Magnetic Origin of Giant Magnetoelectricity in Doped Y-type Hexaferrite

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We investigated site-specific magnetic behaviors of multiferroic Ba0.5Sr1.5Zn2(Fe1−xAlx)12O22 using Fe L2,3-edge x-ray magnetic circular dichroism. The Al dopants mostly replace the Fe3+ ions at octahedral (O6) sites, which contribute unquenched angular momenta through off-centering displacements. This replacement greatly reduces the magnetic anisotropy energy to change the magnetic order from a helical to a heliconical type with enhanced magnetoelectric susceptibility (αME). The tetrahedral (T4) Fe sites exhibit magnetic hysteresis distinguishable from that of the O6 sites, especially at low magnetic fields. These results provide essential clues for the heliconical order with a giant αME and multibit memory effects in the Al-doped Y-type hexaferrite.

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Multiferroic materials, in which magnetism and ferroelectricity coexist with a cross coupling, the so-called magnetoelectric (ME) effect, have been intensively studied experimentally and theoretically over the past decade due to their potential technological applications as next-generation multibit memory devices [1–3]. The ME effect was demonstrated in various multiferroic materials such as chromates, manganites, ferrites, etc. [1–6], and spiral, cycloidal, or noncollinear helical magnetic orders were known to be essential for a large ME effect [7–11]. Multiferroicity is well explained by an inverse Dzyaloshinskii-Moriya interaction [12,13] or a spin-current model [14]. However, most of the materials were recognized to face the difficulty of application barriers due to the low ME response, low ME temperature, and/or the requirement of a high magnetic field. Recently, hexaferrites with several different types have attracted much attention as candidates for possible multiferroic application materials with a giant ME susceptibility (αME) at a relatively high temperature [4,15–17], and even nonvolatile multistate behaviors were demonstrated at room temperature [18]. Particularly in Y-type hexaferrites (Ba, Sr)2Zn3Fe12O22, small Al doping greatly enhances αME at a low magnetic field [16].

Y-type hexaferrites Ba0.5Sr1.5Zn2(Fe1−xAlx)12O22 are crystallized in a stacked hexagonal structure at a R3m space group [19,20] with spinel structured blocks consisting of octahedral (O6) and tetrahedral (T4) Fe sites as shown in Fig. 1(a). The magnetic structure is conventionally described in terms of alternative stacked L and S blocks with large and small magnetic moments, respectively [4,20]. The magnetic ordering temperatures were reported to be 337 K for x = 0.00 and 263 K for x = 0.08 [16]. The spin structures are schematically depicted in Fig. 1(b). For x = 0.00, both L and S block spins are aligned in a helical order under an in-plane magnetic field H∥ab (~1 T) [20]. The ferroelectricity was

FIG. 1 (color online). (a) Crystal structure of Y-type hexaferrite. (b) Spin structures of Ba0.5Sr1.5Zn2(Fe1−xAlx)12O22 for x = 0.00 and 0.08 at H = 6000 Oe. (c) M vs H curves.
proposed to be induced by an inversion symmetry breaking [4]. Meanwhile, for $x = 0.08$, the spin order changes into a helicalon type with a certain $c$-direction magnetic component in the $S$ block under $H_{\parallel ab}$ [16, 21, 22]. The cone-shaped spin blocks lead ferroelectricity with a greatly enhanced $\alpha_{ME}$ through the spin-current mechanism katsura. The change in the spin structure was attributed to reduction of the in-plane magnetic anisotropy energy [15–17]. Indeed, the difference between the in-plane and out-of-plane magnetizations decreases with the doping in a 0.1–1 T region as shown in Fig. 1(c). Moreover, one can also recognize a certain in-plane remanent magnetization for $x = 0.08$, which is essential for multi-bit memory device applications [15, 18].

In this Letter, we performed x-ray magnetic circular dichroism (XMCD) measurements on the Y-type hexaferrites $\text{Ba}_{0.5}\text{Sr}_{1-x}\text{Zn}_2(\text{Fe}_{1-x}\text{Al}_x)_{12}\text{O}_{32}$ ($x = 0.00, 0.08$) to explore a microscopic origin for the changes in the magnetic behavior with the doping and to find out a clue for the remanent magnetization. The results show unquenched orbital magnetic moments for both $x = 0.00$ and 0.08. The orbital moment $m_o$, which is mostly induced from off-centered octahedral ($O_h$) Fe sites, is reduced with the doping, resulting in a decrease of the in-plane magnetic anisotropy energy to change the spin structure with a largely enhanced $\alpha_{ME}$. We also determined site-specific magnetic hystereses for the $O_h$ and $T_d$ Fe sites. The $T_d$ site hysteric behavior is distinguishable from that of the $O_h$ site with Al doping and originates a certain increase of remanent magnetization for the multistate behavior.

$\text{Ba}_{0.5}\text{Sr}_{1-x}\text{Zn}_2(\text{Fe}_{1-x}\text{Al}_x)_{12}\text{O}_{32}$ ($x = 0.00, 0.08$) single crystals were grown by a flux method. Samples were cleaved in situ in a vacuum better than $5 \times 10^{-10}$ Torr. XMCD measurements were performed at the 2A soft x-ray elliptically polarized undulator beam line in Pohang Light Source. The results were obtained at 80 K with ~95% circularly polarized light. A 0.5 T electromagnet was used for magnetization switching, the photon incident angle is 22.5° off from the $H$ direction ($H || c$ or $H || ab$), and XMCD spectra were collected in the total electron yield mode. The magnetization data were obtained by using a Quantum Design physical property measurement system.

To explore magnetic anisotropy of the system, we performed Fe $L_{2,3}$-edge XMCD measurements. The net spin moment direction was flipped to be parallel ($\rho_+$) and antiparallel ($\rho_-$) to the photon helicity vector at each data point. The spectra were averaged over right and left helicities to minimize artificial effects. Figures 2(a) and 2(b) present the results of the absorption spectra ($\rho_+$ and $\rho_-$), dichroisms ($\Delta \rho = \rho_+ - \rho_-$), and integrations $\int (\Delta \rho) dE$ of the undoped ($x = 0.00$) and Al-doped ($x = 0.08$) samples, respectively. The degree of circular polarization and the geometry factor were taken into account in the spectra. The spectra are roughly divided into the $L_3$ ($2p_{3/2}$) and $L_2$ ($2p_{1/2}$) regions. The integrations over $L_3$ and entire $L_{2,3}$ regions are presented with $p$ and $q$, which are roughly proportional to the spin and orbital magnetic moments $m_s$ and $m_o$, respectively [23]. The obtained $p$ values are consistent with the magnetizations at 80 K under $H = 6000$ Oe. Using the sum rule [23], we estimated the orbital to spin moment ratio $m_o/m_s = 2q/(9p - 6q) = -0.018$ for $H || ab$ ($H_a$) and $m_o/m_s = +0.0046$ for $H || c$ ($H_c$). As the spins are fully aligned (eight up- and four down-spin Fe$^{3+}$ ions) [4, 20], the ionic magnetic moment becomes $20 \mu_B$/f.u. (~10% larger than the saturated moment $M_s$ at 10 K), and $m_o = -0.38 \mu_B$/f.u. for $H_a$ and $m_o = +0.09 \mu_B$/f.u. for $H_c$, resulting in in-plane magnetic anisotropy. There exist only half-filled Fe$^{3+}$ ($L = 0$, $S = 5/2$) ions, and off-centering displacements can be considered as the origin of the nonvanishing $m_o$ as discussed in GaFeO$_3$ [24]. Indeed, one can find the off-centering distortions in the Y-type hexaferrite [19, 25].

![Figure 2](image-url)
Figure 2(c) shows the arrangement of (Fe,Zn)O₄ (Td) and FeO₆ (Oh) polyhedra in the undoped hexaferrite with four Td sites (brown) and ten Oh sites per formula unit (f.u.). The Oh sites are classified into three different groups presented with three different colors (two red, six violet, and two blue Oh sites) in the figure. The Td sites are distributed with two Zn²⁺ and two Fe³⁺ ions, while all the Oh sites are occupied by Fe³⁺ ions. The L block contains two Td sites (≈0.67 Fe³⁺) and nine Oh sites (two reds, six violets, and one blue), and the S block has two Td sites (≈1.33 Fe³⁺) and one Oh site (blue) [20,26]. The spin directions are presented with black arrows for H_ab. A large off-centering displacement occurs along the c axis at the red Oh site, while at the violet Oh site a small off-centering displacement does both along the c axis and in the ab plane, as depicted with thick arrows in Fig. 2(d). The off-centering is negligible at the Td and blue Oh sites. The shortest to average Fe-O bond length ratio within an FeO₆ octahedron is 0.93 for the red and 0.98 for the violet [25], indicating that the obtained in-plane m_o = −0.38μB/f.u. mostly comes from the two red sites. The magnitude of m_o is comparable to that of GaFeO₃ with the ratio of 0.92 [24,27]. Considering that the orbital angular momentum is parallel to the spin momentum in an Fe³⁺ [24], its negative sign results from the red site spin direction opposite to the net M direction. Meanwhile, a smaller out-of-plane m_o = +0.09μB/f.u. is mainly from the six violet sites with the spin direction parallel to the M direction.

The Al doping largely reduces the in-plane magnetic anisotropy. For x = 0.08, the ratio was obtained to be m_o/m_s = −0.013 under H_ab = 6000 Oe and m_o/m_s = +0.0044 under H_c = 6000 Oe from the XMCD results. The Al dopants were known to mostly replace the Oh sites [16]. By supposing that those are uniformly distributed only at the Oh sites, the ionic magnetic moment becomes 17.1μB/f.u., and m_o = −0.22μB/f.u. for H_ab and m_o = +0.06μB/f.u. for H_c, resulting in about 40% reduction in the magnetic anisotropy energy. This reduction is responsible for the spin structure change from a helical to a heliconical order [Fig. 1(b)]. One may notice that the reduction in m_o is rather large in comparison with the 0.08 doping rate, which increases up to 9.6% in average under the assumption of all Al dopants at the Oh sites. This large reduction can be attributed to two factors: (i) a certain decrease of the off-centering displacement with a reduction of the c lattice constant and (ii) a preference of the Al replacement for the red Oh site [28]. A recent nuclear magnetic resonance study reported that the Al replacement rate at the off-centered Oh site (red) is considerably larger than the rate at the other Oh sites (violet and blue) [29].

Besides the variations in m_o/m_s, the MCD spectral line shape also varies with the H-field direction and the Al doping. To extract information on the magnetic ordered states, we analyzed the line shapes by using cluster model calculations with full atomic multiplets and configuration interactions, the so-called CI calculations [30]. The calculated MCD spectra for FeO₆ (Oh) and FeO₄ (Td) are extracted by fitting the MCD spectrum of a ferrimagnet γ-Fe₂O₃ [31], in which the Oh and Td Fe³⁺ spins are antiferromagnetically ordered with a 5:3 ratio. In the calculations, the sign results from the red site spin direction opposite to the best fits were obtained with the ratios of 2.3:−1 and 2.7:−1 for the H_ab and H_c, respectively. For the H_ab, the spin structure has a helical order with an in-plane tilting angle ϕ of the L block spin, the so-called intermediate-II phase [4,20], and ϕ = 78° is estimated from the ratio 2.3:−1 and M ≈ 15μB/f.u. (76% of M_s = 17μB at 80 K). Meanwhile, H_c tilts the spins to the c direction and produces a conical order. Considering M ≈ 0.48M_s at 80 K, the cone angles are estimated to be α = 61° for the L block spin and the angle δ = 53° for the S block spin. In both spin structures by H_ab and H_c, the angle between the L and S block spins is nearly maintained to be ~140°.

In the x = 0.08 case (Al doped), the spin structure becomes a heliconical order with a cone angle β for H_ab. The MCD ratio is estimated to be 2.8:−1, which gives a maximum spin moment 16.5μB/f.u. [a net moment of 5.6 × m_o(Oh) minus 2 × m_o(Td)]. This value is consistent with the observed M_s = 16.2μB/f.u., which results in the maximum spin moment 16.4μB/f.u. with m_o/m_s = −0.013. The cone angle is estimated to be β = 48° at H_ab = 6000 Oe from M = 0.67M_s at 80 K. For H_c = 6000 Oe, the spin structure becomes the conical order again [see Fig. 3(d)]. The cone angles γ ≈ 67° and γ′ ≈ 75° were estimated from the Oh to Td ratio of 3.5:−1 and M = 0.41M_s at 80 K. The angle between the L and S block spins reduces to ~120°.

The L₃ MCD line shape shown in Fig. 4(a) presents typical Oh-Td Fe³⁺ ferrimagnet features o, t, and o′ resulting from a ferrimagnetic order of a large Oh site spin and a small Td site spin, as in γ-Fe₂O₃ [24]; the features o and o′ are due to the Oh site up spin, and t is due to the Td site down spin as can be seen in Fig. 3. Thus, we
could obtain the site-specific magnetic hysteresis curves by monitoring the MCD peak intensity of each feature as a function of the \( H \) field. Figures 4(b) and 4(c) show the \( H\parallel ab \) and \( H\parallel c \) magnetic hysteresis curves of the MCD features for \( x = 0.00 \) and \( x = 0.08 \), respectively. In the \( x = 0.00 \) case, all three features display nearly identical hysteresis behaviors for both \( H_{ab} \) and \( H_{c} \), which coincide with one another with normalization factors corresponding to their different MCD intensities. Meanwhile, in the Al-doped \( x = 0.08 \) case, the hystereses for the features \( o \) and \( o' \), which are nearly identical to each other, are somewhat distinguishable from that for the feature \( t \), especially in the low field region \(-0.1 \text{T} < H < 0.1 \text{T} \), indicating that the magnetic response of the \( O_h \) site spin is different from that of the \( T_d \) site spin.

The magnetic hystereses for the \( O_h \) and \( T_d \) site spins can be extracted by taking into account their MCD contributions at the specific photon energies of features \( o \), \( o' \), and \( t \) obtained from the CI calculation fits as presented in Fig. 3. Figures 4(d) and 4(e) show the normalized site-specific magnetic hystereses for \( H\parallel ab \) and \( H\parallel c \), respectively. Effective summations of these site-specific hystereses well reproduce the observed \( M-H \) curves presented in Fig. 1(c) [31]. For \( H\parallel ab \), the \( T_d \) site has slightly larger values in the remanent ratio and coercive field, although its overall hysteresis behavior is similar to that of the \( O_h \) site. On the other hand, the difference in the hysteresis behavior becomes more remarkable for \( H\parallel c \) with much larger values in the ratio and field at the \( T_d \) site. The nonmagnetic Al dopants, which mostly replace the \( O_h \) sites, may loosen the magnetic exchange coupling of the neighboring \( T_d \) site Fe spins to the \( O_h \) site spins to make the magnetic behavior of the \( T_d \) site separated from that of the \( O_h \) site at the low magnetic field. This separated spin behavior may cause the change of the spin structure from helical to heliconical in the low field region in cooperation with the reduced in-plane magnetic anisotropy energy. As a result, the Al doping largely enhances the low field \( \alpha_{ME} \) and increases the remanent magnetization, which is essential for the multibit memory effects demonstrated in the multiferroic hexaferrites [18].

In summary, we reported detailed studies of magnetic origins for improved magnetoelastic effects in the doped Y-type hexaferrite \( \text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_{2}(\text{Fe}_{1-x}\text{Al}_x)_{12}\text{O}_{22} \) \( (x = 0.00) \). \( \beta \), \( \gamma \), and \( \delta \) MCD intensities of the three features as a function of \( H \) for \( (a) x = 0.00 \) and \( (c) x = 0.08 \). Here, the MCD intensity at the feature \( \ell \) is flipped for convenience. \( \alpha \) Normalized site-specific magnetic hystereses of the \( O_h \) and \( T_d \) sites determined from effective summations of the \( H \)-dependent MCD intensities.
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From the reduction value in the saturation magnetic moment with the 8% doping, the replacement rate at the red $O_h$ sites is estimated to be about 70% larger than the rates at other $O_h$ sites.