Structural, electronic and magnetic properties of metal thiophosphate $InPS_4$

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Abstract. The non-centrosymmetric crystal, $InPS_4$,has been investigated by means of density functional theory (DFT). In this paper we have calculated the structural parameters, electronic band structures, density of states plot and magnetic properties using full potential linearized augmented plane wave (FP-LAPW) method. The exchange correlation has been solved employing the generalised gradient approximation due to Perdew-Burke-Ernzerhof. The calculations are performed both without spin as well as spin polarized. The results show that $InPS_4$ is an indirect band gap semiconductor with (N-Γ) energy gap of 2.32eV (without spin) and 1.86eV in spin up and down channels.The obtained lattice parameters and energy gap agree well with the experimental results. Our reported magnetic moment results show that the property of $InPS_4$is nonmagnetic.

1. Introduction

Modern technological developments require more research in the physical properties of material such as mechanical properties, which are closely linked to crystalline and electronic structure of materials. Chalcogenide materials show rich structural and compositional diversity [1]. The ternary semiconducting compounds of chemical formula $M^{III}PS_4(InPS_4)$ crystallize in a non-centrosymmetric structure with a crystallographically ordered array of vacancies in the *I-4* space group. Their crystallographic structure belongs to the so called "*twice defective chalcopyrite"* [2]. Several groups of researchers have made these compounds the object of their experimental studies. And to the author's knowledge, no theoretical calculations of magnetic properties of our compounds have been reported till so far.The crystallographic structure was determined by Carpentier et al. [3]. It is a three dimensional structure made of corner-connected $[PS_4]$ and $[InS_4]$ tetrahedrons. In 1993 Bolcatto et al. used tight-binding method to calculate the electronic structures of the MPS_4 (M=B, Al, Ga, and In) thiophosphate family [4]. This paper is organized as follow; after introduction, gives the computational details, calculated results and through discussion on structural, electronic and magnetic properties of our material and in last conclusions is presented.

2. Computational details

We have carried out structural, electronic and magnetic properties of the $InPS_4$with the framework of density functional theory (DFT) [5] while taking into account the spic effect as well using the full potential linear augmented plane wavemethod as implemented in wien2k code [6]. The generalized gradient approximation (GGA) is used employing the scheme of Perdew-Burke-Ernzerhof (PBE) [7] to find the solution of exchange correlation functional. We have performed non-magnetic calculation

and spin polarize calculations. We have taken the atomic positions of In, P and Sand take their convergent muffin tin radius. The muffin-tin radius is chosen in such a way that they do not overlap each other and core charge do not leak out the spheres. We expand the basis function up to $R_{MT}*k_{max}=7$, where R_{MT} is the radius of muffin tin and k_{max} is the maximum value of the reciprocal lattice vectors.The dependency of the total energy on the number of k-points in the irreducible wedge of Brillouin zone was optimized and the size of mesh has been set of 512 K-points. The equilibrium lattice constants for $InPS_4$ compound are determined by minimization of the total energy with respect to volume of the unit cells. The self-consistent calculation stops only when the total energy and the charge of the system meet the convergent limit of the order 10^{-4}Ry and $10^{-3}e^{-}$, respectively.

3. Results and discussions

3.1Structural properties

The structural properties are very important for understanding the solid properties from microscopic view point. $InPS_4$ crystallizes in the body-centered tetragonal space group *I-4* with the following cell parameters: a=5.70Å and c=9.18Å. The unit cell structure of $InPS_4$is shown in figure 1.We have investigated the structural parameters of $InPS_4$ at ambient condition. In order to compute the ground state properties we made symmetric structural optimization. The total energy has been calculated corresponding to different cell volume and fitted to theMurnaghan equation of state [8]. Our obtained structural lattice parameters, bulk modulus and its pressure derivative are listed in table 1. Earlier reported theoretical results have also been given for the comparison purpose.

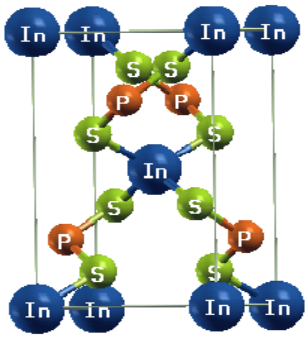

Figure 1. The unit cell structure of $InPS_4$ in space group I-4.

Table 1. Optimized results for equilibrium lattice constants (a, c), c/a ratio, unit cell volumeV_0, bulk modulus B and its first pressure derivative B′ for $InPS_4$in BCT structure.

Spin effect	a(Å)	c(Å)	c/a ratio	V_0 (a.u.^3)	B(GPa)	B’	Results
Without Spin	5.70	9.18	1.61	1007.8771	62.0490	5.000	P.W.
	5.60	9.02	1.61	……	…….	……..	Other work
With Spin	5.72	9.21	1.61	1019.5823	61.9169	4.5535	P.W.

3.2 Electronic properties

The electronic properties of solids are important to determine the energy distribution of electrons in the valence band and the conduction band. The equilibrium constants are used to calculate the electronic band structures and density of states for $InPS_4$ compound. First of all we have used non-spin polarized

GGA (PBE) approach and after that spin-polarized to calculate the electronic band structure of the $InPS_4$ in their most stable ground state at ambient conditions. The self consistent electronic band structure in non-spin and spin-up and spin-down channels of $InPS_4$for BCT phase are presented in figure 2. In both cases $InPS_4$ compound shows semiconductor nature with (N-Γ) indirect band gap 2.32eV and spin-up and spin-down 1.86eV, 1.86eV, respectively. In order to explicate band structures, total and partial densities of state (DOS) for In, P and S atoms are shown in figure.3. DOS plots show that the valence band near Fermi energy level is formed by In-*p*and *d*, S-*p* and P-*p*, states. While a prominent peak of P-*p* state is found in valence band. Near the Fermi level, the spin-up and spin-downDOS has a band gap between occupied states and unoccupied states. The In atom is relatively dominating in lower valence band and upper conduction band. In the energy range -4 eV to 0 eV In-*p* and In-*d* states are strongly degenerate and hybridize with S-*p* states. The top of the valence band corresponds mainly to S-*p* states.

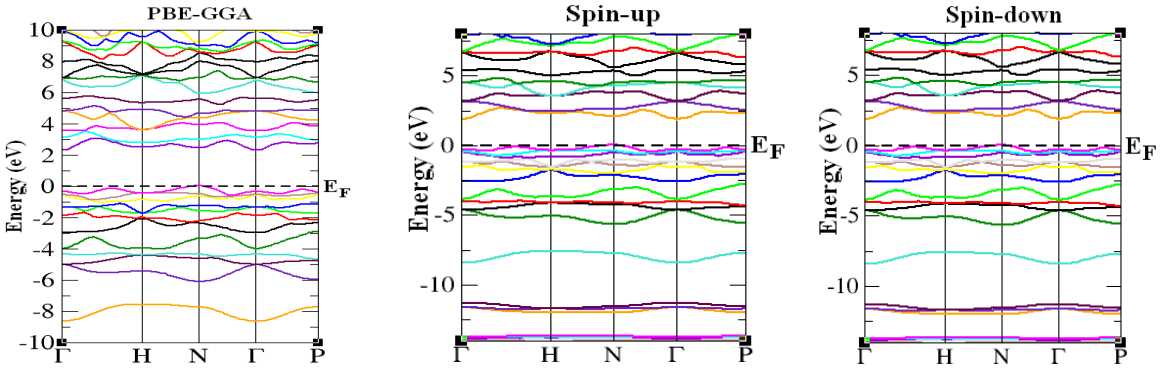

Figure 2. Electronic band structures of $InPS_4$ in BCT phase at ambient pressure and temperature (a) non-spin (b) spin-up and (c) spin-down channel.

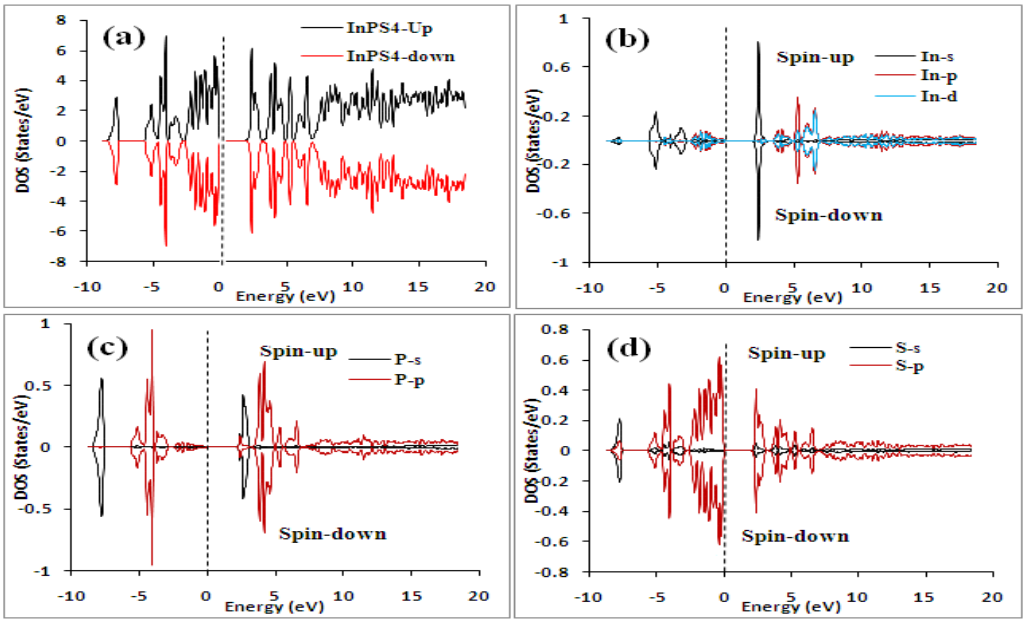

Figure 3. Total and partial DOS (including *s, p* and *d*-state of In, *s* and *p*-state of P and S atom) for $InPS_4$ compound in body-cantered tetragonal structure.

3.3 Magnetic properties

Magnetic moment of any compound shows internal contribution of spin electrons. Magnetic moments of interstitial region, atoms In, P and S, total magnetic moment of $InPS_4$ has been analysed at different cell volumes using PBE-GGA scheme. The calculated values of magnetic moments for $InPS_4$ compound are listed in table 2. The interstitial magnetic moments are negative. The electronic configuration of In is [Kr] $4d^{10}$, $5s^2$ $5p^1$, P is $1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^3$ and S is $1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^4$. In spite of differences in the number of spin up and spin down valance electrons in constituent atoms of $InPS_4$its total magnetic moment is found to be zero.

Table 2. Calculated values of magnetic moments of interstitial region, atoms In, P and S, total magnetic moment for $InPS_4$.

Lattice Constant		Magnetic moment (μB)				
a(bohr)	c(bohr)	m^{int}	m^{In}	m^{P}	m^{S}	M^{total}
10.39	16.74	-0.00191	0.00061	0.00113	-0.00003	-0.00030
10.58	17.05	-0.00097	-0.00011	-0.00010	0.00036	0.00026
10.77	17.34	-0.00118	-0.00006	-0.00013	0.00039	0.00020
10.94	17.63	-0.00129	-0.00005	-0.00013	0.00039	0.00007
11.11	17.90	-0.00139	-0.00004	-0.00013	0.00036	-0.00011

4. Conclusions

Present paper includes theoretical investigation of structural, electronic and magnetic properties of $InPS_4$ using FP-LAPW method. The PBE-GGA is opted to perform all the calculations related to exchange-correlation functional. The optimized results for equilibrium lattice constants, c/a ratio for stabilisation, unit cell volumes, bulk modulus and its first pressure derivative have been reported. The electronic band structures and density of states (DOS) plots show semiconductor nature in both spin-up and spin-down channels. Our reported results show that its character is non magnetic.To the best of our knowledge, the theoretical predictions on magnetic properties (spin polarized band structure and DOS) of metal thio phosphate ($InPS_4$) have been reported for the first time.

References

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