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Crystal structures of the $ScCuSe_2$ and $Sc_3CuSn_3Se_{11}$ compounds

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Abstract

The crystal structure of the $ScCuSe_2$ compound was investigated using X-ray powder diffraction (space group $P2$, $a = 0.67108(5)$ nm, $b = 0.38949(3)$ nm, $c = 1.27879(6)$ nm, $\beta = 90.281(6)^\circ$, Pearson symbol $mP16.08$, $R_I = 0.0839$). The structure of $ScCuSe_2$ represents a distinctive $\sqrt{3}a \times a \times 2c$ superstructure of $Er_{2/3}Cu_2S_2$. The Se atoms are stacked in a close-packed arrangement with layers in the sequence AB. The Sc atoms occupy half of the octahedral sites, the Cu atoms are located in 3/8 of the tetrahedral sites. The crystal structure of the $Sc_3CuSn_3Se_{11}$ compound (space group $Fd3m$, $a = 1.08827(4)$ nm, Pearson symbol $cF52.48$, $R_I = 0.0386$) was also determined by means of X-ray powder diffraction. The Se atoms are stacked in a close-packed arrangement with layers in the sequence ABC. The Sc atoms and a statistical mixture M (Sc + Sn) are located in all octahedral sites, the Cu atoms in 1/8 of the tetrahedral sites.

Keywords: Chalcogenides; Sc compounds; Cu compounds; Sn compounds; Se compounds; Crystal structure; X-ray powder diffraction

1. Introduction

The crystal structure of the $ScCuSe_2$ and $Sc_{2/3}Cu_2Se_2$ compounds has been described as $Er_{2/3}Cu_2S_2$ structure type (space group $P\bar{3}$) in [1] and [2]. The lattice parameters have been refined. No quaternary phases in the Sc_2Se_3–Cu_2Se–$SnSe_2$ system have been reported yet in the literature.

The crystal structures of the $ScCuSe_2$ and $Sc_3CuSn_3Se_{11}$ compounds are given in the present paper.

2. Experimental details

The alloys were prepared by melting the high purity elements (the purity of the ingredients was better than 99.9 wt.%) in evacuated quartz ampoules. The synthesis was realized in a shaft furnace with a heating rate of 20 K/h. The ampoules with the samples were heated to a maximal temperature of 1420 K. The samples were kept at the maximal temperature during 4 h. After that they were cooled slowly to 870 K with a rate of 10 K/h and annealed at respective temperature during 240 h. After annealing the ampoules with the samples were quenched in cold water.

X-ray powder diffraction patterns of the samples for the crystal structure determination were recorded using a DRON-4-13 powder diffractometer (Cu Kα radiation, $10^\circ \leq 2\Theta \leq 100^\circ$, step scan mode with a step size of 0.05° and counting time of 20 s per data point).

The crystal structure determination was performed using the CSD [3] and DBWS-9411 [4] programs.

3. Results and discussion

3.1. Crystal structure of the $ScCuSe_2$ compound

The existence of the ternary $ScCuSe_2$ compound was observed during an investigation of the phase relations in the Sc_2Se_3–Cu_2Se system. According to Refs. [1,2] the $ScCuSe_2$ compound crystallizes in the $Er_{2/3}Cu_2S_2$ structure type (space group $P\bar{3}$). The basic peaks of the X-ray powder diffraction pattern of the sample $ScCuSe_2$ were really indexed in a hexagonal unit cell. The obtained lattice parameters were close to those reported in [1,2] for

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Table 1
Results of the crystal structure determination of the $ScCuSe_2$ and $Sc_3CuSn_3Se_{11}$ compounds

	$ScCuSe_2$	$Sc_3CuSn_3Se_{11}$
Number of formula units per unit cell	4	32/11
Space group	*P*2	*Fd*3*m*
a (nm)	0.67108(5)	1.08827(4)
b (nm)	0.38949(3)	
c (nm)	1.27879(6)	
β (°)	90.281(6)	
Cell volume (nm^3)	0.33425(7)	1.2889(1)
Number of atoms in cell	16.08	52.48
Calculated density (g/cm^3)	5.319	5.3461
Radiation and wavelength	Cu (0.154178 nm)	Cu (0.154178 nm)
Diffractometer	Powder DRON-4-13	Powder DRON-4-13
Mode of refinement	Full profile	Full profile
Number of atom sites	11	4
Structure solution and refinement	CSD	DBWS-9411
R_I	0.0839	0.0386
R_P	0.1355	0.0536[a]
Texture axis and parameter	[0 0 1] 0.51(1)	

[a] Presence of the phases Sc_2Se_3 and Cu_2SnSe_3 was taken into account during the refinement procedure (see Fig. 4).

a sample of the corresponding composition. Many additional peaks of low intensity were observed in the X-ray powder diffraction pattern. Taking into account all peaks of the X-ray powder diffraction pattern a monoclinic lattice with the parameters $a = 0.67108(5)$ nm, $b = 0.38949(3)$ nm, $c = 1.27879(6)$ nm, $\beta = 90.281(6)^\circ$ was found for the $ScCuSe_2$ compound. By assuming space group symmetry *P*2 we were able to extract a plausible structural model from the powder X-ray intensities by means of direct methods and difference Fourier syntheses. Table 1 contains the essential technical and crystallographic data of the crystal structure determination. The atomic coordinates and isotropic temperature factors are given in Table 2, whereas the interatomic distances and coordination numbers of the atoms are listed in Table 3 . The positions of the Sc and Se atoms are fully occupied. All positions of the Cu atoms are partially occupied. The experimental and calculated diffractograms and the corresponding difference diagram for $ScCuSe_2$ are shown in Fig. 1. The interatomic distances agree well with the sum of the corresponding ionic radii [5].

The unit cell, the coordination polyhedra of the Sc1 (a), Sc2 (b), Sc3 (c), Sc4 (d), Cu1 (e), Cu2 (f), Cu3 (g), Se1 (h), Se2 (i), Se3 (j), Se4 (k) atoms and the layers of the Se atoms of hexagonal topology in the structure of the $ScCuSe_2$ compound are shown in Fig. 2. Octahedral surrounding exists for the Sc atoms, tetrahedral for the Cu atoms. The Se1 and Se2 atoms are surrounded by seven and five cations, respectively. The neighbors of the Se3 and Se4 atoms form distorted octahedra. The Se atoms in the structure of the $ScCuSe_2$ compound are stacked in a close-packed arrangement with layers in the sequence AB. The Sc atoms occupy half of the octahedral sites. The Cu atoms are located in 3/8 of the tetrahedral sites. Taking into account the occupation factors of the positions of the Cu atoms we can assume that only one quarter of the tetrahedral sites is really occupied by Cu atoms. The layers of the Sc(Er)-centered octahedra and Cu-centered tetrahedra in the structures of the compounds $ScCuSe_2$ and $Er_{2/3}Cu_2S_2$ [6] are shown in Fig. 3. According to Refs. [1,2] the compounds with composition $RCuSe_2$ (R = Y, Tb, Dy, Ho, Er, Tm, Yb and Lu) crystallize in the $Er_{2/3}Cu_2S_2$ structure type. The Se atoms are stacked in a close-packed arrangement with layers in the sequence AB. The R atoms occupy half of the octahedral sites. The Cu atoms of the $RCuSe_2$ compounds are located in half of the tetrahedral sites. Since the occupation

Table 2
Atomic coordinates and isotropic temperature factors for the $ScCuSe_2$ compound

Atom	Position	*x*/*a*	*y*/*b*	*z*/*c*	Occupation	$B_{iso} \times 10^2$ (nm^2)
Sc1	1(a)	0	0.000[a]	0	1.000	0.3(3)
Sc2	1(b)	0	0.080(4)	1/2	1.000	0.4(3)
Sc3	1(c)	1/2	0.556(4)	0	1.000	0.4(3)
Sc4	1(d)	1/2	0.485(5)	1/2	1.000	0.4(3)
Cu1	2(e)	0.649(1)	0.021(4)	0.1906(4)	0.823(6)	0.7(2)
Cu2	2(e)	0.719(2)	0.047(7)	0.7146(8)	0.496(6)	1.6(4)
Cu3	2(e)	0.153(2)	0.503(4)	0.6875(4)	0.722(6)	0.4(2)
Se1	2(e)	0.6603(9)	0.025(2)	0.3801(3)	1.000	0.2(1)
Se2	2(e)	0.6653(9)	0.983(2)	0.8838(3)	1.000	0.28(9)
Se3	2(e)	0.1644(9)	0.500(2)	0.3815(3)	1.000	0.25(9)
Se4	2(e)	0.1646(9)	0.532(2)	0.8796(3)	1.000	0.25(9)

[a] Fixed.