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Application of resonant X-ray diffraction for investigation of crystal and band structures of sulfide photocatalysts derived from ZnS with isovalent substitutions

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Introduction

The materials capable of converting solar energy into chemical energy attract a lot of attention. It was reported recently that solid solutions in ZnS-$CuInS_2$-$AgInS_2$ system exhibit high photocatalytic activity for hydrogen production under visible light irradiation in the presence of sacrificial reagents [1]. In this work, a series of new chalcogenide photocatalytic materials Ag_2ZnSnS_4, Ag_2ZnGeS_4, Cu_2ZnSnS_4, and Cu_2ZnGeS_4 were studied. Although Rietveld refinement using conventional diffraction patterns gives quite reasonable metal-sulfur interatomic distances, further discussion of possible disorder in Ag-Sn, Zn-Cu, Zn-Ge, Zn-Cu-Ge sites is impossible due to close X-ray scattering factors of these elements. The objective of this proposal is to use synchrotron radiation for resonance diffraction near Zn-, Cu- and Ge-K absorption edges, which can provide the unambiguous characterization of real structure of the sulfides. During the first stage of the project, BL-1B beam line was used to collect part of the planed full dataset. The rest of the data will be collected at BL-4B2 considering the results of preliminary analysis.

Experiment

Powder diffraction data were collected at room temperature using Debye-Scherrer camera equipped with imaging plate detector at BL-1B beam station. Ag_2ZnSnS_4, Ag_2ZnGeS_4, Cu_2ZnSnS_4, and Cu_2ZnGeS_4 were carefully ground and packed into the 0.1-0.3 mm glass capillary tubes. Up to four datasets were acquired using 1.38255 Å (Cu-K edge) 1.28642Å (Zn-K edge), 1.11868 Å (Ge-K edge) and 0.70015Å wavelength of the incident X-ray beam. Actual values of wavelength were refined using reference diffraction patterns collected for standard CeO_2 samples. The obtained diffraction patterns of the sulfides were combined for each sample and used for joint refinement of in total three or four patterns for each sample by GSAS package [2]. The f' and f" values of elements at different wavelengths were calculated by FPRIME program included in GSAS package. Absorption correction was made for cylindrical shape assuming 60% packing density. In this report we will focus only on Cu_2ZnSnS_4 because dataset collected at this stage using

BL-1B diffractometer was sufficient for accurate structural characterization of this compound.

Results

Cu_2ZnSnS_4 was found to have stannite type structure (a=5.43267Å, c=10.84395(13)Å, I-42m Zn (0,0,0), Cu(0,1/2,1/4), Sn(1/2,1/2,0), S(0.7532(3), 0.7532(3), 0.8693(2))). Interatomic distances of 2.3676(24)Å (Zn-S), 2.4070(24) Å (Sn-S) and 2.3157(15) Å (Cu-S) allow estimation of bond-valence sums [3] to be 1.86 for Zn, 3.92 for Sn and 1.29 Cu. The high deviation from the valence of Cu can not be explained by the experimental uncertainty. Thus, one should conclude that Zn can substitute for Cu. The unrestrained refinement of occupancies of metal sites yielded relatively large standard deviations. The variation of occupancies in the refined model resulted in the total Rwp values for joint refinement as shown in Fig. 1. One may notice a flat bottom in the range of concentrations ~0.35-0.45, which is responsible for large standard deviations of occupancies. Examination of the refinement results also suggests that substitution into Sn site is unlikely.
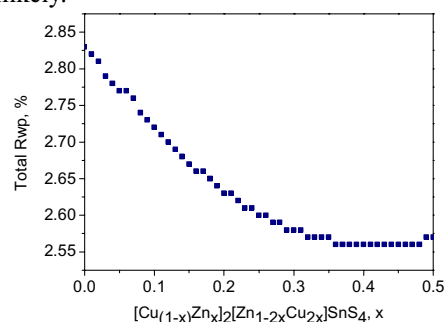

Fig. 1. Final **Rwp** values vs. disorder parameter **x** in the $[Cu_{(1-x)}Zn_x]_2[Zn_{1-2x}Cu_{2x}]SnS_4$ model. in joint refinement of Zn-, Cu-K edge and 0.7A data set.

References

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