Anisotropic spin-driven ferroelectricity and magnetoelectric effect in a Y-type hexaferrite

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ABSTRACT

We report a systematic study on the magnetic, dielectric, and magnetoelectric (ME) properties of the Y-type hexaferrite (Ba0.4Sr1.6)Zn2(Fe11.3Al0.7)O22 single crystal. The phase diagrams were established by the observed magnetic anomalies under magnetic field and temperature scans for the in-plane and out-of-plane cases. Intrinsic large anisotropy in the magnetodielectric and converse ME effects were revealed. The spin-driven electric polarizations induced in the ab-plane and out-of-plane were found to be closely related to the transverse conical and alternating longitudinal conical spin structures, respectively. The amplitudes of varied magnetization ΔM are about ~0.128 μB/f.u and ~0.0178 μB/f.u. in the E oscillating between ±1 MV/m at 100 K, corresponding to the converse ME effect coefficient of ~3500 ps/m and ~480 ps/m for the in-plane and out-of-plane cases, respectively. All these results demonstrate the essential and unique spin-order-induced anisotropic ferroelectricity and ME properties in these Y-type hexaferrites.

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Multiferroicity and magnetoelectric (ME) effects are significant topics in materials science due to their great application potential in next-generation memory and novel spintronic devices.1–3 Spin-driven multiferroics, in which the ferroelectricity originates from broken space inversion symmetry, have attracted intensive interest due to their strong coupling and giant ME effect.4,5 In the past several decades, some spiral multiferroic magnets, such as TbMnO3,6 DyMn2O5,7 Sm2BaCuO5,8 Ca3(Co,Mn)2O6,9 and Fe2Mo3O8,10 were reported. Multiferroics with helical spin order are the most promising candidates for high T and/or low H modulated multiferroics.11–23 Y-type hexaferrites are the most widely studied compounds, which have a general chemical formula of Ba xSr2−xMe2Fe12O33 (Me = Co2+, Zn2+, Ni2+, etc.) with a space group of R-3m.16–23 As shown in Fig. 1(a), the magnetic structure can be described as an alternate stacking of large (L) and small (S) spin blocks along the [001] direction. The spins (Fe3+ and Me2+) in each block are known to be ferrimagnetically aligned and yield a large magnetic moment μL on the L block and a small moment μS on the S block.20 The spin configurations in Y-type hexaferrites are complex, as marked in Figs. 1(b)–1(c), which greatly depend on the temperature and magnetic field.21,22 Considering the strong magnetic anisotropies in each block and magnetic frustration at the block boundaries, a helical or conical spin order with a magnetic wavevector k along the c-axis tends to develop.20 It was suggested that these longitudinal conical (LC) spin configurations are paraelectric (PE) without breaking the centro-symmetry. Once an ab-plane magnetic field (Hab) is applied, the LC spin configuration will be driven into the so-called commensurate transverse conical (TC) phase [Fig. 1(c)]. Consequently, a ferroelectric (FE) polarization would be induced with the ab-plane polarizations Pab ⊥ Hab in terms of the spin-current model or inverse Dzyaloshinskii–Moriya (iDM) interaction: P ∝ ∑ k × (μi × μj), where μi and μj are the neighbor magnetic moments at the lattice sites.24,25 The ferroelectric polarization Pab was reported in many hexaferrites, such as Sr3Co2Fe24O4112 and Ba2Mg2Fe12O22.19
Actually, there exist two distinct types of LC spin structures, as confirmed in a Y-type Ba$_{0.4}$Sr$_{1.6}$Zn$_2$(Fe$_{11.3}$Al$_{0.7}$)O$_{22}$ crystal by neutron diffraction [10]: one is the normal longitudinal conical (NLC) spin configuration [Fig. 1(b)], i.e., ferrimagnetically aligned magnetic moments along the c-axis and the other is the alternating longitudinal conical (ALC) spin configuration [Fig. 1(d)], i.e., [111] magnetic arrangement along the c-axis. Considering the ferroelectric mechanism of symmetric exchange striction (SES): $P \propto \sum_{i}^{N} \mu_i \mu_j^* \Delta$ an out-of-plane electric polarization ($P_\perp$) might occur in the ALC phase. For instance, Shen et al. [28] reported this novel spin-induced ferroelectricity in a Ba$_{0.4}$Sr$_{1.6}$Zn$_2$(Fe$_{11.3}$Al$_{0.7}$)O$_{22}$ crystal. However, the electric polarization $P_\perp$ is scarcely reported. Considering that Y-type hexaferrites are strong magnetically anisotropic, it will be expected that this spin-induced ferroelectricity that originated from different mechanisms might exist simultaneously in a Y-type hexaferrite. Unfortunately, the anisotropic multiferroicity with different ferroelectric origins is scarcely reported in a single-phase material.

Under this motivation, in this paper, an intriguing example of anisotropic ferroelectricity induced by the two different mechanisms is explored in a Y-type hexaferrite (Ba$_0.3$Sr$_{1.7}$Co$_2$Fe$_{11.3}$Al$_{0.7}$)O$_{22}$ (BSZFAO) with a peculiar conical spin structure. Its structure, magnetization, magnetodielectric, and ME effect are systematically investigated. The magnetic phase diagrams for the in-plane and out-of-plane, respectively, are established. The TC spin state exits below 165 K for the ab-plane, while it is the ALC spin state for the out-of-plane around 50–150 K at low $H_c$, corresponding to the in-plane and out-of-plane polarizations, respectively. A large anisotropy in the magnetodielectric is observed. Most importantly, the anisotropic converse ME effect between the in-plane and out-of-plane is confirmed by measuring the $M$ controlled by $E$.

In our experiment, a single crystal of Y-type hexaferrite (Ba$_0.3$Sr$_{1.7}$Co$_2$Fe$_{11.3}$Al$_{0.7}$)O$_{22}$ (BSZFAO) was prepared using the Na$_2$O–Fe$_2$O$_3$ flux method in air. The detailed preparation process could be found in previous reports [18,20]. To reduce the oxygen vacancy and enhance the resistivity, the as-grown crystal was annealed at 900 °C under an O$_2$ atmosphere for 8 days [20]. The X-ray diffraction (XRD), energy dispersive spectrometer (EDS) and X-ray photoelectron spectroscopy (XPS) analysis, as shown in Figs. S1–S3, supplementary material, respectively, revealed the high quality and normal composition of our crystals. Finally, the crystal was cut into thin plates along the (120) and (001) planes in the hexagonal setting.

The magnetization ($M$) as a function of temperature ($T$) and/or magnetic field ($H$) was measured using a vibrating sample magnetometer (VSM) integrated with a Physical Property Measurement System (PPMS). For electrical measurements, Au electrodes were deposited on the parallel end surfaces of the two cut samples. The dielectric constant and converse ME effects were measured by a LCR meter (Agilent, 4980A) and a homemade sample holder, respectively, in the PPMS system.

Figures 2(a) and 2(b) display the T dependence of $M$ of the crystal at $H = 100$ Oe for applying $H$ perpendicular and parallel to the c-axis, respectively. For the H//c-axis case, the $M(T)$ curve exhibits two clear anomalies around $T_1 \sim 50$ K and $T_2 \sim 220$ K. The former experiences a broadened bump and the latter undergoes a rapid increase. Meanwhile, a small jump at $T_2 \sim 165$ K can be observed. Based on the early neutron diffraction results reported on Y-type hexaferrites [22,26], the anomaly at $T_1$ marks a typical magnetic transition from the NLC to ALC phase. The jump at $T_2$ indicates a transition from ALC to a proper screw (P-S) phase [Fig. 1(d)] and the anomaly at $T_3$ corresponds to a transition from P-S to the collinear ferrimagnetic phase [25]. While for the $H \perp$ c-axis case, the $M(T)$ behavior is significantly different: one is that the amplitude of $M$ is much higher in the low T region ($<T_2$) but lower at high-T ($>T_2$) compared with the H//c-axis case, implying a significant magnetic anisotropy. Another is that $M$ undergoes an abrupt change at $T_2 \sim 165$ K. It was suggested that a giant bump can be observed near $T_1$, corresponding to a transition from the ALC to TC phase. The abrupt drop at $T_3$ means that the TC state is no longer stable and likely changed to a P-S phase [17]. The detailed magnetic phase transformations are indicated correspondingly in Figs. 2(a) and 2(b). Similar features were extensively illustrated in other Y-type hexaferrites [17,26,29]. To further verify the phase transition temperature, the specific heat capacity ($C_p$) of our Y-type crystal was measured, and the result is shown in Fig. S4, supplementary material. It is noted that no evident $\lambda$-type peak, corresponding to the magnetic structure transition, is identified during T ranging from 10 K to 300 K. The reason might be attributed to two aspects: one is that the phonon and magnon coupling in the Y-type hexaferrite are non-sensitive to the heat transport although the magnetic structures could be definitely clarified by a neutron diffraction technique [19,25,30]. Another is that the contribution of the magnon self-interaction to the heat capacity can be overwhelmed by the electron–phonon interaction in the Y-type BSZFAO hexaferrite.

The evolutions of $M(T)$ behaviors of our crystal under different H are illustrated in Figs. 2(c) and 2(d) for $H//c$ and H//c configurations, respectively. As shown in Fig. 2(c) for $H//c$, it can be seen with increasing $H$ that $T_1$ is gradually suppressed and shifted toward the lower T region and disappeared until $H//c \sim 0.5$ T. This means the ALC phase gradually disappears and finally transforms into the TC phase by applying $H//c$. However, $T_3$ is gradually shifted toward the higher T region. As for $H//c$, as displayed in Fig. 2(d), these critical temperatures ($T_1$, $T_2$ and $T_3$, marked by the arrows) remain identifiable at $H//c \leq 0.5$ T, in which $T_1$ moves toward higher T upon increasing $H$. This indicates that the ALC phase is more likely transformed into the NLC phase under a low $H//c$ and completely disappears once $H//c > 0.5$ T.
Figures 2(e) and 2(f) show the $H$ dependence of $M$ measured at different $T$ for $H\perp c$ and $H//c$, respectively. As for $H\perp c$, $M$ first abruptly increases, and linearly ascends, and finally gets saturated in the low-$T$ region ($\leq 100$ K). This feature of two-step saturation is attributed to the successive evolution of the TC phase. It is worth mentioning that a hysteresis loop can be seen at the very low $H_{c1}$, as shown in the inset of Fig. 2(e). Such loops are probably caused by a kind of weak ferromagnetism due to spin transition between ALC and TC phases. Once $T$ goes above 100 K, the abrupt increase at low $H_{c1}$ is absent, corresponding to the magnetic structure transition from the TC to P-S phase. It is noted that the saturation $H$ presents a shifting toward a lower level upon increasing $T$. Finally, only the linear $M(H)$ curve can be observed at high $T$ ($> 300$ K), implying the appearance of a simple planar ferrimagnet structure. As for $H//c$ [Fig. 2(f)], $M$ increases gradually up to saturation in the low $T$ region ($\leq 200$ K). An abruptly increased step at the very low $H_{c1}$ is presented at $T = 200$ K, as shown in the inset of Fig. 2(f). This change of $M(H)$ shape means a significant magnetic structure transition from the ALC structure to the NLC structure. According to the magnetic anomalies under $T$ and $H$, we summarize its $H$–$T$ phase diagrams in Figs. 3(a) and 3(b) for $H\perp c$ and $H//c$, respectively. It is found in the $H\perp c$-axis that the TC phase always exists below $T_2$ and the ALC phase could be transitioned into the TC phase under a sweeping process of low $H_{c1}$ while the ALC phase in the $H//c$-axis case is confined to the small magnetic field ($H_c < 0.5$ T) between $T_1$ and $T_2$. A significant discrepancy between the two phase diagrams further verifies the large anisotropy in spin ordering. It is noted that the non-continuous phase boundaries (dot lines) are owing to the absence of well-defined anomalies in estimating the transition points.

To verify the nature of spin-driven ferroelectricity, we measured the in-plane ($H/[100]$ and $E/[120]$) and out-of-plane ($H/E/[001]$) magnetoelectric properties at different $T$. As for the in-plane case, the relative change of the dielectric constant, $\Delta \varepsilon(H)/\varepsilon(10$ kOe) = $[\varepsilon(H) - \varepsilon(10$ kOe)]/\varepsilon(10$ kOe), is shown in Fig. 4(a). Obviously, the sharp peak near zero-$H_{c1}$ is related to the switching of FE polarity. Moreover, two shoulder peaks can be observed at high $\pm H_{c1}$. This behavior is a typical transition between paraelectric (PE) and FE phases. Upon increasing $T$, the two shoulder peaks are shifted gradually toward low $\pm H_{c1}$, and the intensity of the sharp peak gradually decreases. Both the shoulder and sharp peaks are totally inhibited above 200 K, implying the disappearance of the FE phase. These results are in good agreement with the previous reports. As for the out-of-plane case, the relative change of the dielectric constant, $\Delta \varepsilon(H)/\varepsilon(10$ kOe) = $[\varepsilon(H) - \varepsilon(10$ kOe)]/\varepsilon(10$ kOe), is presented in Figs. 4(b) and 4(c) for the low $T$ region ($< 100$ K). The dielectric hysteresis effect against $H$, particularly at the very low $T$ (< 15 K), is due to the magnetic-thermal effect. The linear-like magnetodielectric curve reveals that the associated spin order is the non- FE NLC phase. Once $T$ is above 100 K, the two dielectric peaks at low $H_c$ are presented, as shown in Fig. 4(c), indicating the appearance of the ALC phase. It is worth noting that a dielectric plateau can be observed in the high $H_{c1}$.
implying that the high \( H_c \) can destroy the ALC phase, leading to the appearance of a non-FE NLC phase. A similar result has been reported by Shen et al., who revealed that the reversal of the ALC state can induce an electric polarization.

To explore the ME coupling effect of the BSZFAO crystal, the \( M \) controlled by \( E \) was measured by applying \( E \) in a sequence: \(-1 \text{ MV/m} \text{–} 1 \text{ MV/m} \text{–} 0 \text{ MV/m} \text{–} 0 \) both in the in-plane and out-of-plane. For the in-plane case, the measurement was carried out at 100 K and \(-20 \text{ Oe} \text{ H}_{ab} \) bias, and the result is plotted in Fig. 5(a). Obviously, the polarity reversal of \( M \) by \( E \) is clearly identifiable. The varied magnitude of \( \Delta M \) is \(-0.128 \mu \text{C/cm}^2\). The converse ME effect coefficient defined as \( \Delta M/\Delta E \) is estimated to be \(-\approx 3500 \text{ ps/m} \). Similar results have been reported in other spiral multiferroic magnets, such as \(-8.1 \text{ ps/m} \text{ in Sm}_2\text{BaCuO}_5^8 \) and \(-5700 \text{ ps/m} \text{ in Fe}_3\text{Mo}_2\text{O}_{19}^9 \). In contrast, the polarity reversal in the out-of-plane case is still observable, as depicted in Fig. 5(b) at 100 K and \(-20 \text{ Oe} \text{ H}_{ab} \) bias. Although \( M \) is slightly delayed against the pulsed \( E \), the magnitude of \( \Delta M \) is up to \(-0.178 \times 10^{-1} \mu \text{C/cm}^2\). The converse ME coefficient is estimated to be \(-\approx 480 \text{ ps/m} \). These results reveal the significantly anisotropic converse ME effect or multiferroic property of the BSZFAO crystal. Next, a similar measurement was performed by applying \( E \) in a sequence: \(-1 \text{ MV/m} \text{–} 0 \text{ MV/m} \text{–} -1 \text{ MV/m} \text{–} 0 \). Here, only the measurement for the in-plane case was carried out at 15 K and zero \( H_{ab} \) bias. As shown in Fig. 5(c), \( M \) reduces/increases at negative/positive \( E \), attributed to the clamped/released \( M \) and \( P \) orders. Interestingly, when \( E \) is removed from \(-1 \text{ MV/m} \text{ to zero} \), \( M \) values are distinctly different due to the hysteresis effect. The four \( M \) values are clearly identifiable with good repeatability, which has an application potential for non-volatile four state memory.

It was suggested that the ALC spin configuration in the in-plane case can be driven into the TC phase by applying \( H_{ab} \), leading to the FE phase with \( P_{ab} \| H_{ab} \). That is to say, the TC and ALC spin configurations respond to the FE phase. The FE phase can persist below the critical temperature \( T_c \) as confirmed by the \( H–T \) phase diagram in Fig. 3(a). It should be noted that the TC spin configuration will be inhibited at high \( H_{ab} \), yielding a PE phase, as shown in Fig. 2(c). A similar conclusion has been revealed by Jakub Višič in Y-type \( \text{Ba}_3\text{Sr}_2\text{Co}_2\text{Zn}_2\text{Fe}_{14}\text{A}_{10}\text{O}_{22} \). Actually, the converse ME effect i.e., the manipulation of \( M \) by \( E \) is considered as a result of the compound domain wall movement. The double \( M \) states during \(-E \) back to zero might be due to the resistance of domain wall movement. While for the out-of-plane case, the ALC exists below \( T_c \) \(-165 \text{ K} \), the broken space inversion symmetry can lead to its \( c \)-axis spin component alignment into the \( [1 1 0] \) collinear order, which is responsible for the origin of FE in terms of the SES mechanism. It should be mentioned that this ALC or FE phase is not stable and only exists in low field in our experiment, see Fig. 3(b).

In summary, the Y-type BSZFAO hexaferrite single crystal has been fabricated. The detailed \( H–T \) phase diagram for the in-plane and out-of-plane cases were established by the magnetic anomalies under \( T \) and \( H \). The magnetodielectric measurement revealed the anisotropy that the ab-plane electric polarization is induced by the transverse conical (TC) spin structure, while for the out-of-plane, the ALC structure also generates electric polarization below 165 K. The measured control of \( M \) by \( E \) revealed the anisotropic converse ME effect or multiferroic property. Their ME coefficients were obtained to be \(-\approx 3500 \text{ ps/m} \text{ and } \approx 480 \text{ ps/m} \) for the in-plane and out-of-plane, respectively. Our results demonstrate the spin-order-induced anisotropic ferroelectricity and magnetoelectric effect in Y-type hexaferrites.
See the Supplementary Material for more details of the x-ray diffraction pattern, EDS XPS, and specific heat capacity of the Y-type hexaferrite (Ba0.4Sr1.6)Zn2(Fe11.3Al0.7)O22 single crystal sample.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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