Large anisotropy in the magnetodielectric effect of orthorhombic HoMnO$_3$ thin films

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Abstract. Orthorhombic HoMnO$_3$ thin films of thickness 80 nm were grown epitaxially on Nb-doped SrTiO$_3$(111) substrates using pulsed laser deposition. Magnetization and dielectric constant measurements reveal that antiferromagnetic Mn$^{3+}$ spin ordering occurs at approximately 40 K while Ho$^{3+}$ ordering does at about 13 K. The films show sizable magnetodielectric effects (MDE) below 25 K and, in particular, they manifest a large directional anisotropy in the MDE, that is, the MDE depends sensitively on the relative direction of an external magnetic field with respect to the film normal.

1. Introduction

A material with a strong coupling between electric and magnetic degrees of freedom is not only of fundamental interest but also of eminent significance for applications. While the first experimental realization of magnetoelectric coupling effects occurred in Cr$_2$O$_3$ several decades ago [1], not too many other examples were reported since. More recently materials such as Gd$_2$CuO$_4$ [2], YMnO$_3$ [3], and BiMnO$_3$ [4] were studied, but the smallness of the effects found in these materials has subdued continued efforts. Intense interest in so-called magnetoelectrics, however, has revived due to the discovery of gigantic magnetoelectric and/or magnetodielectric effects in some rare earth manganite compounds [5].

Manganite compounds AMnO$_3$ with A being a rare earth or alkaline earth metal crystallize in two structural phases: cubic and hexagonal. It turned out that the structure is primarily determined by the size of the A-site ion. LaMnO$_3$, for example, is orthorhombic, while the smaller rare earth in LuMnO$_3$ stabilizes a hexagonal structure. AMnO$_3$ with A-site rare earth ions between Ho and Dy crystallize in either of the two phases, hexagonal or orthorhombic. The hexagonal phase shows ferroelectricity (FE) with a high transition temperature, 590~1000 K, and also exhibits antiferromagnetism (AFM) below a low transition point, ~100 K. On the other hand, both FE and AFM transition temperatures appear below 50 K in the orthorhombic phase. It is also known that some of the hexagonal compounds can be synthesized in a metastable orthorhombic form by high pressure synthesis [6]. For instance, large magnetodielectric effects were observed in the orthorhombic phase of polycrystalline YMnO$_3$ and HoMnO$_3$ both of which are normally hexagonal [7, 8]. One naturally expects even larger magnetodielectric effects of the orthorhombic phase in single crystals. Unfortunately, however, single crystals of orthorhombic HoMnO$_3$ are not easily available, and we investigated epitaxial thin films of orthorhombic
HoMnO$_3$ instead because they can be synthesized with much less difficulty by judicially choosing substrates and synthesis conditions.

2. Experimentals

HoMnO$_3$ epitaxial thin films were deposited by the pulsed laser deposition (PLD) technique using a HoMnO$_3$ (hexagonal phase) bulk target on Nb-doped SrTiO$_3$(111) substrates. A Nd-YAG pulsed laser of wavelength 266 nm, frequency 4 Hz, and fluence $\sim$2.5 J/cm$^2$ was used. Substrate temperature and oxygen pressure were maintained during deposition at 830 $^\circ$C and at 30 mTorr, respectively. The HoMnO$_3$ bulk target was synthesized using a conventional solid state reaction method. The stoichiometric amount of Ho$_2$O$_3$ and Mn$_2$O$_3$ powders with high purity was mixed, ground, and fired at 1100 $^\circ$C for 24 hrs. The resulting powder was then pelletized and fired again at 1300$^\circ$C in air for 24 hrs followed by furnace cooling. The crystal structure, surface roughness, and surface morphology of the films were characterized by X-ray diffraction (XRD) with Cu K$\alpha$ radiation and atomic force microscopy (AFM). The thickness was measured by X-ray reflectivity, and the typical thickness of the films was 80 nm. Macroscopic physical properties were measured with a Quantum Design PPMS; the films were subject to a magnetic field $H$ up to 7 T and dielectric constant was measured at 1 kHz with a measuring electric field both parallel and perpendicular to the magnetic field.

3. Results and discussion

XRD measurements were first performed to determine the structure of HoMnO$_3$ thin films; Fig. 1(a) displays the results. The (202) and (404) peaks of the orthorhombic phase are seen from the figure, and the unit cell parameters were determined to be: $a = 5.25722$ Å, $b = 5.83536$ Å, and $c = 7.36060$ Å. The inset shows that the full width at half maximum (FWHM) of the (202) rocking curve is about 0.122 $^\circ$. Fig. 1(b) is an AFM micrograph and it shows that the surface roughness of the film is approximately 7 Å. These structural data indicate that good epitaxial growth occurred along the [101] direction.

Fig. 2 shows the temperature dependence of the zero-field-cooled (ZFC) magnetization ($M$, filled squares) of an orthorhombic HoMnO$_3$ film measured with a magnetic field of 5 kOe. The $M$ curve exhibits two anomalies at 13 and 40 K. The former is attributed to the antiferromagnetic ordering of the Ho$^{3+}$ moments [7, 8], and the latter is due to the ordering of the Mn$^{3+}$ moments. The inset of Fig. 2 illustrates the temperature dependence of FC and ZFC $M$; the splitting of the two curves at 13K is due to the AFM ordering of the Ho$^{3+}$ moments. The temperature dependence of the dielectric constant of the film is also shown in Fig. 2 (open squares). As temperature is reduced below 40 K, the dielectric constant rises rapidly, reaches a maximum value at 13 K, and then decreases. This behavior is similar to that found in a polycrystalline sample reported previously [7].

Magnetodielectric effects (MDE), which signifies a magnetic tunability of the dielectric properties of HoMnO$_3$ films, were measured at $H = 0, 3, 5,$ and 7 T for both $E \parallel H$ and $E \perp H$ configurations. (Note that the magnetic field direction can be either $\perp$ or $\parallel$ to the surface normal of the film, which is the electric field direction.) Fig. 3(a) shows variations of the dielectric constant, as a function of temperature, at various field strength with $H \parallel E$. The maximum in the dielectric constant decreases and shifts to lower temperatures as the strength of the magnetic field is increased. The MDE (with $E \parallel H$) at various temperatures is shown in Fig. 3(b). The magnetic field dependence of the dielectric constant disappears above approximately 30 K, while a magnetic field causes sizable variations of the dielectric constant below this temperature. It is noted that the MDE increases rapidly, in particular, below 25 K. The origin of this MDE behavior probably lies in the appearance of a ferroelectric polarization below this temperature [9]. The maximum value of the MDE (measured at 7 T) reaches about 1.8 % at 13 K. From Fig. 3(b) it is also observed that the curve shapes of the MDE change at
Figure 1. (a) XRD pattern of a HoMnO$_3$ film grown on a SrTiO$_3$(111) substrate. Inset shows rocking curve for the (202) peak. (b) AFM image of the film. (1.5 µm × 1.5 µm)

Figure 2. Temperature dependence of the magnetization and the dielectric constant of the HoMnO$_3$ thin film measured under zero field cooled (ZFC) condition. Inset: Magnetization from 3 to 20 K at H = 5 kOe.

this temperature. At temperatures above 13 K negative MDE is generally seen; however, below this temperature a positive MDE appears for a field less than 1.5 T in addition to the overall negative MDE at higher fields. This peculiar behavior is related to the metamagnetic transition which is observed at $H \approx 1.5$ T only below the Ho ordering temperature [10]. The AFM order of the Ho spins below 13 K is also observed to reduce the magnetic field effect on the dielectric constant at low fields ($\leq 1.5$ T).

Perhaps the most interesting phenomenon observed in orthorhombic HoMnO$_3$ thin films is a strong directional dependence of MDE illustrated in Fig. 4. First, Figure 4(a) displays the temperature dependence of the dielectric constant and loss measured with a magnetic field of 7 T in comparison with the zero-field case. When the magnetic field is applied along the surface normal (E $\parallel$ H), the deviation of the dielectric constant from the zero field values is smaller than that associated with E $\perp$ H. Thus the MDE shows a directional dependence. Fig. 4(b) illustrates more clearly this directional dependence; as the angle between the magnetic field and the surface normal changes, the dielectric constant shows minima when H and E are parallel and maxima when H and E are perpendicular. The magnitude of the angular variation of the dielectric constant is about 0.9% with 9 T at 10 K. In a previous study [10], the Ho moments were found to lie in the (110) planes. Thus an external magnetic field can induce a rotation of the moments toward the field direction, which then gives rise to a change in magnetization and an associated change in, via magnetoelastic effect, the dielectric constant. Although the MDE of the present HoMnO$_3$ thin film is smaller than that of a polycrystalline bulk, larger MDE may be obtained if one controls the strain and growth direction of thin films with suitable substrates.
Figure 3. Dielectric properties of the orthorhombic HoMnO$_3$ thin film measured at 1 kHz. (a) Temperature dependence of the dielectric constant at various fields. (b) Magnetodielectric effect with an external magnetic field parallel to the surface normal.

Figure 4. Directional anisotropy of the magnetodielectric effect in orthorhombic HoMnO$_3$ thin films (a) Temperature dependence of dielectric constant and dielectric loss with in-plane and out-of-plane field of 7T. (b) Directional dependence of the magnetodielectric effect at various fields at 10K.

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