CHAPTER 1

Electronic Structure and the Influence of Replacing Ge by Si in the Chalcogenide Quaternary Sulfides Ag_2In_2Ge (Si) S_6 Single Crystals: Experiment XPS and XRD and Theory

Ag_2In_2Ge (Si) S_6 and Ag_2InSiS_6 are two interesting quaternary sulfides single crystals. Taking off from our previous investigation of $Ag_2In_2GeS_6$ single crystals, the Ag_2In_2Ge (Si) S_6 is investigated here. We demonstrate the effect of replacing Ge by Si on the electronic structure and the bonding properties. We have taken our X-Ray Diffraction Data (XRD) for Ag_2In_2Ge (Si) 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 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 0.76eV while for the modified Becke-Johnson approximation (mBJ) the energy gap increases to 1.98 eV. We should emphasize that this energy gap in Ag_2In_2Ge (Si) S_6 is almost the same as that obtained for Ag_2In_2Ge S_6 (1.96 eV). Another significant finding is that when we replace Ge by Si the conductions 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 EF (TDOS-VB) of Ag_2In_2Ge (Si) S_6 single crystals is compared with our experimentally measured X-Ray Photoelectron Spectroscopy (XPS-VB). The theoretical spectrum reproduces the general features structure of the measured XPS-VB faithfully.

1.1 Historical Review

In recent years, the chalcogenide semiconducting compounds have received much attention due to their possible applications as materials for visible-infrared spectral range [1–7]. They form a large group of semiconducting materials with diverse optical, electrical, structural properties. The energy gap is formed from p-chalcogenic delocalized states from the valance band and by relatively more localized s- and d-cationic states from the conduction band [8]. The acentric crystal structure of these chalcogenides is one of the reasons to forecast their possible application as non-linear optical materials [9]. The chalcogenide is a chemical compound consisting of at least one chalcogen ion and at least one more electropositive element. Although all group 16 elements of the periodic table are defined as chalcogens, the term is more commonly used for sulfides, selenides, and tellurides, rather than oxides.

Recently, Chmiel *et al.* [10] have presented a complex spectral studies of near-band gap and photoconductive spectra for novel Ag_2In_2Ge (Si) S_6 single crystals. The spectral dependences of photoconductivity clearly show an existence of spectral maxima within the 450 nm–540 nm and 780 nm–920 nm. The fundamental absorption edge is analyzed by Urbach rule. The authors [10] discussed the origin of the spectral photoconductivity spectral maxima. The obtained spectral features suggest that, the titled compound could be a photosensors. Yet, up to now there is no comprehensive work that concerns the electronic structure of the Ag_2In_2Ge (Si) S_6 compounds. Therefore, it is interesting to perform ab initio calculations using a full potential method. In last decade, ab initio calculations have been successfully used to obtain different properties of materials. The structural parameters and dynamical properties of crystals determine a wide range of microscopic and macroscopic behavior: diffraction, sound velocity, elastic constants, Raman and infrared absorption, inelastic neutron scattering and specific heat. The Full Potential Linear Augmented Plane Wave (FP-LAPW) method has proved to be one of the most accurate