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Crystalline Structure of Cu_4SSe

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Abstract—Ternary compound Cu_4SSe has been first synthesized by alloying the Cu, S, and Se elements taken in stoichiometric ratios. An X-ray diffraction study of polycrystalline samples has revealed the synthesized material to be crystallized into the trigonal system with unit-cell parameters $a = 4.021(1)$ Å, $c = 6.838(1)$ Å, and $V = 95.75(4)$ Å^3; sp. gr. $P\bar{3}m1$; $Z = 1$; $D_x = 6.333(3)$ g/cm^3. The crystal structure has been solved and refined to the reliability factor $R_{\text{Bragg}} = 0.40\%$.

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INTRODUCTION

Compounds and solid solutions of copper chalcogenides are of interest for researchers due to their diverse physicochemical properties and structural features [1–3]. Compounds of Cu–S, Cu–Se, and Cu–Te systems have a low activation energy of the intrinsic defect formation and belong to materials with ion–covalent chemical bonding [4]. Despite the large number of publications on these compounds [5–14], questions concerning the characterization of their crystal structure are still debatable. Apparently, this is related to the variable valence of copper atom, which facilitates the formation of a number of nonstoichiometric crystalline phases; in turn, these phases are characterized by numerous temperature phase transformations.

In this paper we report the results of synthesizing the new compound Cu_4SSe and determining its crystal structure and perform a crystallochemical analysis of the results.

SYNTHESIS AND PHASE ANALYSIS OF Cu_4SSe

Cu_4SSe sample was obtained by alloying the initial elements Cu, S, and Se (of purity no less than 99.9998%), taken in stoichiometric ratios for Cu_4SSe composition, with a total weight of 5 g. To this end, a quartz ampoule filled with the components was evacuated to a residual pressure of 10^{-4} Torr and placed in a furnace with a previously set temperature $T = 500°C$. After a 1-h exposure at this temperature, the ampoule was heated at a rate of 50°C/h to 1100°C and kept at 1100°C for 1.5 h. Then the furnace temperature is reduced to 400°C, and, to provide alloy homogenization, the sample is annealed for 100 h. A visual inspection of the synthesized sample with the microscope showed the alloy sample to have a compact shape and brown color with metallic luster.

X-ray diffraction data for polycrystalline Cu_4SSe samples are obtained using an XRD D8-ADVANCE diffractometer (BRUKER) under the following conditions: tube voltage 40 kV, tube current 40 mA, and CuK_α radiation. Figure 1 shows a diffraction pattern of the synthesized Cu_4SSe sample. One can clearly see a hump in the range $2\theta = 20°–60°$,which indicates the presence of a certain amount of amorphous component in the sample composition (Fig. 1, the area between the dotted line and the spectrum).

An analysis of the diffraction pattern with the aid of the EVA and TOPAS-4.2 programs showed that Cu_4SSe samples are crystallized into the trigonal system with the unit-cell parameters $a = 4.021(1)$ Å, $c = 6.838(1)$ Å, and $V = 95.75(4)$ Å^3; sp. gr. $P\bar{3}m1$; $Z = 1$; and $D_x = 6.333(3)$ g/cm^3. The diffraction pattern exhibits a pronounced wide peak at $2\theta = 27.1°$ and $d = 3.285$ Å, which is not related to the chosen cell and suggests the presence of the second crystalline phase in the sample composition. This peak corresponds to the 111 reflection of the cubic Cu_2Se lattice with the unit-cell parameter $a = 5.707(2)$; sp. gr. $Fm\bar{3}m$ [15].

DETERMINATION OF Cu_4SSe CRYSTAL STRUCTURE AND DISCUSSION OF RESULTS

Note that the unit-cell parameters of the compound are similar to the parameters of Cu_2Te crystal, whose structure was solved by Nowotny [9] as early as in 1946.That structural study is one of the most frequently cited among works devoted to binary chalcogenide semiconductors. According to the results obtained in [9], covalent bonds of the Cu–Cu

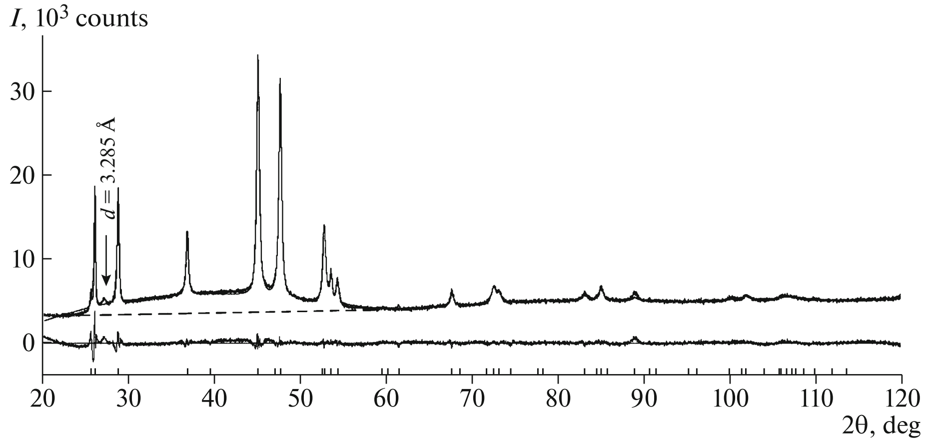

Fig. 1. Diffraction pattern of Cu_4SSe. The difference between the experimental and calculated values is shown in the bottom.

Table 1. X-ray diffraction data for Cu_4SSe at 20°C

2θ, deg	d, Å	I/I_0, %	h	k	l
25.56	3.48228	9.5	1	0	0
26.041	3.419	49.2	0	0	2
28.746	3.10308	48.7	1	0	−1
28.747	3.10307	48.7	1	0	1
36.811	2.43966	25.6	1	0	2
36.811	2.43967	25.6	1	0	−2
45.057	2.0105	100	1	1	0
47.076	1.92885	7.5	1	1	1
47.646	1.90711	89.3	1	0	3
47.645	1.90712	89.3	1	0	−3
52.516	1.74114	15.2	2	0	0
52.779	1.73306	31.7	1	1	2
53.564	1.7095	14.3	0	0	4
54.327	1.6873	10.5	2	0	1
54.326	1.6873	10.5	2	0	−1
59.534	1.55154	1.7	2	0	−2
59.534	1.55154	1.7	2	0	2
67.659	1.38364	5.2	2	0	3
67.658	1.38364	5.2	2	0	−3
68.562	1.3676	0.4	0	0	5
72.523	1.30235	7.7	1	1	4
73.168	1.29246	4.4	2	1	−1
73.168	1.29245	4.4	2	1	1
74.476	1.27295	1.2	1	0	−5
74.476	1.27295	1.2	1	0	5
77.676	1.22831	0.5	2	1	−2
77.677	1.22831	0.5	2	1	2
78.319	1.21983	0.9	2	0	−4
78.319	1.21983	0.9	2	0	4

(2.326 and 3 × 2.442 Å) and Te–Te (2.820 Å) types arise in this structure between copper atoms and between tellurium atoms. Note that the corresponding distances in pure copper and pure tellurium are 2.572 and 2.864 Å, respectively.There are many examples of crystal structures containing one of these anion–anion or cation–cation covalent bonds, e.g., GaSe (Ga–Ga) [16, 17], FeS_2 (S–S) [18, 19], and Fe_3S_4 (Fe–Fe) [20]. Such structural solutions generally occur in nature when one of the ion bond types is in excess. It is rather difficult to find examples of crystal structures containing simultaneously bonds of both types.At the same time, in the case under consideration, proceeding from the stoichiometry of synthesized Cu_4SSe compound, one would expect bonds of the Cu–Cu type to be presented in its structure with rather a high probability. The absence of reflections of the 00l type with odd indices l among the diffraction peaks in the experimentally observed diffraction pattern (Table 1) stimulated the search for a new model, differing from the structure solved by Nowotny.

The crystal structure of Cu_4SSe compound has been solved by Rietveld method [21] (using the TOPAS-4.2 program) based on powder diffraction data (Fig. 1). The difference between the experimental and calculated intensities is shown in the bottom of the diffraction pattern.

A projection of Cu_4SSe crystal structure on the (101) plane is shown in Fig. 2. The chalcogen (S/Se) atoms in the structure form a hexagonal close packing. The copper atoms are localized at 2d and 2c sites, whereas the sulfur and selenium (S/Se) atoms statistically occupy 2d sites. The structural parameters, atomic coordinates, and interatomic distances are listed in Tables 1–3, respectively. The unit cell of Cu_4SSe crystal contains two independent copper atoms. One of them, Cu(1), is coordinated by four S/Se atoms to form a tetrahedron. The translationally identical tetrahedra, located along the a and b axes,

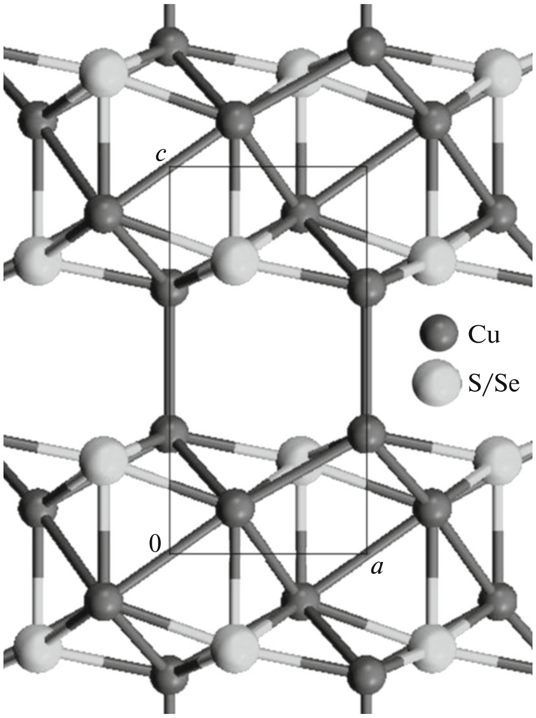

Fig. 2. Projection of Cu_4SSe crystal structure on the (101) plane.

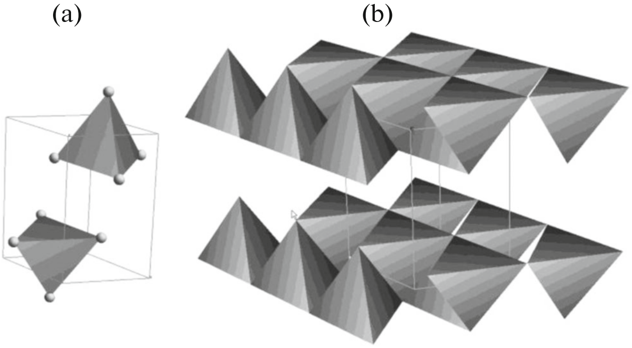

Fig. 3. (a) $Cu(1)(S/Se)_4$ tetrahedra and (b) their two-dimensional layer in Cu_4SSe structure.

share vertices to form a trigonal network. Each such network shares edges with the tetrahedra of the identical network reflected by the center of symmetry to form a rigid two-dimensional framework, oriented perpendicular to z axis (Fig. 3). Similar structures can be found in Li_2O and $NaCu_6Se_4$ crystal structures [22, 23]. The other independent copper atom, Cu(2), is bonded with its symmetric equivalent along the z axis to form a dumbbell configuration. Each of these copper atoms, being coordinated by three more atoms (S/Se) from the two neighboring layers, links them into a three-dimensional framework.

Figure 4 shows a schematic of Cu_4SSe crystal structure. As it is noted above, the anions (S/Se) in the structure obey the principle of hexagonal close packing. Tetrahedral and octahedral voids are known to be formed in close-packed structures. These voids are generally occupied by cations with small and intermediate ionic radii, respectively. In this context, the structure under consideration is not an exception. Cu(1) atoms occupy all tetrahedral voids located between two neighboring trigonal layers of (S/Se) atoms, oriented perpendicular to z axis. As a result, a rigid two-dimensional block of tetrahedra consisting of four atomic layers, (S/Se)–Cu–Cu–(S/Se), is formed. A schematic diagram of these blocks is presented in Fig. 3. Their composition can be written as $[(CuS/Se)_2^{2-}]_n$. Copper atoms Cu(2) occupy all octahedral voids between the next two neighboring trigonal layers of (S/Se) atoms. However, it should be noted that in this case each octahedron contains two copper atoms linked by a covalent bond. Each of these

Table 2. Crystallographic data for Cu_4SSe

Chemical formula	Cu_4SSe
Cell	Trigonal
a, c, Å	4.021(1), 6.838(1)
V, Å^3	95.75 (4)
Sp. gr.	$P\bar{3}1m$
D_x,, g/cm^3	6.333 (3)
Number of atoms per cell	6
Diffractometer	D8 ADVANCE
Radiation; λ, Å	CuK_α; 1.5406
μ, cm^{-1}	390.5(2)
Calculation technique	Full-profile analysis
R_{Bragg}, %	0.404
Preferred crystallite orientation	1: 001; 1.19(3)

Table 3. Atomic coordinates in Cu_4SSe structure

Atoms	Site	x/a	y/b	z/c	B_j, Å^2	Occupancy
S/Se	2d	2/3	1/3	0.242(3)	1.01	0.5/0.5
Cu(1)	2d	1/3	2/3	0.091(3)	2.88	1
Cu(2)	2c	0	0	0.311(4)	2.80	1

Table 4. Interatomic distances in Cu_4SSe structure

Bond	d, Å
Cu(1)–(S/Se) × 3	2.54(1)
Cu(1)–(S/Se)	2.28(3)
Cu(1)–Cu(1)	2.63(2)
Cu(2)–(S/Se) × 3	2.37(1)
Cu(2)–Cu(2)	2.58(6)
Cu(1)–Cu(2)	2.77(2)

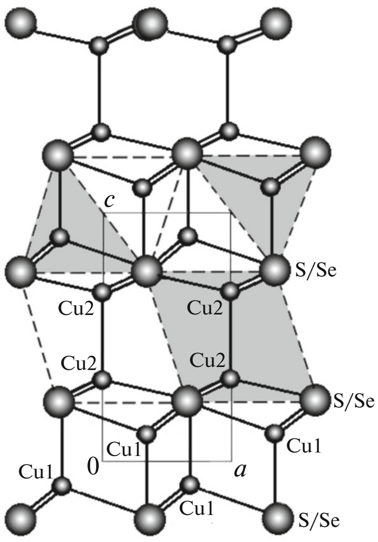

Fig. 4. Cu_4SSe crystal structure. Dual parallel lines connecting atoms indicate that Cu(1) atoms are simultaneously linked with two translationally identical anions.

pairs of copper atoms is linked with three more atoms (S/Se) from the aforementioned blocks to combine them into the three-dimensional framework. As it is noted above, a similar design is observed in the GaSe structure [18, 19].

The crystallographic data are deposited with the Inorganic Crystal Structure Database (ICSD) (CSD no. 430647).

CONCLUSIONS

A new Cu_4SSe compound has been first synthesized and its crystal structure is solved as a trigonal lattice with unit-cell parameters a = 4.021(1) Å, c = 6.838(2) Å, and V = 95.75(4) Å^3; sp. gr. $P\bar{3}m1$; and $Z = 1$.

Copper atoms were found to be coordinated in two different ways. Cu(1) atoms, located at the 2d site, occupy all tetrahedral voids, whereas Cu(2) atoms (located at the 2c site) occupy all octahedral voids. Cu(2) atoms are linked to their symmetric equivalent to form a dumbbell configuration, as in GaSe.

It was established that four-layer block $[(\mathrm{CuS/Se})_2^{2-}]_n$, oriented perpendicular to the c axis, is an important element for the formation of structures of $Cu_{2-x}X$ ($0 \leq x \leq 1$; X = S, Se, Te) composition and similar compounds.

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