{\text{app}(h\,k\,l)} = \frac{\text{Peak height } (h\,k\,l)}{\text{Peak height } (2\,0\,4)} \times 100 \qquad (1)$$

These I_{app} values were converted to true.intensities by multiplying with the absorption correction A*(θ)

$$I_{\text{true}(h\,k\,l)} = I_{\text{app}(h\,k\,l)} A^*(\theta_{h\,k\,l})/A^*(\theta_{204}) \qquad (2)$$

The squares of the structure factors, F^2, were obtained by dividing the I_{true} values by Lorentz, polarization and multiplicity factors;

$$F^2_{\text{true}(h\,k\,l)} = \frac{I_{\text{true}(h\,k\,l)}}{L_{h\,k\,l}p_{h\,k\,l}j_{h\,k\,l}} L_{204}p_{204}j_{204}. \qquad (3)$$

These observed squares of the relative structure factors were compared with those calculated theoretically. Theoretical values were obtained from the Equation 4 for space group (I$\bar{4}$) [14]

$$F^2_{\text{cal}(hkl)} = (A^2_{hkl} + A^2_{\bar{h}\bar{k}l} + B^2_{hkl} + B^2_{\bar{h}\bar{k}l})/F^2_{\text{cal}(204)} \qquad (4)$$

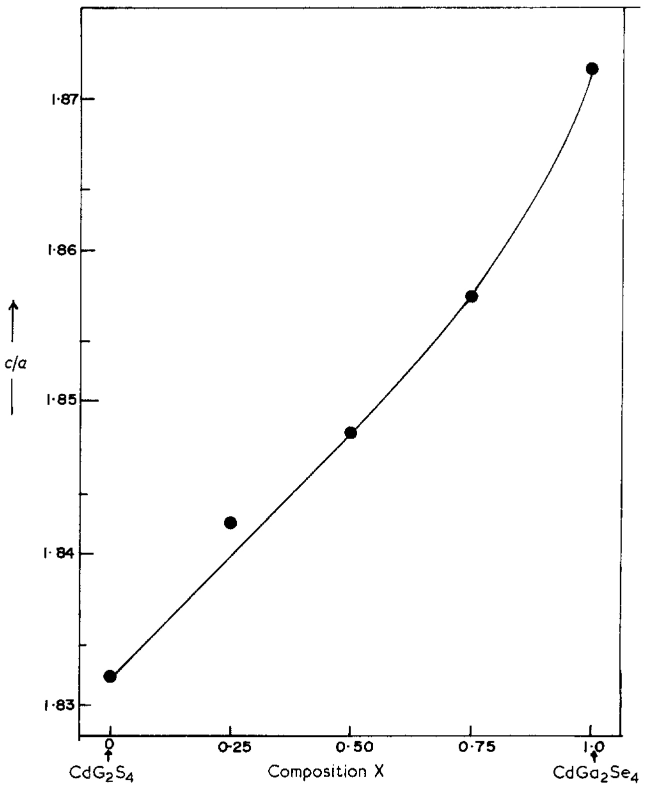

Figure 3 Variation of c/a versus composition

where

$$A = 2f_{\mathrm{Cd}} + 2f_{\mathrm{Ga}}\left[\cos \pi l + \cos \frac{\pi}{2}(h+k) \cos \frac{\pi}{2}(h-k) \cos \frac{\pi}{2} l\right] + 8f_{\mathrm{Se}} \cos \pi [(h-k)x + (h+k)y] \cos \pi [(h+k)x - (h-k)y] \cos (2\pi l z) \qquad (5)$$

$$B = 2f_{\mathrm{Ga}}\left[\sin\left(\frac{(h+k)}{2}\pi\right) \sin\left(\frac{(h-k)}{2}\pi\right) \sin\left(\frac{\pi}{2}\right) l\right] - 8f_{\mathrm{Se}}[\sin \pi(p) \sin \pi(q) \sin (2\pi l z)] \qquad (6)$$

where $p = (h-k)x + (h+k)y$ and $q = (h+k)x - (h-k)y$. $f_{\mathrm{Cd}}, f_{\mathrm{Ga}}, f_{\mathrm{Se}}$ are the scattering powers of Cd, Ga and Se respectively. $B = 0$ if $h = k = 0$ or $l = 0$.

Acknowledgement

The authors are grateful to Mr G. D. Shahapure for carrying out chemical analysis for sulphur and selenium contents.

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Received 27 September 1976 and accepted 4 April 1977.