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Magnetodielectric effect in lead-free multiferroic $CoFe_2O_4/K_{0.5}Na_{0.5}NbO_3$ bilayers

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ABSTRACT

In this letter we presented the investigations of magnetodielectric (MD) effect in lead-free multiferroic $CoFe_2O_4/Na_{0.5}K_{0.5}NbO_3$ (CFO/KNN) bilayers with constant volumes. The CFO/KNN bilayers were synthesized on conductive Nb-doped $SrTiO_3$ (001) single-crystal substrates by radio frequency magnetron sputtering. Noticeable MD effect was observed in these CFO/KNN bilayers. The MD coefficient depends on the volume fraction of CFO layer. A maximum MD coefficient of about 7% at 12 kOe at 2 kHz was observed in 0.6CFO/0.4 KNN bilayer. The MD effect is attributed to strain-mediated magnetoelectric effect and magnetoresistance effect combined with the Maxwell–Wagner effect. The MD effect may have possible applications in magnetic field sensing devices.

1. Introduction

Multiferroic materials have drawn increasing interests due to their attractive physical properties and potential applications in sensors, transducers, data storage devices [1,2]. However, single phase multiferroics are relatively rare in nature, and most of them are in fact ferroelectric weak ferromagnets (or antiferromagnets) with weak magnetoelectric (ME) coupling at low temperature [1,3]. For practical application, alternative artificial multiferroic composites are being extensively studied, which can be obtained by combining a ferroelectric phase and a ferromagnetic phase at room temperature relying on strain [4], charge or magnetic interaction through the interface [5]. These multiferroic composites exhibit stronger ME coupling. Moreover, the ME coefficient is tunable by modulating the composite structures and component ratio [6]. Recently, many investigations have been performed on ME effect in multiferroic composite, for example $Co_{1.2-y}Mn_yFe_{1.8}O_4$–$BaZr_{0.08}Ti_{0.92}O_3$ [7], $Pb(Zr,Ti)O_3$–$(Co,Zn)Fe_2O_4$ [8], and $CuFe_2O_4$–$BiFeO_3$ [9], etc. Since many ferroelectric films are in fact poor insulators, making it difficult to sustain the electric field necessary to switch ferroelectric polarization [10], it is a relatively simple alternative way to investigate the magnetodielectric (MD) effect. Up to now, MD effect has been widely reported in multilayered films [11], nanocomposite structures [12], and bulk laminates [13], etc.

$K_{0.5}Na_{0.5}NbO_3$ (KNN) is one of the promising lead-free piezoelectric materials due to its biocompatibility, excellent piezoelectric and ferroelectric properties [14,15]. $K_xNa_{1-x}NbO_3$ is composed of ferroelectric $KNbO_3$ and antiferroelectric $NaNbO_3$, and forms a morphotropic phase boundary near $x=0.5$. However, investigations of KNN-based multiferroic films are rarely reported [8,12]. To our knowledge, few investigations on MD effect in KNN-based bilayers were reported until now. In this work, we investigated the MD effect in KNN-based multiferroic bilayers. $CoFe_2O_4$ (CFO) was adopted as the magnetic phase for its high magnetostriction coefficient [16].

2. Experimental

Multiferroic CFO/KNN bilayers were prepared by radio-frequency magnetron sputtering. KNN and CFO targets were prepared through a standard solid reaction sintering process. KNN films were grown on conductive Nd-doped $SrTiO_3$ (NSTO) (001) single crystal substrates before depositing CFO films. During deposition of KNN, the working pressure was 0.6 Pa of a mixture gas of Ar/O_2 with ratio of 20:1. Amorphous CFO layers were grown on the top of KNN at 350 °C. Two hundred nanometer-thick xCFO/$(1-x)$KNN bilayers with $x=0.4$, 0.5 and 0.6 were achieved, which were then annealed in air at 800 °C.

The crystal structure was characterized by x-ray diffraction (XRD). For electrical measurements, 100 nm-thick Au top electrodes with diameter of 300 μm were prepared through a lift-off technique. Dielectric properties were performed using an impedance analyzer in a frequency range from 1 kHz to 1 MHz. Magnetic hysteresis loops were measured by alternating gradient magnetometer (AGM) at room temperature. The MD effects were

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carried out by measuring the frequency dependence of dielectric constant under a variety of magnetic fields.

3. Results and discussion

Fig. 1(a) shows the XRD $\theta-2\theta$ scans of as-grown KNN films deposited at temperatures of 500, 600, 700 and 800 °C. KNN film with perovskite structure can be obtained at growth temperature of 800 °C. The KNN films are polycrystalline without preferential orientation. K–Nb–O second phase is observed in these films due to the sublimation of Na at high growth temperature [17]. A post annealing treatment at 800 °C in air only slightly improves the crystallinity of KNN film, as shown in Fig. 1(a). However, the annealing treatment remarkably enhances the dielectric constants, as shown in Fig. 1(b). This enhancement is probably attributed to denser grains and recombination of oxygen vacancies during annealing in air.

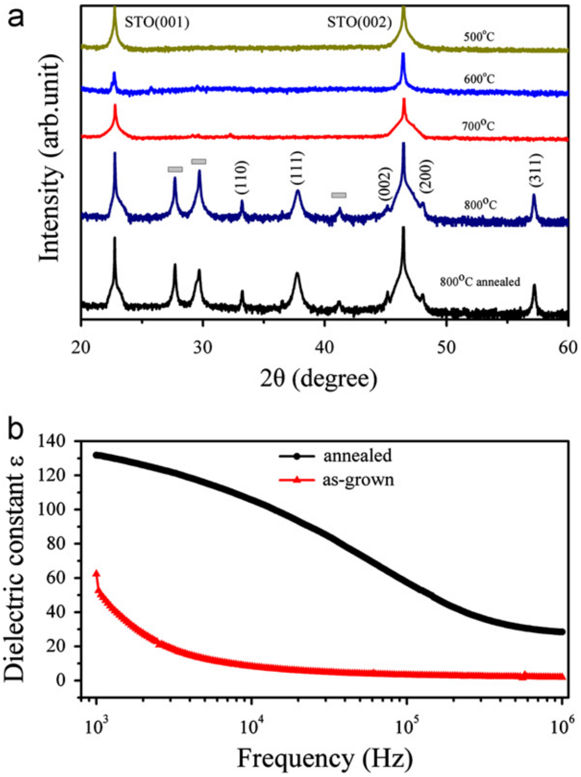

Fig. 1. (a) XRD $\theta-2\theta$ diffraction patterns of as-grown KNN films deposited at substrate temperature of 500, 600, 700 and 800 °C. XRD pattern of KNN film deposited at 800 °C with annealing treatment is also shown. "▭" represents Na-deficient K–Nb–O second phase and (b) frequency dependence of dielectric constant of KNN films grown at 800 °C with and without annealing treatment.

The magnetic hysteresis loops (M–H) of xCFO/(1 $-x$)KNN bilayers are shown in Fig. 2(a). The saturated magnetization (Ms) depends on the volume fraction of CFO layer, which are 203, 246 and 299 emu/cm^3 for $x=0.4$, 0.5 and 0.6, respectively. The normalized Ms for CFO layer are 507, 492 and 498 emu/cm^3, which are comparable to 530 emu/cm^3 in CFO single layer [18]. It indicates that the CFO layer maintains its good magnetic properties in KNN/CFO bilayers. Fig. 2(b) shows the dielectric constant ε of xCFO/(1 $-x$)KNN bilayers. Ascribed to lower dielectric constant and higher conductivity nature of CFO comparing with KNN, the dielectric constant of xCFO/(1 $-x$)KNN decreases with increasing volume fraction of CFO. The values of dielectric constant at 1 kHz are 121, 80 and 71 for xCFO/(1 $-x$)KNN films with $x=0.4$, 0.5 and 0.6, respectively. Since the measured capacitance is very small (a few hundred pF with the electrode radius of 300 μm), the defect mediated space charge carrier may easily cause disturbances of the frequency dependent dielectric constant, as seen in Fig. 2(b).

Fig. 3(a) shows the dielectric constant of 0.4CFO/0.6 KNN bilayer under an in-plane magnetic field. The ε increases with increasing applied magnetic field at low-frequency region, as the zoom-in curves presented in the inset of Fig. 3(a). The magnetic field induced variation of dielectric constant is characterized by MD effect. The MD coefficient is defined as:

$$\mathrm{MD}(\%) = [\varepsilon(H) - \varepsilon(0)]/\varepsilon(0) \times 100\%$$

where $\varepsilon(H)$ and $\varepsilon(0)$ are dielectric constants at magnetic field H and 0 at same frequency. The frequency dependence of MD at room temperature is shown in Fig. 3(b). The MD coefficient has positive value. It is noted that peaks of MD near 135 kHz are observed in Fig. 3(b), which is attributed to the Maxwell–Wagner effect combined with Magnetoresistance [10]. According to Catalan's argument [10], samples with heterogeneous nature, either accidental (interfacial or grain-boundary layers) or intentional (superlattice), can be described by a Maxwell-Wagner capacitor model. If the resistance of the sample is changed by a magnetic field, so will the measured dielectric constant, resulting in MD effect. At low frequency the charge carriers in the low resistivity layer do respond to the field, but at high frequency charge carriers do not have time to response to the field, so a cutoff forms (RC time constant) in the frequency dependent dielectric constant. The difference of the frequency dependent dielectric constant with and without magnetic field results in a MD maximum around the frequency of 1/RC [10]. In our work, it corresponds to the MD maxima near 135 kHz. The MD peak is very small (almost disappear) up to 10 kOe. The reason for the peak disappearance is unclear. It might be due to the depth change of charge depleted interfacial layers in KNN/CFO layers, where the

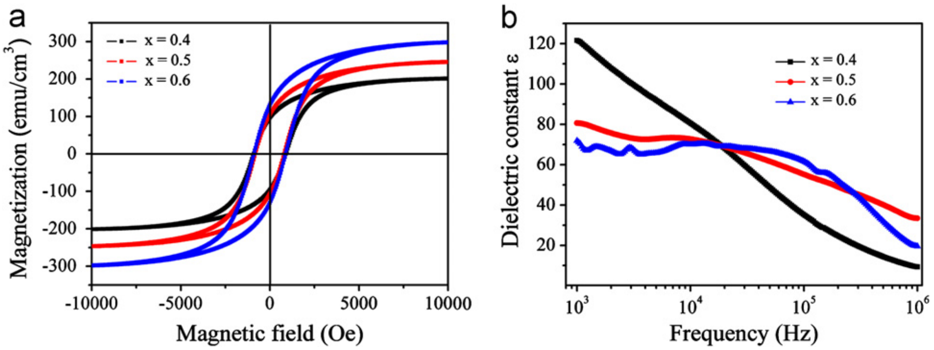

Fig. 2. (a) Magnetic hysteresis loops of xCFO/(1 $-x$)KNN bilayers with $x=0.4$, 0.5 and 0.6 and (b) frequency dependence of dielectric constant of xCFO/(1 $-x$)KNN ($x=0.4$, 0.5 and 0.6) bilayers.