

THE STANNITE GROUP COMPOUNDS: STRUCTURES, ATOM VALENCY, AND CHEMICAL BONDS

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Based on our recent investigations of kuramite - stannite isomorphous series the valent state of metallic atoms (Fe, Cu, and Sn) could be discussed for compounds of stannite family. According to the data obtained the end member of this series close to stannite in the composition has a near completely disordered cubic structure ($P\bar{4}3m$, $a = 5.4179$ (3)) with two tetrahedral positions differently fulfilled by metallic atoms. This compound is considered as the synthetic analogue of mineral isostannite. Its high-temperature modification (550°C) is tetragonal. The structures of intermediate members of this series belong to the $sp.gr. I\bar{4}$. The exit of S from the mirror planes and the different fraction of Fe in three positions occupied mainly by Cu determine the symmetry decreasing in comparison with stannite structure. The analysis of relations cell parameters - composition in the series shows the deviation from Vegard's rule caused by the complex character of isomorphous replacement Cu-Fe. ^{57}Fe and ^{119}Sn nuclei peculiarity of kuramite - stannite series compounds was studied with Mossbauer spectroscopy. The parameters of ^{57}Fe and ^{119}Sn nuclei superfine interactions are obtained. Fe valency is dramatically decreased from $3+$ to $2+$ at the Fe 0.45 ± 0.02 (in formula units). The average valences of other atoms are not changed. At the lower Fe content ($x0.45$ f.u.) the gradual decreasing of Cu valency from $1.5+$ to $1.25+$ is noted. These data and the monotone reducing of ^{119}Sn and ^{57}Fe Mossbauer line shifts with the Fe-content increasing are used to discuss the isomorphism and structure orderliness. For compare the characteristics of Fe and Sn atoms in structures of stannite family compounds with Metal : Sulfur 1:1 the X-ray and Mossbauer study has been done for synthetic stannoidite -, and chatkalite - mawsonite series members. Results of this study and recently published data are discussed also from the point of view of block isomorphism