Materials Science

Evolution of Crystal and Electronic Structures in $(Ag,In)_xZn_{2-2x}S_2$ solid solutions

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Introduction

$Ag_xIn_xZn_{2-2x}S_2$ solid solutions exhibit high photocatalytic activity for hydrogen production under visible light in the presence of sacrificial reagents [1]. The activity in this series demonstrates a pronounced maximum vs. **x** (Ag and In concentration) in the range of 0.15-0.5. It means that electronic band structure of the semiconducting samples undergoes a significant change in the investigated Ag and In concentration range and it has a remarkable impact on the photocatalytic properties. Structural characterization of these materials is difficult when conventional laboratory XRD equipment is used - it provides information only about 50 reflections, and even the simplest refinement procedure is quite unstable. In addition, Ag^+ and In^{+3} have similar X-ray scattering factors at $CuK\alpha$ and it is not possible to refine their positions separately. On the other hand, computations of electronic structures rely on accurate structural information. The goal of this proposal was to obtain accurate structural parameters for these solid solutions using synchrotron radiation. The obtained data will be used for computations of electronic band structures.

Experiment

Six specimens of $Ag_xIn_xZn_{2-2x}S_2$ solid solutions (x=0.18, 0.22, 0.28, 0.33, 0.4, 0.5) were carefully ground and packed into the 0.3 mm capillary tubes. Powder diffraction data for all samples were collected at room temperature using Debye-Scherrer camera equipped with imaging plate detector at BL-1B beam station and in the flat plate geometry using Multi Detector System at BL-4B2 beam station for four samples (x=0.18, 0.28, 0.33, 0.5). At BL-1B two datasets were acquired using 1.28843Å (Zn-K edge) and 0.69801Å wavelength of the incident X-ray beam, while at BL-4B2 only 1.306348 Å wavelength was used. The obtained diffraction patterns were combined with the patterns collected at SPring-8 near Ag-K and In-K absorption edges and used for joint refinement of in total four/five diffraction patterns for each sample by GSAS package [2].

Results

It was found that all solid solutions in the system $Ag_xIn_xZn_{2-2x}S_2$ (x=0.18, 0.22, 0.28, 0.33, 0.4, 0.5) possess wurtzite structure. No superstructural reflections have been detected in the diffraction patterns. The lattice

parameters of the hexagonal unit cell show linear trend vs. composition. The site symmetry of metal and sulfur positions allows variation of z parameters for metal ions and sulfur. However only the relative value of $z_S - z_M$ (metal-sulfur distance) should be considered as an independent parameter. Therefore during the last stage of the Rietveld refinement, all z parameters except for Zn were allowed to vary. Fig.1 summarizes two types of metal-sulfur distances in the distorted metal-sulfur tetrahedron. One can see that the distortion of $M-S_4$ tetrahedron decreases with increasing **x** and the distances tend towards usual In-S and Ag-S distances in $AgInS_2$ compound (2.468Å). The release and refinement of the other z coordinates yields the sets of Ag-S, In-S and Zn-S distances that are clustering around "average" points in Fig.1. However for x=0.18 unreasonable distances of 2.63Å for Ag-S, and 2.28 Å for Ag-S and In-S were obtained during independent refinement of z, which could be due to either intergrowth of sphalerite structure (this composition x=0.18 is close to cubic-hexagonal transition) or uncertainty introduced by the complex shape of background from the capillary combined with low concentration of Ag and In.
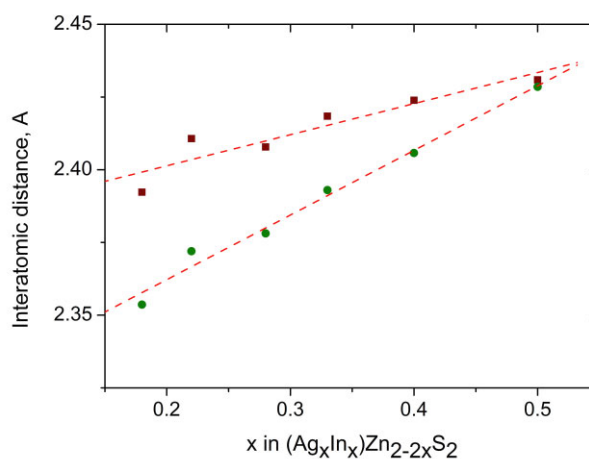

Fig. 1. Interatomic distances in the metal – sulfur tetrahedra vs. composition **x**.

References

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