

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

Solid solutions in ZnS-CuInS₂-AgInS₂ system exhibit high photocatalytic activity for hydrogen production under visible light irradiation [1]. We investigated a series of new chalcogenide photocatalytic materials Cu₂ZnGeS₄, Ag₂ZnGeS₄, AgCuZnGeS₄, Cu₂ZnSnS₄, Ag₂ZnSnS₄, AgCuZnSnS₄ in this work. The diffraction patterns of these compounds can be indexed assuming the stannite type unit cell. Although general packing of atoms in the stannite structure is well understood, relatively little work has been done to analyze actual site occupancies [2]. For most of the compounds with stannite structure conventional Rietveld refinement does not provide such information due to the similar scattering factors of the elements constituting the crystal. In this proposal synchrotron radiation was applied for resonance diffraction near Zn-, Cu- and Ge-K absorption edges, which can provide the unambiguous information on site occupancies in these sulfides.

Experiment

Powder diffraction data were collected at room temperature using Debye-Scherrer camera equipped with imaging plate detector at BL-1B beam station. The samples were 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) 1.28642 Å (Zn-K edge), 1.11868 Å (Ge-K edge) and 0.70015 Å wavelength. Actual values of wavelength were refined using diffraction patterns of CeO₂ standard. The diffraction patterns of the sulfides were combined for each sample and used for joint refinement by GSAS package [3]. The f' and f'' values of elements at different wavelengths were calculated by FPRIME program included in GSAS.

After refinement of BL-1B data, a limited set of samples was selected for additional data acquisition with higher resolution at BL-4B2 beamline. The diffraction patterns were obtained in the backscattering setup with the step size of 0.005-0.008° and acquisition time of 2-4 s/step depending on sample. The diffraction data collected with MultiArm Detector System were merged into the single pattern using the approach described in [4] and coded as IgorPro script. The wavelengths were determined by measuring 8-13 peaks of Si standard.

Results

The summary of the refinement results is presented in Table 1. The most important conclusion from the obtained data can be described as follows: i) Ge and Sn sites in stannites are exclusively occupied with these tetravalent cations; ii) there is a considerable disorder between Cu and Zn sites and Cu(I) has a preference to occupy metal sites close to Ge(IV) or Sn(IV), while Zn tends to stay in the site, which is normally considered as Cu-site; iii) for Ag-containing compounds, silver completely substitutes Zn in the neighborhood of Ge and Sn due to the interplay of size and charge effect; iv) all crystals structures are little strained because analysis of bond valence sums gives $BVS(Cu^+) \approx 1.2$, $BVS(Ge^{4+}) \approx 3.85$ and $BVS(Sn^{4+}) \approx 3.9$ although preliminary calculations of electron density of states (DOS) on basis of DFT method show a clear energy gap between Cu-3d (fully filled) and Ge-4s(4p) (empty) indicating no redistribution of electrons between these metals. A more detailed analysis of the obtained data is currently in progress.

Table 1. Refined site occupancies and lattice parameters for the analyzed sulfides .

Refined Composition	Lattice Parameters, Å
(Cu _{0.70} Zn _{0.30}) ₂ Zn _{0.36} Cu _{0.63} GeS ₄ (tetragonal)	a=5.34462(1) c=10.51699(2)
(Cu _{0.96} Zn _{0.04}) ₂ Zn _{0.80} Cu _{0.03} GeS ₄ (orthorhombic)	a=7.50947(36) b=6.48468(31) c=6.19345(29)
(Ag _{0.5} Zn _{0.5}) ₂ AgGeS ₄	a=5.74852(6) c=10.34011(14)
(Cu _{0.5} Zn _{0.5}) ₂ AgGeS ₄	a=5.56883(6) c=10.30627(12)
(Cu _{0.55} Zn _{0.45}) ₂ Zn _{0.1} Cu _{0.9} SnS ₄	a=5.43267(4) c=10.84403(13)

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