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The electronic structure and room temperature ferromagnetism in non-magnetic element X (X = Al, Mg and Li) doped $SrSnO_3$ from hybrid functional calculations

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ABSTRACT

The remarkable properties of diluted magnetic semiconductors have renewed interest in the perovskite materials with unique magnetic attributes. The magnetic properties of perovskite cubic and orthorhombic $SrSnO_3$ with non-magnetic element X (X = Al, Mg and Li) doping have been theoretically investigated using the state-of-the-art hybrid density functional calculations. The X doping at the Sn site was observed to obtain the spontaneous magnetization and the surrounding oxygen atoms were polarized. Moreover, the induced magnetic moments increase with the hole density introduced by the dopants. Additionally, the induced magnetic moment and its stability are closely dependent on the host crystal symmetry. The calculated Curie temperature of T_C for Li and Mg doped $SrSnO_3$ is much higher than the room temperature, indicating that the room temperature ferromagnetism can be achieved by hole doping. And the doping systems are more energetically stable under the O-rich condition.

1. Introduction

The perovskite-type oxides symbolize a significant category of materials which demonstrate numerous attractive physical properties, such as ferroelectric, superconductivity, photocatalytic and piezoelectric [1–5]. Therefore, they have been extensively used in many applications [6]. Recently, the great interest has been raised in applying perovskite oxides for spintronic applications [7] and the physical properties of perovskites under high-pressure [8]. The realization of spintronic applications needs to be accomplished by the specific properties of materials which have both semiconductor and room temperature ferromagnetism [9]. However, the pure perovskite-type oxides do not exhibit ferromagnetism under normal circumstances.

Strontium stannate, $SrSnO_3$, is a multifunctional perovskite material due to its wide band gap (4.10 eV) [10], superior conductivity [11] and outstanding photocatalytic properties [12]. And the cubic [13,14] and orthorhombic [15] crystal structures are usually considered for the polymorphs of SSO in experiment and theory. According to the advantages of SSO, there have been a lot of technical applications in different fields such as humidity sensors [16], thermally stable capacitors [17] and electronic devices [18,19]. Recently, the experimental and theoretical investigations have been performed on the optical and transport properties of SSO [20,21], but few reports on the magnetic properties of SSO can be found until now [14,22,23]. In order to yield the perovskite oxides spin-polarization, numerous efforts have been devoted both theoretically and experimentally, affirming that the doped perovskite oxides can possess the ferromagnetism [7,22–24]. As for the magnetic origin aspect, the previous theoretical reports pointed out that the formation of magnetic moment (MM) may be in connection with hole doping in the perovskites and oxides with large band gap [25–30]. For example, Liu et al. investigated the hole doped $SrTiO_3$ with non-magnetic elements, and observed the formation of localized MM which can realize the ferromagnetism [7]. Moreover, Peng et al. have proposed the association between hole density and ferromagnetism in the defect-induced oxides. It indicates that the origin of the robust ferromagnetism is the localized nature of O-2*p* states. The sufficient hole density is essential to emerge spin-polarization [26].

To realize spin-polarization in SSO, it is necessary to introduce hole defect in SSO system. Since both the anion-substitution and the intrinsic defect are controlled the hole density in the experiment with difficulty, the pure SSO was fit by the cation-substitution with non-magnetic element X (X = Al, Mg and Li). Since the number of valence electron of Al, Mg and Li is on the decrease, the introduced hole density can be increased in the

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sequence of Al-substitution > Mg-substitution > Li-substitution cases. To keep the structural stability, the size of the doping element should be close to the replaced host atom, which can avoid large lattice distortion and reduce the doping formation energy [31,32]. Therefore, the Sn of the SSO was proposed to be replaced by Li, Mg and Al here, because their ionic radiuses (R(Al) = 0.51 Å, R(Mg) = 0.66 Å, R(Li) = 0.68 Å) are similar with that of Sn (R(Sn) = 0.69 Å). Fortunately, the ferromagnetism was successfully observed after hole doping in both cubic and orthorhombic SSO. And the induced MM are significantly dependent on the crystal symmetry and hole density in the doped crystals. These will give more insights into understanding the d^0 magnetism in the perovskite materials.

2. Calculation details

All calculations in this work were performed via the projector-augmented-wave method [33] which was implemented by the Vienna ab initio Simulation Package (VASP) based on spin-polarized density functional theory [34]. The exchange correlation has adopted the generalized gradient approximation (GGA) parameterized by Perdew-Burke-Ernzerhof (PBE) [35]. It is known that GGA functional ignores the Hartree–Fock exact exchange part which usually gives inaccurate electronic structure, such as smaller band gap for semiconductors and insulators [36–39]. Thus, the electronic structure and magnetic properties were calculated using the state-of-the-art Heyde-Scuseriae-Ernzerhof (HSE06) hybrid functional [40]. Before investigating the properties of SSO, the convergence test for supercell size with 40-atoms and 80-atoms was performed. The details for the 40-atoms and 80-atoms supercells of the cubic and orthorhombic SSO were shown in Fig. S1. The lattice parameters (volume) of the 40-atom supercell for the cubic and orthorhombic SSO are a_0 = 8.16 Å (543.43 Å^3) and a_0 = 8.07 Å (523.79 Å^3), which successfully avoid the interaction between the nearest doping atoms. Similar supercell size was also used for the perovskite calculations in previous literatures [7]. The 80-atoms supercells were also used for testing the convergence of the property calculations. The supercells with different sizes give similar results. Therefore, to balance the computation time, we choose the 40-atom supercells for our property calculations. The k-points meshes in Monkhorst-Pack scheme were set as $3 \times 3 \times 3$ for the cubic and orthorhombic SSO supercells. The numbers of k-points for cubic and orthorhombic SSO are 4 and 14, respectively. The electronic states are expanded using plane wave up to a cutoff energy of 500 eV. For the total energy, the convergence is lower than 1×10^{-5} eV/atom. All atomic coordinates and lattice constants were optimized until the residual forces became less than 0.01 eV/Å.

3. Results and discussion

3.1. The structural and electronic properties of undoped SSO

Firstly, the crystal structure of un-doped primitive bulk SSO was calculated to check the accuracy and reliability of calculation parameters used in this work. The primitive cell of SSO was selected for the determination of bulk properties. The Brillouin-Zone interactions with Monkhorst-Pack special k-point grids of $8 \times 8 \times 8$ (35 k points) and $4 \times 4 \times 3$ (18 k points) were applied for cubic and orthorhombic SSO. The calculated crystal structural parameters, bulk modulus (B), valance band width (VBW) and band gap (E_g) of SSO are demonstrated in the Tables 1and 2, where the previous theoretical and experimental values are also shown as references. Upon lattice parameters and atomic position optimization, unit-cell parameters are slightly overestimated compared with the experimental values [42,45]. It is well-known that the GGA exchange-correlation functional tends to underestimate the strength of interatomic forces, leading to larger lattice parameters [44]. On the other hand, our calculated unit-cell parameters are close to the previous theoretical values for the cubic SSO, since the similar calculation method was used [41]. However, as for the orthorhombic SSO, the unit-cell parameters in this work are a little larger than the previous theoretical values. This difference may come from the ultra-soft pseudopotential used in the previous theoretical work [44]. Meanwhile, the HSE06 functional also reproduces the valence band widths of SSO which is close to the previous theoretical reports [41,44]. In addition, it could be found that HSE06 functional results in the larger band gap for both structures than PBE functional. And the band gaps from HSE06 functional are closer to the experimental results compared with the PBE functional, indicating that the HSE06 functional can improve the description of electronic structure for SSO systems. Hence, the electronic structure and magnetic properties will be calculated with the HSE06 functional in the following sections.

The band structures of cubic and orthorhombic SSO from the HSE06 functional were presented in Fig. 2. It can be seen that the valence band maximum (VBM) of cubic SSO is situated at the R point and the conduction band minimum (CBM) is at the Γ point, indicating that the cubic SSO is an indirect bandgap (2.95 eV) semiconductor. Similarly, the calculated orthorhombic SSO also possesses an indirect bandgap about 3.29 eV (S → Γ), which is smaller than the previous hybrid functional theoretical value by 0.23 eV [47]. This difference should be attributed to that all calculation process including geometry optimization in Ref. [47] was adopted the hybrid functional method. Besides the equilibrium structure, the band gap of SSO under external pressure was also obtained. As shown in Fig. S2, the band gap of both cubic and orthorhombic SSO increases with the pressure, since the band gap of materials was sensitive to the structural modification from strain [36,51]. And it is different from the band gap narrowing of $CaMoO_4$ under high pressure [37]. This results from the decrease of the Sn—O bond length with the compressive pressure, presented in Fig. S3, which enhances the Sn—O hybridization and opens the band gap.

To understand the electronic structure characteristics of cubic and orthorhombic SSO, the total and projected DOS were calculated and displayed in Fig. 1. Obviously, a set of dispersive bands between −9.19 eV and −4.88 eV dominantly arises from Sn 5s and O 2p orbital in the cubic SSO valence band. And another set of bands form between −4.88 eV and 0.0 eV with dominant contribution from O 2p orbitals with small Sn 5p states, as shown in the Fig. 1(b). The similar electronic structure also could be found in the orthorhombic SSO. The Sr atom states have almost no contribution in the valence band of SSO, which is consistent with the previous reports [41,44]. The hybridization between the Sn and O atom orbitals in the occupied states indicates the covalent bond character, which is well known for the perovskite-like compound. Additionally, the crystal structure of the cubic SSO is different from that of the orthorhombic SSO, which leads to variation of distribution of Sn 4d orbitals. For the cubic SSO, the crystal field effect results in the Sn 4d orbitals splitting into Sn d t_{2g} and e_g states, as shown in Fig. 3(a). The middle part of valence band for the cubic SSO is composed of Sn d t_{2g} states, while the bottom and top part of the valence band are combined in Sn d e_g states. And the bottom portion of the conduction band mainly consists of Sn d e_g states [23]. Compared with the cubic SSO, the Sn d orbitals of orthorhombic SSO can't generate the orbital splitting since the crystal field effect does not exist in the orthorhombic SSO, as shown in the Fig. 3(b).

3.2. The magnetic properties of the X doped cubic SSO

The magnetic property of the cubic SSO was systematically analyzed in this section. The substitution site in the supercells of SSO