Computational and experimental study on the cation distribution of La−Cu substituted barium hexaferrites

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ABSTRACT

The total energies and forces of the $Ba_{0.5}La_{0.5}Fe_{11.5}Cu_{0.5}O_{19}$ structure were calculated using the density functional theory (DFT) and generalized gradient approximation (GGA). The calculations demonstrated that at 0 K, the magnetic ions Cu^{2+} preferentially occupy Fe^{3+} at the $4f_2(0)$ and $4f_2(1)$ configurations. For the site occupancy at the higher temperature (0−1500 K, except 0 K), we computed the formation probability of twenty inequivalent configurations using the Maxwell−Boltzmann statistical distribution. Correspondingly, the Cu^{2+} ions prefer to enter the $4f_2$ and $2b$ sites, especially close to lanthanum layer. In order to confirm the computational conclusions, La−Cu substituted barium hexaferrites with the chemical formula of $Ba_{1-x}La_xFe_{12-x}Cu_xO_{19}$ ($x = 0.0, 0.1, 0.3,$ and 0.5), prepared by a conventional ceramic method, were investigated by the Raman spectra and Rietveld refinement of X-ray diffraction patterns (XRD). The experiments revealed that the Cu^{2+} ions are partitioned at the $2b$ and $4f_2$ sites in the ratio of around 1:2.

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1. Introduction

Barium hexaferrites [$BaFe_{12}O_{19}$, BaM] are of great interest for microwave magnetic devices, permanent magnets and magnetic recording materials in virtue of their fairly large magnetocrystalline anisotropy, high Curie temperature, and relatively large saturation magnetization [1,2]. The magnetoplumbite structure is described as RSR^*S^*, where $R = (Ba^{2+}Fe_6^{3+}O^{2-}_{11})^{2-}$ is a barium containing hexagonal block with three oxygen layers, and $S = (Fe_6^{3+}O^{2-}_8)^{2+}$ is a spinel block with only two layers: R^* and S^* are obtained from R and S blocks, respectively, by a rotation of 180° about c axis [3,4]. 24 Fe^{3+} ions of barium hexaferrites are distributed over five different sublattices: 3 parallel ($12k$, $2a$ and $2b$) sites and 2 antiparallel ($4f_1$ and $4f_2$) sites [5,6].

To improve the intrinsic magnetic properties of barium hexaferrites, many attempts have been made by doping on the Fe or Ba (Sr) sublattices, such as Al^{3+} [7], Cr^{3+} [8], $Mg^{2+}−Zr^{4+}$ [9], and $Mg^{2+}−Mn^{2+}−Co^{2+}−Ti^{4+}$ [10]. However, the substitutions of Al^{3+} and Cr^{3+} could bring the enhancement in the coercivity (H_c), along with the prominent decrease of the saturation magnetization (M_s). The $Mg^{2+}−Zr^{4+}$ and $Mg^{2+}−Mn^{2+}−Co^{2+}−Ti^{4+}$ substitutions could improve the M_s at the expense of the decrease of H_c. It was concluded that, for the substituted barium hexaferrites, quite generally either the M_s, or H_c, or both decrease until the reports of rare-earth-based representatives [11].

With respect to the rare-earth substitutions, Peng et al. [12] had prepared the $Sr_{1-x}La_xFe_{12-x}Co_xO_{19}$ ($x = 0−0.5$) samples using the microwave sintering method, and confirmed that both the specific saturation magnetization σ_s and the coercivity H_c have great improvements. Yang et al. [13] had reported that the H_c of the Sr−Ca−La−Co sintered ferrites could reach 300 kA/m with high remanent magnetic induction $B_r = 0.43T$. Based on the effects of Cu^{2+} introductions in NiZn ferrites, Qiao et al. [14] had adopted the self-propagating high-temperature synthesis (SHS) to investigate the magnetic properties of $Sr_{1-x}La_xFe_{12-x}Cu_xO_{19}$ ($x = 0−0.6$) samples. The results manifested that the improvements in B_r and H_c at $x = 0.3$ are 10% and 14%, respectively. All those improvements in intrinsic magnetic properties mainly stem from the modified site occupancy.

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There have been several investigations on the site occupancy of rare-earth substituted barium hexaferrites. Pieper et al. [11] had detected that, for La−Co substitutions, cobalt ions occupy $4f_1$ and $4f_2$ sites with nuclear magnetic resonance (NMR) at the low temperature. La occupying Ba had been widely confirmed by DFT [15,16] and Mössbauer spectrometry [17,18]. However, the mechanism on copper preferential site assignments still remains to be obscure and unreported [14].

Therefore, in this current work, we used the first-principle total-energy calculations to study the site occupancy of $Ba_{1-x}La_xFe_{12-x-}Cu_xO_{19}$ with $x = 0.5$, and then computed the formation probability of twenty inequivalent configurations at the elevated temperature. Based on the computational study, we prepared the $Ba_{1-x}La_x$-$Fe_{12-x}Cu_xO_{19}$ ($x = 0.0, 0.1, 0.3$ and 0.5) samples to investigate the cation distribution of La−Cu substituted barium hexaferrites by the Raman spectra and Rietveld refinement of X-ray diffraction patterns (XRD).

2. Experimental details

2.1. Computational details

The total energies and forces were calculated using the density-functional theory (DFT) with the Generalized Gradient Approximation (GGA) as parameterized by the Perdew−Burke−Ernzerhof (PBE) in VASP [19−21]. In structure optimization, we employed the Conjugate Gradient (CG) method to optimize the lattice parameters and the position of ions until the force on each ion was less than 0.03 eV/Å. The plane-wave cutoff energy and convergence criteria were 500 eV and 10^{-7} eV, respectively. The reciprocal space was sampled with an $11 \times 11 \times 1$ Monkhorst-Pack mesh [22]. All the calculations were spin polarized according to the Gorter's ferrimagnetic ordering of the magnetic moments [23]. For the structure of $Ba_{0.5}La_{0.5}Fe_{11.5}Cu_{0.5}O_{19}$ (BLFCO), La occupying Ba could break the symmetry of barium hexaferrites, and thus the twenty calculations on Cu occupying Fe are required. As shown in Fig. 1, Fig. 1(a) shows a unit cell of $BaLaFe_{12}O_{19}$ (BLFO), and Fig. 1(b) presents 20 inequivalent configurations of Cu occupying Fe.

To improve the description of strongly correlated $3d$ electrons of

Fig. 1. (a) A unit cell of $BaLaFe_{24}O_{38}$: Purple, red, blue, and gold spheres denote Ba, O, La, and Fe atoms, respectively; (b) A schematic diagram of twenty inequivalent configurations of Cu occupying Fe: the arrows represent the local magnetic moment at each atom site, and the $2a(0)$ and $2a(1)$ show the different configurations at the $2a$ site. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fe, the generalized gradient approximation with the Coulomb and exchange interaction effects (GGA + U) were employed, where an on-site potential is added to introduce intra-atomic interactions between the strongly correlated electrons [24]. We adopted the effective U value (U_{eff}) equal to the difference between the Hubbard parameter U and the exchange parameter J [25]. In this present work, the U_{eff} equal to 6.7 eV for Fe $3d$ electrons were considered on the basis of many rigorous calculations [16,26,27] of barium hexaferrites.

2.2. Experimental procedures

Barium hexaferrites with a composition of $Ba_{1-x}La_xFe_{12-x}Cu_xO_{19}$ ($x = 0.0, 0.1, 0.3$ and 0.5) were fabricated by a conventional ceramic method. The analytical-grade raw materials, $BaCO_3$, La_2O_3, CuO and Fe_2O_3 were weighed in stoichiometric proportion and mixed homogeneously in zirconia ball mills for 12 h. The slurries, after being dried, were calcined at 800 °C for 2 h and then second-milled with 3.0wt% Bi_2O_3 for 8 h. After being further dried at 90 °C, the powders were granulated, pressed and sintered at 980 °C (1253 K) for 2 h in air. The Raman scattering spectra was acquired using a Renishaw (New Mills, UK) inVia confocal micro-Raman spectroscopy. The X-ray diffraction (XRD) patterns were identified on Bruker D8 Advance X-ray diffractometer with Cu-Kα radiation, and then the Rietveld refinement of XRD patterns was done by GSAS software.

3. Results and discussion

For the optimized crystal structure of $BaFe_{12}O_{19}$, we obtained the lattice parameters $a = 5.886$ Å, and $c = 23.134$ Å in good agreement with the experimental values of $a = 5.891$ Å and $c = 23.091$ Å. In the case of $Ba_{0.5}La_{0.5}Fe_{11.5}Cu_{0.5}O_{19}$, the lattice parameters a and c were calculated to be 5.875 Å and 23.11 Å, respectively, where the deviations between the theoretical and experimental values are less than 1%. As known, the substitution energy of Cu in BLFCO is calculated by the following expression:

$$E_{sub} = E(BLFCO) - E(BFO) - \sum_\alpha n_\alpha \xi(\alpha) \tag{1}$$

where $E(BLFCO)$ and $E(BFO)$ are the total energy per unit cell at 0 K for BLFCO and BFO, respectively. $\xi(\alpha)$ is the total energy per atom for the element α (α = Ba, La, Cu, and Fe) at 0 K in its most stable crystal structure. n_α is the number of the atoms of the type α added or removed: if two atoms are added, then $n_\alpha = +2$ while $n_\alpha = -1$ when one atom is removed. In the BLFCO calculations, the $\sum n_\alpha \xi(\alpha)$ is equal to $E(Cu) + E(La) - E(Fe) - E(Ba)$, where $E(Cu)$, $E(La)$, $E(Fe)$, and $E(Ba)$ are the total energies per atom at 0 K for metallic Cu, La, Fe, and Ba, respectively. The configuration with the lowest energy E_{sub} is concluded to be the ground state configuration.

The variation of the substitution energies at the different Fe sites originates from their different chemical and structural environments. As shown in Table 1, the lowest E_{sub} is observed at the $4f_2(0)$ and $4f_2(1)$ configurations, and the followings are $2b(0)$, $4f_2(2)$, $4f_2(3)$, and $2b(1)$ configurations. Moreover, the configurations close to lanthanum layer (such as $4f_2(0)$, and $4f_2(1)$) pose the lower energies. Those calculation results could imply that at 0 K, the Cu^{2+} ions tends to occupy the $4f_2$ sites, especially close to lanthanum layer.

To understand the occupation preference of Cu at each Fe site at higher temperature, we computed the formation probability P_i of the configuration i using th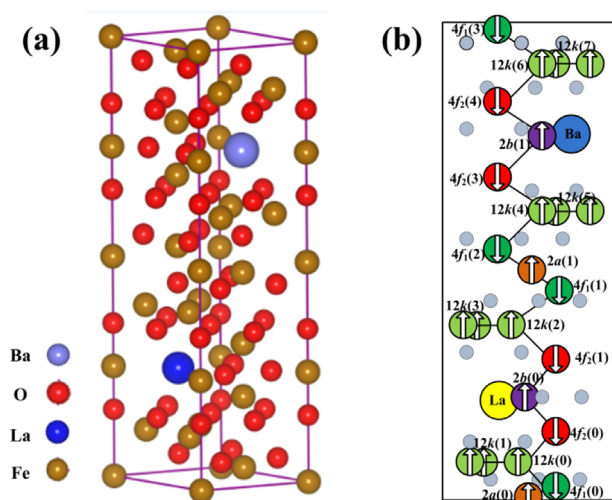e Maxwell−Boltzmann statistical distribution [28]: