

Preliminary X-ray Absorption Spectroscopy study of synthetic nanokuramite, Cu_3SnS_4

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The task for renewable energy resources is stimulating the research for new materials allowing to set up low cost and high conversion efficiency solar cells. The kesterite-like quaternary chalcogenides ($\text{Cu}_2\text{ZnSnS}_4$, or CZTS) attracted a relevant interest from worldwide researchers, due to their good performances (up to 10 % conversion efficiency) and to the absence of relevant economic or environmental concerns associated with their use in the solar cells production.

A recent reconsideration of materials belonging to the pseudoternary system $\text{Cu}_2\text{FeSnS}_4$ (stannite) - $\text{Cu}_2\text{ZnSnS}_4$ (kesterite) - Cu_3SnS_4 (kuramite), to which CZTS belongs, evidenced promising phases which can be related to CZTS adding band-gap tunability thanks to the isomorphous replacement of Cu with Fe, Zn ions.

Kuramite nanoparticles, synthesised through solvothermal approach, were the object of a study aimed to verify the structural, magnetic and electronic properties associated to the nanometric powders, in relation to what already known for bulk microcrystalline Cu_3SnS_4 (Di Benedetto et al., 2011). Two key aspects, for the consideration of kuramite in advanced technological devices, were fostered but not finally assessed: a) the possible occurrence of divalent Cu as a formal discrete state, and b) the synthesis-dependent random metal distribution in the structural sites. Both aspects have been re-examined, in the present study, through X-ray Absorption Spectroscopy at Cu K-edge.

Spectra were collected in the transmission mode at room temperature, with high detail in the pre-edge, XANES and EXAFS regions. The nanokuramite sample reveals a XAS spectrum (in particular the XANES and EXAFS regions) fully comparable with those of the most common sulphide minerals having Cu in tetrahedral coordination by S anions: chalcopyrite and enargite, but also tetrahedrite and covellite (where Cu is partly tri-coordinated in triangular arrangements). The EXAFS region was fitted starting from the structural model of kuramite, confirming the first shell tetrahedral coordination for Cu at 2.28(2) Å. This value agrees well with the shortest Cu-S bond distances in sulfide minerals having at least a part of formally divalent Cu (e.g. natural kuramite, 2.31 Å, covellite, 2.30 Å, tetrahedrite, 2.25 Å). Moreover, the pre-edge region of the spectrum reveals the presence of a very weak peak, before the absorption jump, which is clearly observed in several Cu(II) standards (e.g. malachite and CuO). Although in the reference samples this pre-edge feature is more marked, the present data, including the first shell bond distance, suggest that Cu(II) can be considered at least in part as a discrete state effectively occurring in the sample (as necessary to achieve the charge balance). Finally, it is noteworthy to mention that the fitting of successive coordination shells appears suggestive of the possible occurrence of random metal distribution (traced by the scattering of the heavy Sn ions).

References:

Di Benedetto, Borrini, Caneschi, et al. (2011), *Phys. Chem. Minerals*, 38, 483-490.