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Investigation of ferromagnetic semiconducting and opto-electronic properties of $Zn_{1-x}Mn_xS$ ($0 \leq x \leq 1$) alloys: A DFT-mBJ approach

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ABSTRACT

In this study, we report the mechanical, structural, electronic, magnetic and optical behaviors in $Zn_{1-x}Mn_xS$ ($0 \leq x \leq 1$), which are determined by employing Wein2K code. The ferromagnetic (FM) state stability of the $Zn_{1-x}Mn_xS$ alloys has been elucidated from the calculated values of enthalpy of formation. The elastic constant (C_{11}, C_{12}, C_{14}) are calculated to find various useful mechanical parameters, which depend upon Mn concentrations. The calculated electronic band structure and density of states (DOS) have demonstrated that exchange splitting through p-d hybridization, arising due to Mn impurities, stabilize a ferromagnetic state. The exchange splitting of the bands is further elucidated from the sharing of magnetic moment, charge and spin, between the impurity cations and the host lattice anions. Various parameters like direct spin-exchange splitting $\Delta_x(d)$, exchange constants $N_0\alpha$ and $N_0\beta$ have also confirmed a stable ferromagnetic state. Various calculated optical parameters have indicated that the studied compounds respond to visible and ultraviolet energies. Moreover, the calculated optical band gap and static dielectric constant $\varepsilon_1(0)$ verify Penn's model. The studied compounds of $Zn_{1-x}Mn_xS$ have been shown theoretically that they find potential spintronic and optical device applications.

1. Introduction

The realization of ferromagnetism in traditional semiconductors keeps immense interest for researchers because both charge and spin can simultaneously be manipulated. In magnetic semiconductors, a magnetic impurity can induce ferromagnetism in the nonmagnetic semiconducting host lattice and can be used to elucidate the material properties in a vast composition range. On the other hand, in diluted magnetic semiconductors (DMSs) the composition of magnetic impurity is limited to a very small range. The non-oxide magnetic semiconductors have a major limitation of having Curie temperature (T_C) below room temperature (RT). Various magnetic semiconductors like, GdN [1,2], GaMnAs [3], $Ge_{1-x}Mn_x$ [4], $Si_{1-x}Mn_x$ [5], CdMnTe [6], GaMnN [7] and GeMnTe [8,9] etc., have been investigated to enhance T_C. There are also few reports about T_C above room temperature but that is explained by the presence of precipitates or clusters of magnetic impurity ions [10–12].

An enormous amount of work exists on oxide based magnetic semiconductors. Although room temperature ferromagnetism (RTFM) has been reported for $Zn_{1-x}Ni_xO$ [13], $Ti_{1-x}Fe_xO_2$ [14] and $Sn_{1-x}Co_xO_2$ [15] etc., but the real cause of ferromagnetism (FM) is not clear because even the un-doped oxide semiconductors have shown RTFM [16–19]. In such systems, it is believed that FM may arise due to cations or anions vacancies and interstitials [20–24]. Moreover, as predicted by Dietl et al. [25], the composition of magnetic ions is related to T_C. In this context, epitaxial thin films of Mn-doped GeTe with high Mn content, ~50%, have shown that Mn addition enhances T_C and may affect the crystal structure, while the single phase of $Ge_{1-x}Mn_xTe$ is maintained [8,9].

Wide band gap semiconductors have important technological applications such as optical waveguides, blue laser, devices operating at high power levels, visible light emitting devices etc. ZnS is an important II-VI semiconductor, which crystallizes into cubic Zinc blende (ZB) phase ($a = 5.41$ Å) or hexagonal wurtzite phase ($a = 3.82$ Å, $c = 6.26$ Å). The ZB phase is a low-temperature phase, which could be transformed to the high-temperature wurtzite phase around 1296 K [26]. At room temperature (RT), the band gap of ZnS is 3.72 eV [27] and 3.77 eV [28], for the cubic and the

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hexagonal wurtzite phases, respectively.

ZnS has been doped, experimentally, with transition elements like Co [28], Cr and Fe [29] etc., and RTFM have been reported. From various experimental reports on $Zn_{1-x}Mn_xS$, it is evident that highest x_{Mn} achieved is not greater than 0.30 [30–32]. Therefore, non-equilibrium growth conditions, as employed in MBE, are expected to increase the solubility limit of a dopant in the host semiconductor lattice [8,9]. In this context, it is important to perform density functional theory (DFT) calculations for $Zn_{1-x}Mn_xS$, to find various properties within the full composition range. Various DFT calculations have been performed for first-row transition metal doping in ZnS, and it has been observed that Cr, Fe, Ni doping results in half metallic ferromagnetism (HMFM) due to double exchange while Mn and Co doping induces ferromagnetic semiconducting properties due to super-exchange [33–36]. Recently, Ni and Fe-doped ZnS thin films fabricated by using chemical bath (CBD) method have been investigated experimentally as well as theoretically, and results show that both dopants exhibit half metallic ferromagnetic properties [37,38]. The ferromagnetism with half-metallic and semiconducting nature has also been demonstrated in ZnS due to Carbon (C) and Copper (Cu) doping, respectively [39,40].

Although, N. Benkhettou and D. Ben have theoretically determined various physical properties of $Zn_{1-x}Mn_xS$ for the whole composition range x_{Mn} = 0.00, 0.25, 0.50, 0.75 and 1.0 [41], however, reports about the optical properties and application of recently developed mBJ functional are scarce in the literature. According to our best knowledge, no comprehensive report on Mn-doped ZnS for the full composition range exists to relate structural, electronic, mechanical and magnetic properties. Moreover, the DFT calculations of the optical properties of Mn doped ZnS, for the whole composition range, do not exist in the literature. In this work, we present the results of DFT calculations to explore the structural, elastic, electronic, magnetic and optical properties of $Zn_{1-x}Mn_xS$ (x = 0, 0.25, 0.50, 0.75, 1.0).

2. Computational details

Ab-initio modeling is commonly used to explore materials, which are intended for advanced device applications. To elucidate the presence of a stable ferromagnetic semiconducting ground state in $Zn_{1-x}Mn_xS$ (x = 0, 0.25, 0.50, 0.75, 1.0), we have used FP-LAPW + lo technique, implemented in the Wein2k [42], which is based on spin-polarized density functional theory (DFT). The structural and electronic characteristics are calculated from the Wu and Cohen generalized gradient approximation (WC-GGA), by self consistently evaluating the Kohn-Sham orbitals [43]. The recently developed modified Becke–Johnson (mBJ) functional [44], is used to find the accurate electronic and optical properties, in excellent agreement with the experiments [45]. As compared to the already employed functionals, modified Becke Johnson (mBJ) functional calculates the band gap that is very close to the experimental values. For example, the band gap of ZnS calculated with LDA functional is 1.84 eV, which highly deviates from the experimental value of 3.54 eV [71]. While calculated band gap of pure ZnS (non spin-polarized) in the present study is 3.46 eV, which shows that the presented calculations are in excellent agreement with the experiment. A comparison of the band gaps calculated by using various functionals, showing advantage of mBJ functional, is available in reference [44].

The end binaries of ZnS and MnS with cubic zinc-blende (ZB) B3 phase and space group $F\bar{4}$ 3m (No. 216) along with $Zn_{1-x}Mn_xS$ (x = 0.25, 0.50 and 0.75) are computed by employing a supercell consisting of 8 atoms. For x = 0.25 and x = 0.75, the host lattice exhibit a cubic structure with space group $P\bar{4}$ 3m (No. 215), while for x = 0.50, the crystal structure has been observed to exhibit a tetragonal space group $P\bar{4}$ m2 (No. 115). The computations are carried out by optimizing the experimental lattice parameters using WC-GGA. The cut-off parameter, which is product of radius of the muffin-tin sphere and maximum plane wave vector K_{max}, has been adjusted to 8. The potential within the interstitial region is evaluated by using G_{max} = 18 a.u.$^{-1}$. The muffin-tin radii (a.u.) for Zn, Mn, and S atoms are, respectively, taken as 2.5, 2.5 and 2.4. Brillion zone integration is carried out over a 10 × 10 × 10 k-mesh. The total energy and the charge have preferably been allowed to be converged below 10^{-4} Ry and 10^{-3} e, respectively.

3. Results and discussion

3.1. Structural and mechanical stability

The calculated volume and energies for $Zn_{1-x}Mn_xS$ (x = 0.00, 0.25, 0.50, 0.75, 0.10) are optimized and fitted with Birch-Murnghan equation [46], which yields the optimized lattice parameters (*a*) as well as the bulk modulii (B), as listed in Table 1. The bulk modulus represents the ability of the crystal to withstand deformations, in response to the uniform pressure, and demonstrates the hardness of the crystal. The calculated lattice parameters and the bulk modulii for ZnS and MnS are in nice agreement with the experimental and the other theoretical reports [47–50], verifying the accuracy of our presented calculations. The increase in Mn content results in increase of *a* and decrease of B, depicting that *a* is inversely related to B [51]. Increase in lattice constant can be justified by the relatively larger ionic radii (0.80 Å) of Mn^{+2} ions, those are replacing Zn^{+2} cations with a smaller ionic radius (0.74 Å). Therefore, increase in Mn^{+2} concentration results in an expansion of the host lattice and hence the lattice constant enhances [52]. The stability of the ferromagnetic (FM) state as compared to the paramagnetic (PM) state has been investigated by comparing their total energies, by using the equation, $\Delta E_1 = E_{PM} - E_{FM}$. The positive values of ΔE_1, as given in Table 1, confirm the stability of the FM phase. The stability of this FM phase has again been confirmed from the negative sign of the computed enthalpy of formation (ΔH_f), which is determined by employing Eq. (1).

$$\Delta H = E_{Total}(Mn_lZn_mS_n) - lE_{Mn} - mE_{Zn} - nE_S \quad (1)$$

where the $E_{Total}(Mn_lZn_mS_n)$ represents the compound ground state, and E_{Mn}, E_{Zn} and E_S demonstrate the ground state energies of Mn, Zn and S, respectively. The subscript *l*, *m* and *n* represent the number of respective atoms per unit cell.

In order to investigate the stability and the stiffness of the cubic $Zn_{1-x}Mn_xS$ lattice, C_{11}, C_{12} and C_{44} elastic constants are calculated by using Charpin method [42], in which total energy response to different lattice strains is investigated. The bulk B, shear G and Young's modulii E, Kleinman parameter ξ, Poisson's ratio ν, anisotropy factor A and Pugh ratio (B/G) have been calculated by using the following relations [53–59].

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \quad (2)$$

$$G = \frac{1}{2}(G_V + G_R) \quad (3)$$

where,

$$G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})}$$