Synthetic Mn-substituted analogues of stannite $\text{Cu}_2(\text{Fe}_{x-1}\text{Mn}_x)\text{SnS}_4$ – alternative photovoltaic and photocatalytic material

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To be sustainable, future electronic materials must deliver desirable optoelectronic properties while containing only abundant and benign elements. Semiconductor properties of stannite $\text{Cu}_2\text{FeSnS}_4$ make it a potential candidate for application as an absorber layer in thin film solar cells. In the nature, it is a common sulfide mineral which is formed as a result of hydrothermal processes. Its crystal structure allows for numerous substitutions including replacement of Fe by Mn.

The aim of this study is development of a simple method of synthesis of stannite analogues and validation of the effect of Mn$^{2+}$ substitution for Fe$^{2+}$ in the series of $\text{Cu}_2(\text{Fe}_{x-1}\text{Mn}_x)\text{SnS}_4$ on the crystal structure and optoelectronic properties. Six members of the series were cost-effectively synthesized by hydrothermal reactions of metal salts and sulfur in hot ethylene glycol at presence PVP solution in an autoclave at 195°C. The products were identified with powder X-ray diffraction and analyzed with electron microscopy SEM/EDS and Raman spectroscopy. The XRD patterns of the synthesized nanoparticles correspond to stannite structure with reflections coming from (112), (200), (204), and (312) planes shifted systematically with the extent of substitution. The increase of the lattice parameters and lattice volume is in agreement with the increasing ionic radius of the substituting element (Mn$^{2+}$=83pm, Fe$^{2+}$=78pm). It is evident from SEM imaging that the aggregates of nanocrystals display characteristic, nearly spherical shape with concentric structure. The average size of grains is ca. 1±0.5 µm. Raman spectroscopy confirms the phase purity of the precipitates.

In summary, pure members of $\text{Cu}_2(\text{Fe}_{x-1}\text{Mn}_x)\text{SnS}_4$ solid solution series can be successfully synthesized via a relatively simple hydrothermal method. The composition of the final product can be precisely controlled by the composition of the reactants. The synthesis results in pure and promising material of uniform morphology. The crystal structure of the phases is similar to the established CIGS type photovoltaic materials. Future work will concentrate on photoelectronic properties and application in photocatalysis. Photocatalytic processes using semiconductor materials have attracted much attention as a promising advanced oxidation technology to decompose refractory pollutants in the environmental application.

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