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Magnetoelectric effect in $PbCoTiFe_{10}O_{19}$ multiferroic ceramic

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Abstract

Magnetoelectric hexaferrites have attracted more and more attention recently owing to their high operation temperature and large magnetoelectric effect. In this paper, we report the multiferroicity and magnetoelectric coupling in an M-type hexaferrite, $PbCoTiFe_{10}O_{19}$. The electric polarization of this multiferroics decreases sharply around 240 K, which is consistent with the onset temperature of conical spin structure, suggesting the intrinsic coupling between magnetic and electric orders. Moreover, cross-control of magnetism and ferroelectricity is simultaneously realized in this magnetoelectric hexaferrite. The origin of magnetoelectric effect in $PbCoTiFe_{10}O_{19}$ is discussed.

Keywords: A. Powders: solid state reaction; C. Magnetic properties; D. Ferrites; Magnetoelectric coupling

1. Introduction

The type-II multiferroics, in which the ferroelectricity is induced by some special magnetic structures, are extensively investigated in recent years due to their large magnetoelectric effects [1–4]. However, the multiferroic properties in most of these magnetic ferroelectrics present only at low temperature, which limits their practical applications to a large extent. Therefore, exploring multiferroics with large magnetoelectric effect as well as high operating temperature is greatly desired. In this context, multiferroic hexaferrites are promising candidates for the design of magnetoelectric devices, since they can show excellent magnetoelectric performance near or above room temperature [5–8].

Hexaferrites can be classified into different types, such as M, W, X, Y, U, and Z due to the different stacking sequences of three basic blocks, called S ($Me_2Fe_4O_8$), R ($MeFe_6O_{11}$) and T ($Me_2Fe_8O_{14}$), where Me^{2+} represents the divalent metal ions [9]. Magnetoelectric coupling of hexaferrite was first reported in a Y-type hexaferrite $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ [10] in 2005 and has been extensively studied in M-type [6,11], Z-type [5,7,12,13], U-type [14] and other Y-type hexaferrites recently [15–18]. By doping proper ions or optimizing synthesis method, large room-temperature magnetoelectric effects are reported in some Z-type [5,7] and M-type [11] hexaferrites, which promote these multiferroics toward practical applications effectively. The electric polarization emerged in these hexaferrites can be understood in the scenario of spin current or inverse Dzyaloshinskii–Moriya models [19,20], which can be expressed as

$$P = \sum A \vec{e}_{ij} \times (\vec{s}_i \vec{s}_j) \quad (1)$$

(A is a coupling constant depend on exchange coupling and spin orbital coupling, e_{ij} denotes a propagation vector connecting s_i and s_j). According to this model, the interaction between noncollinear spins can produce the local polarization through the spin–orbit interaction. It is known that the electric-field-controlled magnetization, i.e. converse magnetoelectric effect, is a promising subject of multiferroic hexaferrites due to the potentials in low-energy consuming magnetoelectric devices [21,22]. However, this investigation is always hampered in many multiferroic hexaferrites owing to their low resistivity [22]. As we know, doping foreign elements is a commonly used method to optimize magnetoelectric performance in multiferroic hexaferrites [6,17,18]. Base on the

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earlier reports, in order to obtain large magnetoelectric effect in high temperature, the substituting ions should meet two preconditions: (i) they should modify the superexchange interaction, leading to the formation of a noncollinear spin structure. Meanwhile, the spin rotation axis should not be parallel to the propagation vector e_{ij}. (ii) They should be helpful to obtain an insulating sample, which has resistivity high enough to sustain a substantial macroscopic ferroelectric polarization. Along these conditions, we prepare a single-phase polycrystalline M-type hexaferrite $PbCoTiFe_{10}O_{19}$, in which the magnetization and electric polarization are simultaneously observed near room temperature. The magnetic field manipulation of electric polarization as well as electric field control of magnetization is realized in this multiferroic hexaferrite simultaneously.

2. Experimental details

Polycrystalline sample of $PbCoTiFe_{10}O_{19}$ was synthesized by solid state reaction. Analytic grade purity powders of PbO, Co_2O_3, TiO_2, and Fe_2O_3 were used as raw material. To avoid lead deficiency during the sintering process, a 1.5 wt% excess of PbO over the stoichiometry was added. All the reagents were weighted precisely then mixed and grounded carefully. The mixture was calcined at 1173 K for 2 h in air, leading to the conversion from Co_2O_3 to CoO [23]. After that, the sample was milled into powders and then pressed into pellets under a pressure of 40 MPa, followed by sintering at 1323 K for 2 h in oxygen atmosphere. It is reported that the substitution of a Co^{2+}–Ti^{4+} pair for two Fe^{3+} ions can maintain the average 3+ valence state and prevent the formation of Fe^{2+} ions effectively, which would reduce the electron hopping between Fe^{2+} and Fe^{3+} in our sample [24]. In addition, annealing in oxygen is also beneficial to increase the resistivity. As a result, the resistivity of $PbCoTiFe_{10}O_{19}$ reaches up to 14 GΩ cm at room temperature and even higher at lower temperature, which is high enough to sustain an electric field and ensure the following magnetoelectric measurements.

The phase purity of the sample was characterized by X-ray powder diffraction (XRD) using Cu Kα radiation (BRUKER, D8 ADVANCE) at room temperature. The measurements of magnetic properties were performed on a superconducting quantum interference device magnetometer (Quantum Design, MPMS-XL) and vibration sample magnetometer (VSM, ADE-EV7). For the electric measurement, silver pastes were painted as electrodes on both sides of the samples. The temperature dependence of electric polarization was obtained by integrating the pyroelectric current, which was measured by an electrometer (Keithley, model 6514) with temperature controlled by the physical property measurement system (Quantum Design, PPMS) at a warming rate of 4 K/min. The change of electric polarization as a function of magnetic field was measured at 200 K. The electric field manipulation of magnetism as performed by measuring temperature profile of magnetization with electric voltage applying on the sample.

3. Results and discussion

The crystal structure of M-type hexaferrite $AFe_{12}O_{19}$ (A = Ba, Sr, Pb, etc.) belongs to the space group $P6_3/mmc$, which can be described as the stacking sequence of RSR^*S^* (star represents 180° rotation around c axis). Here, R and S represent (AFe_6O_{11}) and (Fe_6O_8), respectively [9]. As illustrated in Fig. 1(a), there are five different Fe^{3+} crystallographic sites, such as three octahedral (12k, $4f_2$, 2a) sites, one tetrahedral ($4f_1$) site and one bipyramidal (2b) site in M-type hexaferrite [25]. Due to large uniaxial magnetocrystalline anisotropy, M-type hexaferrite is widely used as permanent

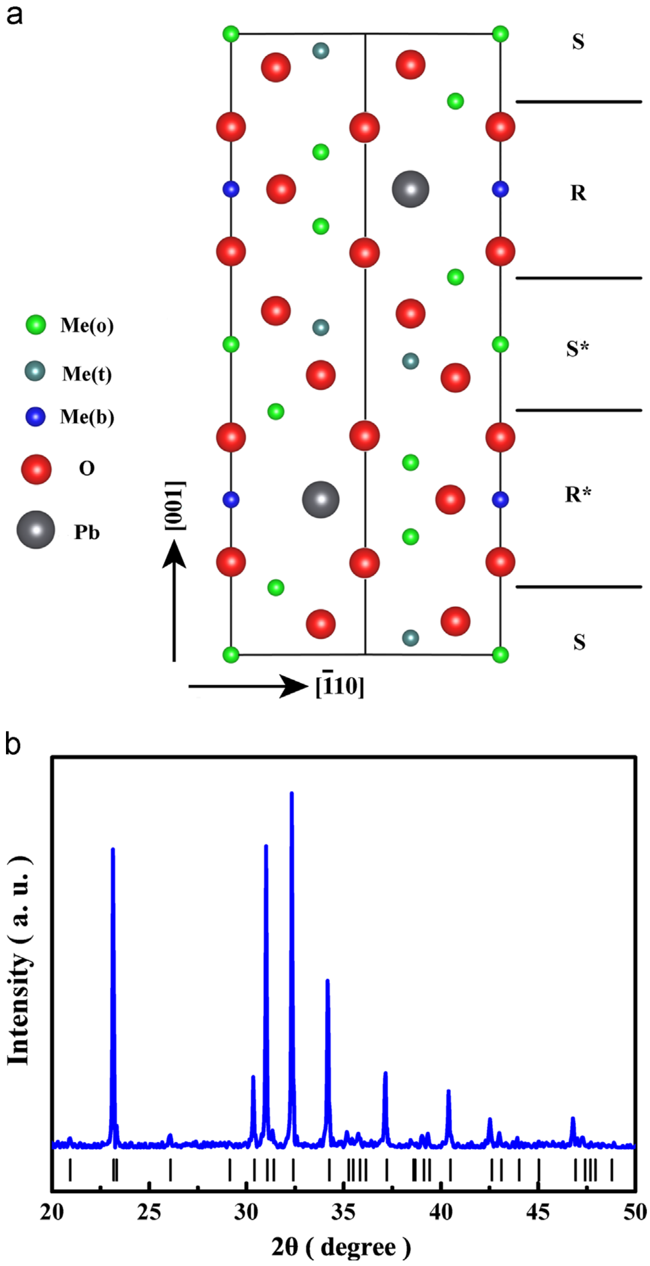

Fig. 1. (a) Illustration of the crystal structure for M-type hexaferrite $PbCoTiFe_{10}O_{19}$. Me denotes Fe, Co, and Ti; Me(o), Me(t) and Me(b) denote Me in octahedral site, tetrahedral site and bipyramidal site, respectively. (b) XRD pattern for $PbCoTiFe_{10}O_{19}$ measured at room temperature.