

Structural Characterization of AgGaS₂-type Photocatalysts for Hydrogen Production from Water Under Visible Light

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Abstract. Bulky AgGaS₂ was synthesized as a p-type semiconductor photocatalyst by a conventional solid state reaction under N₂ flow for hydrogen production under visible light. To remove the impurity phase involved in the synthesized material and improve its crystallinity, the material was treated at various temperatures of 873-1123 K under H₂S flow. Impurity phases were identified as β -Ga₂O₃ and Ag₉GaS₆ with Rietveld analysis of XRD, and the local coordination structure around gallium atom in AgGaS₂ was investigated by EXAFS. As the H₂S-treatment temperature increased, the contribution from impurity phase was diminished. When the temperature reached 1123 K, the impurity phases were completely removed and the material showed the highest photocatalytic activity.

Keywords: AgGaS₂, p-type semiconductor photocatalyst, EXAFS, impurity phase.

PACS: 61.10.Ht, 61.10.Nz, 61.43.Gt, 61.72.-y

INTRODUCTION

Sulfide photocatalysts have been known to be active for hydrogen production from aqueous electrolyte solutions containing a sacrificial electron donor (Na₂S or/and Na₂SO₃) under visible light irradiation [1,2]. In contrast to oxide photocatalysts, the band gap energy and band positions of sulfide photocatalysts can drive both oxidation and reduction of water under visible light irradiation. The multicomponent metal sulfides such as chalcogenide (AB₂X₄) and chalcopyrite (ABX₂) are stable and show high photocatalytic activity under visible light [3,4]. AgGaS₂ is a p-type material of the I-III-VI ternary semiconductors, which crystallize in the chalcopyrite structure.

In this study, bulky AgGaS₂ was prepared by a conventional solid state reaction at various temperatures under N₂ flow. To remove the impurity phase and the defect which might cause a low photocatalytic activity for hydrogen production, the material was treated at elevated temperatures under H₂S flow. Before and after H₂S treatment, we investigated the structure of the materials mainly by synchrotron radiation techniques of x-ray diffraction and x-ray absorption fine structure (XAFS). The

relationship between impurity phases of the materials and their photocatalytic activity was studied.

EXPERIMENTAL

For the preparation of AgGaS₂ materials, stoichiometric amounts of Ag₂S and Ga₂S₃ were mixed and ground in the presence of ethanol and dried in and oven. Their pelletized form was calcined at 873 – 1073 K for 5 h under N₂ flow. Then, the powders calcined at 1073 K were treated with H₂S at 873 - 1123 K for 3 h.

The crystal phases of the materials were determined by powder x-ray diffraction. The XRD patterns were taken at BL 8C2 of Pohang Accelerator Laboratory (PAL) in Korea. Full-profile refinements through Rietveld analysis were performed with *FULLPROF2K* (Rodriguez-Carvajal, 1990).

The local structure around gallium in AgGaS₂ was characterized by EXAFS. X-ray absorption measurements for Ga K-edges were conducted on BL 7C1 of PAL (2.5GeV; stored current of 120-180 mA). After treated at the desired temperatures, the materials were cooled and their spectra were measured at room temperature in transmission mode. The obtained data were analyzed using the IFEFFIT suite of software programs [5] and the FEFF 8.2 code [6].

RESULTS AND DISCUSSION

A multicomponent sulfide photocatalyst, which was prepared by a conventional solid state reaction, showed an increased activity in hydrogen production from an aqueous electrolyte solution containing Na_2S and Na_2SO_3 under visible light (using a cutoff filter of $\lambda \geq 420$ nm) as the calcination temperature in the preparation of materials increased. In the powder x-ray diffraction patterns for these materials, most reflections were indexed to tetragonal phase AgGaS_2 . However, there exist some peaks due to impurity phases even for AgGaS_2 calcined at 1073 K.

H_2S -Treatment of AgGaS_2

The post-synthetic H_2S treatment is a plausible method to minimize the impurity phases for the sulfide photocatalyst so that the photocatalytic performance over H_2S -treated AgGaS_2 should be optimized. Figure 1 shows XRD patterns before (A) and after (B) H_2S -treatment of the material, with a fit of full-profile structure refinements.

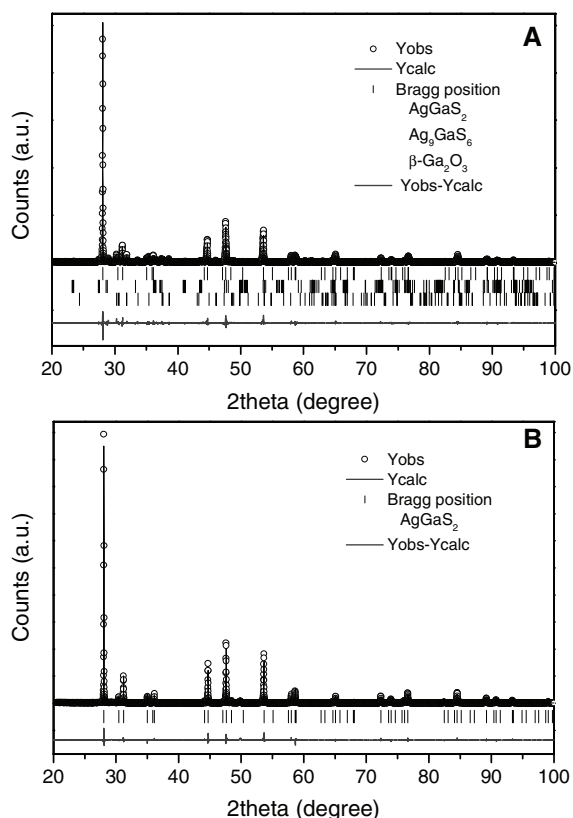


FIGURE 1. Observed (solid line) and calculated (dots) x-ray diffraction patterns of (A) untreated AgGaS_2 , and (B) H_2S -treated AgGaS_2 at 1123 K.

The Rietveld analysis has demonstrated that untreated AgGaS_2 prepared at the calcination temperature of 1073 K consists of three phases of AgGaS_2 , Ag_9GaS_6 , and $\beta\text{-Ga}_2\text{O}_3$. The evolution of $\beta\text{-Ga}_2\text{O}_3$ phase could be understood as the impurity originated from precursor Ga_2S_3 , because both crystals are monoclinic with cell dimensions in order of $a > c > b$. The existence of Ag_9GaS_6 , for which only the space group and lattice parameters but not the structure were known, could be controversial. But, the phase diagram of silver-gallium-sulfur suggests that two additional phases of Ag_9GaS_6 and $\text{Ag}_2\text{Ga}_{20}\text{S}_2$ could co-exist together with the chalcopyrite analog AgGaS_2 in the preparation of AgGaS_2 [7]. The lack of structural information on Ag_9GaS_6 made it impossible to determine the amount of the three phases. On the other hand, H_2S -treated AgGaS_2 at 1123 K has a chalcopyrite structure without impurity phases. Therefore, we could rationalize that the post-synthetic treatment under H_2S flow would change the structure of the solids.

EXAFS of Untreated and H_2S -Treated AgGaS_2

The radial structural functions (RSF) calculated from Ga K-edge EXAFS data are given Figure 2.

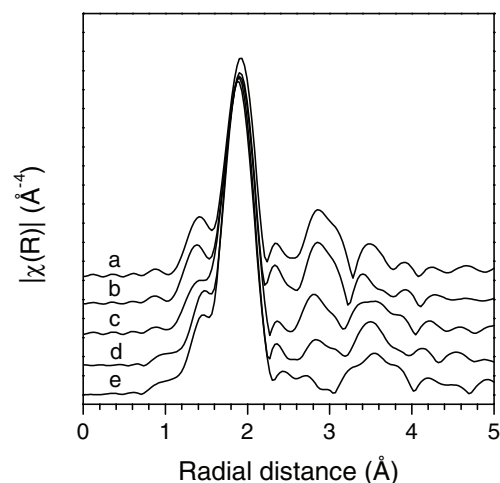


FIGURE 2. Fourier-transforms of $k^3\chi(k)$ of (a) untreated AgGaS_2 , (b) AgGaS_2 -873K, (c) AgGaS_2 -973K, (d) AgGaS_2 -1073K, and (e) AgGaS_2 -1123 K.

Regardless of H_2S -treatment and treatment temperatures, all materials show a distinct peak at $1.2 - 2.3$ Å, which could be assigned as the Ga-S interaction. However, the peaks above 2.3 Å change in a systematic manner with increasing H_2S -treatment temperatures. The peak at $2.3 - 3.3$ Å decreases in magnitude of Fourier-transformed data as the sample

is treated up to 1073 K under H₂S flow. At 1123 K, its RSF exhibits different features in the position of peaks as well as in intensity of peaks. The peak at 2.3 – 3.3 Å which was initially present in the untreated sample, almost disappears and a new peak at 3.0 – 4.0 Å is observed. In consideration of the powder diffraction result, we fitted the experimental EXAFS data up to

4.07 Å with theoretically generated data of AgGaS₂. For other samples which were untreated and H₂S-treated up to 1073 K, only the first shell at 1.2 – 2.3 Å was inverse-Fourier transformed and fitted in *k*-space in order to prevent EXAFS fit from over-calculating structural parameters. The results of EXAFS least-square fits are given in Table 1.

TABLE 1. EXAFS least-square fitting results for untreated and H₂S-treated AgGaS₂ at different temperatures.

H ₂ S-treatment Temp.	N _{Ga-S}	R _{Ga-S} (Å)	σ ² _{Ga-S} (Å ²)	ΔE ₀ (eV)	R-factor
Untreated	2.6(4)	2.29(1)	0.0043(10)	4.1	0.0173
873 K	2.8(4)	2.29(1)	0.0042(9)	2.7	0.0154
973 K	3.5(3)	2.29(1)	0.0051(6)	3.4	0.0071
1073 K	3.6(3)	2.29(1)	0.0047(6)	2.2	0.0047
*1123 K	4.0	2.29(1)	0.0044(1)	2.4	0.0141

* Fitted to 4.07 Å with fixed coordination numbers which are already revealed with XRD of AgGaS₂. Its fit up to four shells results in R_{Ga-Ag} = 3.88 Å, R_{Ga-Ga} = 3.88 Å, and R_{Ga-2Ag} = 4.09 Å with σ²_{Ga-Ag} = σ²_{Ga-2Ag} = 0.0213 Å², σ²_{Ga-Ga} = 0.0114 Å², ΔE_{0,Ga-Ag} = ΔE_{0,Ga-2Ag} = -1.1 eV, and ΔE_{0,Ga-Ga} = 3.1 eV as well as parameters in the Table.

The features at higher shells in RSF (the peaks above 2.3 Å) having a systematic change during heat-treatment of H₂S flow, can be explained with the aids of Feff simulations of β-Ga₂O₃ and AgGaS₂. The imaginary function of the second shell of untreated AgGaS₂ at 2.3 – 3.3 Å has the same feature as that of the second shell of Ga₂O₃ at 2.3 – 3.3 Å. The latter reflects both single scattering of Ga-Ga and multiple scattering of Ga-O-O. Since the backscattering amplitude from a heavier element dominates contribution from a light backscatterer, we could say that the peak at 2.3 – 3.3 Å for untreated AgGaS₂ originates from the surrounding gallium in Ga₂O₃. In a similar way, the peak at 3.0 – 4.0 Å in RSF of H₂S-treated material at 1123 K was identified as Ga-Ag, Ga-Ga, and Ga-Ag scatterings at distances of 3.86 – 4.07 Å.

In conclusion, as the H₂S-treatment temperature increases, the contribution from the second shell of Ga₂O₃ is suppressed and that of AgGaS₂ becomes clearer because the content of the impurity phases is diminished. The EXAFS fitting results in Table 1 confirms that the decrease of impurity phase causes the increased Ga-S coordination number with increasing H₂S treatment temperature. Thus, obtained AgGaS₂ having no impurity and high crystallinity exhibited a high photocatalytic activity under visible light.

ACKNOWLEDGMENTS

This work was supported by the Hydrogen Energy R&D Center, one of the 21st Century Frontier R&D Program, National Research Laboratory, General Motors R&D Center, National R&D Project for Nanaoscience and Technology. The power XRD and XAFS experiments at PLS were supported in part by MOST and POSTECH.

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