

Structure Refinement of ZnIn_2Se_4

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The structure of ZnIn_2Se_4 has been refined to $R = 0.079$ and found to be defect chalcopyrite in type (space group $I\bar{4}$). The vacancies form an ordered array while Zn and In atoms are randomly distributed within the cationic sublattice. This type of disorder may explain the lack of excitonic structures and some features of the luminescence spectra of ZnIn_2Se_4 . © 1987 Academic Press, Inc.

Introduction

Studies of defect chalcopyrite compounds of the general formula AB_2X_4 have been carried out with growing interest in recent years. Indeed, these compounds show interesting photoconductive and non-linear optical properties, which suggest that they may be promising materials for the design of new devices (1-5).

Future applications of this class of materials are related not only to progress in growing films and large single crystals of optical quality and controlled compositions but also to a more accurate knowledge of their structural properties. Indeed, the crystal lattices of these systems are characterized by a vacancy sublattice and a distorted cationic sublattice which can be occupied by metal atoms *A* and *B* with a different degree of order, which creates different structural models. Due to this fact, different polytypes of the same compound can be isolated, depending on the temperature and crystal growth method (6, 7) and a simple relationship between structure and

physical properties is often difficult to discern.

In the case of AGa_2X_4 compounds ($A = \text{Co, Cd, Hg}$; $X = \text{S, Se, Te}$), which are interesting materials for opto- and quantum electronics, several accurate crystal structures have been refined and a simple relationship between the c/a ratio and the ordering in the cationic sublattice has been suggested (8). Although several AIn_2X_4 compounds show interesting electro-optical properties (5, 9-10), very little is known about the structure of these materials.

This paper deals with the structure refinement of ZnIn_2Se_4 , the photoconductivity and luminescence properties of which have been widely investigated (11-14).

Experimental

Single crystals of ZnIn_2Se_4 were obtained by heating a stoichiometric mixture of the corresponding binary selenides (99.99% micropure) in an evacuated (4×10^{-5} Torr) quartz ampoule. The ampoule was kept for 4 days at $T = 900^\circ\text{C}$; then the

TABLE I
CRYSTAL DATA, FRACTIONAL ATOMIC PARAMETERS, ANISOTROPIC TEMPERATURE FACTORS ($\times 10^4$), AND
ATOMIC OCCUPANCY FOR ZnIn_2Se_4

Site	Atom	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{13}	U_{23}	U_{12}
2a	Zn	0.0833	0.0	0.0	0.0	18(10)	18(10)	15(10)			
	In	0.1666				145(27)	145(27)	148(30)			
2b	Zn	0.0833	0.0	0.0	0.5	27(11)	27(11)	20(12)			
	In	0.1666				140(20)	140(20)	100(18)			
2c	Zn	0.0833	0.0	0.5	0.25	15(10)	15(10)	14(11)			
	In	0.1666				130(30)	130(30)	120(35)			
8i	Se	1.00	0.2716(3)	0.2285(4)	0.1346(1)	89(7)	121(8)	100(4)	-10(2)	-14(5)	-6(2)

Note. ZnIn_2Se_4 ; $M = 610.9$; tetragonal $\bar{I}4$; $a = 5.705(2)$, $c = 11.448(3)$ Å; $V = 372.60$ Å³; $Z = 2$; $F(000) = 564.84$; $\mu(\text{MoK}\alpha) = 336.5$ mm⁻¹.

temperature was lowered to 600°C at a rate of 1°C/h; and finally, the sample was quenched in air.

Crystal data were collected on a Syntex P21 diffractometer with MoK α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The hkl , $\bar{h}kl$, and $h\bar{k}l$ reflections were collected up to $2\theta_{\text{max}} = 85^\circ$ and then the symmetry equivalent intensities were averaged. Independent reflections (566) with $I > 3\sigma(I)$, were measured. L_p and semiempirical absorption corrections, based on a 360° ψ scan around the scattering vector of selected reflections, were applied.

The structure was solved by means of three-dimensional Fourier synthesis and refined by full-matrix least-squares calculations using the SHELX 76 program system (15). The scattering factors and the correction for the anomalous scattering were taken from the "International Tables for X-Ray Crystallography." An isotropic refinement using an intermediate cation confirmed that the cationic disorder found was, indeed, correct. Final anisotropic refinement led to an R factor of 0.079.

Crystal data, final atomic coordinates, and anisotropic temperature factors are listed in Table I. Bond lengths and bond angles are reported in Table II.

Results and Discussion

As reported in Table I, ZnIn_2Se_4 crystallizes in a tetragonal cell of space group $\bar{I}4$ with parameters $a = 5.705(2)$ Å, $c = 11.448(3)$ Å, and $c/a = 2.0$. The structure of ZnIn_2Se_4 is a defect chalcopyrite in type (Fig. 1) with the vacancies fixed on special positions and the metal atoms randomly distributed within the cationic sublattice.

Each Se atom is tetrahedrally surrounded by a vacancy and three cationic sites occupied by the metal atoms in the ratio 2/3 of In and 1/3 of Zn. The presence of a vacant site in the tetrahedral coordination of Se allows the anion to displace far from the metal ions and toward the vacancy. Indeed, the distance Se-vacancy (2.268 Å) is measurably shorter than the distance (2.473 Å) between the vacant site and the ideal anionic position (1/4, 1/4, 1/8). Due to the fact that the vacancies are fixed on special positions we have a uniquely defined Se-vacancy distance.

The metal-Se distances are determined by the positional parameters x , y , z of the selenium. While in completely ordered defect chalcopyrites (8), CdGa_2S_4 , CdGa_2Se_4 , and HgGa_2Se_4 , two different bond distances were found between Se and the cations, in

TABLE II
BOND LENGTHS (Å) AND BOND ANGLES (°) FOR ZnIn_2Se_4

Tetrahedron $\text{Se}-M_3-\square$			
$M(2a)-\text{Se}$	2.545(2) Å	$M(2a)-\text{Se}-M(2b)$	104.9(1)°
$M(2b)-\text{Se}$	2.544(1) Å	$M(2a)-\text{Se}-M(2c)$	104.7(1)°
$M(2c)-\text{Se}$	2.558(2) Å	$M(2b)-\text{Se}-M(2c)$	104.7(1)°
Tetrahedron $M(2a)-\text{Se}_4$			
$M(2a)-\text{Se}$	2.545(2) Å	$\text{Se}-M(2a)-\text{Se}$	111.5(1)°
			105.5(1)°
Tetrahedron $M(2b)-\text{Se}_4$			
$M(2b)-\text{Se}$	2.544(1) Å	$\text{Se}-M(2b)-\text{Se}$	111.5(1)°
			105.4(1)°
Tetrahedron $M(2c)-\text{Se}_4$			
$M(2c)-\text{Se}$	2.558(2) Å	$\text{Se}-M(2c)-\text{Se}$	117.8(1)°
			105.5(1)°

Note. Estimated standard deviations are in parentheses.

ZnIn_2Se_4 only one bond length is found: $M(2a)-\text{Se} = M(2b)-\text{Se} = M(2c)-\text{Se}$ (Table II). This fact is a consequence of the random distribution of zinc and indium atoms within the cationic sublattice.

Another feature, in contrast to the above-mentioned ordered AGa_2X_4 compounds, is the different degrees of distortion found in the cationic tetrahedra $2a$, $2b$, and $2c$.

Two parameters play an important role in these internal distortions: the tetragonal compression of the unit cell along the c axis, which is measured by the c/a ratio, and the anion relaxation arising from the displacement of the anion with respect to the ideal position $1/4, 1/4, 1/8$. The tetragonal distortion leads to the same compression for all of the cationic tetrahedra.

As the z of the anion increases, this produces a strong compression of only the $2c$ tetrahedral site along the $\bar{4}$ axis and a slight elongation of the $2a$ and $2b$ tetrahedral sites. Simultaneously, the deviation of x and y from the value $1/4, 1/4$ introduces a slight rotation of the tetrahedra about the $\bar{4}$ axis. For tetrahedral coordination of symmetry $\bar{4}$ the axial distortion is measured by

$3\cos^2\theta - 1$ (where 2θ is the angle to the $\bar{4}$ axis) and this expression will be positive for an elongated tetrahedron, negative for a

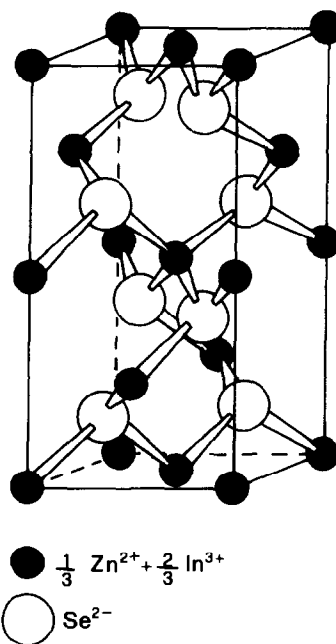


FIG. 1. Crystal structure of ZnIn_2Se_4 .

TABLE III
STRUCTURAL PROPERTIES OF ZnIn_2Se_4
AND SOME AGa_2X_4 COMPOUNDS

Bond angles	CdGa_2S_4	CdGa_2Se_4	HgGa_2Se_4	ZnIn_2Se_4
$X-M(2a)-X$	107.5	109.3	109.2	105.4
$X-M(2b)-X$	104.7	104.9	103.2	105.4
$X-M(2c)-X$	119.3	119.4	119.5	117.8
$3\cos^2 \theta(1)-1$	0.049	0.004	0.007	0.102
$3\cos^2 \theta(2)-1$	0.119	0.114	0.157	0.102
$3\cos^2 \theta(3)-1$	-0.234	-0.236	-0.238	-0.200

Note. $X-M(2a)-X = 2\theta(1)$; $X-M(2b)-X = 2\theta(2)$; $X-M(2c)-X = 2\theta(3)$.

compressed one, and equal to zero for an ideal tetrahedron ($2\theta = 109.47$).

As reported in Table III the ordered chalcopyrites show different degrees of elongation for the $2a$ and $2b$ tetrahedra (the M^{2+} tetrahedra results are less distorted) and a strong compression for the $2c$ tetrahedra. In ZnIn_2Se_4 , the cationic sites $2a$ and $2b$ show an equal elongation, whereas the $2c$ site shows a strong compression.

Conclusions

The physical properties of ZnIn_2Se_4 (11–14) were explained assuming the presence of a large number of localized states. These localized states can arise from the following causes:

- (1) presence of accidental impurities;
- (2) failure of a crystallographic long-range order;
- (3) failure of a periodic array of stoichiometric voids;
- (4) antisite defects due to A ions in B sublattice and B ions in A sublattice.

Accidental impurities are generally due to iodine used in crystal growth processes, but they are usually an order of magnitude less than the number of quasi-continuously distributed traps. The failure of a long-range order can play a significant role in

layer compounds like ZnIn_2S_4 , but it seems ineffective in ZnIn_2Se_4 , which has a defect chalcopyrite structure. The structure model adopted for ZnIn_2Se_4 allows us to say that the main contribution to the formation of traps is from the antisite defects. In fact, in ZnIn_2Se_4 the vacancies are fixed on special positions and it follows that the random distribution of In and Zn within the cationic sublattice gives rise to the lack of excitonic structure (13). Nevertheless, this exchange of Zn and In in their lattice positions may explain the formation of the A center responsible for the ZnIn_2Se_4 luminescence (11).

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