

X-ray powder diffraction study of the semiconducting alloy $\text{Cu}_2\text{Cd}_{0.5}\text{Mn}_{0.5}\text{GeSe}_4$

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The structure of the semiconducting alloy $\text{Cu}_2\text{Cd}_{0.5}\text{Mn}_{0.5}\text{GeSe}_4$ was refined from an X-ray powder diffraction pattern using the Rietveld method. The present alloy crystallizes in the wurtz-stannite structure, space group $\text{Pmn}2_1$ (N° 31), and unit cell parameters values of $a = 8.0253(2)$ Å, $b = 6.8591(2)$ Å, $c = 6.5734(2)$ Å and $V = 361.84(2)$ Å³. The structure exhibits a three-dimensional arrangement of slightly distorted CuSe_4 , $\text{Cd}(\text{Mn})\text{Se}_4$ and GeSe_4 tetrahedras connected by corners.

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1 Introduction

Diluted magnetic semiconductors and alloys containing manganese are of interest because of the large magneto-optical effects, which can occur in these materials. Some materials where it occurs are the I₂-II-IV-VI₄ compounds, which belong to one of the two possible families of the four-fold normal derivatives of the II VI binary semiconductors [1]. Structural studies carried out on some members of this family indicate that they crystallize in a sphalerite derivative structure with tetragonal space group I-42m (N° 121) [2], or a wurtzite derivative structure with orthorhombic space group $\text{Pmn}2_1$ (N° 31) [3]. In particular, for the $\text{Cu}_2\text{Cd}_{(1-x)}\text{Mn}_{(x)}\text{GeSe}_4$ system, the substitution of Cd by Mn had been magnetically studied and the reciprocal of the susceptibility data showed that the samples have antiferromagnetic behaviour [4]. On the other hand, in this system, the phase with $x = 0$ ($\text{Cu}_2\text{CdGeSe}_4$) crystallizes in the tetragonal system [5] while for the phase with $x = 1$ ($\text{Cu}_2\text{MnGeSe}_4$) an orthorhombic cell was proposed [6]. Therefore, a crystallographic phase transition in the range $x = 0$ to 1 is expected.

In this work, the crystal structure analysis for the semiconducting $\text{Cu}_2\text{Cd}_{0.5}\text{Mn}_{0.5}\text{GeSe}_4$ alloy by using the Rietveld method from X-ray powder diffraction data is reported.

2 Experiment

The sample of $\text{Cu}_2\text{Cd}_{0.5}\text{Mn}_{0.5}\text{GeSe}_4$ was prepared by the melt and anneal technique as described elsewhere [4]. A small quantity of the sample was ground mechanically in an agate mortar and pestle and then sieved to 106 µm to get a homogeneous grain size. The specimen was mounted on a zero-background holder. X-ray powder diffraction data was collected at room temperature on a Siemens D5005 diffractometer, using Bragg-Brentano

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geometry, in θ/θ reflection mode. This instrument is equipped with an X-ray tube (CuK α radiation: $\lambda = 1.5418$ Å; 30kV, 15mA), a diffracted beam graphite monochromator and a scintillation detector. A fixed aperture and divergence slit of 1 mm, a 1 mm monochromator slit, and 0.6 mm detector slit were used. The diffraction pattern was collected by steps of 0.02° (2θ) over the angular range 10 - 100° , with a counting time of 25 s per step. Quartz was used as an external standard. The Bruker analytical software was used to establish the precise positions of the peaks.

3 Results and discussion

The powder pattern was examined using the PDF-ICDD Database [7] and no secondary phases were found. The indexing of the X-ray powder diffraction was performed by means of the DICVOL91 program [8] and the unit cell refinement by using the NBS*AIDS program [9]. These analyses showed that the present alloy crystallize in the orthorhombic system with unit cell parameters $a = 8.021(1)$ Å, $b = 6.856(1)$ Å, $c = 6.566(1)$ Å and figures of merit $M_{20} = 38.4$ [10] and $F_{20} = 20.0$ [11]. Systematic absences indicate a P-type lattice. Pattern revision taking into account the sample composition, unit cell parameters and the lattice-type, suggested that this material is isostructural with the $\text{Cu}_2\text{CdGeS}_4$ compound [3], which crystallize in the $\text{Pmn}2_1$ ($N^\circ 31$) space group.

The structure of $\text{Cu}_2\text{Cd}_{0.5}\text{Mn}_{0.5}\text{GeSe}_4$ was refined by the Rietveld method [12] using the FULLPROF program [13]. The atomic coordinates of $\text{Cu}_2\text{CdGeS}_4$ [3] were used as starting parameters. A parameterized pseudo-Voigt profile function was used to fit the peak shapes and a polynomial with six coefficients was used to model the background. The results of the Rietveld refinement are summarized in Table 1. Figure 1 shows the final Rietveld adjust. Figure 2 show the unit cell diagram of $\text{Cu}_2\text{Cd}_{0.5}\text{Mn}_{0.5}\text{GeSe}_4$. Atomic coordinates, occupation and isotropic temperature factor are given in Table 2. Distances and angles are given in Table 3.

Table 1 Results of Rietveld refinement for $\text{Cu}_2\text{Cd}_{0.5}\text{Mn}_{0.5}\text{GeSe}_4$.

Molecular Formula	$\text{Cu}_2\text{Cd}_{0.5}\text{Mn}_{0.5}\text{GeSe}_4$	D_{calc} (g/cm^3)	5.51
Molecular weight (g/mol)	599.22	N° step intensities	4501
Crystal system	Orthorhombic	N° independent reflections	227
Space group	$\text{Pmn}2_1$ ($N^\circ 31$)	Peak-shape profile	Pseudo-Voigt
Z	2	R_p (%)	6.5
a (Å)	8.0253(2)	R_{wp} (%)	8.1
b (Å)	6.8591(2)	R_{exp} (%)	6.1
c (Å)	6.5734(2)	R_B (%)	8.3
V (Å ³)	361.84(2)	S	1.3

Table 2 Atomic coordinates, occupancy factors and isotropic temperature factor for $\text{Cu}_2\text{Cd}_{0.5}\text{Mn}_{0.5}\text{GeSe}_4$.

Atom	Ox.	Site	x	Y	z	foc	B_{iso} (Å ²)
Cu	+1	$4b$	0.253(2)	0.820(2)	0.196(3)	1	2.04(5)
Cd	+2					0.52(2)	
		$2a$	0	0.658(2)	-0.301(2)		2.04(5)
Mn	+2					0.48(2)	
Ge	+4	$2a$	0	0.321(2)	0.191(2)	1	2.04(5)
Se1	-2	$4b$	0.236(1)	0.159(1)	0.065(3)	1	2.04(5)
Se2	-2	$2a$	0	0.655(2)	0.089(3)	1	2.04(5)
Se3	-2	$2a$	0	0.310(2)	0.559(3)	1	2.04(5)

The structure of $\text{Cu}_2\text{Cd}_{0.5}\text{Mn}_{0.5}\text{GeSe}_4$ is characterized by a three-dimensional arrangement of slightly distorted CuSe_4 , $\text{Cd}(\text{Mn})\text{Se}_4$ and GeSe_4 tetrahedras connected by corners. In this structure two Cu, one Cd or Mn and

one Ge ion coordinate each anion, and each cation is coordinated by 4 anions. This array is expected for adamantane compounds [14]. It is observed from Table 2 that the occupancy factors for Cd^{+2} and Mn^{+2} cations are in good agreement with the expected value for $x = 0.5$ for the chemical composition. It is also found that the tetrahedra containing the $\text{Cd}(\text{Mn})$ cations [mean Se-Se distance 4.23(2) Å] are slightly larger than those containing the Cu cations [mean Se-Se distance 3.95(2) Å] and Ge [mean Se-Se distance 3.88(2) Å] cations, respectively. The mean bond distance values for Cu-Se [2.42(2) Å] and Ge-Se [2.38(2) Å] agree very well with the average distances Cu-Se (2.42 Å) and Ge-Se (2.38 Å) observed in the adamantane structures: Cu_2GeSe_3 [15], CuInSe_2 [16], $\text{Cu}_2\text{FeSnSe}_4$ [17], Fe_2GeSe_4 [18], $\text{Cu}_2\text{ZnGeSe}_4$ [19], $\text{Cu}_2\text{ZnSnSe}_4$ [20], $\text{Cu}_2\text{CdSnSe}_4$ [20], $\text{Cu}_2\text{HgSnSe}_4$ [20], $\text{Cu}_2\text{CdGeSe}_4$ [5], and Cu_2SnSe_3 [21]. The distance $\text{Cd}(\text{Mn})\text{-Se}$ [mean value 2.59(2) Å] is smaller than the average Cd-Se distance of 2.64 found in the CdGa_2Se_4 [22], CdAl_2Se_4 [23] and $\text{Cu}_2\text{CdGeSe}_4$ [5] adamantane compounds, which is expected to be due to the Mn^{+2} (0.66 Å) ionic radii which is smaller than the one for Cd^{+2} (0.78 Å) [24].

4 Conclusions

The $\text{Cu}_2\text{Cd}_{0.5}\text{Mn}_{0.5}\text{GeSe}_4$ alloy crystallizes in the wurtz-stannite structure, space group $\text{Pmn}2_1$ (N° 31) characterized by a three-dimensional arrangement of slightly distorted CuSe_4 , $\text{Cd}(\text{Mn})\text{Se}_4$ and GeSe_4 tetrahedras connected by corners.

Fig. 1 Final Rietveld refinement plot for $\text{Cu}_2\text{Cd}_{0.5}\text{Mn}_{0.5}\text{GeSe}_4$. The lower trace is the difference curve between observed and calculated patterns. The Bragg reflections are indicated by vertical bars.

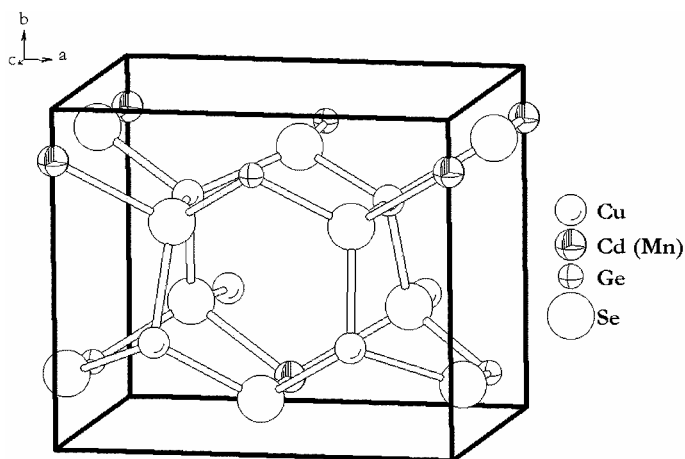
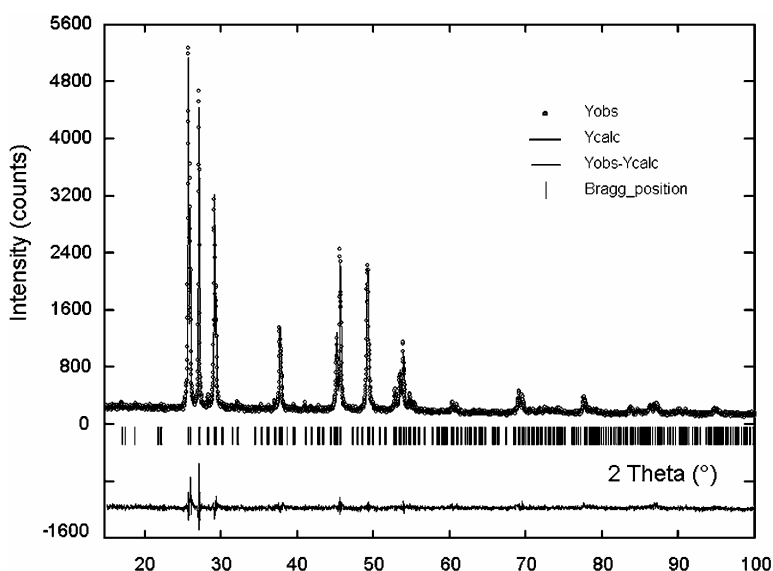


Fig. 2 Unit cell diagram for $\text{Cu}_2\text{Cd}_{0.5}\text{Mn}_{0.5}\text{GeSe}_4$.

Table 3 Distance lengths (Å) and bond angles (°) for $\text{Cu}_2\text{Cd}_{0.5}\text{Mn}_{0.5}\text{GeSe}_4$.

Cu-Se3 ⁱ	2.35(2)	Ge-Se1	2.35(1)	Cd(Mn)-Se1 ⁱ	2.62(1)
Cu-Se2	2.43(2)	Ge-Se1 ^{iv}	2.35(1)	Cd(Mn)-Se3 ^v	2.56(2)
Cu-Se1 ⁱⁱ	2.43(3)	Ge-Se3	2.42(3)	Cd(Mn)-Se1 ^{vi}	2.62(1)
Cu-Se1 ⁱⁱⁱ	2.48(2)	Ge-Se2	2.39(2)	Cd(Mn)-Se2	2.56(2)
Se3 ⁱ -Cu-Se1 ⁱⁱ	111.9(8)	Se2-Cu-Se1 ⁱⁱⁱ	106.9(6)	Se3 ⁱ -Cu-Se1 ⁱⁱⁱ	105.6(6)
Se1 ⁱⁱ -Cu-Se1 ⁱⁱⁱ	107.0(8)	Se3 ⁱ -Cu-Se2	114.6(7)	Se1 ⁱⁱ -Cu-Se2	110.3(7)
Se1-Ge-Se3	109.8(4)	Se1-Ge-Se1 ^{iv}	107.6(3)	Se3-Ge-Se1 ^{iv}	109.8(4)
Se1-Ge-Se2	110.8(2)	Se3-Ge-Se2	108.1(9)	Se1 ^{iv} -Ge-Se2	110.8(2)
Se1 ⁱ -Cd(Mn)-Se3 ^v	109.1(2)	Se3 ^v -Cd(Mn)-Se2	110.6(7)	Se1 ^{vi} -Cd(Mn)-Se1 ⁱ	108.2(3)
Se1 ^{vi} -Cd(Mn)-Se3 ^v	109.1(2)	Se ^{vi} -Cd(Mn)-Se2	109.9(4)	Se2-Cd(Mn)-Se3 ^v	110.6(7)

Symmetry codes: (i) 0.5-x, 1-y, -0.5+z (ii) 0.5-x, 1-y, 0.5+z (iii) x, 1+y, z (iv) -x, y, z (v) x, y, -1+z (vi) -0.5+x, 1-y, -0.5+z

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