Journal of Alloys and Compounds 573 (2013) 83–89

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Electronic structure and half-metallic ferromagnetism in (C, Si, Ge and Sn) doped alkaline-earth sulfides: A first principles approach

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ARTICLE INFO

Article history:
Received 6 October 2012
Received in revised form 28 March 2013
Accepted 29 March 2013
Available online 6 April 2013

Keywords:
Alkaline-earth chalcogenides
First principles calculations
Half-metallicity
Non-magnetic dopants

ABSTRACT

The electronic structure and magnetic properties of $AeS_{1-x}M_x$ (Ae = Mg, Ca and Sr; M = C, Si, Ge and Sn; x = 0.125, 0.25, 0.50 and 1.00) in the rock salt structure was studied using full potential linear augmented plane wave (FP-LAPW) method within the spin density functional theory. The calculation reveals that the non-magnetic dopants can induce stable ferromagnetic state in alkaline-earth sulfides. Also it is found that the alkaline-earth sulfides exhibit half-metallicity with an integer magnetic moment of 2.00 μ_B/f.u., with group IV elements as dopants (except for Si, Ge and Sn in MgS). The calculated results show that the minority spin electrons are metallic in nature, while the majority spin electrons show an energy gap around the Fermi level. It also found that the HM gap decreases with the increase of atomic size and concentration of the dopant atoms. The half-metallicity originates from the spin-polarized *np* like states of dopant atoms in these compounds.

1. Introduction

Half-metallic (HM) ferromagnets [1] are believed to be a promising material for spintronic devices. They are magnetic materials with semiconducting or insulating behavior for one spin channel and metallic in other spin channel at the Fermi level. Therefore they can exhibit 100% spin-polarization around the Fermi level. Recently the existence of half-metallic ferromagnetism has been reported in undoped oxides such as HfO_2, ZnO, CaO and TiO_2 [2–7] by the creation of cation vacancy. The creation of magnetic moment in these materials is mainly due to cation vacancy. No magnetic impurities were used to induce magnetism in these materials; this phenomenon is called as d^0 ferromagnetism. More recently, it is found that the substitution of anion with a nonmetal atom of smaller valence introduces finite bandgap for majority spin channel and a vanishing bandgap for minority spin channel at the Fermi level. The concept of anion doping was first introduced by Kenmochi et al. [8] in his study on electronic and magnetic properties of B, C and N doped CaO. Since then, several work have been reported showing that 2*p* light elements doped at anion site can induce HM ferromagnetism in oxide, sulfide and nitride based materials such as MgO, CaO, SrO, BaO, In_2O_3, ZnO, TiO_2, CeO_2, SnO_2, CdS, ZnS, and AlN [9–24]. Further several groups have reported that the non-magnetic dopant materials like Mg, Ca and Cu [25–28] can induce ferromagnetism in host material. Small concentration of Si or Ge doping at sulfur site in K_2S [29] induces ferromagnetism. Also HM ferromagnetism is found in I_2-VI compounds by anion doping with group IV and group V elements [30,31]. Recently electronic structure and trends of MgO systems doped with III, IV and V main group elements for a concentration of 25% was reported by Liu et al. [32] using plane wave ultrasoft pseudopotential method. Liu et al. [33] have studied that the C doping in alkaline-earth chalcogenides (O and S) produce HM ferromagnetism. Very recently we have investigated the electronic structure and HM ferromagnetism in alkaline-earth chalcogenides doped with B, C and N [34,35] using TB-LMTO method.

Alkaline-earth sulfides are found to be important wide bandgap semiconducting materials, since it can produce excitons with large binding energy. Hence they have ample technological application in the areas of luminescent devices, catalysis, radiation dosimetry and microelectronics [36,37]. They are the important closed shell ionic system which crystallizes in NaCl-structure at ambient conditions. So realization of ferromagnetism in these alkaline-earth sulfides has been expected to advance the development of spin-injection electrode materials and magneto-optical devices. The aim of the present paper is to explore the possibility of HM ferromagnetism in AeS (Ae = Mg, Ca and Sr) by doping with group IV non-magnetic elements such as C, Si, Ge and Sn at anion site for various concentrations (x = 0.125, 0.25, 0.50 and 1.00). In order to study the stability of ferromagnetic state, both spin-polarized and spin-unpolarized calculations have been performed. Also the equilibrium lattice constant, bond length, HM gap and magnetic moments of $AeS_{1-x}M_x$(Ae = Mg, Ca and Sr; M = C, Si, Ge and Sn; x = 0.125, 0.25, 0.50 and 1.00) compounds have been calculated using full potential linear augmented plane wave (FP-LAPW) meth-

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0925-8388/$ - see front matter © 2013 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.jallcom.2013.03.275

od within generalized gradient approximation with Perdew–Burke–Ernzerhof parameterization (GGA–PBE) scheme. The outline of the paper is as follows; computational details are briefly given in Section 2. The results of the calculations and their discussions are given in Section 3. Finally the concluding remarks are given in Section 4.

2. Computational frameworks

The spin-polarized calculation for $AeS_{1-x}M_x$ (Ae = Mg, Ca and Sr; M = C, Si, Ge and Sn; x = 0.125, 0.25, 0.50 and 1.00) were performed using FP-LAPW method based on density functional theory, as implemented in WIEN2k [38] code. There is no shape approximation made to charge and potential expansions in this method. To construct exchange–correlation (XC) potentials in the calculation, GGA–PBE [39] has been used. The radii R_{MT} of the muffin tins chosen for the present study is found to be approximately proportional to the corresponding ionic radii and is as large as possible under the condition that the spheres do not overlap. We expand the $R_{MT} \times K_{max}$ = 8.0, where R_{MT} is the smallest value of the muffin-tin (MT) spheres and K_{max} is the maximum value of the reciprocal lattice vectors. The maximum value for partial wave expansion inside the atomic spheres was confined to l_{max} = 10. The cutoff energy, which defines the separation of valence and core states were chosen as −6.0 Ry. For accurate Brillouin zone integration, the tetrahedron method [40] with 2000 k-points were used. We neglect the effect of spin–orbit coupling. In order to find the possibility of HM ferromagnetism in alkaline-earth chalcogenides with group IV elements (C, Si, Ge and Sn), 2 × 2 × 2 supercell (Ae_8S_7M) with cubic symmetry was constructed. The self-consistency is considered to be converged when the integrated charge density per formula unit, $\int|\rho_n - \rho_{n-1}|\,dr$ between the input charge density ρ_{n-1} and the output charge density ρ_n is less than 0.0001 e/a.u^3.

3. Results and discussion

3.1. Ground state properties

As a first step, total energy vs reduced volume was calculated for the binary host compounds MgS, CaS and SrS within GGA–PBE, from which the equilibrium lattice constants were calculated and tabulated in Table 1. The calculated lattice constant is in good agreement with the experimental as well as other theoretical values [42–48]. To study the effect of dopants in alkaline-earth sulfides, 2 × 2 × 2 supercell containing 16 atoms was constructed at their calculated equilibrium lattice constant. Atomic position and lattice size have strong effects on magnetic and electronic properties. So before doing the electronic and magnetic calculations, full atomic position and volume optimization was performed for $AeS_{1-x}M_x$ (Ae = Mg, Ca and Sr; M = C, Si, Ge and Sn; x = 0.125, 0.25, 0.50 and 1.00) compounds. In order to determine the equilibrium lattice constant (a_0) and bulk modulus (B_0) for doped systems, the total energies were calculated as a function of relative volume for both non-magnetic and ferromagnetic states and fitted into Birch–Murnaghan equation of state [49]. The calculated equilibrium lattice constant and bulk modulus are tabulated in Table 1. The equilibrium lattice constant (Table 1) of C-doped AeS (Ae = Mg, Ca and Sr) is small as compared to the equilibrium lattice constants of host compounds and it decreases on increasing the dopant concentration from x = 0.125 to 1.00. This is because the atomic size of

Table 1
Calculated equilibrium lattice constant (a_0) Å, bulk modulus (B_0) GPa for both non-magnetic (NM) and ferromagnetic (FM) phases, total energy difference (ΔE) in meV, bond length (Å) and half-metallic gap (eV) of $AeS_{0.875}M_{0.125}$ (AE = Mg, Ca and Sr; M = C, Si, Ge and Sn) using GGA–PBE.

Compounds	(a_0) Å		(B_0) GPa		ΔE (meV)	Bond length (Å)	Half-metallic gap (eV)
	NM	FM	NM	FM			
MgS						2.6159	
Present	5.231		83.30				
Experiment	5.19[a]						
Others	5.23[b]		84.0[b]				
	5.244[c]						
$MgS_{0.875}C_{0.125}$	5.187	5.190	78.20	74.86	407.8	2.5953	0.552
$MgS_{0.875}Si_{0.125}$	5.286	5.292	77.98	74.84	31.4	2.6475	–
$MgS_{0.875}Ge_{0.125}$	5.293	5.300	76.54	75.79	23.3	2.6470	–
$MgS_{0.875}Sn_{0.125}$	5.359	5.361	73.89	73.54	–	2.6805	–
CaS						2.7826	
Present	5.716		67.16				
Experiment	5.689[d]						
Others	5.717[e]		67.40[e]				
$CaS_{0.875}C_{0.125}$	5.679	5.681	66.88	67.43	538.8	2.8407	0.888
$CaS_{0.875}Si_{0.125}$	5.769	5.772	62.56	61.12	208.4	2.8620	0.208
$CaS_{0.875}Ge_{0.125}$	5.774	5.778	60.56	59.89	187.0	2.8890	0.172
$CaS_{0.875}Sn_{0.125}$	5.831	5.837	57.81	58.77	136.0	2.9170	0.007
SrS						3.0301	
Present	6.060		58.64				
Experiment	6.024[f]		58				
Others	6.076[h]		62[g]				
$SrS_{0.875}C_{0.125}$	6.021	6.024	58.24	57.91	594.0	3.0120	1.069
$SrS_{0.875}Si_{0.125}$	6.111	6.114	54.03	53.91	290.0	3.0571	0.412
$SrS_{0.875}Ge_{0.125}$	6.116	6.119	54.56	53.82	275.0	3.0595	0.369
$SrS_{0.875}Sn_{0.125}$	6.171	6.175	50.64	51.45	205.0	3.0876	0.210

[a] Ref. [41].
[b] Ref. [42].
[c] Ref. [43].
[d] Ref. [44].
[e] Ref. [45].
[f] Ref. [46].
[g] Ref. [47].
[h] Ref. [48].