Theory of magnetic enhancement in strontium hexaferrite through Zn–Sn pair substitution

Laalitha S.I. Liyanage [a,b], Sungho Kim [c], Yang-Ki Hong [d], Ji-Hoon Park [d], Steven C. Erwin [e], Seong-Gon Kim [a,c,*]

[a] Department of Physics and Astronomy, Mississippi State University, Mississippi State, MS 39762, USA
[b] Center for Advanced Vehicular Systems, Mississippi State University, Mississippi State, MS 39762, USA
[c] Center for Computational Sciences, Mississippi State University, Mississippi State, MS 39762, USA
[d] Department of Electrical and Computer Engineering and MINT Center, The University of Alabama, Tuscaloosa, AL 35487, USA
[e] Center for Computational Materials Science, Naval Research Laboratory, Washington, DC 20375, USA

ABSTRACT

We study the site occupancy and magnetic properties of Zn–Sn substituted M-type Sr-hexaferrite $SrFe_{12-x}(Zn_{0.5}Sn_{0.5})_xO_{19}$ with $x=1$ using first-principles total-energy calculations. We find that in the lowest-energy configuration Zn^{2+} and Sn^{4+} ions preferentially occupy the $4f_1$ and $4f_2$ sites, respectively, in contrast to the model previously suggested by Ghasemi et al. [J. Appl. Phys, **107**, 09A734 (2010)], where Zn^{2+} and Sn^{4+} ions occupy the $2b$ and $4f_2$ sites. Density-functional theory calculations show that our model has a lower total energy by more than 0.2 eV per unit cell compared to Ghasemi's model. More importantly, the latter does not show an increase in saturation magnetization (M_s) compared to the pure M-type Sr-hexaferrite, in disagreement with the experiment. On the other hand, our model correctly predicts a rapid increase in M_s as well as a decrease in magnetic anisotropy compared to the pure M-type Sr-hexaferrite, consistent with experimental measurements.

1. Introduction

Strontium hexaferrite $SrFe_{12}O_{19}$ (SFO) is widely used as a material for permanent magnets, along with other M-type hexaferrites X $Fe_{12}O_{19}$ (X=Sr, Ba, Pb), due to their high Curie temperatures, large saturation magnetization, high coercivity, excellent chemical stability and low cost [1–3]. As shown in Fig. 1, magnetism in SFO results from Fe^{3+} ions occupying five crystallographically inequivalent sites in the unit cell: three octahedral sites ($2a$, $12k$, and $4f_2$), one tetrahedral site ($4f_1$), and one trigonal bipyramid site ($2b$). SFO is a ferrimagnetic material that has 16 Fe^{3+} ions with spins in the majority direction ($2a$, $2b$, and $12k$ sites) and 8 Fe^{3+} ions with spins in the minority direction ($4f_1$ and $4f_2$ sites) as shown in Fig. 1(c). Therefore, the substitution of nonmagnetic ions into Fe sites with the minority spin direction has the potential to increase the saturation magnetization of SFO by reducing the negative contribution toward the saturation magnetization (M_s). Consequently, investigations to improve the magnetic properties of M-type hexaferrites have been made using various nonmagnetic impurities [1–20]. Zr–Cd substituted SFO ($SrFe_{12-x}(Zr_{0.5}Cd_{0.5})_xO_{19}$) showed

an increase of M_s up to $x=0.2$, while the coercivity decreased continuously with increasing Zr–Cd concentration [10]. For Er–Ni substituted SFO, M_s and coercivity steadily increased with Er–Ni concentration [3]. Substitution by Zn–Nb [18], Zn–Sn [6,20] and Sn–Mg [2] increased M_s and decreased coercivity. These results call for a systematic understanding, from first principles, of why certain combinations of dopants lead to particular results. This theoretical understanding will open the door to systematically optimizing the properties of SFO.

There have been several previous first-principles investigations of SFO. Fang et al. investigated the electronic structure of SFO using density-functional theory (DFT) [21]. Novak et al. calculated the electronic structure and exchange interactions of barium hexaferrite using DFT [22]. In spite of the importance of substituted SFO, only a few theoretical investigations have been done, and have focused on La substitution [23,24]. To our knowledge, no electronic structure calculation has been done on Zn–Sn substituted SFO.

In this work we use first-principles total-energy calculations to study the site preference and magnetic properties of Zn–Sn substituted M-type Sr-hexaferrite $SrFe_{12-x}(Zn_{0.5}Sn_{0.5})_xO_{19}$ with $x=1$. Based on total energy calculations, we conclude that in the ground-state configuration Zn and Sn ions preferentially occupy $4f_1$ and $4f_2$ sites, respectively. This is different from the model suggested by Ghasemi and co-workers [6,20], where Zn and Sn ions occupy $2b$ and $4f_2$ sites, respectively. We further show that our model predicts an

* Corresponding author at: Department of Physics and Astronomy, Mississippi State University, Mississippi State, MS 39762, USA. Tel.: +1 662 325 8031.
E-mail address: kimsg@ccs.msstate.edu (S.-G. Kim).
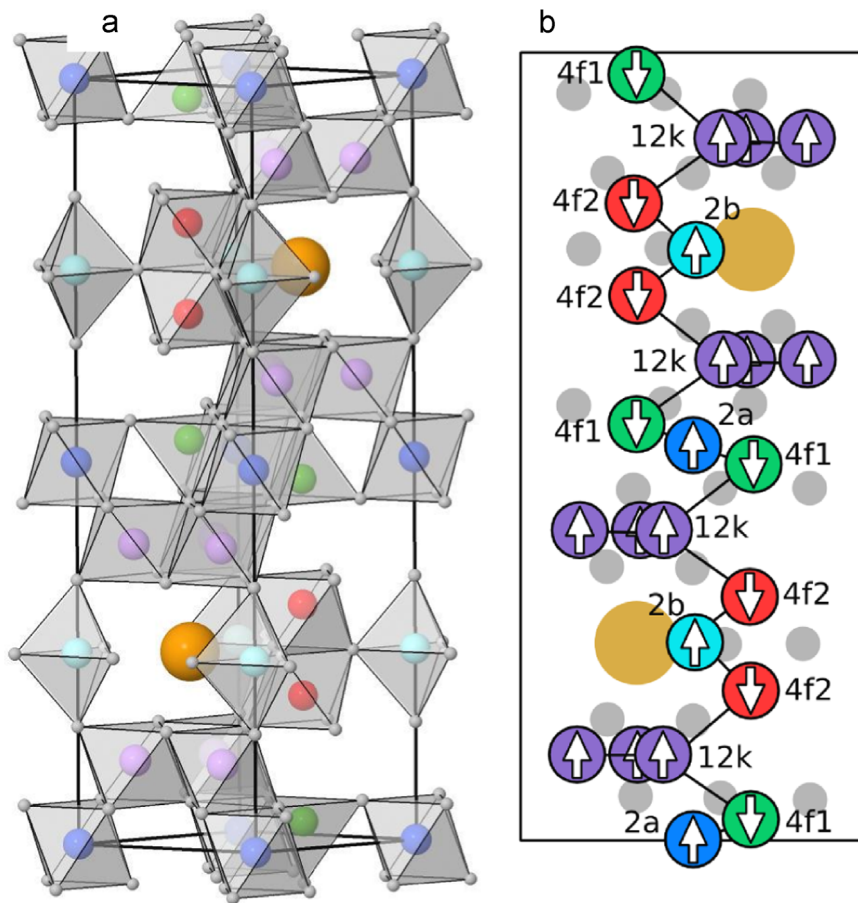
Fig. 1. (a) One double formula unit cell of $SrFe_{12}O_{19}$. Two large gold spheres are Sr atoms and small gray spheres are O atoms. Colored spheres enclosed by polyhedra formed by O atoms represent Fe^{3+} ions in different inequivalent sites: $2a$ (blue), $2b$ (cyan), $12k$ (purple), $4f_1$ (green), and $4f_2$ (red). (b) A schematic diagram of the lowest-energy spin configuration of Fe^{3+} ions of $SrFe_{12}O_{19}$. The arrows represent the local magnetic moment at each atomic site. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

increase of saturation magnetization as well as a decrease in magnetic anisotropy energy (MAE) compared to the pure *M*-type SFO ($x=0$) consistent with experimental observations.

2. Methods

To determine the site preference of Zn and Sn atoms in Sr-hexaferrite, we use first-principles total-energy calculations for configurations of $SrFe_{12-x}(Zn_{0.5} Sn_{0.5})_xO_{19}$ at $x=0$ and $x=1$. We used a unit cell which contains two formula units of SFO. The $x=1$ configuration was constructed by substituting Zn and Sn, one atom each, into the Fe sublattices of SFO. Total energies and forces were calculated using density-functional theory (DFT) with projector augmented wave (PAW) potentials as implemented in VASP [25,26]. All calculations were spin polarized according to the ferrimagnetic ordering of Fe spins as shown in Fig. 1(b) as first proposed by Gorter [21,27]. A plane-wave energy cutoff of 520 eV was used for pure SFO and 400 eV for $SrFe_{12-x}(Zn_{0.5} Sn_{0.5})_xO_{19}$ with $x=1$. Reciprocal space was sampled with a $7 \times 7 \times 1$ Monkhorst–Pack mesh [28] with a Fermi-level smearing of 0.2 eV applied through the Methfessel–Paxton method [29] for relaxations and the tetrahedron method [30] for static calculations. We performed geometric optimizations to relax the positions of ions and cell shape until the largest force component on any ion was less than 0.01 eV/Å. Electron exchange and correlation were treated with the generalized gradient approximation (GGA) as parameterized by the Perdew–Burke–Ernzerhof (PBE) scheme [31].

To improve the description of localized Fe $3d$ electrons, we employed the GGA+U method in the simplified rotationally invariant approach described by Dudarev et al. [32]. The method requires an effective U value (U_{eff}) equal to the difference between the Hubbard parameter U and the exchange parameter J. The effective U (simply U from now on) parameter can be determined in a number of ways so as to reproduce various experimental or theoretical results of particular interest. Here we choose the value of U that best reproduces the local magnetic moments of the Fe ions obtained from a more rigorous calculation using the hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE) [33–35]. Thus our computational approach consisted of the following sequence. (1) Use PBE to optimize the volume and internal coordinates of pure SFO. (2) Use HSE to determine the individual Fe local moments of pure SFO. (3) Within GGA+U, determine the value of U that best reproduces the HSE local moments. (4) Use GGA+U to investigate the effects of varying the sites on which Zn and Sn substitute for Fe.

3. Results

3.1. Pure $SrFe_{12}O_{19}$

Pure SFO ($SrFe_{12-x}(Zn_{0.5} Sn_{0.5})_xO_{19}$ with $x=0$) has the hexagonal crystal structure and the space group $P6_3/mmc$ as shown in Fig. 1. As shown in Table 1, the unit cell has 11 inequivalent sites: one Sr site of multiplicity 2, five Fe sites of multiplicity 2, 2, 4, 4 and 12, and five oxygen sites of multiplicity 4, 4, 6, 12, and 12.