Submitted for publication Sept. 2007

Magnetoelectric nano-$Fe_3O_4/CoFe_2O_4//PbZr_{0.53}Ti_{0.47}O_3$ Composite

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Abstract

A new magnetoelectric hybrid device composed of a nano-particulate magnetostrictive iron oxide-cobalt ferrite film on a piezoelectric PZT crystal serving as both substrate and straining medium, is described. Nano-$Fe_3O_4/CoFe_2O_4$ particles, ranging from 5nm to 42nm, were prepared using a variation of the sol-gel method . A small electric field, 5-10 kV cm^{-1}, applied at the coercive field of the nano $Fe_3O_4/CoFe_2O_4$ component modulates the film magnetization up to 10% of the saturation magnetization of ferrite. At the smallest particle size of 5nm the coercive field is as low as 25 Oe and the ME_E voltage coefficients as high as 10.1 V/cm Oe.

85.80.Jm Magnetoelectric devices
81.20.Fw Sol–gel processing
81.40.Rs Electrical and magnetic properties (related to treatment conditions)
75.70.Ak Magnetic properties of monolayers and thin films
75.30.Hx Magnetic impurity interactions

The recent surge of papers describing magnetoelectric composites (MECs) may be divided into two groups, the first consisting of papers reporting on metal-oxide composites and the second containing those publications dealing with oxide-oxide structures. High MEC susceptibilities at low magnetic fields are achieved with metal-oxide MECs by choosing either glassy metals or designing highly magnetostrictive metallic components with zero demagnetization factor.[1,2] Similar approaches are not as readily accessible for oxide/oxide ME composites as these are predominantly fabricated by thin film technologies, e.g.,[3] and the oxide featuring the highest magnetostriction, CFO, possesses a large magnetocrystalline anisotropy. The fully epitaxial self-assembled 3-1 CFO/BTO ME composites[4] represent somewhat of an exception. Therefore, in an effort to reduce the effective magnetocrystalline anisotropy and thereby the coercive force of CFO, we developed a nano-$Fe_3O_4/CoFe_2O_4$//PZT MEC whose fabrication and properties are described in the following.

To achieve a high effective magneto-electric signal, ME composites require high piezoelectric and magnetic susceptibilities.[5,6] $Pb(Zr_{0.53}Ti_{0.47})O_3$ is a well-understood piezoelectric material fulfilling this requirement. Ferromagnetic bulk Co- ferrite is a good choice due to its high magnetostriction. But, because of its high magneto-crystalline anisotropy[7] it has a low magnetostrictive initial susceptibility that results in a low magnetoelectric susceptibility, $d\lambda/dH$. In nano-particles the effective magneto-crystalline anisotropy is lowered and $d\lambda/dH$ can be increased while maintaining its high saturation [8] as has been also demonstrated for Co- ferrite.[9] Therefore, in order to create an all-oxide MEC with a large ME coupling coefficient, a nano-$Fe_3O_4/CoFe_2O_4$/ $Pb(Zr_{0.53}Ti_{0.47})O_3$ was developed. This composite yields giant ME voltages under significantly lower

magnetic bias fields than previously reported for CFO/PZT MECs.[10] Its manufacture and properties will be described next.

The composite was manufactured by spinning a CFO sol-gel[11] onto a mirror polished PZT single crystal substrate, obtained from Fuji Ceramics, Inc.. The deposition technique and substrate were chosen to obtain lower sintering temperatures and good homogeneity of the film as well as proper stress transfer between the components of the composite by avoiding large surface roughness. The sol solution of $CoFe_2O_4$ with a molar ratio of Co^{2+}:Fe^{3+}= 1:2 was repeatedly spin coated onto the PZT substrate until a smooth precursor film was obtained.[12] Subsequently, the composite was annealed 15 minuets at different temperature, 450°C ~ 650°C, to obtain different nano-sizes and compositions between Fe_3O_4 and $CoFe_2O_4$. The final composite consisted of a 5μm thick film of nano-$CoFe_2O_4$ on 100μm PZT. Special attention was given to heat treatment at compositions intermediate between Fe_3O_4 and $CoFe_2O_4$ as Bickford et al. have shown that addition of only a small amount of cobalt ferrite to magnetite changes the sign of the anisotropy constant from negative to positive.[13] Our experiments extend this idea to additions to cobalt ferrite.

The structure of the composites was characterized using scanning x-ray micro-diffraction (D8 DISCOVER with GADDS for combinatorial screening by Bruker-AXS). XRD shows the typical signature of the composite: Two sets of well-defined peaks are observed belonging to PZT and $CoFe_2O_4$. No additional or intermediate phase peaks can be identified. The minor constituent Fe_3O_4 (see below) was not specifically identified as its XRD signature is almost identical to that of CFO. The broad CFO XRD peaks are indicative of nanoparticle formation. The morphology and cross-section examination of

the film was made using an environmental scanning electron microscope (ESEM) and an atomic force microscopy (AFM). A well bonded interface was discerned.

Magnetic properties of the nano-CFO films were measured using a superconducting quantum interference device (SQUID). We measured the field dependent magnetization at room temperature by applying magnetic fields parallel to the plane of the film. The magnetic hysteresis loops of the films demonstrate the effect of the different annealing temperature (450 ^{0}C~ 700 ^{0}C) on the coercivity as well as saturation magnetization. It was observed that the value of the coercive field gradually decreases with decreasing annealing temperature (Fig. 1), as expected. At an annealing temperature of 450 ^{0}C the coercivity $H_c \approx 25$ Oe. The saturation magnetizations of in-plane loops yielded 375 emu/cm^3 independent of the particle size. The temperature dependence of the saturation magnetization of a 22 nm-CFO film yields Curie temperatures of 700K and 860K indicating that the particles consisted of approximately 91% CFO and 9% Fe_3O_4.

In order to demonstrate the ME coupling of the ferro-electric and –magnetic components of the composite the average in-plane magnetization of the CFO nano-particles was determined as the PZT substrate was alternately poled.[14,15] Fig. 2 displays the variation of the magnetization at the coercive field of 80 Oe as the electric field was sinusoidally varied as a function of time. These data yield a magnetoelectric coefficient ME_E= 10.1 V/Oe cm which compares favorably with published values.[16]

It is clear from Fig. 2 that the processing temperature significantly affects the sensitivity output of ME composites. The maximum ME_E sensitivity was observed for a sample annealed at T=550 ^{0}C. After annealing at this temperature the domain size is significantly smaller than after annealing at all other temperatures, see Fig. 3. It is

proposed that the fine domain structure obtained after the anneal at 550^{o}C increases the fraction of 90 degree domains and hence the elastic response of the ferromagnetic component of the MEC.

In summary, a very simple, inexpensive, double-layer all oxide nano-Fe_3O_4/CFO//PZT multiferroic 2-2 composite heterostructure has been prepared and studied. Ferromagnetic films of nano-Fe_3O_4 /$CoFe_2O_4$ were obtained by a spinning a suitable sol-gel onto a $Pb(Zr_{0.53}Ti_{0.47})O_3$ substrate. The double-layer film contains PZT and Fe_3O_4 /CFO phases and shows good electric-field-induced magnetoelectric properties. We can obtain a very low coercivity value of magnetostrictive Fe_3O_4 /$CoFe_2O_4$ phase, less than 100 Oe through controlled sol-gel and annealing processing. The resulting ME laminates have very large inverse ME voltage coefficients. The bias field obtained in this study can be further reduced by changing the ratio between Fe_3O_4 and CFO component by targeted annealing.

The support of the National Science Foundation, grant DMR0354740, and the Office of Naval Research, contract No. N000140110761 is acknowledged. The authors are also grateful to Dr. I. Lloyd for her hospitality and to the UMD-MRSEC program, DMR-00-0520471, for permission to use its equipment.

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Fig. 1: The coercivity field, determined at room temperature, of the nano-$Fe_3O_4/CoFe_2O_4$ component of the MEC as a function of the annealing temperature.

Fig. 2: (a), top, electrically induced magnetic switching, the moment of magnetization dependence of external applying electric field (-10^6~10^6V/m);

(b), bottom, room temperature magnetoelectric susceptibility, $\alpha_{ME} = \frac{\Delta E}{4\pi\Delta M}$, of the MEC as a function of the annealing temperature, corresponding to the top figure.

Fig. 3: MFM images of nano-$Fe_3O_4/CoFe_2O_4//PbZr_{0.53}Ti_{0.47}O_3$ MECS processed at temperatures of 450 ^{0}C (a), 500 ^{0}C (b), 550 ^{0}C (c) and 600 ^{0}C (d).

Figure 1

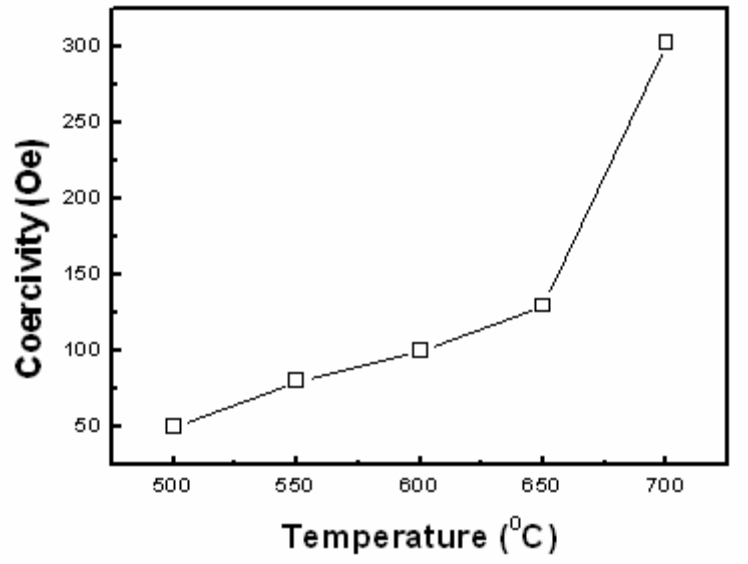
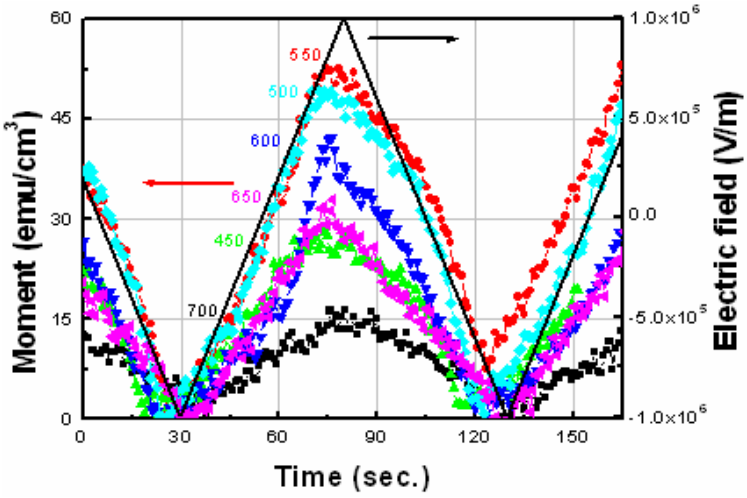

Coercivity (Oe)
300
250
200
150
100
50
500
550
600
650
700
Temperature (^{0}C)

Figure 2


Moment (emu/cm^3)
Electric field (V/m)
Time (sec.)
550
500
600
650
450
700
60
45
30
15
0
0
30
60
90
120
150
1.0x10^6
5.0x10^5
0.0
-5.0x10^5
-1.0x10^6

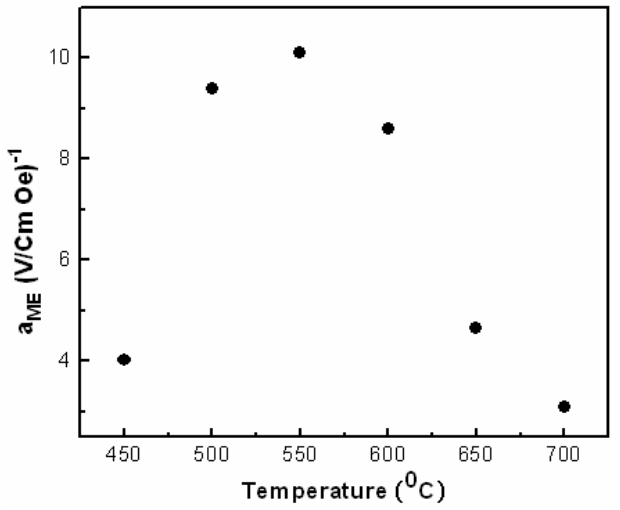

a_{ME} (V/Cm Oe)$^{-1}$
Temperature (^{0}C)
10
8
6
4
450
500
550
600
650
700

Figure 3