UDK 548.32

ISOMORPHISM IN THE MINERALS OF STANNITE-FAMILY

Tat'yana L. Evstigneeva
Institute of Geology of Ore Deposits (IGEM RAS), Moscow, evst@igem.ru
Vyacheslav S. Rusakov
Physics Department, Lomonosov Moscow State University, Moscow, rusakov@moss.phys.msu.su
Yurii K. Kabalov
Geology Department, Lomonosov Moscow State University, Moscow, kabalov@geol.msu.ru

The crystals structures of stannite group minerals and mechanism of isomorphic substitution were studied using a complex of analytical techniques. Ten members of the kuramite-stannite series, $Cu_{3-x}Fe_xSnS_4$ ($0<x<1$), synthesized by ~0.1 formula units, pure stannite, and kesterite were chosen for this study. The methods used included microprobe and profile analysis (Rietveld method), Mössbauer spectroscopy, scanning and transmitting electron microscopy, and X-ray photoelectron spectroscopy. The intermediate members of the kuramite-stannite series are structurally similar homogeneous phases of tetragonal symmetry with regularly changing unit cell parameters (c/a~2). According to the structural analysis, four compounds of the series $Cu_{3-x}Fe_xSnS_4$ with $x = 0.3, 0.6, 0.8$, and 1.0 have tetragonal structures, which differ from stannite by their lower symmetry ($I\,4$) and distribution of atoms among tetrahedral positions.

According to the Mössbauer, the compounds of this mineral group contain divalent and trivalent iron atoms. Below the limiting iron atom concentration Fe (x) ~ 0.5 data shows that all Fe atoms are trivalent and occupy the sulfur octahedra. At $0<x<0.5$, the substitution of atoms and the change of the structural positions and atom valence is carried out according to the scheme: $2Cu^{2+}(T_d) \rightarrow Cu^{1+}(T_d) + (T_d) + Fe^{3+}(O_h)$. The formula of the intermediate compounds can be expressed as

$Cu^{1+}{}_2Cu^{2+}{}_{1-2x}Fe^{3+}{}_xCu^{1+}{}_xSn^{4+}S_4$. The rend phase of this process is $Cu^{1+}{}_{2.5}Fe^{3+}{}_{0.5}Sn^{4+}S_4$. At the concentration ($x>0.5$), the mechanism of isomorphism is different: $Cu^{1+}(T_d) + Fe^{3+}(O_h) + (T_d) \rightarrow 2Fe^{2+}(T_d)$, and the end phase of this process is $Cu^{1+}{}_2Fe^{2+}Sn^{4+}S_4$.

Based on the results of the Mössbauer analysis, the structure of the intermediate phase $Cu_{3-x}Fe_xSnS_4$ with x~0.6 was refined. It has been shown that Fe^{3+} atoms have octahedral coordination and occupy the positions that are free in the «normal» ordered sphalerite structure.

The Fe^{3+} atoms (high-spin state) in kesterite with low Fe content are distributed among octahedral positions, which are vacant in the structure of pure Cu_2ZnSnS_4. This result is in good agreement with the complex scheme of isomorphism in $Cu_{3-x}Fe_xSnS_4$ series.

2 tables, 3 figures and 11 references.

Introduction

Compared to the significant progress in studying the crystal structures of silicates and multi-atom compounds (organic substances, metalloorganic compounds, semiconductors of new types, etc.), the level of knowledge for structures of relatively simple compounds has not almost changed for the last 20–30 years. First of all this concerns intermetallides (Cu_3Au, CuAu) or similar phases (NiAs, MnP, Fe_2P, Ni_2Si), sulfides (ZnS, $CuFeS_2$, Cu_2FeSnS_4, FeS_2), and their analogs. The main reason for this situation is the absence of high-quality material. Another reason is the widespread opinion about the «simplicity» of these crystal structures.

Most of the above-mentioned compounds have a high isomorphic capacity and always contain impurities (sometimes up to tens of atom percent). All these compounds are characterized by covalent or mixed (ionic-covalent, covalent-metallic, etc.) type of chemical bond. The presence of vacancies in many structural types and the different degree of ordering in the distribution of isomorphic components among structural positions are also typical for these minerals.

The problem of isomorphism in ore minerals, primarily sulfides, is quite important because many commercial elements are present as impurities and are now extracted from their host minerals. Investigation of the forms of occurrence of these elements is necessary to understand the reasons for the loss of useful components during ore processing and to develop new technologies. The different elements distribution in crystal structures, the possibility of isomorphic substitution of atoms, and, as a consequence, the ordering of atoms

Table 1. **Stannite group minerals**

Mineral	Formula	Sp.gr.	*a* (A)	*b*(A)	*c*(A)	Z	Reference
Stannite	Cu_2FeSnS_4	$I\bar{4}2m$	5.449	5.449	10.757	2	(Hall *et al.*,1978)
Kesterite	Cu_2ZnSnS_4	$I\bar{4}$	5.427	5.427	10.871	2	(Hall *et al.*,1978; Kissin, 1989)
Sakuraiite	$Cu_2Zn(In,Sn)S_4$	$I\bar{4}2m^*$	5.45	5.45	10.91	2	(Chvileva *et al.*,1988)
Okartite	Ag_2FeSnS_4	$I\bar{4}2m$	5.72	5.72	10.98	2	—«—«—«
Briartite	Cu_2FeGeS_4	$I\bar{4}2m$	5.32	5.32	10.51	2	—«—«—«
Gernyite	Cu_2CdSnS_4	$I\bar{4}2m$	5.487	5.487	10.848	2	(Szymanski, 1978)
Velikite	Cu_2HgSnS_4	$I\bar{4}$	5.5749	5.5749	10.882	2	(Evstigneeva *et al.*, 1998)
Kuramite	Cu_2CuSnS_4	$I\bar{4}2m$ ($I\bar{4}$)	5.445	5.445	10.75	2	(Kovalenker *et al.*, 1979)

within the structure also need to be known to answer the question about the different behavior of atoms in the nature, further development of crystal chemistry, and synthesis of new compounds. This consideration involves both noble (Au, Ag, PGE) and common (Fe, Zn, Cu, Cd, Pb, etc.) metals.

There is a common opinion that the theory of isomorphism is well developed. Publications by L. Pauling, G. Goldshmidt, N. Belov, G. Bokii, V. Frank-Kamenetskii, and others are quite famous. Discussing chemical composition of minerals (especially ore minerals) mineralogists usually use the terms «substitution isomorphism», «compensation isomorphism», «intercalation isomorphism», «isomorphism of the ions of the same element with a charge change». However, in most cases, the data on the structures of particular compounds under discussion and on the crystallographic positions of the impurity elements are absent. Because of application Pauling's empirical rules, or of data interpolation for similar compounds many conclusions about the isomorphism in sulfides seem to be declarative. This problem primarily concerns the minerals with composition rich in impurities (MRSA) and non-stoichiometric; i.e. fahlores, stannite group, and their close derivatives. The X-ray analysis and spectroscopy techniques could help us to verify existing concepts and to collect new information about the real isomorphic substitution.

The structure of stannite is derivative from the ZnS (sphalerite structure space group $I\bar{4}2m$). The tetragonal unit cell of stannite is doubled *c* in comparison to ZnS: $a = 5.449$, $c = 10.757$ (4) Å, Z = 2. Metal atoms occupy all sulfur tetrahedra with the similar orientation in the cubic close packing: Fe — 2a (000), Sn — 2b (1/2 1/2 0), Cu — 4d (0 1/2 1/4), S — 8i (xxz, x = 0.7551, z = 0.8702) (Hall *et al.*, 1978).

The stannite-group minerals have the common formula A_2BSnS_4, where A = Cu,Ag; B = Fe,Cu,Zn,Cd,Ge,Hg etc. (Table 1). The stannite group includes kuramite (Cu_3SnS_4) (Kovalenker *et al.*, 1979), kesterite (Cu_2ZnSnS_4) (Kissin 1989), okartite (Ag_2FeSnS_4) (Chvileva *et al.*, 1988), velikite (Cu_2HgSnS_4) (Evstigneeva *et al.*, 1998), cernyite (Cu_2CdSnS_4) (Szymanski, 1978), and other species. Stannite minerals have a significant place among natural and synthetic sulfides. Many of those are abundant and characteristic minerals of pyrite, gold, copper-nickel, silver, and other ore deposits. The stannite compounds and their structural analogs are characterized by an extremely diverse composition, containing elements of the I, II, III, IV, V, VI, and VIII groups of the periodic system.

Minerals of the stannite family are characterized by a great number of isomorphic impurities. The most typical of which is iron in kuramite (Cu_3SnS_4) (Kovalenker *et al.*, 1979) and kesterite (Cu_2ZnSnS_4) (Kissin, 1989). The structures of these compounds are derivatives from the cubic sphalerite structure (ZnS). They differ in space symmetry ($I\bar{4}2m$, $I\bar{4}$), distribution of metal atoms in the structural sheets perpendicular to the 4-order axis, and the degree of distortion of the coordination sulfur polyhedra.

The monocrystal method was only used for studying the structures of kesterite (Kissin, 1989) and Gernyite (Szymanski, 1978). These structures differ from the stannite one by the distribution of atoms among tetrahedral positions and by the absence of the diagonal mirror symmetry planes. The latter results in the reduced symmetry ($I\bar{4}$).

The study of synthetic compounds in the Cu_2ZnSnS_4 — Cu_2FeSnS_4 system showed that the Fe-Zn substitution solid solutions exist in the whole range of compositions (Springer, 1979). Due to the close size of the divalent iron and zinc ions, the iron atoms were believed to substitute zinc atoms in the kesterite structure. However, it was suggested (Kissin, 1989) that the isomorphic series exists between kesterite and a polymorphic modification of stannite with kesterite structure. Thus, the problem of the substitution mechanism in the series Cu_2ZnSnS_4 — Cu_2FeSnS_4 remains unsolved (Bernardini *et al.*, 1979).

The existence of the stannite-kuramite series (limited?), with divalent iron substituting divalent copper in kuramite, was suggested according to the compositions, X-ray patterns, and properties (Kovalenker *et al.*, 1979). However, because of the different electron structures the Fe^{2+} and Cu^{2+} ions takes place should be interesting to know if the Fe-Cu substitution really takes place and, if it does, what is the mechanism of this process.

Subjects and methods of study

A complex investigation of the compounds of stannite group was carried out to refine the structural features of some sulfide phases and to determine the mechanism of isomorphic substitution. The kuramite-stannite system and kesterite were chosen as subjects for this study. Ten members of the kuramite-stannite series, $Cu_{3-x}Fe_xSnS_4$ at 0<x<1 (step of x~0.1 formula unit), were synthesized from pure elements in evacuated quartz capsules (heating to 1150°C, annealing at 400°C, 960 hours, quenching in ice-cold water). The composition of kesterite from the Kester deposit (O. Stavrov's sample) was determined as follows (average of 10 analyses, wt.%): Cu 28.79 – 28.98; Zn 12.06 – 12.21; Fe 2.28 – 2.21; Sn 27.09 – 27.15; S 28.96 – 28.29; Σ 99.18 – 98.84; which yields the formula $Cu_{2.00\text{-}2.03}(Zn_{0.81\text{-}0.83}Fe_{0.18})Sn_{1.00\text{-}1.03}S_{3.99\text{-}3.94}$.

The valence and coordination of atoms in the crystal structures were concurrently determined by several methods: microprobe [MS-46 Cameca (IGEM RAS), Camebax Microbeam (Institute of Volcanology, RAS, Far East Branch), 20 kV-10 nA; standards: $CuFeS_2$ (Cu,Fe), Sn_{met} (Sn), FeS_2(Fe)]; profile analysis (Rietveld method) – ADP-2 difractometer (CuKα, Ni filter), calculation by WIRIET program (version 3.3); Mössbauer spectroscopy (MS1001E, ^{57}Co in Rh and ^{119m}Sn in $BaSnO_3$; MSTools software complex); scanning (JSM-5300+Link ISIS) and transmitting (JEM-100C + Kevex 5100 EDD) electron microscopy; X-ray photoelectron spectroscopy [LAS-3000 «Riber» + OPX-150 semispherical photoelectron analyzer, AlK_α (1486.6 eV) at U=12 kV and I=20 mA, calibration by carbon 1s-line (bond energy = 285 kV)]. Use of the modern analytic facilities and software for identification and decoding of experimental data enables determining the coordination and valence of Fe and Sn atoms in structures of common and rare sulfide minerals.

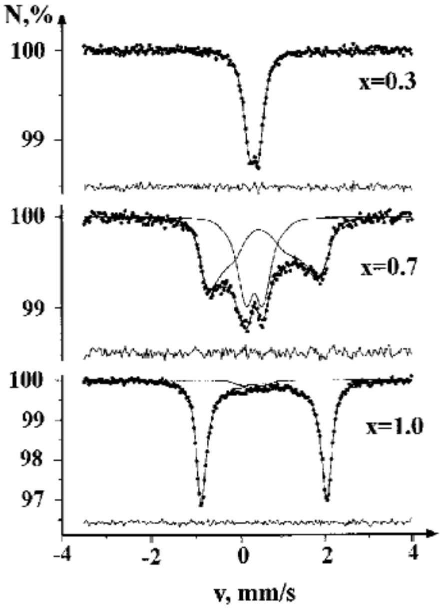

Fig. 1. *Typical Mössbauer spectra of ^{57}Fe for the compounds of the $Cu_{3-x}FexSnS_4$ series. N is the number of impulses (intensity), and v is the counting rate.*

Results

According to SEM and transmitting electron microscopy data, all intermediate members of the kuramite-stannite series are structurally similar homogeneous phases with a tetragonal symmetry and regularly changing unit cell parameters (c/a~2).

The structural study of four phases of the $Cu_{3-x}Fe_xSnS_4$ series (x=0.3, 0.6, 0.8, and 1.0) by Rietveld method indicated that all of them have a tetragonal symmetry and differ from stannite (Cu_2FeSnS_4, $I\bar{4}2m$) by a lower symmetry ($I\bar{4}$) and metal atom distribution among tetrahedral positions. The endmember of this series evidently is the synthetic polymorph of stannite. Attempts to determine how iron replaces copper in different tetrahedral positions in intermediate phases of the kuramite-stannite series lead to ambiguous results in spite of a good R-factor values (3.2-3.8%) (Evstigneeva *et al.*, 2001a).

The Mössbauer analysis showed that the phases of this series contain both divalent and trivalent iron atoms (Fig. 1). It was found that below the limiting concentration (x)~0.5 iron is only trivalent and is octahedrally coordinated by the S atoms.

Within the whole isomorphic series, Sn atoms are tetravalent and have tetrahedral

Table 2. **Composition (wt.%) of synthetic phases in the $Cu_{3-x}Fe_xSnS_4$ system**

x	Cu	Fe	Sn	S	Σ
0.08	41.74	1.08	34.11	24.72	101.65
0.14	42.71	1.56	31.04	23.85	99.16
0.29	39.68	3.79	29.62	29.32	102.41
0.40	40.50	4.83	28.96	23.36	97.65
0.51	39.16	6.60	29.39	26.31	101.46
0.58	35.28	7.88	30.00	29.33	102.49
0.71	35.89	8.89	28.96	27.07	100.81
0.84	32.03	11.18	29.65	29.70	102.56
0.97	33.77	11.52	28.21	25.69	99.16
0.96	29.80	12.88	26.5	29.9	98.1

Note: MS-46 Cameca (IGEM RAS); Analyst: G.N. Muravitskaya; Conditions of analysis: 2 kV – 10 nA; standards: $CuFeS_2$ (Cu,Fe), Snmet (Sn), FeS_2 (Fe)

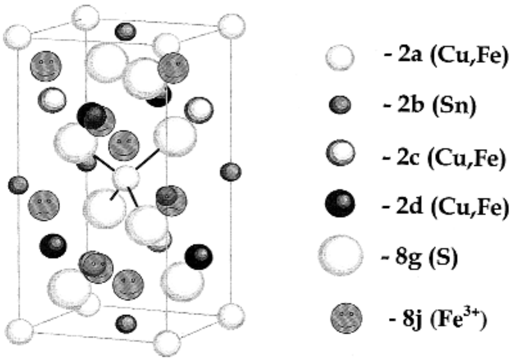

Fig. 2. *Structure of an intermediate member of the kuramite-stannite series*

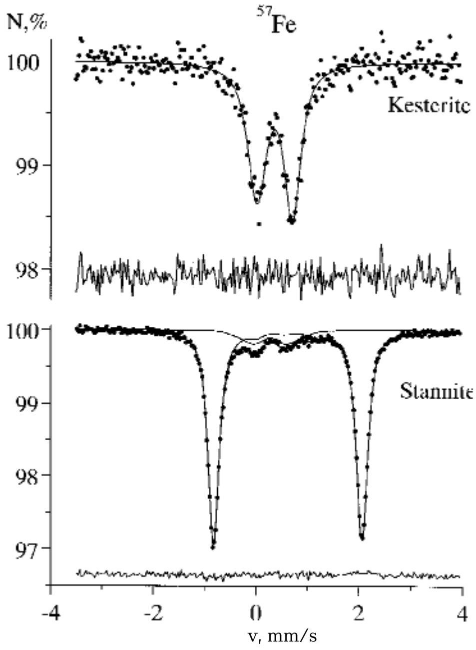

Fig. 3. *Mö ssbauer spectra of ^{57}Fe for natural kesterite and stannite*

coordination in the structure with a high degree of covalence (bonds with S atoms). As the concentration of the Fe atoms increases, the covalence degree of the Fe^{2+}-S and Sn^{4+}-S bonds decreases, while the covalence of the Fe^{3+}-S bonds increases. The magnitude of the effective charge of the Sn atoms in the tetrahedral positions is $Q_{Sn} = 3.38 \pm 0.08$ (Evstigneeva *et al.*, 2001a).

The structure of the intermediate phase $Cu_{3-x}Fe_xSnS_4$ with x = 0.6 was refined on the base of the Mö ssbauer data. The best results (R = 2.69%) were obtained with Fe^{3+}distribution among the octahedral positions that are free in the «normal» ordered sphalerite structure: 8j – xxz (xFe^{3+}~1/4, zFe^{3+}~0.126-0.128, zFe^{3+} = zS/3 + 5/12, zS – z atoms of S – in the structure) (Fig. 2). Correspondingly Me_{Oh}-Me_{Td} = 2.31 – 2.34 Å, that is comparable to the Me_{Td}-S distances but less than the Me_{Oh}-S distance (2.57 – 2.81 Å) (Td and Oh are tetrahedral and octahedral positions, respectively).

Two schemes of isomorphism in the $Cu_{3-x}Fe_xSnS_4$ series are proposed to explain the results obtained in this study:

At 0<x<0.5, the isomorphic substitution and the change of structural position and atom valence of occur as follows: $2Cu^{2+}(T_d) \rightarrow Cu^{1+}(T_d) + (T_d) + Fe^{3+}(O_h)$. The formula intermediate phases can be: $Cu^{1+}{}_2Cu^{2+}{}_{1-2x}Fe^{3+}{}_xCu^{1+}{}_xSn^{4+}S_4$. The complete depletion of Cu^{2+} corresponds the formula $Cu^{1+}{}_{2.5}Fe^{3+}{}_{0.5}Sn^{4+}S_4$.

Above the limiting concentration (x = 0.5), the scheme of isomorphism changes as follows: $Cu^{+}(T_d) + Fe^{3+}(O_h) + (T_d) \rightarrow 2Fe^{2+}(T_d)$, and the end phase of this process is $Cu^{1+}{}_2Fe^{2+}Sn^{4+}S_4$ (Evstigneeva *et al.*, 2001b).

The above-described mechanism of isomorphism could be indirectly confirmed by XPES results: the divalent copper content decreases (relative to monovalent copper) with increasing iron content.

The presence of the trivalent iron (high-spin state) in the octahedral coordination of sulfur atoms in the structure of kesterite pure in iron, $Cu_{2.00-2.03}(Zn_{0.81-0.83}Fe_{0.18})Sn_{1.00-1.03}S_{3.99-3.94}$, was proved by Mö ssbauer spectroscopy (Fig. 3; Rusakov *et al.*, 2001). This result contradicts the structural analysis data for kesterite, according which iron substitutes zinc in tetrahedral positions (Kissin, 1989).

Because the presence of trivalent iron atoms in octahedral positions is in good agreement with the scheme of isomorphism for Fe-poor members of the Cu_3SnS_4 – Cu_2FeSnS_4 series, a similar scheme could be suggested for the Fe-poor kesterite. The tetrahedral positions in the structure become vacant: $Cu^{1+}(T_d)$ + $Zn^{2+}(T_d) \rightarrow (T_d) + Fe^{3+}(O_h)$; that correspond to the formula of the intermediate phases: $Cu^{1+}{}_{2-x}Zn_{1-x}Fe^{3+}{}_{x}Sn^{4+}S_4$.

Conclusions

The isomorphism of Fe atoms in the stannite group compounds has a complex character and involves the formation of tetrahedral vacancies, occupation of octahedral positions, and change of the copper valence.

In the kuramite-stannite series there is the limiting concentration of Fe atoms, below which all Fe atoms are trivalent. In this concentration area, the number of Fe^{3+} and Cu^{1+} ions increases with x, while the number of Cu^{2+} ions decreases. Above the $x>0.5$ value, Fe^{2+} ions appear, and their concentration increases with x, while the number of $Fe^{3+}$and Cu^{1+} atoms decreases.

The presence of trivalent iron atoms in the octahedral positions is also characteristic for Fe-kesterites (Fe < 0.5 formula units). That could prove the similar mechanism of substitution.

This study was supported by the Russian Foundation for Basic Research (RFBR, Project 00-05-64609).

References

Bernardibi, G.P., Bonazzi, P., Corazza, M., Corsini, F., Mezetti, G., Poggi, L., Tanelli, G. New data on the Cu_2FeSnS_4 – Cu_2ZnSnS_4 pseudobinary system at 750 degrees and 550 degrees, C. //Eur. J. Mineral., **1990**, 2(2), pp. 219-225.

Chvileva, T.N., Bezsmetrnaya, M.S., Spiridonov, E.M., et al., Cpravochnik – opredelitel' rudnykh mineralov v otrazhennom svete (Reference Book: Identification of Ore minerals in Reflected Light), Moscow: Nedra, **1988**, p. 504.

Evstigneeva, T., Rusakov, V., Burkovsky, I., and Kabalov, Y. New data on the isomorphism Cu-Fe in sulfides of stannite family. in Mineral Deposits at the Beginning of the 21st Century (Piestrzynski *et al.*, Eds.), Zwets & Zeitlinger B.V., Lisse, The Netherlands, **2001**, pp. 1075-1078.

Evstigneeva, T., Rusakov, V., Kabalov, Y., Trubkin, N., Burkovsky, I., Tschegol'kov, Y. The complex study of Fe-Cu isomorphous replacement in the Cu_3SnS_4-Cu_2FeSnS_4 series, //Bull. Soc. Fr. Miner. Crist., **2001** Vol., 13, no. 3, p.71.

Evstigneeva, T.L., Kabalov, Yu. K., and Spiridonov, F.M., Kristallicheskaya struktura Cu_2HgSnS_4 – sinteticheskogo analoga minerala velikita (Crystal structure of Cu_2HgSnS_4 – synthetic analog of velikite), //Crystallography, **1978**, V. 43, no. 1, pp. 1-7. (Rus.)

Hall, S.R., Szymanski, J.T., and Stewart, J.M. Kesterite, $Cu_2(ZnFe)SnS_4$ and stannite, Cu_2FeSnS_4, structurally similar but distinct minerals, //Canad. Mineral., **1978**, V. 16, pp. 131-137.

Kissin, S.A. A reinvestigation of the stannite (Cu_2FeSnS_4) – kesterite (Cu_2ZnSnS_4) pseudobinary system, //Canad. Mineral., **1989**, V. 27., no. 4, pp. 689-697.

Kovalenker, V.A., Evstigneeva, T.L., Troneva, N.V., and Vyal'sov, L.N. // Kuramit, Cu_3SnS_4, novyi mineral gruppy ctannina (Kuramite, Cu_3SnS_4 – a new mineral from stannite group), //ZVMO, **1979**, Part 108, no. 5, pp. 564-569. (Rus.)

Rusakov, V.S., Evstigneeva, T.L., and Burkovsky, I.A., Messbauerovskaya spektroskopiya kesterita, $Cu_2(Zn,Fe)SnS_4$. Traditzionnye i novye napravleniya v mineralogicheskikh issledovaniyakh. (Mö ssbauer spectroscopy of kesterite, $Cu_2(Zn,Fe)SnS_4$, in Traditional and new directions of mineralogical studies, // Trudy godichnoi sessii MO VMO (Works of annual session of All-Russia Mineral Soc., Matias, V.V., Rusinov, V.L., and Amosov, R.A., Moscow: IGEM RAS, VIMS, MPR RF, **2001**, p. 132.

Springer, G. The pseudobinary system Cu_2FeSnS_4 – Cu_2ZnSnS_4 and its mineralogical significance, //Canad. Mineral., **1972**, V. 11, pp. 535-541.

Szymanski, J.T. The crystal structure of cernyite, Cu_2CdSnS_4, a cadmium analogue of stannite, //Canad. Mineral., **1978**, V. 16, pp. 147-151.