

The effects of Co-Ti co-doping on the magnetic, electrical, and magnetodielectric behaviors of M-type barium hexaferrites

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Magnetic, electrical and magnetodielectric properties have been studied in Co-Ti co-doped M-type hexaferrite $\text{BaCo}_x\text{Ti}_x\text{Fe}_{12-2x}\text{O}_{19}$ ($x = 0 \sim 4$). With the incorporation of Co-Ti, both their ferromagnetic magnetization and coercivity have been greatly changed. The temperature dependent magnetization curve shows a apparent hump at around 420 K, likely in association with more complicated cycloidal spin ordering, which is closely related to ferroelectric polarization. Interestingly, a significantly enhancement in resistivity (~ 3 orders in magnitude) can be obtained in co-doped samples ($x > 2$), which is beneficial for magnetoelectric properties. The magnetoelectric effect were examined by dielectric tunability under external magnetic field, which shows apparent tunability up to $\sim -3\%$ for sample with $x = 2$ at 1T magnetic field, further supporting it is a room temperature single phase multiferroic material. © 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4860948>]

I. INTRODUCTION

Recently there has been an upsurge of research interest in magnetoelectric (ME) effects in hexaferrites. The ME effects have been explored in various hexaferrites, such as Y-type $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$,¹ BaSrCoZnFe₁₁AlO₂₂,² Z-type $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$,^{3,4} U-type $\text{Sr}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60}$,⁵ and M-type $\text{BaFe}_{10.35}\text{Sc}_{1.6}\text{Mg}_{0.05}\text{O}_{19}$.⁶ It was revealed that the magnetically controllable ferroelectricity can be induced with a complicated cycloidal spin order in certain hexaferrites, which has been well described with the spin current model or inverse Dzyaloshinskii-Moriya interaction model.^{1,6-9} In these spiral magnets, the magnetic order and ferroelectricity are inherently coupled and thus pronounced ME effects could be expected. Such spiral magnetic order induced multiferroicity and ME effects have been extensively reported in transition metal magnates (e.g. TbMnO_3),¹⁰ where the ME effects are only available at low temperature and a large magnetic field of several tesla, hampering its further applications. In comparison, hexaferrites enable generating and controlling the ME effects at much higher temperatures and lower magnetic fields, hence being considered as promising candidates for future multiferroic applications.

Among them, M-type barium hexaferrite, $\text{BaFe}_{12}\text{O}_{19}$, denoted as BaM by Braun,¹¹ is the most-studied compound, which has been widely used as commercially permanent magnets, data storage media and microwave devices.¹²⁻¹⁴ Pure M-type hexaferrites $\text{BaFe}_{12}\text{O}_{19}$ has a large mag-

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netoanisotropy, stabilized by the strong exchange interactions among the Fe ions.¹⁵ By substitution of Fe³⁺ with other ions (e.g. Co and Ti), its magnetocrystalline anisotropy can be greatly reduced, and even switched from a perpendicular easy-axis (*c*-axis) to planar anisotropy (*ab*-plane).^{16–20} If properly doped (Co-Ti or Sc-Mg codoping), it may form longitudinal conical cycloidal spin order, producing ferroelectric polarization effects at rather high temperatures.^{6,7,21} However, there are very few investigations on the electric or ME effect on BM hexaferrite. Although it has been reported that longitudinal conical spin state can be observed in BaFe_{10.35}Sc_{1.6}Mg_{0.05}O₁₉, in which spin helicity (vector spin chirality) is robust against magnetic field scans as well as thermal agitations up to room temperature,⁶ it suffers from low resistivity, deleteriously affecting its electric as well as ME properties.

In this work, the magnetic, electrical properties and dielectric tunability of Co-Ti co-doped BaM hexaferrite (BaCo_{*x*}Ti_{*x*}Fe_{12–2*x*}O₁₉, *x* = 0 ~ 4) was explored. It was found that Co-Ti co-doping not only significantly changes the magnetic structures of BaM hexaferrite, but greatly enhances (~3 orders in magnitude) their resistivities. In particular, a magnetic induced dielectric tunability up to ~–3% can be observed for sample with *x* = 2 at 1T magnetic field. These demonstrated that the Co-Ti co-doped hexaferrites are possible candidate for room temperature multiferroics.

II. EXPERIMENTAL DETAILS

Co-Ti co-doping BaM (BaCo_{*x*}Ti_{*x*}Fe_{12–2*x*}O₁₉, *x* = 0 ~ 4) ceramics were prepared through conventional solid-state reaction. The high purity powders of Fe₂O₃, BaCO₃, Co₂O₃ and TiO₂ were weighed to the designed ratios, mixed and well ground. The mixture powders were calcined at 1100°C for 10 h and then pulverized. Finally the powders were pressed into pellets and sintered at 1200°C for 10 h. The crystalline structures were characterized by X-ray diffraction (XRD), using an X' Pert PRO diffractometer (PANalytical). The magnetism of samples was measured using a vibrating sample magnetometer incorporated into a physics properties measurement system (PPMS). For electrical measurements, the sintered pellets were polished into thin plates with a thickness of 0.5 mm, then silver electrodes were then applied onto both surfaces of the samples, and subsequently the samples were fired at 200°C for 20 min to ensure the good contact. The resistivities for the as prepared samples were measured at room temperature by two-probe method using a Keithley source current meter (KEITHLEY 6430). The dielectric properties were tested by a high performance impedance analyzer (Alpha-A, Novocontrol Technology) at a frequency range of 10 Hz to 10 MHz.

III. RESULTS AND DISCUSSION

The XRD diffraction patterns of the sintered samples are showed in Fig. 1(a). All the diffraction peaks can be indexed to the magnetoplumbite structure with a space group of *P6₃/mmc*, which means that the Co-Ti atoms are incorporated into the lattice matrix. Further detailed analysis found that some diffraction peaks are shifted towards lower angles with increasing doping concentration *x*, as shown in Fig. 1(b), indicating an increase in lattice parameters. With rising doping concentration, both lattice constants of *a*-axis and *c*-axis increase, which is clearly demonstrated in Fig. 1(c). It is noted that the radius of Co²⁺ and Ti⁴⁺ ions are 0.72 Å and 0.68 Å, respectively, both of which are slightly larger than that of Fe³⁺ ions (0.64 Å). Therefore it is reasonable that the substitution of Fe³⁺ ions by Co²⁺ and Ti⁴⁺ ions results in the expansion of lattice constant.

The ferromagnetic hysteresis (*M-H*) loops were shown in Fig. 2(a). It is observed that the saturation magnetizations (*M_s*) first increases and then decreases with the rise of *x*. The maximal *M_s* is obtained at *x* = 0.5. While the coercive field (*H_c*) declines monotonously, as shown in the inset of Fig. 2(a). In addition, the coercive field (*H_c*) for sample without doping is of 3.26 kOe, and it starts to reduce remarkably with the increase of *x*. Finally, it drops down to 0.024 kOe at *x* = 4. For pure BaFe₁₂O₁₉, it has a space group of *P6₃/mmc*, in which Fe atoms occupy three octahedral sites (*4f₂*, *12k* and *2a*), one tetrahedral site (*4f₁*), and one trigonal bipyramidal site (*2b*),²² for each unit cell (two formula units). Its magnetic structure can be regarded as collinear ferrimagnetic order with 16 Fe in *b*, *a*, *k* sites moment antiparallel with eight Fe spin in *f₁* and *f₂* per unit cell, producing a net magnetic moment 8μ_{Fe} (40μ_B) at 0 K.¹⁶ The increase of magnetism at initial stage in doped BaFe₁₂O₁₉

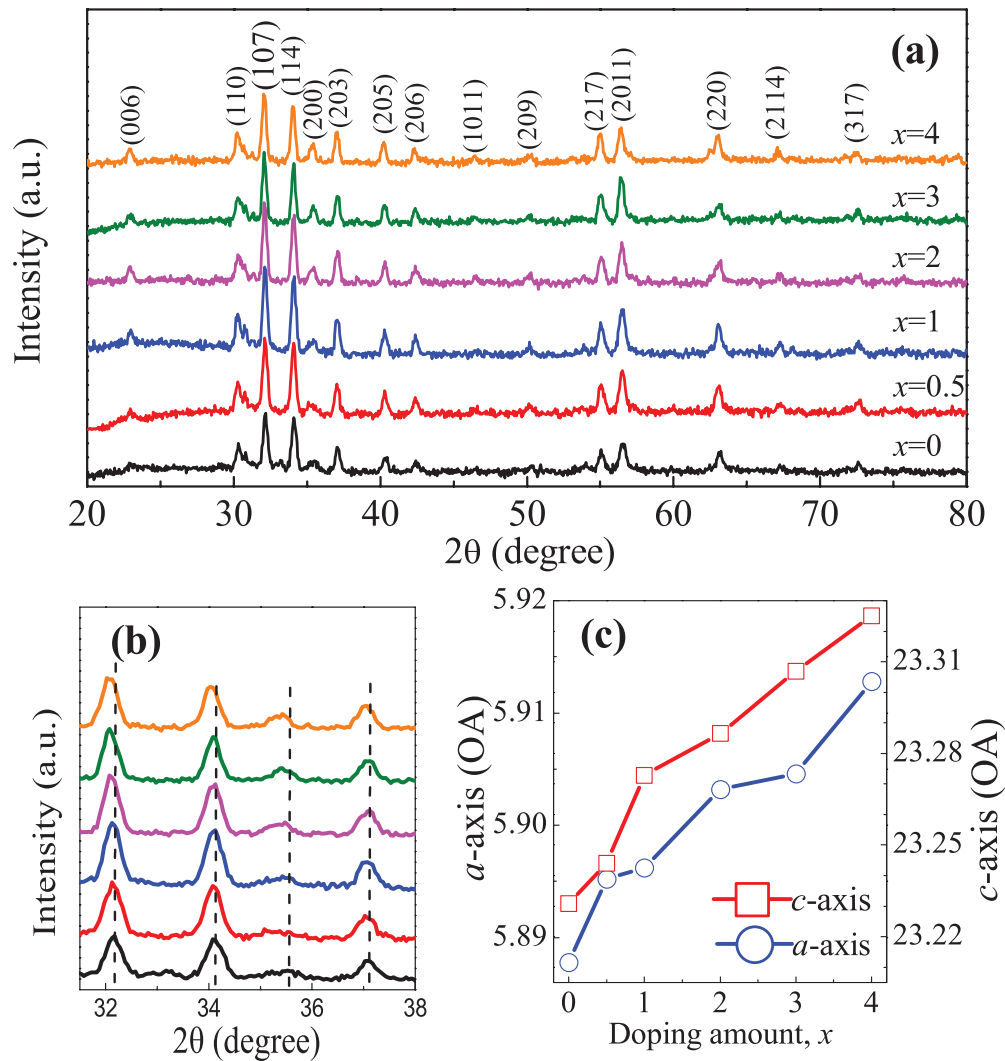


FIG. 1. (a) XRD patterns for the $\text{BaCo}_x\text{Ti}_{1-x}\text{Fe}_{12-2x}\text{O}_{19}$ ($x = 0 \sim 4$) ceramics. (b) Subtle XRD patterns of the peaks in 2θ range $31\text{--}38^\circ$. (c) The lattice constants of a -axis and c -axis as a function of doping amount.

ceramics can be attributed to the partial substitution of Fe^{3+} ions by low spin Co^{2+} ($0.8\mu_B$) on antiparallel f -sites, while replacing of Fe cations in parallel sites (e.g. $12k$) with nonmagnetic Ti^{4+} ions may significantly reduce the local magnetic moments and consequent to the overall drop of magnetization with further increase of doping content. On the other hand, the monotonously drop of coercivity is mainly attributed to the loss of magnetocrystalline anisotropy by Co-Ti codoping,¹⁹ which can be affected by Co^{2+} ions in f_2 -sites.

Furthermore, Co-Ti codoping can also greatly affect the magnetic structures. It is generally accepted that the crystalline structure of BaM hexaferrite is considered as alternative stacking of four block of R , S , R^* , and S^* , in which RS and R^*S^* carry same spin moments.²¹ Without doping, RS and R^*S^* are collinearly aligned at the same orientation, give rising to the observed ferromagnetism. Once Ti^{4+} cations are introduced, they tend to occupy the $12k$ sites of the unit cell, leading to the decoupling of these two blocks,²¹ which promotes the formation of noncollinear magnetic orders. For instance, co-doping may increase the magnetic angle between these RS and R^*S^* blocks, and form conical spin structures. To verify this, we measured temperature dependent magnetization for the $\text{BaCo}_3\text{Ti}_3\text{Fe}_6\text{O}_{19}$ ceramics ($x = 3$), as shown in Fig. 2(b). With temperature increasing from 300 K, the magnetization first increases at lower temperature region, and then gradually decreases at

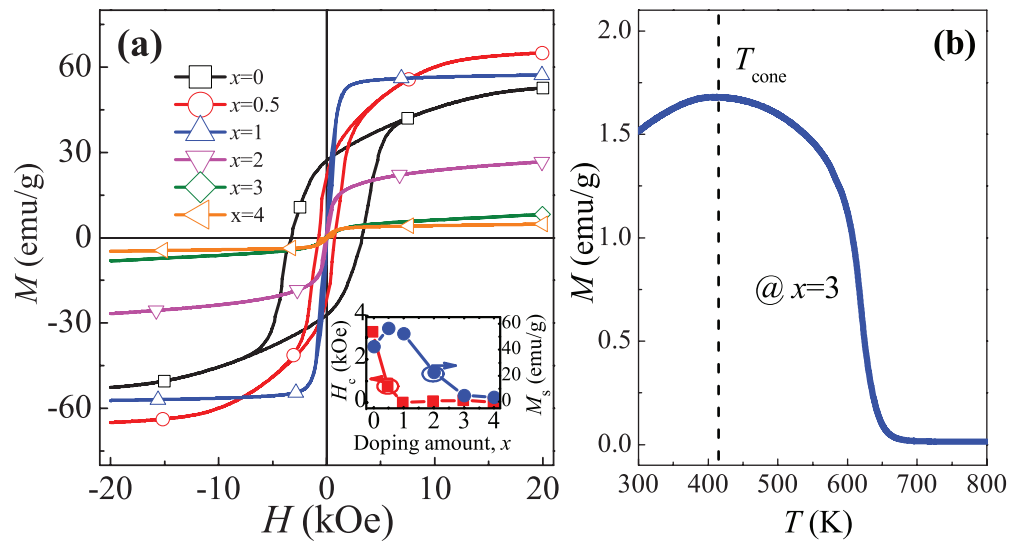


FIG. 2. (a) Magnetic hysteresis loops for the $\text{BaCo}_x\text{Ti}_x\text{Fe}_{12-2x}\text{O}_{19}$ ($x = 0 \sim 4$) ceramics and the insert shows the saturation magnetization and the coercive field as a function of doping amount. (b) Temperature dependence of the magnetization for $\text{BaCo}_3\text{Ti}_3\text{Fe}_6\text{O}_{19}$ measured at 0.05 T during field heating process.

higher temperature region. The maximal magnetization of 1.68 emu/g is obtained at 410 K, likely correspondent to the transition from collinear ferrimagnetic to conical spin structures as reported in Ref. 6. Our results show that the conical spin structure in $\text{BaFe}_{12}\text{O}_{19}$ ceramic can be stabilized up to 410 K in case of Co-Ti co-doping. Further increase of the temperature to 620 K, the magnetization dramatically decreased to a value close to zero and remains constant at higher temperature. This is in association with a transition from paramagnetic to ferromagnetic phases occurred at 620 K.

Figure 3 shows the frequency dependence of dielectric constant (ϵ') and dielectric loss ($\tan \delta$) of $\text{BaCo}_x\text{Ti}_x\text{Fe}_{12-2x}\text{O}_{19}$ ($x = 0 \sim 4$) measured at room temperature. For all the samples, both ϵ' and $\tan \delta$ decrease gradually with increasing frequency. This feature is consistent with previous report.²⁰ It can also be observed that higher content of doping will lead to lower ϵ' and $\tan \delta$. The high ϵ' and large $\tan \delta$ at low frequencies in pure $\text{BaFe}_{12}\text{O}_{19}$ ceramic can be attributed to high concentration of charge carriers related to space charge relaxation. For the samples with high doping concentration of $x > 2$, the ϵ' exhibits rather frequency independent behaviors, and the $\tan \delta$ reduced by two orders in magnitude as shown in Fig. 3(b). These above results show that Co-Ti co-doping can greatly improve the frequency stability of the dielectric constant and decrease the dielectric loss of $\text{BaCo}_x\text{Ti}_x\text{Fe}_{12-2x}\text{O}_{19}$ ceramics. This is also attributed to the significant enhancement of resistivity in samples with high concentration of doping, as will discuss later.

More interesting result is that the resistivity of the BaM hexaferrite ceramics can be greatly increased by Co-Ti co-doping, as shown in Fig. 4(a). Compared with undoped $\text{BaFe}_{12}\text{O}_{19}$, the resistivity of Co-Ti co-doping ceramics has been greatly increased. For example, the obtained resistivity of $\text{BaCo}_4\text{Ti}_4\text{Fe}_4\text{O}_{19}$ ceramic is $4.36 \times 10^{10} \Omega \cdot \text{cm}$, which shows three orders of magnitude higher than $1.50 \times 10^7 \Omega \cdot \text{cm}$ for the pure $\text{BaFe}_{12}\text{O}_{19}$. The increase of the resistivity may be attributed to two mechanisms. One is the suppression of electron hopping between Fe^{3+} and Fe^{2+} , which is main source for high conductive loss in ferrites.²³ Substitution of Fe^{3+} by Co^{2+} and Ti^{4+} in octahedral sites can obviously reduce oxygen vacancy concentration due to decreased Fe ions,²⁴ in responding to the suppression of electron hopping among $\text{Fe}^{3+}/\text{Fe}^{2+}$. The other reason is that the lattice distortion induced by Co-Ti co-doping further confines the electron hopping between Fe^{3+} and Fe^{2+} .²⁵ The mechanism proposed here is consistent with that of Iqbal's reported for Zr-Cu substituted strontium hexaferrites system.²⁰

To examine the magnetoelectric effect, a dielectric measurement under a magnetic field was performed at room temperature. Here, we define the dielectric tunability as $[\epsilon(H) - \epsilon(0)]/\epsilon(0)$, where $\epsilon(H)$ and $\epsilon(0)$ are the dielectric constant with and without a magnetic field, respectively.

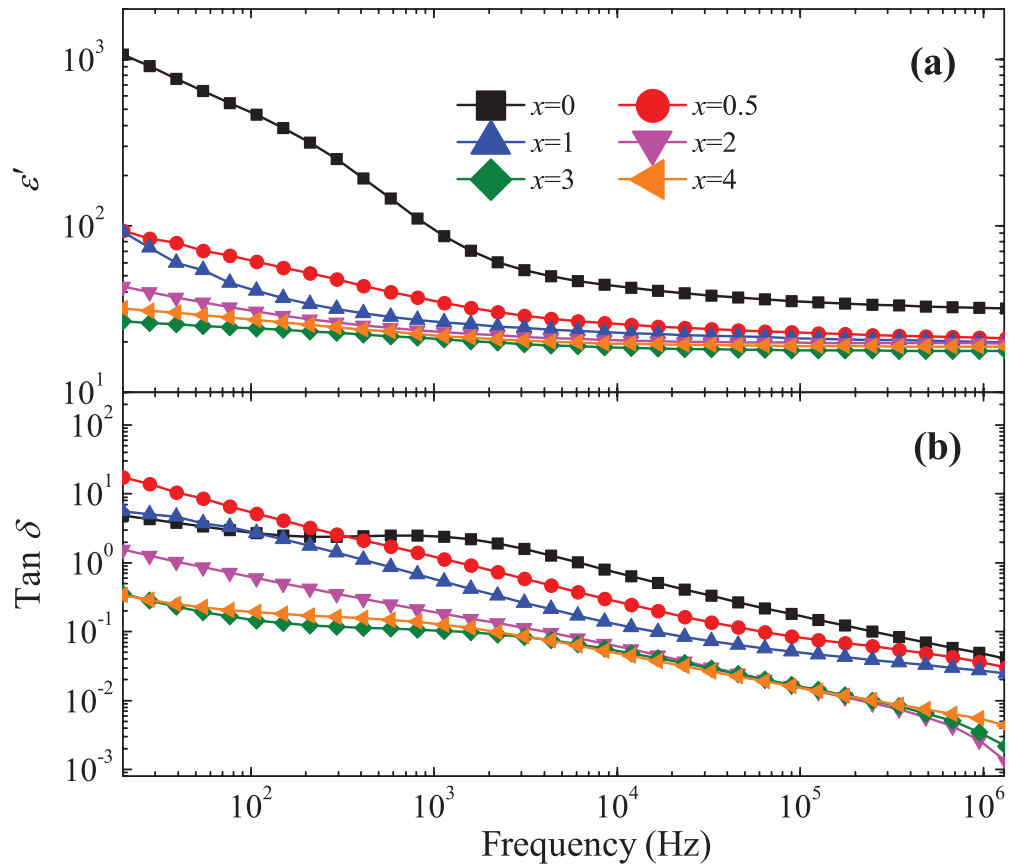


FIG. 3. Frequency dependence of (a) relative dielectric constant (ϵ') and (b) dielectric loss ($\text{Tan } \delta$) for the $\text{BaCo}_x\text{Ti}_x\text{Fe}_{12-2x}\text{O}_{19}$ ($x = 0 \sim 4$) samples measured at room temperature.

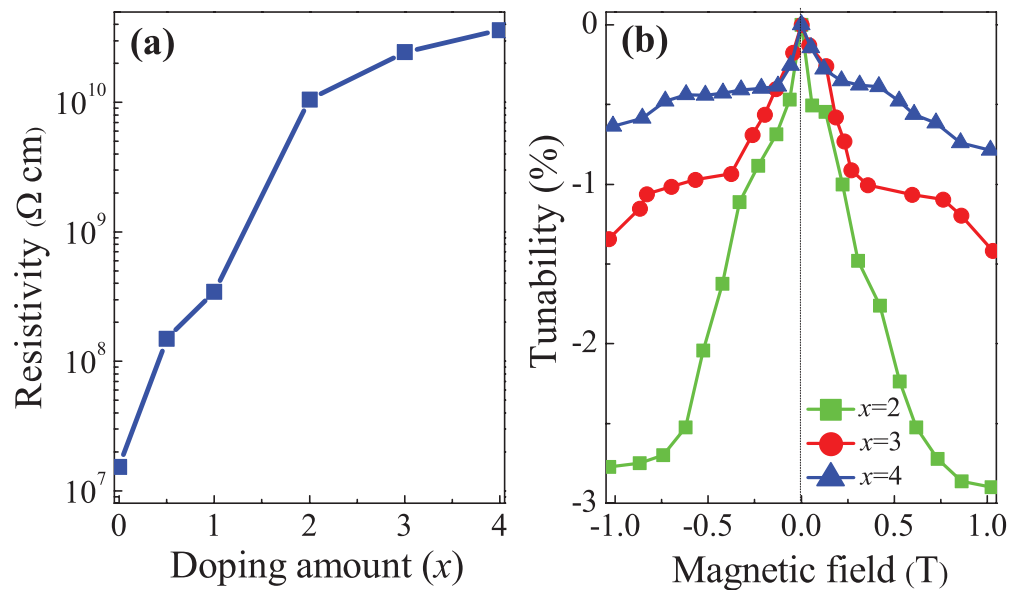


FIG. 4. (a) Resistivity as a function of doping amount. (b) Dielectric tunability as a function of applied magnetic fields at a frequency of 10 kHz.

The dielectric tunability as a function of magnetic field is shown in Fig. 4(b). It is found that the dielectric tunability for samples with $x < 2$ cannot be observed due to the high leakage current. Due to the increase of the resistivity with higher doping concentration, clear dielectric tunability can be observed for high concentration of doping. For examples, dielectric tunability of $\sim -3\%$ and $\sim -1.4\%$ have been observed for samples with $x = 2$ and $x = 3$ at 1T. The dielectric tunability by magnetic field is believed to be due to the change of electric polarization induced by magnetic field, i.e. ME effects. This has been supported by the results in the Z-type hexaferrite $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ and Y-type hexaferrite $\text{BaSrCoZnFe}_{11}\text{AlO}_{22}$ at low temperature.²⁻⁴ Our results demonstrate that the substitution of Fe^{3+} by $\text{Co}^{2+}\text{-Ti}^{4+}$ for BaM hexaferrites can push forward its applications as new type of room temperature magnetoelectric materials, and more studies are still needed to explore its other room temperature ME properties.

IV. CONCLUSIONS

The single-phase Co-Ti co-doping BaM $\text{BaCo}_x\text{Ti}_x\text{Fe}_{12-2x}\text{O}_{19}$ ($x = 0 \sim 4$) have been synthesized successfully by conventional solid-state reaction. It was found that Co-Ti co-doping can greatly change its saturate magnetization, coercivity, as well as induce complicated cycloidal spin orderings. More interestingly, it can also significantly enhance (~ 3 orders in magnitude) resistivity of the M-type Barium hexaferrites, which enable further investigation of room temperature electric properties. A dielectric tunability up to $\sim -3\%$ was obtained at 1T for sample with $x = 2$, which demonstrates a clear magnetodielectric effect. These indicate that proper Co-Ti co-doping into BaM hexaferrites is an effective way to make it a room temperature magnetoelectric materials.

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