THE COMPARATIVE ANALYSIS OF ISOMORHISM PECULIARITIES IN THE SYSTEMS $Cu_{3-X}Fe_XSnS_4$ AND $Cu_2Zn_{1-X}Fe_XSnS_4$

Evstigneeva T.L., Rusakov V.S., Kabalov Yu.K.
evst@igem.ru; rusakov@moss.phys.msu.su; kabalov@geol.msu.ru

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Mineral stannite has the structure derivative from the ZnS (sphalerite) one. It is characterized by Sp.Gr. $I\bar{4}2m$, and by tetragonal cell, doubled by “c” in comparison to ZnS: a = 5.449, c = 10.757 (4) Ǻ, Z=2. Metal atoms occupy all equally director tetrahedral positions in close packing of S atoms: 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). Among minerals of stannite family there are kuramite (Cu_3SnS_4), kesterite (Cu_2ZnSnS_4), hokartite (Ag_2FeSnS_4), velikite (Cu_2HgSnS_4), cherniite (Cu_2CdSnS_4) etc. Many isomorphous elements are typical for minerals of this family. The most known amongst them is Fe in kuramite (Cu_3SnS_4) [1] and kesterite (Cu_2ZnSnS_4) [2]. X-ray powder data of all mentioned minerals and of stannite are near identical, but could be distinguished only by cell parameters. Only the structures of kesterite and cherniite have been studied using monocrystal methods [3]. It was proved that their structures differ from stannite one by both, the atom distribution among tetrahedral positions and by the absence of diagonal mirror planes. Based on the close ion radius similarity of Fe^{2+} and Zn^{2+} the conclusion that Fe replaces Zn in kesterite structure. The composition, properties, and x-ray characteristics of kuramite and stannite also caused the opinion that in kuramite Cu^{2+} is replaces by Fe^{2+} [1].

For check these suppositions the isomorphism peculiarities, valence state, and coordination of Fe- and Sn- atoms in structures of stannite family compounds have been studied. The system kuramite-stannite and mineral kesterite were chosen as objects to study. The eleven members of the series kuramite-stannite, $Cu_{3-x}Fe_xSnS_4$ (0<x<1, every x~0.1 f.u.) were synthesized in vacuumed quartz ampoules from pure elements (heated till 1150° C, annealed at 400 ° C during 960 h., and quenched to ice water). The composition of kesterite from Kester deposit (Chukotka, Far-East of Russia) (average from 10 analysis, 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. It corresponds to $Cu_{2.00÷2.03}(Zn_{0.81-0.83}Fe_{0.18})Sn_{2.00-2.03}S_{3.99-3.94}$.

The complex of methods used: microprobe [MS-46 Cameca (IGEM RAS) Camebax Microbeam (Institute of volcanology Far-East Branch of RAS), 20 kV-10 nA; standards – $CuFeS_2$ (Cu, Fe), Sn_{met} (Sn), FeS_2 (Fe)]; profile analysis (Rietveld method) – diffractometer ADP-2 (CuKα, Ni filter), calculations have been done using WIRIET program (version 3.3); moessbauer spectroscopy (MS1001E; ^{57}Co in Rh and ^{119m}Sn in $BaSnO_3$; program complex MSTools); scanning (JSM-5300 + Link ISIS) and transmission (JEM-100C + Kevex 5100 EDD) electron microscopy; x-ray photoelectron spectroscopy, XPES [LAS-3000 “Riber” + OPX-150 semispherical photoelectrode analyzer, AlK_α (1486.6 eV) at U=12 kV and I=20 mA, calibration after C1s line (bond energy = 285 kV)].

According to SEM and TEM data all intermediate members of the series kuramite-stannite, $Cu_{3-x}Fe_xSnS_4$, are structurally similar homogeny tetragonal phases with regularly variable cell parameters (at c/a~2). The results of structural determination shows that three intermediate compounds, $Cu_{3-x}Fe_xSnS_4$,, with x=0.3, 0.6, and 0.8, have tetragonal structures differ from stannite one (Cu_2FeSnS_4, $I\bar{4}2m$) by lower symmetry ($I\bar{4}$) and metal atom distribution among tetrahedral positions [4]. It is necessary to note that attempts to determine the mode of Cu replacement by Fe in different structural positions led to not simple results even at good values of R (<3.8%).

Moessbauer spectroscopy shows that compounds of the series contain bi- and three- valent Fe ions. There is the limit value of Fe concentration x = 0.45±0.02, below which these ions are only three valent, and have the octahedral co-ordination of S atoms.

At **$0< x_0 <0.5$** the process of replacement and the change of structural and valence state of metals correspond to the schema **$2Cu^{2+}(T_d) \rightarrow Cu^{1+}(T_d) + \square(T_d) + Fe^{3+}(O_h)$.** The formula of intermediate compounds can be presented as **$Cu^{1+}_2(Cu^{2+}_{1-2x}Fe^{3+}_xCu^{1+}_x)Sn^{4+}S_4$**. If Cu^{2+} is completely existed the formula of final phase corresponds to **$Cu^{1+}_{2.5}Fe^{3+}_{0.5}Sn^{4+}S_4$**. When the limit concentration, x_0, exceeds 0.5 the schema of isomorphism is changed: **$Cu^+(T_d)+Fe^{3+}(O_h) + \square(T_d) \rightarrow 2Fe^{2+}(T_d)$.** The final phase of this process is “normal” stannite, **$Cu^{1+}_2Fe^{2+}Sn^{4+}S_4$** [4].

Along all series studied Sn atoms occupy tetrahedral positions in the structure, and are four-valent. The level of Sn-S bond covalence is high. When the Fe concentration in compounds increases the level of Fe^{2+}-S and Sn^{4+}-S bond covalence falls, but Fe^{3+}-S one increases. The effective charge value of Sn in tetrahedral structural positions is Величина эффективного заряда атомов Sn в тетраэдрических позициях структуры, Q_{Sn}, is3.38±0.08.

According to the data of moessbauer spectroscopy, the structure of $Cu_{3-x}Fe_xSnS_4$ with x=0.6 were redefined. The best results have been obtained when Fe^{3+} have been distributed among octahedral positions free in "normally" ordered sphalerite structure: 8j - xxz (xFe^{3+} ~1/4, zFe^{3+} ~ 0.126-0.128 , $zFe^{3+} = zS/3 + 5/12$) where zS = number of S atoms in the structure. In this case the interatomic distances Me_{Oh} –Me_{Td} = 2.31-2.34 Ă. It is comparable with Me_{Td} –S distances, but less than Me_{Oh}-S (2.57-2.81Ă) (Td и Oh correspond to the tetrahedral and octahedral positions correspondingly).

Results of XPES prove the schema proposed. Data obtained show that along the series the Cu^{2+} concentration decreasing relatively to Cu^{1+} when Fe content increases.

The ^{119}Sn isomeric shift for kesterite is 0.012(3) mm/sec relatively to $BaSnO_3$ and SnO_2, the quadrupole shift = 0.283(3) mm/sec. It corresponds to Sn^{4+} in S tetrahedral. The moessbauer spectra of ^{57}Fe is a little asymmetric. The isomeric shift is 0.361(9) mm/sec relatively to α-Fe. The quadrupole shift = 0.346(9) mm/sec, that is typical for high spin state Fe^{3+} in octahedral environment of S atoms in kesterite structure. [5].

The presence of three-valent Fe in octahedral structural positions conforms well to the schema of isomorphous replacement for Fe-poor members of isomorphous series Cu_3SnS_4 - Cu_2FeSnS_4. On this base we could propose for Fe-poor kesterite the similar schema with tetrahedral vacancies in structure: $\mathbf{Zn^{2+}(T_d)\rightarrow \square(T_d) + Fe^{3+}(O_h)}$. The corresponding formula for intermediate members of the kesterite-stannite series - $\mathbf{Cu^{2+}(Zn_{1-x}Fe^{3+}_{x})\ Sn4^{+}S_4}$.

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