

Electronic and Vibrational Properties of PbSnS_3

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Abstract: A study was made of the electronic band structure and vibrational properties of PbSnS_3 using density functional theory (DFT) and the density perturbation functional theory (DPFT) respectively. For exchange and correlation, the local density approximation (LDA) was used. The study revealed that the material under investigation is a semiconductor with a fundamental indirect band gap of 0.71 eV and an optical direct band gap of 08.3 eV. For the phonon band structure it was found from the calculation that the highest frequency mode of 317.9 cm^{-1} occur at Γ -point. This shows that the material is polar.

Keywords- Density functional theory, density perturbation functional theory, direct and indirect band gap, electronic band structure, local density approximation.

I. Introduction

Lead Tin Sulphide (LTS) PbSnS_3 is a material that has attracted attention because of its technological application in photonic devices [1, 2]. It belongs to a group of semiconductors of the general formula $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{S}_3$ and it is found in nature in tin ore [3]. Suredaite as is also known occurs: (1) as layers up to 1 cm thickness which are composed of tabular prismatic crystals, elongated along [010] and inter-grown in fan-shaped arrangements, and (2) as individual needle-like crystals, embedded in sphalerite. The color is grayish-black with a metallic luster and a black streak. It is a relatively new mineral species, as a result, not much study has been done on it. However, a number of experimental studies have been done [3,4,5] which put the electronic band gap value at 1.04 eV. To the best of our knowledge, this is the first time a theoretical investigation will be carried out on LTS. In this paper, we will be studying the electronic band and vibration properties of PbSnS_3 in the frame work of the density functional theory (DFT) and density functional perturbation theory (DFPT) respectively.

II. Computational Detail

PbSnS_3 crystallizes in an Orthorhombic structure with a space group $Pnma$ (space group number of 62). The lattice parameters are $a = 8.8221 \text{ \AA}$, $b = 3.7728 \text{ \AA}$, $c = 14.0076 \text{ \AA}$. There are four formula units in the unit cell; this gives a total of 20 atoms in five types. The fractional coordinates used in this study were adopted from Paar et al [3] and are listed in Table 1. Fig. 1 shows the structure of PbSnS_3 . In the band structure calculations, we have utilized the local density approximation with the norm-conserving⁶ pseudopotential method within the framework of the density functional theory as implemented in the Abinit package [7,8]. For exchange and correlation, the parametrization of Perdew and Zunger [9] was used. The valence electron of 12, 4 and 6 were used for Lead, Tin and Sulphur respectively. A kinetic energy cutoff of 540 eV was used for the generation of plane waves. A 128 k-point mesh generated by a $4 \times 4 \times 4$ regular shift k-point. The self consistency calculation was well converged when the difference in energy between subsequent iteration was 1.0×10^{-10} . For the phonon calculations, the kinetic energy cut-off of 810 eV was used for the generation of the plane waves. The number of wave vectors (q-point) used is 32. Lattice dynamical calculations (phonon dispersion curves and phonon density of states) are performed within the frame work of the self consistent density functional perturbation theory (DFPT) [10,11,12]. The q-point used gave a good Phonon dispersion curve.

Table 1: Atomic coordinates used in the calculations

Atom	x axis	y axis	z axis
Pb	0.5030	0.75	0.1705
Sn	0.1655	0.25	0.0521
S	-0.0114	0.75	0.1062
S	0.3394	0.75	-0.0066
S	0.2855	0.25	0.2132

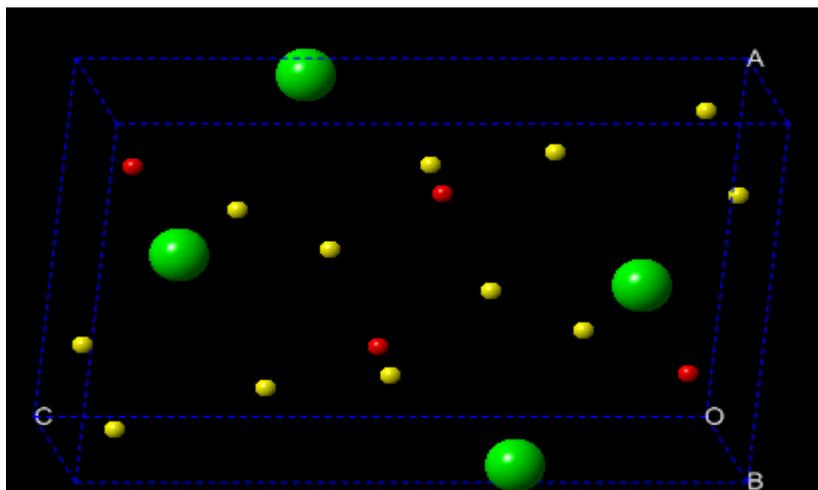


Fig. 1. The structure of $PbSnS_3$ use in the calculation

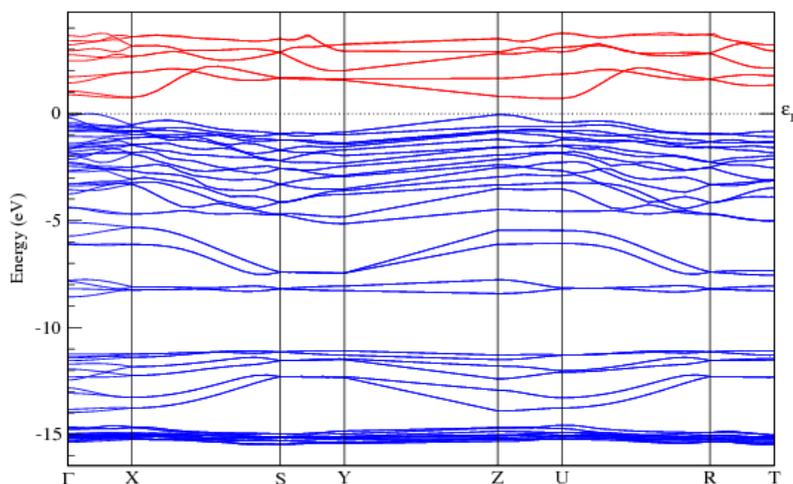


Fig. 2. The electronic band structure of LTS. The Fermi energy is at the zero mark and it's indicated by E_F .

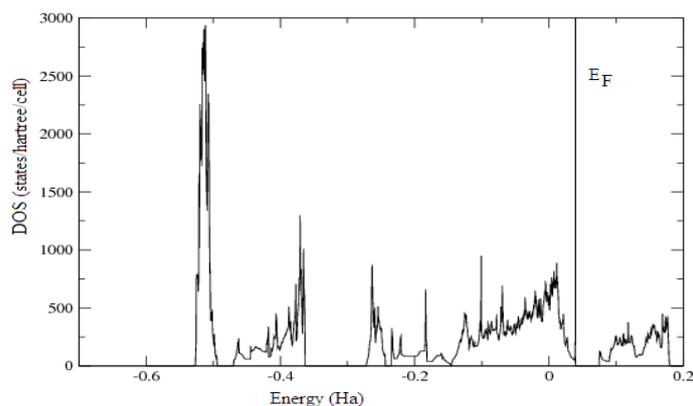


Fig. 3. The density of states (DOS) of LTS. The Fermi energy is at 0.04 Ha and is indicated by E_F .

III. Results And Discussion

The electronic band structure of $PbSnS_3$ along lines of high symmetry in the first Brillouin zone is shown in Fig. 2. The conduction band minimum (CBM) occurred at the U and X-point while the valence band maximum

is at the Z-point and a point mid way between the Γ and X-point. From our calculation, PbSnS_3 is a semiconductor whose fundamental indirect band gap is 0.71 eV, while the optical band gap is 0.83 eV. The density of states is shown in Fig. 3. The valence band is divided into three sections. The states between -0.53 and -0.49 Hartree are dominated by the Pb 5d and Sn 4d orbitals. The states from -0.47 to -0.16 Hartree are dominated by the Pb 6s, S 3s and Sn 5s orbitals while the states at the top of the valence band are of the Pb, S and Sn p characters. The contribution of the various atomic species to the density of states are shown in Figs.4 to 6 for Pb, S and Sn atoms respectively.

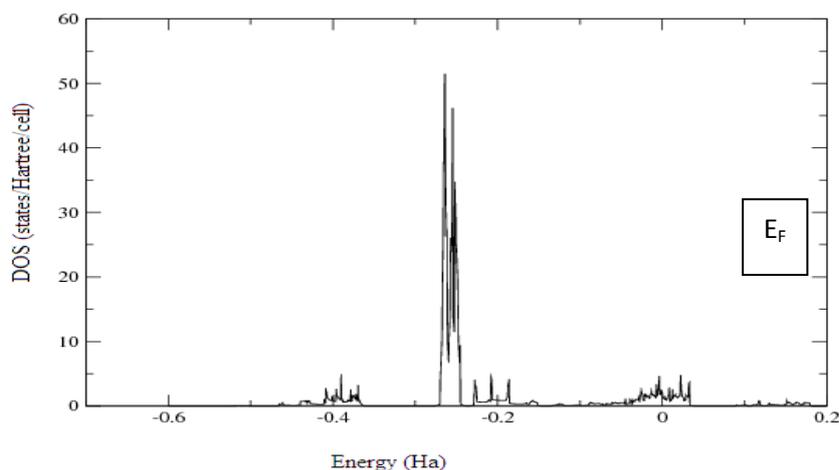


Fig. 4. The partial density of states for Pb. E_F indicates the Fermi energy.

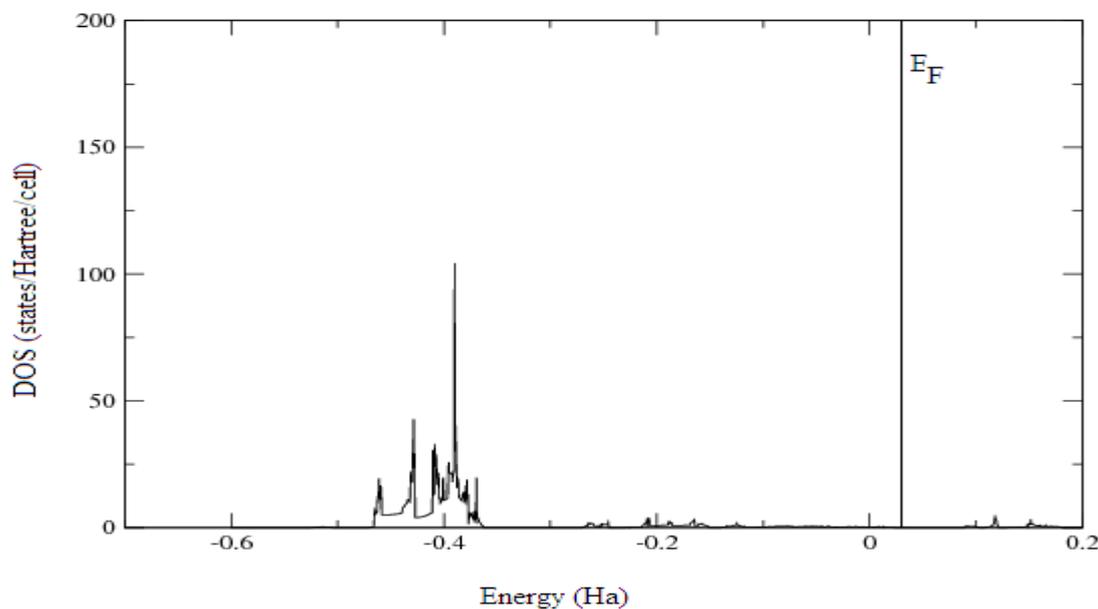


Fig. 5. The partial density of states for S. E_F indicates the Fermi energy.

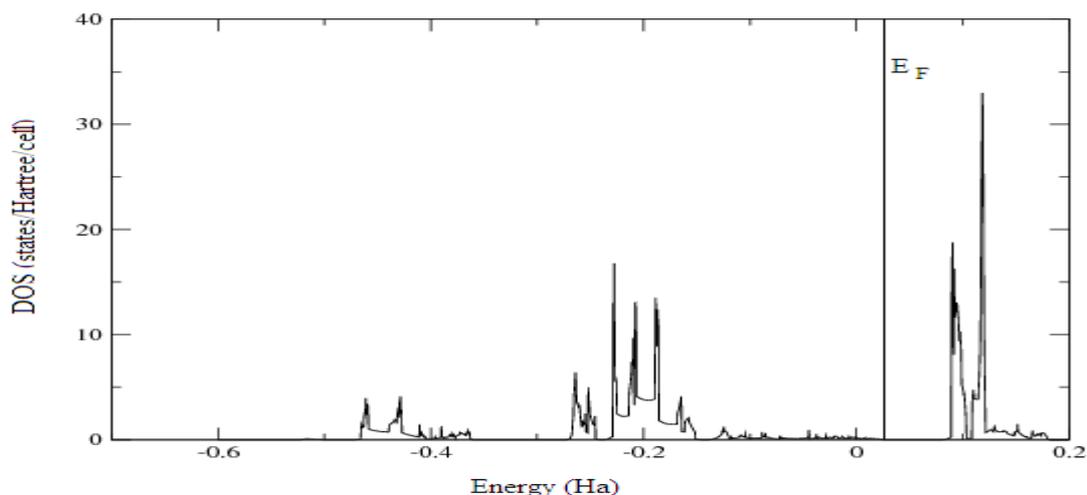


Fig. 6: The partial density of states for Sn. E_F indicates the Fermi energy.

From Fig.4, the Pb states are dominant within the energy range of -0.25 and -0.27 Hartree. Also the states within the energy range -0.47 to -0.36 hartree are predominantly of the S species. This is indicated by the peak points within the energy range in Fig. 5. In Fig. 6, the states belonging to the Sn states are dominant in the energy range of -0.23 to -0.15 Hartree and the states at the bottom of the conduction band.

The phonon dispersion curves of $PbSnS_3$ along several high symmetry lines in the Brillouin zone are displayed in Fig. 7 while the phonon curves along Γ -X, Γ -Z and Γ -U are displayed in Figs. 8, 9 and 10 respectively. There are 20 atoms which are group into five types in the unit cell. This gave a total of 60 frequency modes or bands. All atoms in the unit cell have the C_1 positional symmetry, it therefore follows that all 60 frequency modes can be expanded in terms of the irreducible representations $\Gamma^{crystal} = 15A_g + 15B_g + 15A_u + 15B_u$. Where $1A_u$ and $2B_u$ represent the acoustic modes. The bands are either longitudinal or transverse. So we could have longitudinal acoustic (LA), transverse acoustic (TA), longitudinal optical (LO) and transverse optical (TO). The dispersion spectral in figure 6 shows that the highest energy occurred at the centre or gamma point with energy of 317.9 cm^{-1} . This is an indication that the material is polar. Popovic [13] studied the Raman scattering spectra of $PbGeS_3$, which is a member of the group $A^{II}B^{IV}S_3$ to which $PbSnS_3$ is a member. The highest LO in his study was 404 cm^{-1} . This shows that our result is good. The phonon dispersion curve is divided into two parts by an energy gap. The first part is from 0 to 154.8 cm^{-1} while the other half is from 165.7 cm^{-1} to 317.9 cm^{-1} . Another feature of the phonon spectra is the sharp band crossings close to the gamma line and the flatness of the bands. The bands are generally flat except for the bands in the X-Z and U-Y directions were the bands exhibit some measure of dispersion.

Fig. 8 shows the phonon curve along Γ -X direction. Again, the flatness of the optical branches of the spectra is very visible. There is a degeneration of the LA and TA_1 branches. There is a very small split as the branches approach the X-point. The TA_2 and TA_1 converge to form a degenerate point at the X-point. The two TO branches belonging to the second atom in the unit cell are degenerate at both the Γ and X-point. The softening or small downward bending of the LO branch belonging to this atom forms a degenerate point with the TO's at the X-point.

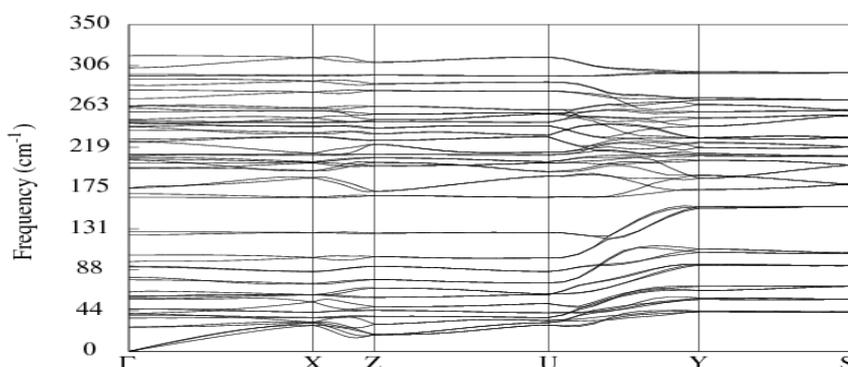
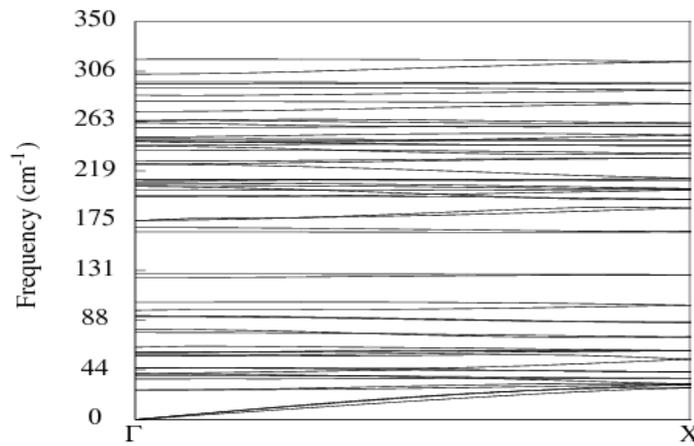
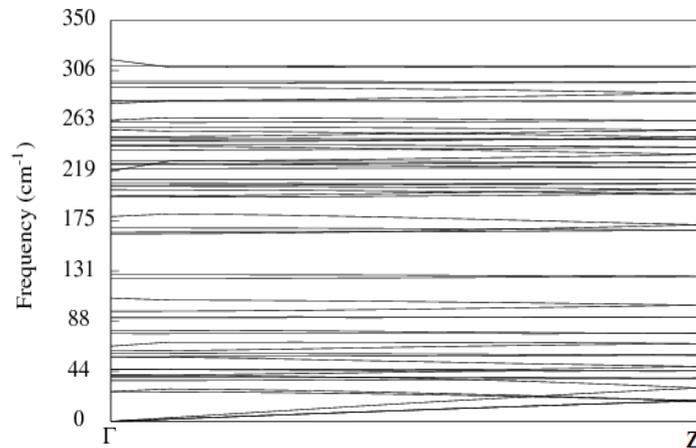
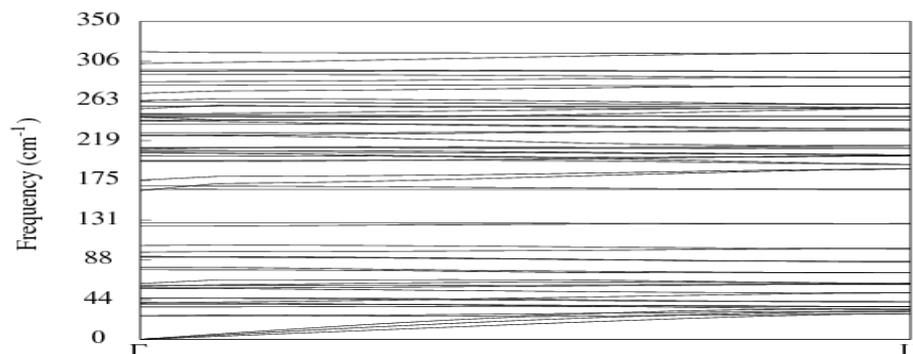


Fig. 7: The Phonon spectra of $PbSnS_3$ along lines of high symmetry in the Brillouin zone.

Fig. 8: The Phonon spectra of $PbSnS_3$ along Γ -X directionFig. 9: The Phonon spectra of $PbSnS_3$ along Γ -Z direction

The phonon spectra for the Γ -Z direction is shown in Fig.9. The acoustic branches are less disperse than those of the Γ -X direction. Also in this direction, TA_1 and TA_2 are degenerate whereas in the Γ -X direction, it is the LA and TA_1 that are degenerate. There is a small downward bending of the TO branches to form a degenerate point with the LA branch at a point close to the Z-point. All the three acoustic branches are well separated at the Γ -point in the Γ -U direction as can be seen in Fig.10. The two TA branches form a degenerate point at the U-point with energy of 29 cm^{-1} while the LA and TO form a degenerate point at the U-point with energy of 31.6 cm^{-1} .

Fig.10: The Phonon spectra of $PbSnS_3$ along Γ -U direction

IV. Conclusion

The electronic and phonon band structure has been calculated in this study. The work was done using density functional theory (DFPT) for the electronic band structure and density functional perturbation theory (DFPT) for the phonon band structure. From our calculation, $PbSnS_3$ was found to be a semiconductor with fundamental and optical band gaps of 0.71 eV and 0.83 eV respectively. For the phonon band structure it was found from the calculation that the highest frequency mode of 317.9 cm^{-1} occur at Γ -point.

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