Correlation between site preference and magnetic properties of Zn-Sn-substituted strontium hexaferrite

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The site preference and magnetic properties of Zn, Sn and Zn-Sn substituted M-type strontium hexaferrite (SrFe12O19) have been investigated using first-principles total energy calculations based on density functional theory. The site occupancy of substituted atoms were estimated by calculating the substitution energies of different configurations. The distribution of different configurations during the annealing process at high temperature was determined using the formation probabilities of configurations to calculate magnetic properties of substituted strontium hexaferrite. We found that the magnetization and magnetocrystalline anisotropy is closely related to the distributions of Zn-Sn ions on the five Fe sites. Our calculation show that in SrFe11.5Zn0.5O19, Zn atoms prefer to occupy 4f1, 12k, and 2a sites with occupation probability of 78%, 10% and 3%, respectively, while in SrFe11.5SnO19, Sn atoms occupy the 12k and 4f2 sites with occupation probability of 54% and 46%, respectively. We also found that in SrFe11Zn0.5Sn0.5O19, (Zn,Sn) atom pairs prefer to occupy the (4f1, 4f2), (4f1, 12k) and (12k, 12k) sites with occupation probability of 82%, 8% and 6%, respectively. Our calculation shows that the increase of magnetization and the reduction of magnetic anisotropy in Zn-Sn substituted M-type strontium hexaferrite as observed experimentally is due to the occupation of (Zn,Sn) pairs at the (4f1, 4f2) sites.

I. INTRODUCTION

Hexagonal strontium hexaferrite SrFe12O19 (SFO), along with other M-type hexaferrites XFe12O19 (X = Sr, Ba, Pb), has large saturation magnetization, high coercivity, and excellent chemical stability [1–3]. Several experimental studies of substituted hexaferrite have been performed where magnetic properties are tailored to fit specific applications by the partial substitution of Fe in its crystallographic sites by divalent, trivalent, tetravalent, and divalent-tetravalent combination of metal atoms. The substitution of rare-earth elements such as Pr [4, 5], La [6, 7], Sm [8], and Nd [9] in M-type hexaferrite has shown to enhance the coercivity without much reduction in magnetization. Rare earth elements increase the spin-orbit coupling which in turn strengthen the magnetocrystalline anisotropy, hence the coercivity. However, reducing the use of rare-earth elements is highly desired for economical reasons. The substitution of Al leads to enhancement in coercivity [10, 11]. Wang et al. [12] have reported coercivity values as high as 17.6 kOe for Al-substituted strontium hexaferrite. Even higher values of coercivity (21.3 kOe) are possible by the double substitution of Ca and Al atoms [13], which is even higher than the coercivity of Nb-based magnets. The substitution of Fe by the trivalent metals such as Al, Ga, and Cr leads to an increase in coercivity and magnetocrystalline anisotropy (MAE) with reduction in magnetization [12]. In particular, the substitution of divalent-tetravalent pairs such as Zn-Nb [15], Zn-Sn [16, 19], and Sn-Mg [2] result in significant enhancement in saturation magnetization with rapid reduction in coercivity.

Theoretical studies on pure and substituted M-type hexaferrite have also been performed. Fang et al. investigated the electronic structure of strontium hexaferrite using density-functional theory (DFT) [20]. Park et al. have calculated the exchange interaction of strontium hexaferrite from the differences of the total energy of different collinear spin configurations [21]. Magnetism in La-substituted strontium hexaferrite has been studied using DFT [22, 23]. Zn-Sn substituted strontium hexaferrite has been studied by Liyanage et al. [24]. The site occupancy and magnetic properties of Al, In, and Ga-substituted strontium hexaferrite has been investigated by Dixit et al. [10, 25].

In this work, we used first-principles total-energy calculations to investigate the relationship between the site occupation and magnetic properties of substituted strontium hexaferrite, SrFe12−xMxO19 with M = Zn or Sn and SrFe12−2x(ZnSn)xO19 with x = 0.5. The Boltzmann distribution function was used to determine the formation probabilities of various configurations at a typical annealing temperature (1000 K) of strontium hexaferrite, which was further used to compute the weighted average of various magnetic properties. We show that our model predicts an increase of saturation magnetization as well as a decrease in magnetic anisotropy energy (MAE) of SrFe11(ZnSn)0.5O19 compared to the pure M-type SFO in good agreement with the experimental observations [19, 26].
SFO belongs to space group $P6_3/mmc$ (No. 194) and has a hexagonal magnetoplumbite crystal structure [27], whose double formula unit cell containing 64 atoms is shown in Fig. 1(a). The unit cell structure of SFO consists of ten oxygen layers and the Fe ions occupy five crystallographically inequivalent sites: three octahedral sites ($2a$, $12k$, and $4f_2$), one tetrahedral site ($4f_1$), and one trigonal bipyramid site ($2b$) as indicated by the coordination polyhedra in Fig. 1(a). As a ferrimagnetic material, SFO 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(b). First-principles total-energy calculations were performed to determine the site preference of Zn and Sn atoms in $M$-type Sr-hexaferrite. Total energies and forces were calculated using density-functional theory (DFT) with projector augmented wave (PAW) potentials as implemented in VASP [28, 29]. The exchange correlation effect was described using the Perdew-Burke-Ernzerhof (PBE) within generalized gradient approximation (GGA) [30]. All calculations were spin polarized according to the ground state ferrimagnetic ordering of Fe spins [20, 31]. Electronic wave functions were expanded in a plane-wave basis with an energy cutoff of 520 eV. Reciprocal space was sampled with a $7 \times 7 \times 1$ Monkhorst-Pack mesh [32] with a Fermi-level smearing of 0.2 eV applied through the Methfessel-Paxton method [33] for relaxations and the tetrahedron method [34] for static calculations. Full geometrical optimization was performed to relax the positions of ions, cell shape, and cell volume until the largest force component on any ion was less than 0.01 eV/Å. Since the on-site Coulomb interactions are particularly strong for localized d electrons, we employed GGA+U method in the simplified rotationally invariant approach in order to avoid the self-interaction error in localized electron state of Fe-3d [35]. Based on our previous study [24], $U_{\text{eff}}$ for Fe atoms was set to 3.7 eV. The $U_{\text{eff}}$ for Zn ($3d^{10}4s^2$), Sn ($5s^25p^2$), Sr ($5s^2$), and O ($2s^22p^2$) were set to zero. Drawings in Fig. 1 are produced using VESTA code [36].

The magnetic properties of SFO can be modified by substitution of foreign atoms for Fe. There are five crystallographic inequivalent Fe sites in SFO. When foreign atoms are substituted in a SFO unit cell, there can be several energetically different configurations. Due to the ferrimagnetic nature of SFO, the magnetization of substituted SFO strongly depends on site preference of the substituted atoms. In order to investigate the effect of substitution on the magnetic properties, it is imperative to understand site preference of substituted atoms. The site preference of the substituted atom can be determined by calculating the substitution energy. The substitution energy $E_{\text{sub}}[i]$ for configuration $i$ at 0 K is given by

\begin{equation}
E_{\text{sub}}[i] = E_{\text{SFXO}}[i] - E_{\text{SFO}} - \sum_{\alpha} n_{\alpha} \epsilon_{\alpha} \tag{1}
\end{equation}

where $E_{\text{SFXO}}[i]$ is the total energy per unit cell of substituted SFO in configuration $i$, while $E_{\text{SFO}}$ is the total energy per unit cell of pure SFO and $\epsilon_{\alpha}$ is the total energy per atom for element $\alpha$ ($\alpha = \text{Zn}, \text{Sn and Fe}$) in its most stable crystal structure. Zn belongs to space group $P6_3/mmc$ (No. 194) has a hexagonal crystal structure while Sn belongs to $Fd\bar{3}m$ (No. 227) with cubic crystal system. $\epsilon_{\text{Zn}}, \epsilon_{\text{Sn}}$, and $\epsilon_{\text{Fe}}$ were found to be $-0.789$ eV, $-3.835$ eV and $-8.461$ eV, respectively. $n_{\alpha}$ is the number of atoms of type $\alpha$ added or removed; if one atom is added then $n_{\alpha} = +1$ while $n_{\alpha} = -1$ when one atom is removed.

The magnetocrystalline anisotropy energy, $E_a$, was also calculated. $E_a$ in the present case, is defined as the difference between the two total energies where the spin quantization axes are aligned along two different directions [37]:

\begin{equation}
E_a = E_{(100)} - E_{(001)} \tag{2}
\end{equation}

where, $E_{(100)}$ is the total energy with spin quantization axis in the magnetically hard plane and $E_{(001)}$ is the total energy with spin quantization axis in the magnetically easy axis. The total energies in Eq. (2) are computed by the non-self-consistent calculations, where the spin densities are kept constant [38].
The uniaxial magnetic anisotropy constant, $K_1$, can be computed as [39, 40]:
\[
K_1 = \frac{E_a}{V \sin^2 \theta}
\]
(3)
where $V$ is the equilibrium volume of the unit cell, and $\theta$ is the angle between the two spin quantization axis orientations (90° in the present case). The anisotropy field, $H_a$, which is related to the coercivity can be expressed as [41]:
\[
H_a = \frac{2K_1}{M_s}
\]
(4)
where $K_1$ is the magneto-crystalline anisotropy constant and $M_s$ is the saturation magnetization.

When the separation between $E_{sub}$ of different configurations is not too big compared to the thermal energy during the synthesis of these hexaferrites at a high-annealing temperature ($\gtrsim 1000$ K), we can expect the site preference of substituted atoms to change at such an elevated temperature. This change in the site occupation preference can be modeled using Maxwell-Boltzmann distribution. The site occupation probability or the formation probability $P_i(T)$ of configuration $i$ at temperature $T$ is given by
\[
P_i(T) = \frac{g_i \exp(-\Delta G_i/k_BT)}{\sum_j g_j \exp(-\Delta G_j/k_BT)}
\]
(5)
where $\Delta G_i = \Delta E_i + P\Delta V_i - T\Delta S_i$
(6)
\[
\Delta S_i = k_B \ln(g_i) - k_B \ln(g_0)
\]
(7)
where $\Delta G_i$, $\Delta E_i$, $\Delta V_i$, and $\Delta S_i$ are the change in free energy, substitution energy, unit cell volume and entropy of the configuration $i$ relative to the ground state configuration. $P$, $k_B$ and $g_i$ are the pressure, Boltzmann constant and multiplicity of configuration $i$. $g_0$ is the multiplicity of the ground state configuration. In our earlier work, we considered $\Delta S_i$ to be the same for all configurations [12]. Eq. (7) improves the model by explicit calculation of change in entropy with respect to the most stable configuration [13].

Therefore, when the formation probability of higher energy configurations become non-negligible at the annealing temperature, it can be concluded that in a sample of substituted SFO there will not be a single configuration but a distribution of several configurations. Any physical quantity of a sample of SFO will then be a weighted average of respective quantity in different configurations:
\[
(Q) = \sum_i P_{1000K}(i) \cdot Q_i
\]
(8)
where $P_{1000K}(i)$ and $Q_i$ are the formation probability at 1000 K and a physical quantity $Q$ of the configuration $i$. During the annealing process when the material is maintained at high temperature, substituted atoms have sufficient energy to overcome the local energy barriers and acquire energetically the various configurations that have sufficient formation probability. We note that the substituted SFO considered in the present work loses its magnetic properties at a typical annealing temperature (1000 K or higher) that is near or above its Curie temperature. When the material is cooled down to a low temperature below the critical temperature, it regains the magnetic properties while the configurations are locked in those with higher substitution energy due to energy barriers between them. Consequently, the weighted average calculated by Eq. (8) is the material’s low temperature property even though $P_{1000K}$ is used for computation.

III. RESULTS AND DISCUSSION

In this work, two types of substitutions have been studied. In the first case one Zn or Sn atom was substituted in a SFO unit cell. In the second case, a pair of Zn and Sn atoms were substituted in a SFO unit cell. Although there are 24 Fe atoms in SFO unit cell, the application of crystallographic symmetry operations shows that many of these Fe sites are equivalent and leaves only five inequivalent sites. Therefore, one foreign atom can be substituted in five different ways, giving rise to five different configurations. We label these inequivalent configurations using the crystallographic name of the Fe site: [2a], [2b], [4f1], [4f2], and [12k]. $E_{sub}$ corresponding to the substitution of one Zn at different inequivalent Fe sites is given in Table I. The lowest $E_{sub}$ was found when a Zn atom was substituted at 4f1 site, followed by the [2a] and [12k] cases. For the case of a single Sn atom substitution (Table II) the lowest $E_{sub}$ was found to be for the substitution at the 4f2 site, and the second lowest $E_{sub}$ was corresponding to the substitution at the 12k site. A high multiplicity of the 12k site and low $E_{sub}$ indicate that at higher temperatures the 12k site is very likely to be occupied. In the second case, where a pair of Zn and Sn atoms were substituted in the SFO unit cell, there can be 5 x 5 = 25 different configurations. $E_{sub}$ corresponding to all these configurations are listed in Table III. The lowest $E_{sub}$ was found to be the configuration where Zn goes to the 4f1 while Sn occupies the 4f2 site.

Fig. 2 shows the variation of site occupation probability with temperature for the inequivalent configurations of SrFe_{12-x}Zn_xO_{19} with $x = 0.5$. In low temperature range the 4f1 site is the most likely to be occupied. However, as temperature rises this probability falls while the site occupation probability of 12k rises. This is due to small substitution energy difference between 4f1 and 12k sites and higher multiplicity of the 12k site. Similar behavior of site occupancy was seen in the case of single Sn atom substitution as shown in Fig. 3. In the elevated temperature regime, the site occupancy of the 4f2 falls, while that of the 12k site rises. In fact, at the annealing temperature of SFO (1000 K), the occupation prob-
### TABLE I. Physical properties of inequivalent configurations of SrFe$_{12-x}$Zn$_x$O$_{19}$ with $x = 0.5$: multiplicity ($g$), substitution energy ($E_{\text{sub}}$), volume of the unit cell ($V$), total magnetic moment ($m_{\text{tot}}$), saturation magnetization ($\sigma_s$), magnetocrystalline anisotropy energy ($E_m$), uniaxial magnetic anisotropy constant ($K_1$), anisotropy field ($H_a$), and the formation probability at 1000 K ($P_{1000K}$). All values are for a double formula unit cell containing 64 atoms.

| config | $g$ | $E_{\text{sub}}$ (eV) | $V$ (Å$^3$) | $m_{\text{tot}}$ ($\mu_B$) | $\sigma_s$ (emu/g) | $E_m$ (meV) | $K_1$ (kJ/m$^3$) | $H_a$ (kOe) | $P_{1000K}$ |
|--------|-----|----------------|--------------|-------------------------|------------------|--------------|----------------|--------------|-------------|
| [4f$_1$, 4f$_2$] | 16 | -5.326 | 717.32 | 50 | 127.13 | 0.70 | 156.35 | 4.72 | 0.819 |
| [2b, 4f$_1$, 4f$_2$] | 8 | -5.124 | 719.68 | 40 | 101.97 | 0.58 | 129.12 | 4.88 | 0.020 |
| [4f$_1$, 4f$_2$, 4f$_3$] | 12 | -5.065 | 716.49 | 40 | 101.68 | 0.82 | 183.36 | 6.91 | 0.010 |
| [2a, 4f$_1$, 4f$_2$] | 8 | -4.991 | 714.67 | 40 | 101.72 | 0.82 | 183.83 | 6.91 | 0.010 |
| [4f$_1$, 12k] | 48 | -4.940 | 717.54 | 40 | 101.72 | 0.83 | 136.21 | 5.14 | 0.014 |
| [12k, 2a] | 48 | -4.697 | 715.33 | 30 | 76.17 | 0.77 | 172.46 | 8.67 | 0.060 |
| [2a, 12k] | 24 | -4.663 | 717.04 | 40 | 101.58 | 0.63 | 140.77 | 5.32 | 0.003 |
| [4f$_1$, 2a] | 8 | -6.650 | 715.16 | 40 | 101.72 | 0.49 | 109.78 | 4.13 | 0.000 |
| [12k, 2a] | 24 | -4.366 | 718.08 | 30 | 76.17 | 0.71 | 158.42 | 7.99 | 0.000 |
| [2a, 2b, 12k] | 24 | -4.207 | 715.13 | 30 | 76.15 | 0.49 | 109.78 | 5.12 | 0.000 |
| [2a, 4f$_1$, 4f$_2$] | 8 | -4.206 | 714.79 | 40 | 101.68 | 0.90 | 210.73 | 7.59 | 0.000 |
| [2b, 4f$_1$, 4f$_2$, 4f$_3$] | 12 | -3.946 | 720.60 | 50 | 127.17 | 0.78 | 173.43 | 5.26 | 0.000 |
| [12k, 4f$_1$, 4f$_2$] | 48 | -3.932 | 717.21 | 40 | 101.59 | 0.84 | 187.67 | 7.09 | 0.000 |
| [4f$_1$, 4f$_2$, 4f$_3$, 4f$_4$] | 12 | -3.876 | 721.34 | 50 | 127.18 | 0.72 | 159.92 | 4.85 | 0.000 |
| [2a, 4f$_1$, 4f$_2$, 4f$_3$, 4f$_4$] | 4 | -3.726 | 717.56 | 30 | 76.58 | 0.79 | 176.39 | 8.83 | 0.000 |
| [2b, 2a] | 4 | -3.706 | 717.50 | 30 | 76.58 | 0.79 | 175.79 | 8.85 | 0.000 |
| [4f$_1$, 12k] | 48 | -3.586 | 723.09 | 40 | 101.86 | 0.75 | 166.12 | 6.31 | 0.000 |
| [4f$_2$, 2a] | 8 | -3.493 | 724.60 | 40 | 101.73 | 1.12 | 246.98 | 9.41 | 0.000 |
| [2b, 4f$_1$, 4f$_2$, 4f$_3$, 4f$_4$] | 8 | -3.297 | 722.28 | 40 | 101.83 | 0.68 | 150.84 | 5.73 | 0.000 |
| [2b, 2b] | 2 | -3.086 | 690.64 | 30 | 76.36 | 0.41 | 95.11 | 4.60 | 0.000 |
| [4f$_2$, 4f$_1$, 4f$_3$, 4f$_4$, 4f$_5$] | 16 | -3.073 | 723.67 | 50 | 127.21 | 0.78 | 172.69 | 5.26 | 0.000 |
FIG. 2. Temperature dependence of the formation probability of different configurations of SrFe_{11.5}Zn_{0.5}O_{19}. The configurations with negligible probability are not shown. The vertical dotted line indicates the annealing temperature of 1000 K.

ability of the 12k site (54%) becomes higher than that of the 4f₂ site (46%), which is the most energetically stable substitution site at 0 K. For the Zn-Sn substitution (SrFe_{11.5}Sn_{0.5}O_{19}), the formation probability of [4f₁, 4f₂] is high in the low as well as high temperature range. Other important configurations with significant formation probability at high temperature (1000 K) are [4f₁, 12k] and [12k, 12k] (Fig. 4). Substituted Zn atoms are most likely to occupy 4f₁ and 12k sites, while Sn atoms occupy 4f₂ and 12k sites.

The total magnetic moment $m_{\text{tot}}$ upon the substitution of a single Zn and Sn atom at various Fe site of SFO is given in Table I and Table II. It is evident that the substitution at the minority spin sites (4f₁ and 4f₂) enhances the net magnetic moment, while moment is reduced for the substitution at the majority spin sites (12k, 2a, and 2b). Similar changes in the total magnetic moment were also noticed for (SrFe_{11.5}Zn_{0.5}Sn_{0.5}O_{19} substitution (Table III). The saturation magnetization $\sigma_s$ values are also listed.

$E_a$, $K_1$, and $H_a$ of various configurations are presented in Table I, II, and III. In these cases, substitutions at 2a site seems to enhance the anisotropy values. Table III also that the reduction of magnetic coercivity in SrFe_{11.5}ZnSn_{0.5}O_{19} as experimentally observed [10] is mainly due to the occupation of (Zn,Sn) pair at the (4f₁, 4f₂) sites. Although the [2b, 4f₂] configuration, the one with second lowest substitution energy at 0 K, has much lower $K_1$ and $H_a$ values, its multiplicity is much lower compared to other low-energy configurations and its formation probability grows merely to 2% (compared to 82% for the [4f₁, 4f₂] configuration) even at 1000 K.

This is a different behavior from the related systems BaFe_{12−x}(Zr_{0.5}Zn_{0.5})_xO_{19} and LaZnFe_{11}O_{19}, where the 2b site plays the main role in the reduction of anisotropy [13, 25].

Table IV shows the weighted average of physical properties of pure and substituted (Zn, Sn, Zn-Sn) strontium hexaferrite based on the formation probabilities.
TABLE IV. Weighted averages of physical properties of pure and substituted (Zn, Sn, Zn-Sn) strontium hexaferrite: volume of the unit cell (V), total magnetic moment (m_{\text{tot}}), saturation magnetization (\sigma_s), magnetocrystalline anisotropy energy (E_a), uniaxial magnetic anisotropy constant (K_1), and anisotropy field (H_a).

| Material           | V (Å³)  | m_{\text{tot}} (μB) | \sigma_s (emu/g) | E_a (meV) | K_1 (kJ/m³) | H_a (kOe) |
|--------------------|---------|---------------------|------------------|-----------|-------------|-----------|
| SrFe_{12}O_{19}    | 706.83  | 39.0                | 110.19           | 0.85      | 193.00      | 7.35      |
| SrFe_{11.5}Zn_{0.5}O_{19} | 706.83  | 41.7                | 109.22           | 0.83      | 187.39      | 6.75      |
| SrFe_{11.5}Sn_{0.5}O_{19} | 718.61  | 39.7                | 101.34           | 0.75      | 168.05      | 6.52      |
| SrFe_{11}(ZnSn)_{0.5}O_{19} | 717.08  | 47.2                | 120.01           | 0.69      | 153.87      | 4.99      |

at the annealing temperature. In all three cases of substituted SFO, the m_{\text{tot}} was estimated to be greater than that of pure SFO. Biggest increase was found in the case of Zn-Sn pair substituted SFO. A reduction in the values of \sigma_s and anisotropy of SrFe_{11.5}Zn_{0.5}O_{19} and SrFe_{11.5}Sn_{0.5}O_{19} is in agreement with previous experimental studies on substituted barium hexaferrite [46, 47]. The saturation magnetization (\sigma_s) of SrFe_{11.5}Zn_{0.5}O_{19} and SrFe_{11}Zn_{0.5}Sn_{0.5}O_{19} were higher than that of pure SFO. In Table V we compare the magnetic properties of Zn-Sn pair substituted SFO in this work with previously reported computed and experimental data. Results from the present work show an increase of 8.2% in the value of \sigma_s, while Ghasemi et al. [18] experimentally observed a similar increase of 7.4%. Quantities related to magnetic anisotropy viz. K_1, and H_a showed reduction compared to pure SFO. SrFe_{11}Zn_{0.5}Sn_{0.5}O_{19} showed a reduction of 20% and 32% in K_1 and H_a, respectively, while experimentally Fang et al. observed a reduction of 25% and 33% in K_1 and H_a values [16]. Table V indicates that our present results are in better agreement with experimental results compared to the previous computed results that was obtained by considering the ground state configurations at 0 K only. Thus, our model based on the formation probability at the annealing temperature successfully explains the reduction in anisotropy of Zn-Sn substituted SFO as well as the increase in magnetization values.

TABLE V. Comparison of calculated and experimental magnetic properties of SrFe_{12−x}(ZnSn)_xO_{19} with x = 0 and x = 0.5: saturation magnetization (\sigma_s), uniaxial magnetic anisotropy constant (K_1), and anisotropy field (H_a). The calculated values are for 0 K while the experimental values are measured at the room temperature. Relative difference w.r.t. pure SFO (x = 0) values are given in parentheses.

| Property            | x = 0       | x = 0.5      | x = 0       | x = 0.5      |
|---------------------|-------------|--------------|-------------|--------------|
| \sigma_s (emu/g)    |             |              |             |              |
| Exp. [16, 18]       | 69.9        | 75.1 (+7.4%) | 280.9       | 210.7 (−25.0%)| 18.7        | 12.5 (−33.0%) |
| Calc. [This work]   | 110.2       | 120.0 (+8.2%)| 193.0       | 153.9 (−20.0%)| 7.4         | 5.0 (−32.0%)  |
| Calc. [24]          | 113.1       | 127.2 (+12.5%)| 190.0       | 100.0 (−47.4%)| 7.1         | 3.0 (−57.0%)  |
| K_1 (kJ/m³)         |             |              |             |              |
| x = 0               |             |              |             |              |
| Exp. [16, 18]       | 280.9       | 210.7 (−25.0%)| 18.7        | 12.5 (−33.0%)|
| Calc. [This work]   | 266.4       | 193.0        | 19.0        | 7.4          |
| Calc. [24]          | 267.5       | 195.1        | 19.1        | 7.5          |
| H_a (kOe)           |             |              |             |              |
| x = 0               |             |              |             |              |
| Exp. [16, 18]       | 18.7        | 12.5 (−33.0%)| 7.1         | 3.0 (−57.0%) |
| Calc. [This work]   | 19.0        | 15.5         | 7.5         | 4.0          |
| Calc. [24]          | 19.0        | 15.5         | 7.5         | 4.0          |

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IV. CONCLUSION

Using first-principles total energy calculations based on density functional theory, we calculated substitution energies of Zn, Sn, and Zn-Sn pair substituted strontium hexaferrite. These energy values were used to determine site preferences of the substituted atoms at 0 K as well as at a high annealing temperature. The site occupation probabilities or the formation probabilities of different configurations were then used to estimate magnetic properties of substituted SFO. We found that in SrFe_{11.5}Zn_{0.5}O_{19}, Zn atoms prefer to occupy 4f_1, 12k, and 2a sites with occupation probability of 78%, 19% and 3%, respectively, while in SrFe_{11.5}Sn_{0.5}O_{19}, Sn atoms occupy the 12k and 4f_2 sites with occupation probability of 54% and 46%, respectively. We further showed that in SrFe_{11}Zn_{0.5}Sn_{0.5}O_{19}, the pair of (Zn,Sn) atoms prefers to occupy the (4f_1, 4f_2), (4f_1, 12k) and (12k, 12k) sites with occupation probability of 82%, 8% and 6%, respectively. The results from our model based on the formation probability were found to be in good agreement with recent experimental observations showing enhancement of magnetization and the reduction in anisotropy for Zn-Sn substituted strontium hexaferrites.
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