CHAPTER 3

Part I

ELECTRONIC STRUCTURE, CHEMICAL BONDING FEATURES AND ELECTRON CHARGE DENSITY OF THE DOUBLE-CUBANE SINGLE CRYSTAL $[Sb_7S_8Br_2](AlCl_4)_3$

The present calculations were performed using all-electron full potential linearized augmented plane wave method based on the density functional theory. We have optimized the structure of the double-cubane single crystal $[Sb_7S_8Br_2](AlCl_4)_3$***, starting with the X-ray diffraction data [1], by minimization of the forces (1 mRy/au) acting on the atoms, keeping the lattice parameters fixed at the experimental values. Our calculations show that*** $[Sb_7S_8Br_2](AlCl_4)_3$ ***possesses a wide energy band gap. The upper valence band has a maximum at S point of the Brillouin zone while the conduction band minimum is located at Y point resulting in an indirect energy band gap of about 2.0 eV (2.5 eV) using LDA (EV-GGA) exchange correlation potentials. To describe the bonding properties we have evaluated the electronic charge space density contour in four planes - namely (001), (110), (100) and (010) which show that this compound possesses a considerable anisotropy. The contour plot shows partial ionic and strong covalent bonding between S-Sb, Al-Cl, S-Br, S-S, Cl-Cl and Sb-Br atoms.***

3.1 HISTORICAL REVIEW

Ionic liquids as supersolvents are now recognized as powerful reaction media for preparing functional materials such as zeolites [2], metal-organic frameworks [2], metal nanoparticles [3], and organic compounds [4] as well as being useful in separations [5], electrochemistry [6], and nanotechnology [7]. Chalcogenides have not only diverse structures but also technologically promising properties such as thermoelectric and solar energy conversion [8], phase change transitions liquids could offer fascinating possibilities for producing new structure in chalcogenides and unprecedented properties [1]. Recently, Zhang *et al.* [1] demonstrated the use of the ionic liquid EMIMBr-$AlCl_3$ (EMIM=1-ethyl-3-methylimidazolium) as solvent in the preparation of a material featuring a cationic chalcogenide. They reported the synthesis of cationic chalcogenide clusters in ionic liquids and showed that chalcogenide polycationic clusters can be conveniently synthesized in ionic liquid media containing Lewis acids or strong acceptors. They found that the red crystals of $[Sb_7S_8Br_2](AlCl_4)_3$ exhibit Nonlinear Optical (NLO) properties, including Difference-Frequency Generation (DFG) and Second Harmonic Generation (SHG).

Single crystals of $[Sb_7S_8Br_2](AlCl_4)_3$ were synthesized by Zhang *et al.* [1] in 42% yield by reacting Sb with S in EMIMBr-$AlCl_3$ ionic liquid (1:11 EMIMBr/$AlCl_3$ molar ration) at 165 °C for 10 days. The structure was determined from single-crystal X-Ray Diffraction (XRD) data collected at 100 K on a STOE 2T imaging-plate diffraction system with graphite-monochromatized Mo Kα radiation. Numerical and empirical absorption correction was applied. The direct methods and full-matrix least-squares refinements against F^2 were performed with the *SHELXTL* package [1]. The single crystal of $[Sb_7S_8Br_2](AlCl_4)_3$ crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12_1$, with Z=4, a=11.989(2) Å, b=16.896(3) Å, c=17.378(4) Å and v=3520.2(12) Å^3. The collection and refinement data was T=100 K; $2\theta_{max}$ (Mo Kα)=53.52°; D_{calc}=3.349 g/cm^3 [1]. The crystal structure of $[Sb_7S_8Br_2](AlCl_4)_3$ is shown in Figure 3.1. It consists of cationic $[Sb_7S_8Br_2]^{3+}$ clusters and $[AlCl_4]^-$ anions. Each cluster adopts a unique double-cubane structure in which two distorted cubic clusters connect by sharing one corner-Sb1 site. The other corners are alternately occupied with Sb and S