

Electronic structure of quaternary chalcogenide $\text{Ag}_2\text{In}_2\text{Ge}(\text{Si})\text{S}_6$ single crystals and the influence of replacing Ge by Si: Experimental X-ray photoelectron

Abstract

$\text{Ag}_2\text{In}_2\text{GeS}_6$ and $\text{Ag}_2\text{In}_2\text{SiS}_6$ are two interesting quaternary-sulfide single crystals. Starting from our previous investigation on $\text{Ag}_2\text{In}_2\text{GeS}_6$ single crystals, the $\text{Ag}_2\text{In}_2\text{SiS}_6$ is investigated here. We demonstrate the effect of replacing Ge by Si on the electronic structure and the bonding properties. We have used X-ray diffraction (XRD) data for $\text{Ag}_2\text{In}_2\text{Ge}(\text{Si})\text{S}_6$ single crystals as input to our theoretical calculations using the all-electron full potential linearized augmented plane wave method to solve the Kohn Sham Density Functional Theory (DFT) equations. As remarkable finding, our calculations show that, on replacing Ge by Si atom, the environment of the S atoms is changed significantly. The energy gap depends on the exchange correlation function. For the local density approximation (LDA) the energy gap is 0.76 eV, while, based on the modified Becke-Johnson approximation (mBJ), the energy gap increases to 1.98 eV. We should emphasize that this energy gap in $\text{Ag}_2\text{In}_2\text{SiS}_6$ is almost the same as that obtained for $\text{Ag}_2\text{In}_2\text{GeS}_6$ (1.96 eV). Another significant finding is that when we replace Ge by Si the conduction bands move away from the Fermi energy while the valence bands are almost unchanged. In order to support the theoretical calculation the calculated total density of states below E_F (TDOS-VB) of $\text{Ag}_2\text{In}_2\text{SiS}_6$ single crystals is compared with our experimentally measured valence-band X-ray photoelectron spectroscopy (XPS-VB). The theoretical spectrum reproduces the general features structure of the measured XPS-VB faithfully.

Keywords; Chalcogenide Quaternary Sulfides, DFT, XPS, XRD