

CHAPTER

5

Part I

X-RAY PHOTOELECTRON SPECTRUM AND ELECTRONIC PROPERTIES OF A NONCENTROSYMMETRIC CHALCOPYRITE COMPOUND HgGa_2S_4 : LDA, GGA AND EV-GGA

An all electron full potential linearized augmented plane wave method has been applied for a theoretical study of the band structure, density of states, and electron charge density of a noncentrosymmetric chalcopyrite compound HgGa_2S_4 using three different approximations for the exchange correlation potential. Our calculations show that the Valence Band Maximum (VBM) and Conduction Band Minimum (CBM) are located at Γ resulting in a direct energy gap of about 2.0, 2.2, and 2.8 eV for Local Density Approximation (LDA), Generalized Gradient Approximation (GGA) and Engel-Vosko (EV-GGA) compared to the experimental value of 2.84 eV. We notice that EVGGA show excellent agreement with the experimental data. This agreement is attributed to the fact that the Engel-Vosko GGA formalism optimizes the corresponding potential for band structure calculations. We make a detailed comparison of the density of states deduced from the X-ray photoelectron spectra with our calculations. We find that there is a strong covalent bond between the Hg and S atoms and Ga and S atoms. The Hg-Hg, Ga-Ga and S-S bonds are found to be weaker than the Hg-S and Ga-S bonds showing that a covalent bond exists between Hg and S atoms and Ga and S atoms.

5.1 HISTORICAL REVIEW

Mercury thiogallate, HgGa_2S_4 (HGS), possess a combination of attractive properties for many applications. HGS crystal is chemically stable in air. It is a "defect" chalcopyrite derived from the I-III-VI₂ chalcopyrite structure by the order substitution of group II atoms and vacancies on the group I sites [1]. It was first synthesized in powder form by Hahn *et al.* [2]. HGS crystals are characterized with high nonlinear susceptibility coefficients, wide transparency range (from 0.5 to 13 μm) and considerable birefringence [3]. The large birefringence ensures phase matching in a wide frequency range [4, 5]. HGS is considered to be very promising for operating in the mid-IR spectral range [6, 7] because of their superior nonlinearity and damage threshold. It can be used for mid-IR parametric oscillator with Nd:YAG laser pumping. HGS has promising values of effective nonlinear susceptibility, a wide transparent region, a low value of absorption coefficient, a variance of refractive indices, and a resistance to laser radiation [8] thus making it useful for optical applications. Their conversion efficiency is more than two times larger than that of silver thiogallate [8]. HGS shows a very large effective second order susceptibility coefficients (in particularly, tensor component d_{36} which is approximately 1.8 times that of AgGaS_2 [5], i.e. about 34 pm/V [9]).

This material can be used for up conversion of the frequency of the CO_2 laser radiation ($\lambda=10.6 \mu\text{m}$) with an efficiency of up to 60%, for detecting radiation in the atmospheric transmission window (10-12 μm), and for visualizing the spectra of fast processes in the range from 8 to 12 μm [1]. Recently, Rotermund and Petrov [10] used HGS crystals as Optical Parametric Generators (OPG) pumped by femtosecond pulses near 1.25 μm from a Cr:forsterite regenerative amplifier. This wavelength is very close to the signal wavelength from a Ti:sapphire laser pumped OPG that can be used for Difference Frequency Generation (DFG) in the 3-12 μm spectral range. HGS is a negative uniaxial crystal ($n_o > n_e$) with an energy gap corresponding to roughly 440 nm.