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X-Ray Investigations in the System $CdIn_2S_4$–$CdIn_2Se_4$

H. HAEUSELER

Universität Siegen, Laboratorium für Anorganische Chemie, D 5900 Siegen 21, West Germany

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The system $CdIn_2S_{4-x}Se_x$ is investigated by means of X-ray diffraction. There are three phases present in the system: (i) a cubic spinel phase for $x = 0$ to $x = 1.25$, (ii) a rhombohedral phase of $ZnIn_2S_4$ type for $x = 1.75$ to $x = 2.75$, and (iii) a tetragonal thiogallate phase for $x = 3.5$ to $x = 4.0$.

Introduction

There are three structure types possible for samples with stoichiometry AB_2X_4 with A = Zn, Cd, Hg; B = Al, Ga, In; and X = O, S, Se, Te, i.e., the cubic spinel structure, tetragonal defective zinc blende structures, and the rhombohedral $ZnIn_2S_4$-type structure (*1–3*). In the case of $CdIn_2X_4$, the compounds with X = O, S crystallize in the spinel type while $CdIn_2Se_4$ and $CdIn_2Te_4$ show tetrahedral structures. We began an investigation of the system $CdIn_2S_4$–$CdIn_2Se_4$ to obtain information about the homogeneity range of both the spinel-type $CdIn_2S_4$ and the tetragonal $CdIn_2Se_4$.

Experimental

The compounds were prepared by the following method: Stoichiometric amounts of the binary chalcogenides CdS (Schuchardt, München), CdSe (99.99%, Schuchardt, München), In_2S_3 (purum, Fluka, Buchs), and In_2Se_3 (99.99%, Ventron, Beverly, Mass.) were ground together, pressed into pellets, and sealed under vacuum in silica tubes. The reactions were carried out at 900°C in a period of 4 days, followed by second and third heat treatments at 800°C for periods of 3 days. The samples were allowed to cool in the furnace. Between firings the products were ground carefully in an agate mortar. X-Ray diffraction patterns were obtained from a Huber Guinier Powder Chamber 621 using $CuK\alpha_1$ radiation. The photographs were calibrated internally with quartz, and the unit cell dimensions (Table I) were refined by a least-squares procedure.

Results and Discussion

Figure 1 shows a plot of the lattice parameters vs composition of the quaternary chalcogenides. The spinel phase has a relative large homogeneity range. Up to 31% of sulfur atoms can be replaced by selenium. With increasing molar ratio of $CdIn_2Se_4$ the unit-cell dimensions of the $CdIn_2S_{4-x}Se_x$ spinel-type mixed crystals increase. The slope of the curve obeys Vegard's law. The lattice constant of a spinel-type $CdIn_2Se_4$ can be extrapolated to be $a_0 = 1140.2$ pm which corresponds well with the value $a_0 = 1134.5$ pm found for spinel-type $CdIn_2Se_4$ prepared by a pressure reaction (*4*).

The tetragonal pseudocubic form of $CdIn_2Se_4$ (space group $P\bar{4}2m$) has a smaller

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TABLE I

UNIT-CELL DIMENSIONS IN THE SERIES $CdIn_2S_{4-x}Se_x$

	Spinel type	$ZnIn_2S_4$ type		$CdIn_2Se_4$ type	
Compound	a_0(pm)	a_0(pm)	c_0(pm)	a_0(pm)	c_0(pm)
$CdIn_2S_4$	1084.3(1)				
$CdIn_2S_{3.75}Se_{0.25}$	1087.7(3)				
$CdIn_2S_{3.5}Se_{0.5}$	1090.8(4)				
$CdIn_2S_{3.25}Se_{0.75}$	1093.9(3)				
$CdIn_2S_{3.0}Se_{1.0}$	1098.4(2)				
$CdIn_2S_{2.75}Se_{1.25}$	1098.9(3)				
$CdIn_2S_{2.5}Se_{1.5}$	1099.7(3)	401.7(1)	3879(2)		
$CdIn_2S_{2.25}Se_{1.75}$		402.0(1)	3871(1)		
$CdIn_2S_{2.0}Se_{2.0}$		403.0(1)	3888(1)		
$CdIn_2S_{1.75}Se_{2.25}$		403.8(1)	3895(1)		
$CdIn_2S_{1.5}Se_{2.5}$		404.6(1)	3912(2)		
$CdIn_2S_{1.25}Se_{2.75}$		405.5(1)	3919(1)		
$CdIn_2S_{1.0}Se_{3.0}$		406.2(1)	3928(1)	578.2(1)	578.0(2)
$CdIn_2S_{0.75}Se_{3.25}$				578.5(1)	578.5(1)
$CdIn_2S_{0.5}Se_{3.5}$				579.2(1)	579.3(1)
$CdIn_2S_{0.25}Se_{3.75}$				580.3(1)	580.4(1)
$CdIn_2Se_4$				582.2(1)	582.2(2)

homogeneity range than the spinel phase. Only up to 12 mole% of $CdIn_2S_4$ are soluble in $CdIn_2Se_4$.

Between 44 and 68 mole% $CdIn_2Se_4$ the mixed crystals crystallize in the rhombohedral $ZnIn_2S_4$-type structure (space group $R3m$). The lattice parameters in Table I are given for a hexagonal description of the lattice. A compound of the same structure has been found by Shand (*5*) in the system CdS–In_2S_3–Ga_2S_3 for the composition $CdInGaS_4$. The $ZnIn_2S_4$ type seems to be an

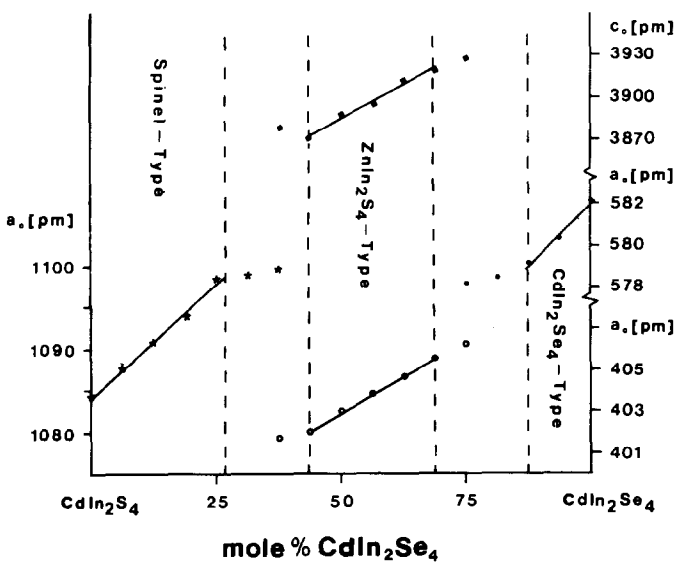

FIG. 1. Plot of unit-cell dimensions vs composition in the series $CdIn_2S_{4-x}Se_x$.

intermediate between the spinel on one hand and tetrahedral structures on the other. It can be formed by changing the composition in both the nonmetal sublattice and the metal sublattice.

The color of the mixed crystals changes with increasing molar ratio of $CdIn_2Se_4$ from red to black for powdered samples. The compounds which crystallize in the $ZnIn_2S_4$-type structure form thin plate-shaped crystals with metallic luster.

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