PART 2

ELECTRONIC, LINEAR AND NONLINEAR OPTICAL PROPERTIES OF CHALCOPYRITE-STRUCTURE CRYSTALS

2.1 INTRODUCTION

In last decade, first-principle 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, specific heat, etc.

The ternary $A^{I}B^{III}C_2^{VI}$ semiconducting compounds which crystallize in the chalcopyrite structure have received much attention in recent years [39-41]. They form a large group of semiconducting materials with diverse optical, electrical, and structural properties [42-49]. Ternary chalcopyrite appears to be promising candidate for solar-cells applications [50], light-emitting diodes [51], nonlinear optics [52], and optical frequency conversion applications in all solid state based tunable laser systems [53]. These have potentially significant advantages over dye lasers because of their easier operation and the potential for more compact devices. Tunable frequency conversion in the mid infrared (IR) is based on optical parametric oscillators (OPO's) using pump lasers in the near IR [53]. On the other hand frequency doubling devices also allow one to expand the range of powerful lasers in the far infrared such as the CO_2 lasers to the mid infrared [53-55].

The specific $A^{XI}B^{XIII}C_2^{XVI}$ chalcopyrite concerned in this book used copper or aluminum as the group *XI* element, indium or gallium as the group *XIII* element, and sulphur or selenium or tellurium as the group *XVI* element. Since these compounds display large birefringence [56], they are potentially interesting as nonlinear optical materials, as well as semiconductors. $CuInTe_2$ has positive birefringent whereas $CuInS_2$ and $CuInSe_2$ has negative birefringent [59,61]. $AgGaTe_2$ has positive birefringent, whereas $AgGaS_2$ and $AgGaSe_2$ have negative birefringent [59-61]. So far, however, the trends of the coupling coefficients in these materials are not well understood. $AgGaS_2$ is mostly in use as near infrared pumped optic parametric oscillators (OPO) [53]. Further the range of transparency of $AgGaSe_2$ in the infrared allows for its use as an efficient frequency doubler and tripler of CO_2 laser lines [53]. Here the first-principle calculations are used to predict enhancement of $\chi^{(2)}(\omega)$ by substitution of S by Se and Te.

2.2 METHODOLOGY

$A^{I}B^{III}C_2^{VI}$ compounds, belong to the group of semiconducting materials crystallizing in the chalcopyrite structure with tetragonal space group $I\bar{4}2d(D_{2d}^{12})$ with four formula units in each unit cell, which is a ternary analog of the diamond structure and essentially a super lattice (or superstructure) of zinc blende. Like the atoms in diamond and zinc blende structures, each constituent atom in these ternary compounds, *XI*, *XIII*, and *XVI*, is tetrahedral coordinated to four neighboring atoms.

The A atom is located at (0,0,0), (0,0.5.0.25), the B atom at (0,0,0.5), (0.0.5.0.75), and C atoms at (x,0.25,0.125), (-x,0.75,0.125), (0.75,x,0.875), (0.25,- x,0.875), where x is equal to 0.28, 0.27, 0.26, 0.20, 0.22, 0.225 for $AgGaS_2$, $AgGaSe_2$, $AgGaTe_2$, $CuInS_2$,