FIRST PRINCIPLES STUDY ON PHASE STABILITIES AND ELECTRONIC STRUCTURES OF STANNNITE-TYPE CuIn₅Se₈ AND RELATED COMPOUNDS, CuIn₅S₈, CuGa₅Se₈, CuGa₅S₈, AgIn₅Se₈, AgIn₅S₈, AnGa₅Se₈, and AgGa₅S₈

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Recently, a group at the Tokyo Institute of Technology obtained high-efficiency Cu(In,Ga)Se₂ (CIGS) solar cells by the insertion of a Cu(In,Ga)₅Se₈ layer at the CdS/CIGS interface [1]. Cu-deficient phases such as CuIn₅Se₅ (1-3-5) and CuIn₅S₈ (1-5-8) are expected to be useful for controlling the valence band offset (ΔEᵥ) at the CdS/Cu(In,Ga)₅Se₈/CIGS interface in CIGS solar cells. Therefore, we studied the crystallographic and optical properties of CuIn₅Se₈, CuIn₅S₈, and CuIn₅S₈ phases in the Cu₅Se-In₅Se₈ system [2]. The crystal structure changed from chalcopyrite-type CuIn₅Se₈ to hexagonal CuIn₅S₈ through stannite-type CuIn₅Se₈ with increasing In₅Se₈ content. In the (1-x)Cu₅Se-xGa₅Se₈ system, there is a wide region of stannite-type phase (x=0.72-0.86) in the Cu₆-poor side of CuIn₅Se₈, and hexagonal CuGa₅Se₈ phase is not observed. In the Cu₅In₃S₈ system, crystal structure changed from tetragonal chalcopyrite-type CuIn₅S₈ to cubic spinel-type CuIn₅S₈, and stannite-type CuIn₅S₈ was not observed. In the Cu₅S-Ga₅S₈ system, CuGa₅S₈ with an unknown crystal structure was reported, and stannite-type CuGa₅S₈ was not observed. Recently, we analysed the crystal structure of CuGa₅S₈ by the Rietveld refinement of the X-ray diffraction data and determined that CuGa₅S₈ had a stannite-type crystal structure [3].

In this study, we examined the phase stability and electronic structures of stannite- and spinel-type CuIn₅Se₈, CuIn₅S₈, CuIn₅S₈, and CuGa₅S₈ by first-principles calculations. Figure 1 shows the enthalpies of formation, ΔH₀, for some stannite-type and spinel-type 1-5-8 compounds, CuIn₅Se₈, CuGa₅Se₈, and CuIn₅S₈. For CuIn₅Se₈, CuGa₅Se₈, and CuGa₅S₈, ΔH₀ for stannite-type were lower than those for spinel-type. On the other hand, for CuIn₅S₈, ΔH₀ for the spinel-type was lower than that for the stannite-type.

There are few studies on the crystal structure and electronic structure of the Ag 1-5-8 chalcogenides. Tetragonal AgIn₅S₈ with an unknown crystal structure and cubic spinel-type AgIn₅S₈ have been reported. However, AgGa₅Se₈ and AgGa₅S₈ are not reported in their phase diagrams. Therefore, we calculated ΔH₀ for the stannite-type and spinel-type AgIn₅Se₈, AgGa₅Se₈, AgGa₅S₈, and AgGa₅S₈. For AgIn₅Se₈, AgGa₅Se₈, and AgGa₅S₈, ΔH₀ for the stannite-type were lower than those for the spinel-type. On the other hand, for AgGa₅S₈, ΔH₀ for the spinel-type was lower than that for the stannite-type. ΔH₀ for AgGa₅Se₈ and AgGa₅S₈ were larger than those for mixed phase of (AgGa₅S₈ + 2Ga₅Se₈) and (AgGa₅Se₈ + 2Ga₅S₈), respectively. We conclude that stannite-type AgIn₅Se₈ and spinel-type AgIn₅S₈ are stable, but AgGa₅Se₈ and AgGa₅S₈ are unstable.

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