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Half-metallic Ferromagnetism in Fe, Co and Ni Doped BaS: First Principles Calculations

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Abstract. The first principle investigation of structural, electronic, magnetic and optical properties of $Ba_{1-x}TM_xS$ (x = 0.25) have been done using FPLAW method within the density functional theory (DFT) using generalized gradient approximation (GGA) for exchange correlation potential using two different functionals which are the PBE-sol and the modified Becke and Johnson local (spin) density approximation (mBJLDA). It was found that mBJLDA functional offer better account for the electronic structure of the Fe, Co and Ni-doped BaS. It was also observed that Fe/Co/Ni d, S p and Ba d states play a major role in determining the electronic properties of this alloy system. Investigation results shows that $Ba_{0.75}(Fe/Co/Ni)_{0.25}S$ is ferromagnetic with magnetic moment of 3.72 μB, 2.73908 μB and 1.74324 μB at Fe, Co and Ni sites respectively. Complex dielectric constant ε(ω) and normal incidence reflectivity R(ω) are also been investigate for broad range of photon energies. These results are compared with the some reported existing experimental values.

INTRODUCTION

Diluted magnetic semiconductors (DMS) have attracted many researchers due to their promising applications in spintronics. BaS is an II-VI compound semiconducting material with noticeable optical and electronic properties. Its unique optical and electronic properties which make these materials suitable for applications in laser diodes, single electron transistors, photoconductors, interference filters, solar cells, IR detectors and so on. BaS undergo first-order phase transition from sodium chloride (halite) structure to the CsCl-crystal structure when pressure is applied. Various researchers have studied BaS experimentally and theoretically due to its properties [1-6]. Most of the experimental studies are focused on absorption and reflectivity properties that are limited to excitonic transitions [4, 5, and 6]. When doping is done to BaS, its electronic and optical properties changes significantly. BaS is a non magnetic semiconductor material nevertheless it can be transformed into a magnetic semiconductor material by adding naturally occurring magnetic elements as impurities. These impurities introduce favorable magnetic properties in a controllable manner. However, the magnetic element concentration is relatively low, so that is called "diluted". The magnetic element which acts as dopant will provide a magnetic moment. In the DMS, the exchange interaction between electrons and the effect of magnetic properties can produce important traits, like the shift of band gap. Recently, Addadi et al. reported electronic and magnetic properties of V doped BaS studied using FPLAPW method [7]. One of the uncovered problem is the effect of transition metal atom doped BaS. Therefore it is required to study it systematically. This paper presents a systematic study of transition metal elements (Fe, Co and Ni) doping in BaS. Changes in electronic and magnetic properties caused by using transition metal doping have been reported. The DFT method is used to find the trends of the shifting of electronic and magnetic properties due to the presence of those transition metal elements as impurities.

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METHODOLOGY

The first principle calculations were performed on the TM doped BaS, using the all-electron full potential linearized augmented plane wave (FP-LAPW) methodology supported density functional theory (DFT), as enforced within the WIEN2K code [8]. The correlation and exchange effects of the electrons were handled with using the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE –sol), as the functional, suggested by Tran and Blaha (mBJLDA) [9] was used to check out the electronic and magnetic properties of TM doped BaS. Self-consistent total energy calculations were performed to the total energy convergence for a value less than 10^{-3} Ry, and the charge is converged to 0.001 e. A dense mesh of 500 K-points is used for the pure and TM-doped compounds. The energy cutoff was used as −11.0 Ry, which represents the separation of valence and core states. The convergence conditions is manipulated by keeping the cut-off parameter $R_{MT}\times K_{max}=7$, where is the radius of the smallest atom and is the magnitude of the largest wave vector in the unit cell.

RESULT AND DISCUSSION

Electronic, optical and magnetic properties of un-doped BaS and TM(TM=Fe, Co, Ni) doped BaS [$Ba_{1-x}TM_xS$ (x = 0.25)] have been calculated and compared. Figure 1 is representation of unit cell structure of pure and Fe, Co and Ni doped BaS alloy. The BaS shows rock-salt type structure with space group of (225) *Fm*-3*m*, where the Ba atom is located at (0, 0, 0) and S atom at (0.5, 0.5, 0.5) Wyckoff position. Concentration of $x = 0.25$ have been obtained by substituting of one Ba cation site at (0, 0, 0) position by Fe/Co/Ni impurity in Ba_8S_8 supercells containing 8 atoms. We get the $Ba_{0.75}TM_{0.25}S$ (TM = Fe, Co and Ni) (1 × 1 × 1) supercells of 8 atoms with concentration $x = 0.25\%$ of tetragonal structure. Structures of pure and doped BaS have been optimized by variation of total energies as a function of equilibrium volumes. Various structural parameters such as equilibrium lattice constants (*a*), bulk modules (*B*) and its volume have been computed for BaS and $Ba_{0.75}TM_{0.25}S$ (TM = Fe, Co and Ni). Table 1 provides various theoretical, experimental and calculated (here) data. Structural optimization calculations show that incorporation of Fe/Co/Ni causes an expansion of crystal lattice when it compared to pure BaS. From band structure calculations (Fig. 1), it can be seen that the valence band maximum (VBM) lies at the Γ point and the conduction band minimum (CBM) is located between L and X points. It indicates that pure BaS is an indirect gap semiconductor whereas doped BaS is closer to direct bandgap semiconductor. The calculated band gap is (PBE-sol=3.75) (mBJLDA=4.63 eV). These values are close to the experimental value that is ~3.90 eV [10]. Minority spin of doped BaS is semiconducting while majority is metallic in nature with many unoccupied states above the Fermi level. It results in 100% spin polarization of conduction carrier. Fig. 2 (a) shows the calculated total density of states for un-doped and doped BaS. For majority-spin electrons, total density of states of Fe/Co/Ni doped BaS is nonzero at Fermi level.

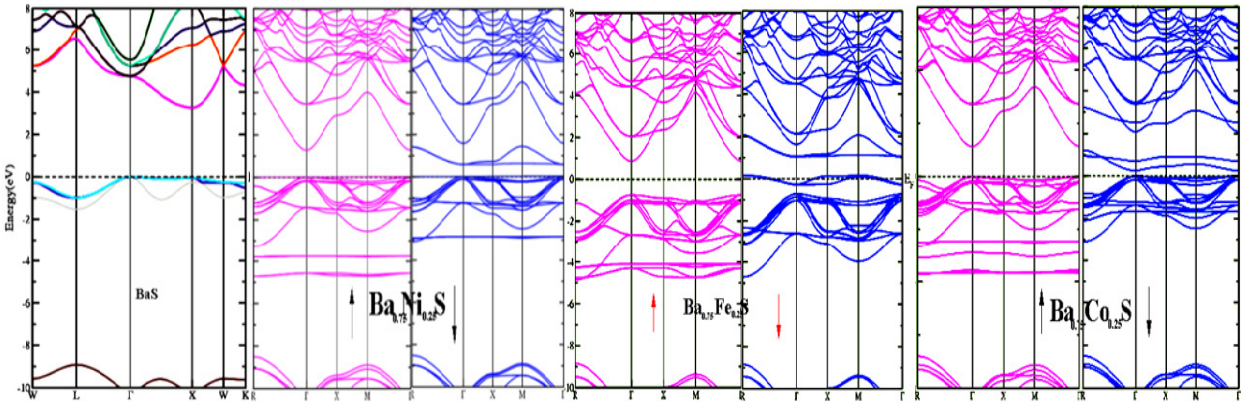
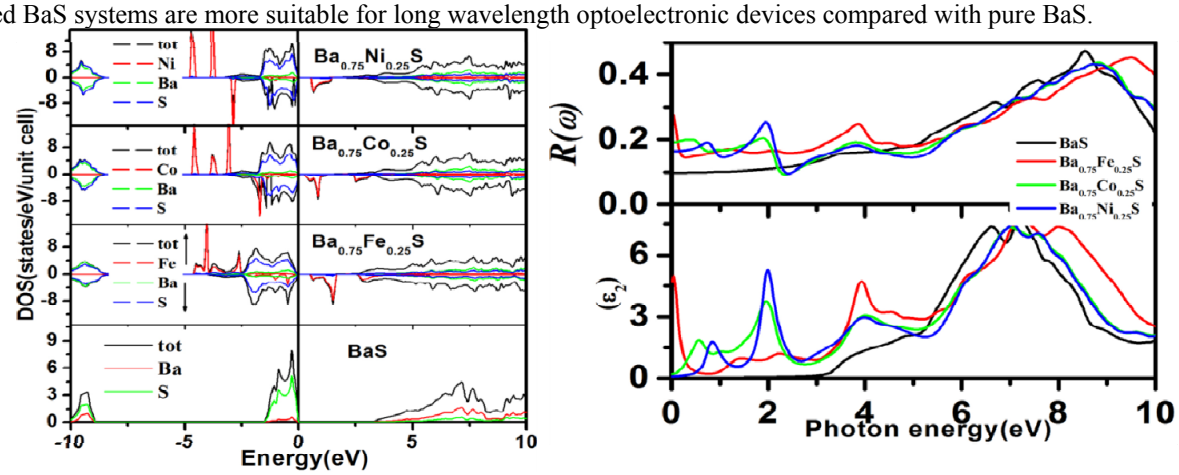


FIGURE 1. The electronic band structures of $Ba_{0.75}TM_{0.25}S$ calculated using mBJLDA at x = 0.25 for spin-up and spin-down

Our results for total density of states show that $Ba_{1-x}TM_xS$ is half-metallic in nature. In the case of undoped BaS, below E_F, main contribution comes from 5d Ba and 3p states. For majority-spin electrons, feature in the DOS at Fermi level is the bonding states of hybridization S 3p and Fe/Co/Ni- 3d states and Ba -5d states which are recognized by the overlapping bands, whereas for minority spin electrons, the separation between the S 3p and Fe/Co/Ni 3d states is large enough to create a band gap. The metallic nature of majority spin results from the large

hybridization between *p* -S and 3*d*-(Fe/Co/Ni) states that occur in the upper part for valence band and crosses the Fermi level, while the 3*d* (Fe/Co/Ni) minority-spin states vanish at Fermi level, resulting in semiconducting band gap. Spin polarization of doped Bas originates from spin polarization of 3d states of Fe/Co/Ni.

The imaginary part spectra of the dielectric function and reflectance for Fe/Co/Ni-doped BaS with 0.25 % doping concentrations are compared with experiment as reported by Kaneko et al. [11] presented in the range 0-12 eV in Fig. 2 (a). For pure BaS, we can see three different peaks, one located at 4.80 eV, which originates the electronic transition from the 3*p* orbital of the S atom in the upper valence band to the 5*s* orbital of the Ba atom in the lowest conduction band. The second peak is located at 7.32 eV, which originates the electronic transition from the 3*p* orbital of the S atom in the valence band to the 5*p* orbital of the Ba atom in the conduction band. The third peak is located at 7.71 eV. It arises due to transitions of S-3p states from valence band to conduction bands. In the case of Fe/Co/Ni-doped BaS systems, significant changes are there and new peaks appear in low energy region; indicating new and distinct channels for the absorption of photons with energies below the gap width of BaS are obtained. The emerging peaks are at 1.38, 0.55 and 0.84 eV for Fe/Co/Ni doping concentrations of 0.25%, respectively, which are due to the electronic intraband transition of the impurity Fe/Co/Ni 3*d* states and the Ba 5*s* states in the conduction band. For the Fe/Co/Ni doped BaS the reflectance enhances in the low energy region due to the impurity bands near the Fermi level. The location of reflectivity and refractivity peaks also agree with the imaginary part spectra of dielectric function. Static reflectivity value has good agreement with reported experimental values. [11]. Doping increases reflectivity coefficients in the UV region of spectra. There is an additional reflectivity peak in each doped system compared to the pure BaS when the energy is lower than 3 eV, indicating that the reflecting ability of BaS can be enhanced when it is doped with Fe/Co/Ni in the low energy area, which originates mainly from the Fe/Co/Ni-3d electrons transition to the Ba 5d states. Therefore , it can be concluded that that doping of Fe/Co/Ni have a significant influence on the optical properties of BaS systems in low energy region, including visible and infrared region, while the effect is barely noticeable in ultraviolet region, which reveals that Fe/Co/Ni-doped BaS systems are more suitable for long wavelength optoelectronic devices compared with pure BaS.



(a) (b)

FIGURE 2. (a) Total density of states (b) Optical property

The total and local magnetic moments of the materials $Ba_{0.75}TM_{0.25}S$ calculated using the mBJLDA are presented in Table 1. Substituting the Ba atom with Fe/Co /Ni provides two of the total five valence electrons to make bonds with S atoms while the rest of valence electrons stay in the impurity bands at E_F. The half-metallic character of these materials is in accordance with their integral magnetic moments. From Table 1, 0.25 % doping concentration, the local magnetic moment of Fe/Co/Ni is less than the total magnetic moment. This is due to the hybridization between S-*3p* states and Fe/Co/ Ni-3d states which induces small magnetic moments on the nonmagnetic (Ba, S) sites. TM extensively contributes to Mtot at 0.25 % doping concentrations. The induced magnetic moment for Ba has positive (negative) sign which is due to the parallel (anti-parallel) alignment with TM. Hence, ferromagnetic interaction exists between TM (Fe, Co and Ni) and Ba/S atoms. It is clear that the dopant-induced impurity level consist a huge contribution of the TM *d* states and S 3*p* states but not only TM *d* states can be found at the Fermi level, S *p* states are also present at the Fermi level which results in p-d coupling.

TABLE 1. Input parameters and their values

Parameters	BaS	$Ba_{0.75}Fe_{0.25}S$	$Ba_{0.75}Co_{0.25}S$	$Ba_{0.75}Ni_{0.25}S$
a (Å)	6.335	5.8265	6.0921	6.1097
B (GPa)	46.37	9.6396	50.84	49.1718
V ($Å^3$)	428.928	1334.8286	1525.81	1539.09
E_g(eV)				
PBE-sol	3.75	No gap↑↓	0.36↑, no gap↓	0.36↑, no gap↓
mBJ-LDA	4.63	0.76↑, 0.93↓	1.29↑, 0.19↓	1.17↑, 0.55↓
Exp.	3.88[10]			
Optical Properties				
R (0)%	0.09	0.27	0.19	0.16
Exp.	0.17[11]			
Magnetic moment(μB)				
Interstitial	--	0.0928	0.04669	0.02078
Fe	--	3.72154	2.73908	1.74324
Ba	--	-0.0193	0.00187	-0.00369
S	--	0.1853	0.21597	0.23967
Tot	--	4	3	1.99999

CONCLUSION

We have investigated the structural, optical and magnetic properties of Fe, Co and Ni doped $Ba_{1-x}TM_xS$ (x = 0.25) alloys are analyzed by first principles in the framework of DFT by Wien2K. The major conclusions drawn from this study are geometry optimization was carried in un-doped and Fe, Co and Ni doped BaS structures. We found that BaS has indirect bandgap semiconductor. From the Spin polarized density of states show the clear evidence of half metallic nature in Fe/Co/Ni doped BaS. Calculations for the dielectric constant, ε(ω), reveal that smaller energy gap results in a larger static dielectric constant $\varepsilon_1(0)$. Direct optical transitions were also observed for doped ε_2 (ω) curves. The calculated reflectivity spectra for the ternary alloys $Ba_{1-x}TM_xS$ (x = 0.25%) shows that there are regions of maximum and minimum reflectivity. The potential use of TM (Fe, Co and Ni) doped BaS in spintronics applications.

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