

First-principle study of the electronic structures and optical properties of six typical hexaferrites



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ARTICLE INFO

Article history:

Received 23 January 2015

Received in revised form 13 April 2015

Accepted 16 April 2015

Available online 16 May 2015

Keywords:

Density functional theory

Hexaferrite

Electronic structure

Static dielectric constant

ABSTRACT

The structural, electronic and optical properties of hexagonal ferrites $MFe_{12}O_{19}$ ($M = Sr, Ba, Pb, Sr_{0.5}Ba_{0.5}, Sr_{0.5}Pb_{0.5}$ and $Ba_{0.5}Pb_{0.5}$) are calculated by plane-wave pseudopotential density functional theory with general gradient approximation (GGA) and GGA+ U . The calculated lattice constants and band gaps are in good agreement with the available experimental and theoretical values. Lattice constants change corresponding to the cation radii at M-sites. The electronic structure shows that all the six hexaferrites are narrow gap semiconductors and Sr^{2+} and Ba^{2+} at M-sites have little contribution to the DOS at the vicinity of Fermi level due to the ionic bond interaction nature between M^{2+} and O^{2-} . It should be noted that for Pb^{2+} , comparing with the narrow localized s-states of Sr^{2+} and Ba^{2+} , there is a significant broadening of its s-states from -7 eV to the Fermi level, indicating its minority donation to the valence band near E_f . The six MFOs (FO refers $Fe_{12}O_{19}$) could be classified into two categories: Pb-containing hexaferrites (PFO, SPFO and BPFO) and others (SFO, BFO and SBFO). The former has larger static dielectric constants. This study will serve as the base for the investigation of the correlation among factors such as site preferences, properties and substitution strategies for MFOs.

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1. Introduction

Hexaferrites $MFe_{12}O_{19}$ (acronym MFO, with $FO = Fe_{12}O_{19}$ and $M = Sr, Pb, Ba$) have been a subject of intensive study for several decades, owing to their intriguing physical and chemical properties such as large saturation magnetization, weak temperature dependent coercivity, excellent chemical stability and low cost [1,2]. Much attention is devoted to their applications in some commercial and military fields, such as electromagnetic wave absorbers, high-density magnetic recording media and microwave devices [3,4]. Attempts have been made to modify the electronic and magnetic properties by introducing impurities to substitute either M^{2+} or Fe^{3+} sites or both due to their complex magnetoplumbite (M-type) structure with mono-substitution and dual-substitution strategies. For mono-substitution, Fe^{3+} is usually replaced by Al^{3+} in order to obtain larger coercivity [5]. In the dual-substitution strategy, Fe–Fe pairs substituted by Zr–Cd [6], Er–Ni [7], Zn–Nb [8], Zn–Sn [9–11], Sn–Mg [12] Ti–Mg [13] and Ti–Co [13] pairs are investigated to tune saturation magnetization and coercivity

of hexaferrites. La–Co pair replacement of Sr–Fe pair is also reported [14–17]. Studies on M-type hexaferrites were mainly focused on experimental approaches to the material preparation, microstructure characterization and physical properties measurement. There are only limited publications of first principle study on the intrinsic electronic, optical and magnetic properties of hexaferrites. In an early work, Fang et al investigated the electronic and magnetic structure of SFO using density functional theory (DFT) method [18] and confirmed Gorter's prediction [19], that the most stable form of this hexaferrite is a ferrimagnet with Fe^{3+} in 4f1 and 4f2 sites having the spin polarization anti-parallel to the other Fe^{3+} cations. In 2005, Novak and coworkers group calculated the exchange interactions in BFO [20]. Recently, Feng et al investigated the magnetic anisotropy change of Co–Ti pair substituted SFO [21]. The site preferences for impurity cations in SFO and BFO were also studied using DFT method [11,22]. To our best knowledge, systematic study on electronic properties variation caused by the cations change at M-sites has not been reported, and theoretical analysis of how cations affect electronic, optical and magnetic properties in MFOs is still need. In this study, six typical hexaferrites MFOs ($M = Sr, Pb, Ba, Sr_{0.5}Ba_{0.5}, Sr_{0.5}Pb_{0.5}$ and $Ba_{0.5}Pb_{0.5}$) are selected as versatile precursors to explore the influence of geometrical, electronic and optical properties with the

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cations variation at M-sites. This work will be a basis for establishing the correlation between factors such as site occupancy preferences, properties and substitution strategies for MFOs, which paves the way toward the hexaferrites design for special applications.

2. Method

The calculations were performed within the framework of DFT, using the plane-wave basis-set and Vanderbilt-type ultrasoft pseudopotential [23]. The valence shells for Sr, Ba, Pb, Fe and O are $4s4p5s$, $5s5p6s$, $5d6s6p$, $3d4s$ and $2s2p$, respectively. The Perdew–Burke–Ernzerhof (PBE) parameterization utilizing generalized-gradient approximation (GGA) scheme was adopted to deal with the exchange–correlation interactions [24]. Since local approach (LDA) or GGA for exchange and correlation failed to correctly describe the band gap. In order to obtain an accurate electronic structure, a Coulomb correction of $U = 3.7$ eV in GGA+ U was implemented to overcome this well-known shortcoming. The parameter U was tested and we chose a value of convergence for the local magnetic moments in SFO, as explained in Section 3.2. A plane wave energy cutoff of 500 eV was applied, and Brillouin zone integration was performed over $5 \times 5 \times 1$ grid points using the Monkhorst–Pack scheme [25]. The convergence with respect to k -point density has been thoroughly checked. The lattice constant of SFO does not change with denser k points samplings such as $7 \times 7 \times 2$ and $10 \times 10 \times 2$. A denser k -point grid ($10 \times 10 \times 2$) decreased the total energy only 2.5 meV. Geometry optimizations were performed to fully relax the atomic internal coordinates (within the BFGS minimization algorithm [26]) and the lattice parameters till the total energy convergence of 1.0×10^{-6} eV per atom and residual force to 0.03 eV/Å. Using the electronic structure, we can get the linear optical properties, which are described by the complex dielectric function defined by

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 \quad (1)$$

where ε_1 and ε_2 are the real and imaginary components of the dielectric constant, respectively. The imaginary part is directly related to the electronic band structure and optical matrix elements, which can describe the absorptive behavior. By summing all possible transitions from occupied to unoccupied states, the interband contribution to the imaginary part can be calculated. In the simple dipole approximation, the imaginary part has the following expression:

$$\varepsilon_2(\omega) = \left(\frac{4\pi^2 e^2}{m^2 \omega^2} \right) \sum_{ij} \int_k \langle i|M|j \rangle^2 f_i(1-f_j) \times \delta(E_{j,k} - E_{i,k} - \omega) d^3k \quad (2)$$

where e is the charge of free electrons, m is the mass of free electrons, ω is the frequency of incident photons, i and j are the initial and final states, respectively, M is the dipole matrix, f_i is the Fermi distribution on the i -th states and $E_{i,k}$ is the electronic energy on i -th state with reciprocal crystal vector k . Summing over k is actually samples the whole region of Brillouin zone in the k space. Within the long wavelength limit, once ε_2 is calculated as a function of frequency, the real part ε_1 is derived out via Kramer–Kronig relationship [27]. Formula 1 and 2 show the ε_1 and ε_2 are the response of the incident light. In industrial applications, low-cost and reliable polycrystalline ferrites are used, hence in our calculation, only polycrystalline polarization is set for simplicity, where optical properties are averaged over all polarization directions as a fully isotropic average, thereby imitating an experiment on a polycrystalline sample. All the total energy calculations were performed in the reciprocal space using the Cambridge serial total energy package (CASTEP) code [28].

3. Results and discussion

3.1. The structures of MFO ($M = \text{Sr, Ba, Pb, Sr}_{0.5}\text{Ba}_{0.5}, \text{Sr}_{0.5}\text{Pb}_{0.5}$ and $\text{Ba}_{0.5}\text{Pb}_{0.5}$)

The crystal structure of hexaferrites belongs to the space group $P6_3/m$. The optimized geometry of SFO is shown in Fig. 1. The lattice parameters for SFO obtained in our DFT calculation are $a = 5.864$ and $c = 23.105$ Å which agrees fairly well with parameters measured experimentally ($a = 5.883$ and $c = 23.038$ Å) [29]. All the lattice parameters for the six optimized hexaferrites are listed in Table 1. The results show that BFO has the largest c , followed by PFO and SFO. It correlates with the effective radii of cations in M-sites (Ba^{2+} (135 pm) > Pb^{2+} (119 pm) > Sr^{2+} (118 pm)) [30]. Lattice constants from our DFT optimized BFO are also in good agreement with the experimental values [31], indicating our calculation method is reasonable and valid. The primitive cell has 11 inequivalent sites: one Sr site of multiplicity 2, five oxygen sites of multiplicity 4, 4, 6, 12 and 12 and five iron sites of multiplicity 2, 2, 4, 4 and 12, respectively. Based on their coordination with oxygen, the Fe^{3+} cations are positioned at five crystallographically different sites as shown in Fig. 1, namely 2a, 2b, 4f1, 4f2 and 12k. It is worth noting that in our calculation, we adopt the most stable spin configuration following Gorter's prediction [19] and Fang's calculation [18], that is, spin polarization of Fe^{3+} in 4f1 and 4f2 sites are opposite to that of the other Fe^{3+} cations. According to the previous reports, all the other spin configurations would cost at least 0.84 eV for BFO [22] and 1.44 eV for SFO [18], respectively.

3.2. The electronic properties of MFO ($M = \text{Sr, Ba, Pb, Sr}_{0.5}\text{Ba}_{0.5}, \text{Sr}_{0.5}\text{Pb}_{0.5}$ and $\text{Ba}_{0.5}\text{Pb}_{0.5}$)

As mentioned above, traditional DFT methods fail to obtain the accurate band gap in solid state physical calculations. Nowadays,

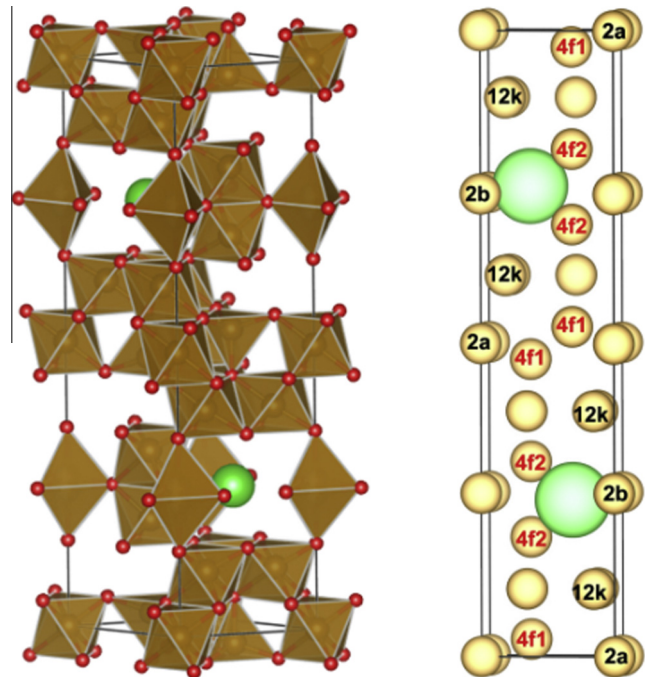


Fig. 1. Crystal structure of M-type hexaferrite. Red, brown and green colored spheres represent oxygen, iron and M atoms ($M = \text{Sr, Ba, and Pb}$). In the right graph, the spin directions for different Fe^{3+} at 2a, 2b, 12k, 4f1 and 4f2 are labeled with different colors (black and red). In order to make it clear, oxygen atoms are not displayed inside. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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