Magnetodielectric response in epitaxial thin films of multiferroic Bi_2NiMnO_6

2008 J. Phys.: Condens. Matter 20 355003

(http://iopscience.iop.org/0953-8984/20/35/355003)

J. Phys.: Condens. Matter **20** (2008) 355003 (4pp) doi:10.1088/0953-8984/20/35/355003

Magnetodielectric response in epitaxial thin films of multiferroic Bi_2NiMnO_6

P Padhan[1], P LeClair[1], A Gupta[1,3] and G Srinivasan[2]

[1] Center for Materials for Information Technology, University of Alabama, Tuscaloosa, AL 35487, USA
[2] Physics Department, Oakland University, Rochester, MI 48309, USA

E-mail: agupta@mint.ua.edu

Received 25 April 2008, in final form 9 July 2008
Published 1 August 2008
Online at stacks.iop.org/JPhysCM/20/355003

Abstract

Thin films of multiferroic Bi_2NiMnO_6 (BNMO) have been epitaxially stabilized on various lattice-matched substrates using the pulsed laser deposition technique. BNMO films deposited on conducting Nb doped $SrTiO_3$ substrates exhibit a magnetodielectric effect, in which the effective dielectric constant is dependent on the applied magnetic field and measurement frequency. A rapid change in the effective dielectric constant with a corresponding maximum in the magnetodielectric effect is observed near the ferromagnetic transition temperature of BNMO. The temperature-dependent magnetodielectric effect is attributed to the coupling between *electric* dipole ordering and fluctuations and *magnetic* ordering and fluctuations.

1. Introduction

The perovskites and double perovskites exhibit a wide variety of electrical and magnetic ordering behavior that can be tuned by compositional changes, making them a natural choice to search for 'multiferroic' materials, in which magnetic and dielectric processes coexist. For example, the local distortion of the transition metal octahedra in TiO_6-based compounds induces polar electric domains [1], and in Bi-cation-containing perovskites, this leads to ferroelectric order [2, 3]. On the other hand, ferromagnetic order in *double* perovskites arises from a 180° superexchange interaction between two transition metal cations (Goodenough–Kanamori rules) [4].

Bismuth-based perovskite ferroelectrics are being seriously considered as materials for nonvolatile ferroelectric random access memory devices to replace the more toxic Pb-based compounds, and also because of their fast switching characteristics [5]. Generally, the dielectric properties of ferroelectric thin films are strongly influenced by the finite screening length of the electrode material, soft-mode hardening of surface dipoles, and the thickness-dependent strain relaxation [6].

Ferroelectric ordering at ∼485 K has recently been observed in bulk Bi-based double perovskite Bi_2NiMnO_6 (BNMO) samples synthesized at high pressures [7]. Interestingly, these samples also exhibit magnetic ordering below ∼140 K, which is significantly lower than the ferroelectric ordering temperature. BNMO has a heavily distorted double perovskite structure with Ni^{2+} and Mn^{4+} ions ordered in a rock-salt configuration similar to La_2NiMnO_6 (LNMO). The presence of the $6s^2$ lone pairs of Bi^{3+} ions and the covalent Bi–O bonds results in ferroelectric properties, while the $–Ni^{2+}–O–Mn^{4+}–O–Ni^{2+}–$ magnetic path leads to ferromagnetism [7]. Thin films of BNMO have been grown on lattice-matched $SrTiO_3$ substrates via epitaxial stabilization that exhibit ferromagnetic and ferroelectric ordering [8]. The lower value of the saturation magnetization ($M_S \sim 4.1$–$4.5\ \mu_B$ at 5 K) of BNMO compared to the theoretical prediction of $M_S \sim 5\ \mu_B$, obtained in both bulk and thin film samples [7, 8], has been explained based on partial B-site disorder of the Ni^{2+} and Mn^{4+} [9].

We have successfully stabilized thin films of BNMO on various substrates which provide different degrees of lattice mismatch. The interesting feature observed in these films is the remarkable change of the effective dielectric constant at the ferromagnetic transition temperature of about 130 K, compared to a very small anomaly at T_C observed in [8]. Our BNMO films also exhibit a 'magnetodielectric effect' in which the effective dielectric constant is dependent on the applied magnetic field. We find a maximum magnetodielectric effect around the ferromagnetic transition temperature.

2. Experimental details

Pulsed laser deposition was used to grow epitaxial thin films of Bi_2NiMnO_6 (BNMO) on (001)-oriented 1.0 wt% Nb doped

[3] Author to whom any correspondence should be addressed.

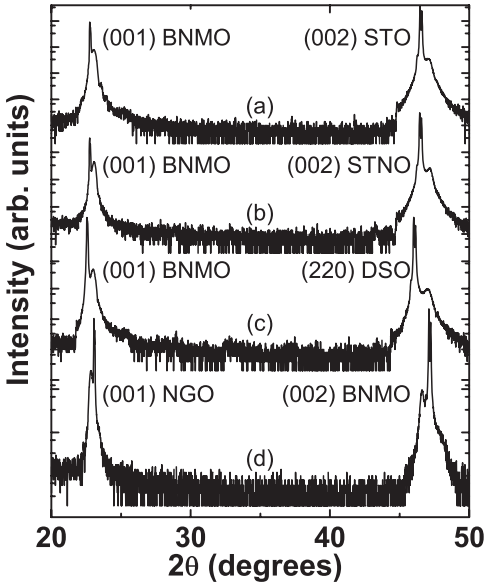

Figure 1. θ–2θ x-ray scan of thin films of BNMO grown on: (a) (001) STO, (b) (001) STNO, (c) (110) DSO and (d) (001) NGO substrates.

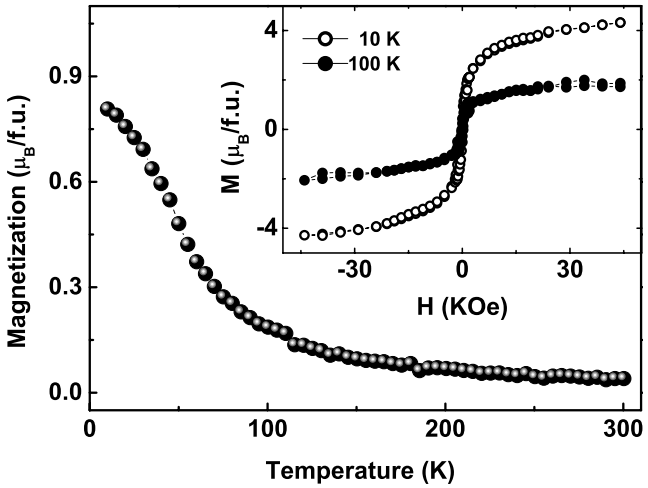

Figure 2. Temperature-dependent magnetization of a ∼350 Å thick BNMO film grown on (001)-oriented STO substrate measured with field cooling in 5 kG. Inset shows magnetic hysteresis curves of the BNMO film grown on (001)-oriented STO at 10 and 100 K.

$SrTiO_3$ (STNO), pure $SrTiO_3$ (STO), $NdGaO_3$ (NGO), and (110)-oriented $DyScO_3$ (DSO) substrates. A KrF excimer laser beam was focused on a target with Bi:Ni:Mn ratio of 2.3:1:1 prepared from the elemental oxides to yield an energy density of ∼1.0 J cm^{-2}. Film deposition was carried out at 700 °C in 800 mTorr pressure of oxygen. After deposition of 200–500 Å thick BNMO layers, the films were cooled to 470 °C in 760 Torr oxygen at 15 °C min^{-1}. The films were subsequently annealed for 1h at 470 °C in the same oxygen pressure and then cooled to room temperature at 15 °C min^{-1}. The crystalline quality of our samples was analyzed using a Philip's X'Pert x-ray diffraction (XRD) system. The Bi:Ni:Mn ratio in the thin films was measured using energy dispersive x-ray spectroscopy (EDS) and determined to be close to the desired stoichiometry of 2:1:1. Circular 1 mm diameter Au contact pads were sputter deposited on top of the BNMO and STNO to perform two probe AC impedance measurements using a HP4294A impedance analyzer. Impedance (Z) and phase angle (θ) were recorded as a function of frequency, temperature, and with in-plane or out-of-plane magnetic field in a Physical Property Measurement System (PPMS, Quantum Design) after cooling the sample down to the desired measurement temperature without any electric or magnetic field.

3. Results and discussion

In figure 1 we show the θ–2θ x-ray scan of the BNMO film grown on various substrates. The observation of only the pseudo-cubic (00l) reflections of the BNMO film and substrate suggest epitaxial growth of the BNMO film. The average in-plane lattice parameter of (001) STO, (110) DSO and (001) NGO substrates are 3.905 Å, 3.9386 Å and 3.8641 Å, respectively, while the pseudo-cubic lattice parameter of BNMO is 3.8775 Å [7]. The STO(001), DSO(110) and NGO(001) substrates thus provide 0.7%, 1.55% and −0.35% lattice mismatch for the epitaxial growth of BNMO. The effect of substrate-induced strain is clearly reflected in the angular position of (00l) x-ray reflections of BNMO on STO, NGO and DSO, which yielded strained out-of-plane pseudo-cubic lattice parameters for BNMO of 3.857 Å, 3.865 Å and 3.889 Å on STO, NGO, and DSO respectively. The remarkably small range of the full width at half maximum values in the rocking curve of BNMO on those substrates (∼0.02° − 0.064°, not shown) indicates good crystalline quality. These BNMO films further show four-fold symmetry in the ϕ-scan of the asymmetric plane consistent with epitaxial film growth. Because of the similar x-ray scattering amplitudes for Ni and Mn, the superstructure reflection resulting from B-site ordering will be very weak and is not observed. Confirmation of B-site ordering for similarly grown BNMO films has been obtained by Shimkawa *et al* based on observation of the (1/2 1/2 1/2) superstructure reflection peak using high-flux synchrotron x-ray diffraction measurements [10]. The intensity of (1/2 1/2 1/2) superstructure reflection is only about 1% of the fundamental refection [10]—in the present experiments, this is well below the noise threshold for detection.

Magnetization (M) versus temperature (T) was measured while cooling in a 0.5 T in-plane magnetic field using a Quantum Design SQUID, and is shown in figure 2 for a 320 Å thick BNMO film on STO. The $M(T)$ curve shows ferromagnetic ordering below a Curie temperature of T_C ∼ 130 K, slightly lower than the bulk value 140 K [7]. The zero-field-cooled magnetization versus field curves at 10 K and 100 K for the same sample are shown in the inset of figure 2, after correcting for the diamagnetic signal originating from the substrate. A saturation magnetization (M_S) value of 4.3 μ_B/fu at 10 K is observed. The smaller value of M_S compared to the theoretical value (5 μ_B/fu) [9] is consistent with previously reported results [7, 8], and is probably due to some degree of B-site antisite disorder of Ni^{2+} and Mn^{4+} ions [3] and/or a deviation from a linear bonding of Ni^{2+}–O–Mn^{4+}.

Ferromagnetic ordering arises from a 180° superexchange interaction between Ni^{2+} and Mn^{4+} across O^{2-}, according to Kanamori–Goodenough rules [4], and both antisite disorder and a deviation from linear bonding of Ni^{2+}–O–Mn^{4+} can lead to reduced ferromagnetism.

Using low resistivity (∼5 mΩ cm) STNO substrate as the bottom electrode, we have measured the resistivity of BNMO across the films' normal axis (i.e., transport perpendicular to the film plane) with a dc excitation voltage. The temperature-dependent out-of-plane resistivity of BNMO shows thermally activated behavior. A fit to the relatively higher temperature resistivity (200–300 K) gives an activation energy value of 0.024 eV. We have also measured the out-of-plane transport properties using a 10 mV or 100 mV RMS ac voltage as a function of temperatures (T), frequency (f), and magnetic field (H). Initially, we focus on the frequency-and temperature-dependent zero magnetic field results. To study the nature of the capacitive (dielectric) response, we modeled the film as a parallel network of an effective resistor (R) and an effective capacitor (C_{eff}) with a complex dielectric function, $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. Both the effective resistance and capacitance can be uniquely determined from impedance (Z) and angle (θ) versus frequency spectra [11, 12].

The effective dielectric constant and dissipation factor ($\tan\delta$) of BNMO films with Au top electrodes has been determined from the impedance and phase measurements at various frequencies for different temperatures. At room temperature, the 100 kHz effective dielectric constant of a 345 Å thick BNMO film with an Au electrode was determined to be 450 (see figure 3). The effective dielectric constant is somewhat higher than that the reported bulk value of ∼200 measured at 10 kHz [7]. As the temperature decreases below room temperature, the effective dielectric constant decreases down to 150 K, after which it remains essentially constant down to the lowest temperatures. As a voltage is applied, electric charges are built up at the interface of BNMO and metal electrode due to the large contrast in resistivities between BNMO and the metallic electrodes. Consequently, the charge built up at the interface leads to the well known electron screening effect, causing electric field penetration into the metal. The interface screening length depends on the work function of the electrode, which is known to strongly influence the dielectric properties in ferroelectric thin films [13, 14]. A complete analysis for the determination of the actual film dielectric constant would require separate inclusion of the impedance contributions from the top electrode-BNMO and the BNMO–STNO substrate. An intriguing feature in our BNMO film is the rapid change of the effective dielectric constant (measured at 100 kHz) at the ferromagnetic transition temperature of about 130 K as compared to the very small anomaly at T_C, as seen in [8]. Because of the leakage characteristics of very thick BNMO films, we could not directly measure their ferroelectric properties.

The qualitative behavior of the temperature-dependent effective dielectric constant at 7 T is similar to the zero-field variation shown in figure 3. The change in the effective dielectric constant with magnetic field (the 'effective magnetodielectric constant', or MDC) for various

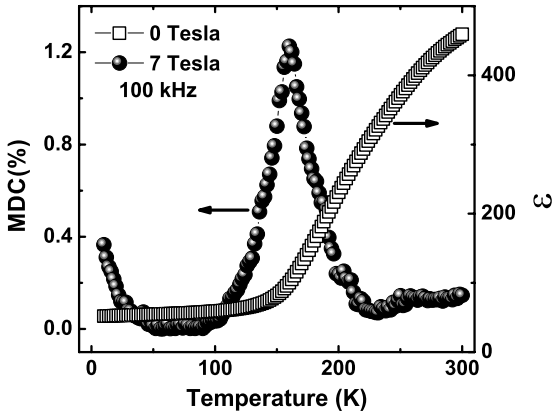

Figure 3. Temperature-dependent effective dielectric constant and magnetodielectric constant of BNMO film grown on a (100)-oriented 1.0 wt% Nb doped STO substrate at 100 kHz.

temperatures has been calculated using the definition MDC $= (\varepsilon_1(\omega, H) - \varepsilon_1(\omega, 0))/\varepsilon_1(\omega, 0)$. The 100 kHz MDC of BNMO is 0.4% at 10 K, decreasing very slowly with increasing temperature, followed by an increase around ∼80 K to reach a maximum at ∼160 K, thereafter decreasing rapidly to ∼0.1% at 200 K. Above 200 K, the variation of the MDC is negligible. The temperature-dependent MDC is attributed to the coupling between *electric* dipole ordering and fluctuations and *magnetic* ordering and fluctuations [11, 15, 16]. The magnitude, field, and temperature dependence of the MDC agrees well with that found for bulk BNMO [7].

Using the same methodology and parallel RC network as above, we have also calculated for these samples the effective dielectric constant as a function of magnetic field. The 'magneto-loss' is defined in terms of the loss tangent, analogously to the MDC. The field-dependent magneto-loss and MDC (MDC(H)) of BNMO with the magnetic field aligned along the [100] and [001] direction of the substrate at 100 kHz and $T = 150$ K are shown in figure 4. The magnitude of the magneto-loss is somewhat larger than that of the MDC. The magnitude of both the MDC and magneto-loss increase with increasing magnetic field, suggesting that the variation is not due to the magnetoresistance of BNMO or the BNMO-electrode interfaces [11, 13]. Further, these values are independent of the orientation of magnetic field with respect to the out-of-plane excitation current, consistent with the fact that the observed magnetodielectric effect does not result from the accumulated space charge at the interface and does not originate from the interaction of the carriers with the magnetic field itself.

The effect of magnetic field on the dielectric constant has been studied from the perspective of exchange magnetoelectronic interaction [15, 16]. The exchange magnetoelectronic interaction is of the form of $\gamma P^2 M^2$, where P and M are the polarization and magnetization respectively [16]. The coupling constant γ is typically a function of temperature. The exchange magnetoelectronic interaction will result in the MDC below the magnetic transition temperature. Since the ferroelectric transition temperature (∼485 K) of BNMO is much larger than the magnetic transition temperature (∼130 K), we can neglect the

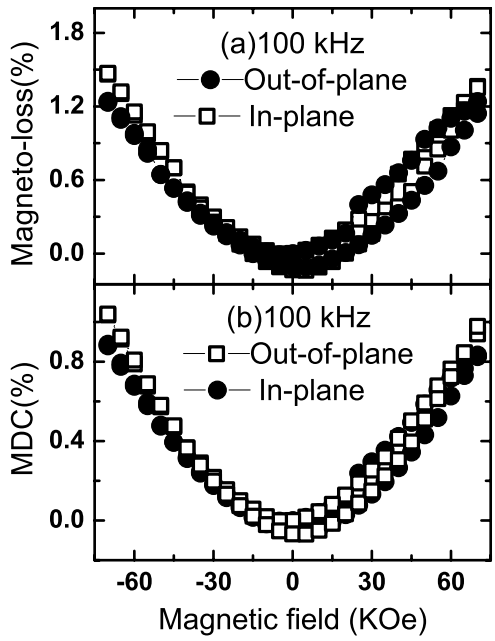

Figure 4. In-plane and out-of-plane magnetic field-dependent (a) magneto-loss and (b) magnetodielectric constant at 150 K for a BNMO film grown on 1.0 wt% Nb doped STO with measurement frequencies of 100 kHz.

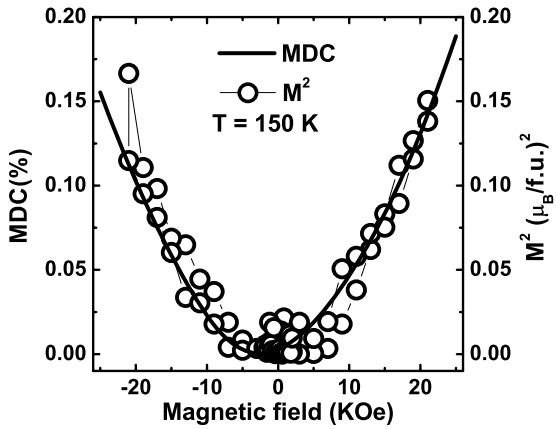

Figure 5. Plots of MDC at 100 kHz and M^2 of BNMO at 150 K as a function of applied magnetic field.

dependence of the electric parameter on temperature near the magnetic transition temperature. Thus, the MDC would simply be proportional to the square of the magnetization. To examine the effect of magnetic field on the dielectric constant, we have plotted the MDC and M^2 of a BNMO film measured at 150 K as a function of magnetic field in figure 5. The overlap of the field-dependent MDC and M^2 data indicate that the exchange interaction between *electric* dipole ordering and fluctuations and *magnetic* ordering and fluctuations is likely responsible for the observed MDC of BNMO.

4. Conclusions

Thin films of multiferroic Bi_2NiMnO_6 (BNMO) have been epitaxially stabilized on various lattice-matched substrates using the pulsed laser deposition technique. The ac transport measurements of BNMO films deposited on conducting Nb doped $SrTiO_3$ substrates as a function of magnetic field exhibit a magnetodielectric effect, and the magnetodielectric constant strongly depends on the applied magnetic field and the measurement frequency. The temperature-dependent magnetodielectric effect is attributed to the exchange interaction between *electric* dipole ordering and fluctuations and *magnetic* ordering and fluctuations.

Acknowledgments

This work was supported by ONR Grant No. N000140610226 (C E Wood) and NSF NIRT Grant No. CMS-0609377.

References

[1] Homes C C, Vogt T, Shapiro S M, Wakimoto S and Ramirez A P 2001 *Science* **293** 673
[2] Kuroiwa Y, Aoyagi S, Sawada A, Harada J, Nishibori E, Takata M and Sakata M 2001 *Phys. Rev. Lett.* **87** 217601
[3] Ranjith R, Kundu A K, Filippi M, Kundys B, Prellier W, Raveau B, Laverdière J, Singh M P and Jandl S 2008 *Appl. Phys. Lett.* **92** 062909
[4] Goodenough J B 1976 *Magnetism and the Chemical Bond* vol 1 (New York: Interscience) chapter 3
[5] Baettig P, Schelle C F, LeSar R, Waghmare U V and Spaldin N A 2005 *Chem. Mater.* **17** 1376
Araujo C A, Cuhair J D, McMillan L D, Scott M C and Scott J F 1995 *Nature* **374** 627
[6] Dawber M, Sinnamon L J, Scott J F and Gregg J M 2002 *Ferroelectrics* **268** 455
[7] Azuma M, Takata K, Saito T, Ishiwata S, Shimakawa Y and Takano M 2005 *J. Am. Chem. Soc.* **127** 8889
[8] Sakai M, Masuno A, Kan D, Hashisaka M, Takata K, Azuma M, Takano M and Shimakawa Y 2007 *Appl. Phys. Lett.* **90** 072903
[9] Ciucivara A, Sahu B and Kleinman L 2007 *Phys. Rev.* B **76** 064412
[10] Shimakawa Y, Kan D, Kawai M, Sakai M, Inoue S, Azuma M, Kimura S and Sakata O 2007 *Japan. J. Appl. Phys.* **46** L845
[11] Padhan P, Guo H Z, LeClair P and Gupta A 2008 *Appl. Phys. Lett.* **92** 022909
[12] Padhan P, LeClair P, Gupta A, Tsunekawa K and Djayaprawira D D 2007 *Appl. Phys. Lett.* **90** 142105
[13] Catalan G 2006 *Appl. Phys. Lett.* **88** 102902
[14] Filippi M, Kundys B, Ranjith R, Kundu A K and Prellier W 2008 *Appl. Phys. Lett.* **92** 212905
[15] Lawes G, Ramirez A P, Varma C M and Subramanian M A 2003 *Phys. Rev. Lett.* **91** 257208
[16] Kimura T, Kawamoto S, Yamada I, Azuma M, Takano Y and Tokura Y 2003 *Phys. Rev.* B **67** 180401