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## Multiferroic thin film of $\text{Bi}_2\text{NiMnO}_6$ with ordered double-perovskite structure

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Epitaxial thin films of  $\text{Bi}_2\text{NiMnO}_6$  were synthesized on  $\text{SrTiO}_3$  substrates by pulsed laser deposition. The resulting film had the rock-salt-type arrangement of  $\text{Ni}^{2+}$  and  $\text{Mn}^{4+}$  ions in a double-perovskite unit cell. The films clearly showed multiferroic properties, both ferromagnetic behavior with a Curie temperature of about 100 K and ferroelectric behavior with a saturated polarization of about  $5 \mu\text{C}/\text{cm}^2$ . © 2007 American Institute of Physics. [DOI: 10.1063/1.2539575]

Multiferroic materials, in which both ferromagnetic and ferroelectric orders coexist, have attracted lots of attention because of their technological applications as well as fundamental physical characteristics. Despite their potential usefulness, however, multiferroic materials are rare in nature and none of them have been used in practical applications so far due to their small response to an external field.

An example of a multiferroic material is  $\text{BiFeO}_3$ .<sup>1,2</sup> Bulk  $\text{BiFeO}_3$  intrinsically shows weak ferromagnetism and ferroelectricity at room temperature. Although this compound is an antiferromagnet, the canted moment of the antiferromagnetically ordered spins gives rise to the weak ferromagnetism. The ferroelectric property, on the other hand, originates from a noncentrosymmetric crystal structure, in which  $\text{Bi}^{3+}$  ions play an important role in the large structural distortion.<sup>3,4</sup> During the last few years, special attention has been devoted to  $\text{BiFeO}_3$  thin films because there were a few reports on enhanced multiferroic properties.<sup>5-9</sup> Although intrinsic ferroelectric and ferromagnetic properties are under debate on  $\text{BiFeO}_3$ , multiferroic properties in the thin films have accelerated research on potential applications of multiferroic materials.

Another example of multiferroic materials is  $\text{Bi}_2\text{NiMnO}_6$  (BNMO) with a double-perovskite structure. We recently prepared bulk BNMO by means of high-pressure synthesis. This compound shows both ferromagnetic [ferromagnetic transition temperature ( $T_{\text{CM}}$ ), 140 K] and ferroelectric [ferroelectric transition temperature ( $T_{\text{CE}}$ ), 485 K] properties. In contrast to the weak ferromagnetism of antiferromagnetically ordered spins in  $\text{BiFeO}_3$ , BNMO shows large moment of ferromagnetically coupled Ni and Mn spins.<sup>10-12</sup> It is noted that BNMO is a metastable phase and is stabilized by means of synthesis under high pressure. This fact reminds us of another important technique for stabilizing a metastable phase, that is, epitaxial growth of a constrained thin film on a substrate. In this study, we synthesized BNMO thin films that were epitaxially grown on  $\text{SrTiO}_3$  substrates by a pulsed laser deposition method. The resulting films have ferromagnetic and ferroelectric behaviors.

$\text{Bi}_2\text{NiMnO}_6$  thin films were synthesized by a pulsed laser deposition (PLD) method with a KrF excimer laser ( $\lambda=248 \text{ nm}$ ). A ceramic target was prepared by sintering from a stoichiometric mixture of  $\text{Bi}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ , and  $\text{NiO}$ .

(0 0 1)-oriented  $\text{SrTiO}_3$  (STO) substrates were used. Substrate temperature and oxygen pressure during the deposition were  $630 \text{ }^\circ\text{C}$  and 0.4 Torr, respectively. The films were deposited at a rate of  $0.6 \text{ \AA}/\text{s}$  to the thickness of  $1000 \text{ \AA}$ . After the deposition, the films were cooled to  $450 \text{ }^\circ\text{C}$  and annealed at that temperature for 1 h. The crystal structure of the obtained films was examined by x-ray diffraction (XRD) with  $\text{Cu K}\alpha$  radiation. The magnetic properties of the films were measured with a superconducting quantum interference device magnetometer by applying magnetic fields parallel to the film plane. The magnetization's temperature dependence was measured under a magnetic field of 100 Oe. Ferroelectric properties were measured for a  $\phi 100 \mu\text{m}$  capacitor fabricated by conventional photolithography and Ar-milling techniques. Nb-0.05 wt % doped conductive STO substrate was used as a bottom electrode and Pt-30 nm/Ti-30 nm/Au-50 nm was deposited as a top electrode.  $P$ (polarization)- $E$ (electric field) hysteresis was recorded by measuring the polarization charge with a 5 kHz triangular wave form at various temperatures. The temperature dependence of the dielectric constant was also measured with a conventional LCR meter with ac frequencies of 1 MHz.

Figure 1 shows a typical  $\theta$ - $2\theta$  XRD pattern of the BNMO thin film grown on the STO (0 0 1) substrate. In XRD only (0 0  $l$ ) reflections of the perovskite structure are observed, and the out-of-plane lattice parameter ( $c=3.87 \text{ \AA}$ ) is obtained from the data. Figure 2 shows a logarithmic intensity mapping in reciprocal lattice space around the (1 0 3) reflection for the BNMO thin film. The in-plane lattice parameter of the film matches that of the substrate perovskite structure ( $a=3.91 \text{ \AA}$ ) while the out-of-plane lattice parameter is smaller than the substrate cell. All the re-

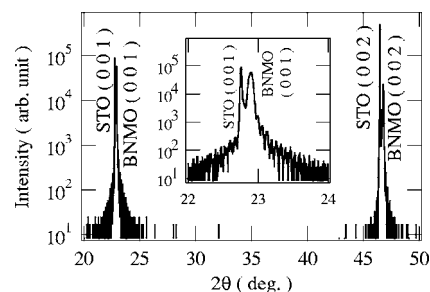


FIG. 1. X-ray diffraction patterns of  $\text{Bi}_2\text{NiMnO}_6$  thin films grown on  $\text{SrTiO}_3$  (0 0 1) substrate.

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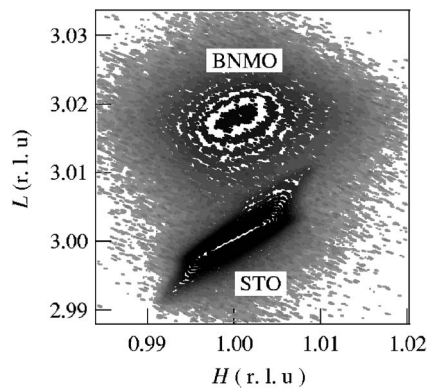


FIG. 2. Logarithmic intensity mapping around (1 0 3) peak in reciprocal space of BNMO thin film grown on STO (0 0 1) substrate.

sults of the XRD measurements indicate that the perovskite BNMO thin film epitaxially grows on the (0 0 1)-oriented STO substrate. In addition, the reflection high energy diffraction (RHEED) pattern (Fig. 3) strongly suggests a double-perovskite structure. Electron beam incidence from the (1 1 0) direction gives weak streaks of the twofold superstructure, whereas the (1 0 0) incidence shows none such a superstructure reflection. These results imply that the synthesized BNMO thin film has  $\sqrt{2}a \times \sqrt{2}a$  superstructure, which originates from a rock-salt-type ordering of the B site ions in the double-perovskite structure.

Figure 4 shows an  $M$ (magnetization)- $H$ (magnetic field) behavior of the BNMO film at 5 K. The observed saturated magnetization is  $4.5 \mu_B/\text{f.u.}$ , which is close to the  $5 \mu_B/\text{f.u.}$  that would be expected from the ferromagnetic ordering of  $\text{Ni}^{2+}$  ( $S=1$ ) and  $\text{Mn}^{4+}$  ( $S=3/2$ ) spins.<sup>10-14</sup> Since a  $\text{Ni}^{2+}$  ion has  $e_g$  electrons while a  $\text{Mn}^{4+}$  has no  $e_g$  electrons, a linear arrangement of  $\text{Ni}^{2+}$ -O- $\text{Mn}^{4+}$  gives rise to a ferromagnetic interaction according to Kanamori-Goodenough's rule. Such a linear arrangement is realized in the rock-salt-type configuration of the  $\text{Ni}^{2+}$  and  $\text{Mn}^{4+}$  ions in the double-perovskite structure, and this rock-salt-type double-perovskite structure is consistent with the superstructure observed in the RHEED pattern. Figure 5(a) shows the temperature dependence of the magnetization of the BNMO thin film measured under a 100 Oe magnetic field applied to the in-plane direction. The magnetization increases below about 100 K. Although it is difficult to determine the transition temperature exactly from

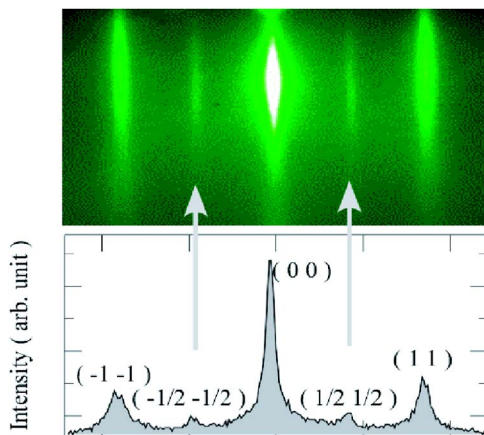


FIG. 3. RHEED pattern and its integrated intensity of BNMO thin film with the (110) beam incidence. The twofold superstructure peaks confirm the double-perovskite structure.

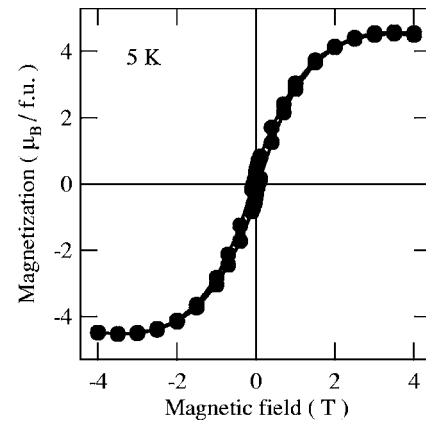


FIG. 4. Magnetic field dependence of magnetization of BNMO thin film measured at 5 K.

the measured magnetic data due to the large diamagnetic moment from the substrate, the ferromagnetic transition of the present BNMO film appears to be around 100 K.

The ferroelectric behavior of the BNMO thin film is confirmed by the  $P$ - $E$  hysteresis loop measured at 7 K, as shown in Fig. 6. Although the observed slightly distorted hysteresis loop includes an effect of leakage current, we can see that the saturated polarization is about  $5 \mu\text{C}/\text{cm}^2$  above  $80 \text{ kV}/\text{cm}$ . It was, however, difficult to observe such ferroelectric hysteresis at higher temperatures because of the increased leakage of the film. The increased leakage current at elevated temperatures is also indicated by the observed increase in the dielectric constant. Accordingly, we cannot confirm the ferroelectric transition temperature of the BNMO film from the ferroelectric hysteresis and dielectric measurements.

The most important point is that our BNMO thin film shows both ferromagnetic and ferroelectric properties at low temperatures. In other words, we clearly confirmed the multiferroic property of the film. Then, it should be interesting to look at the coupling between the magnetic and dielectric properties of our BNMO film. As shown in Fig. 5(b), the observed dielectric constant shows a very small anomaly at the ferromagnetic transition temperature of about 100 K. Although the change is very small, the anomaly at  $T_{\text{CM}}$  appears

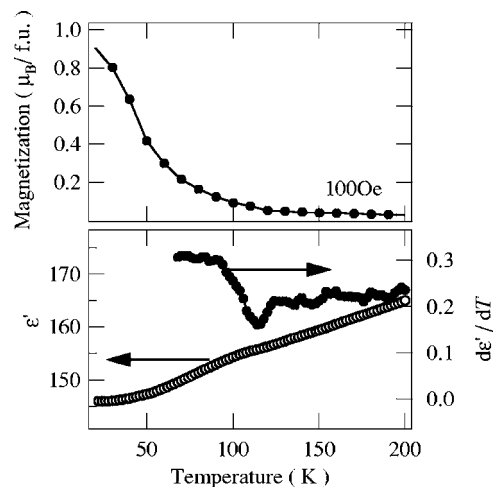


FIG. 5. (a) Temperature dependence of magnetization of BNMO thin film measured under an external field of 100 Oe. Diamagnetic signals of the substrate are subtracted. (b) Temperature dependence of dielectric constant measured with 1 MHz and its derivative.

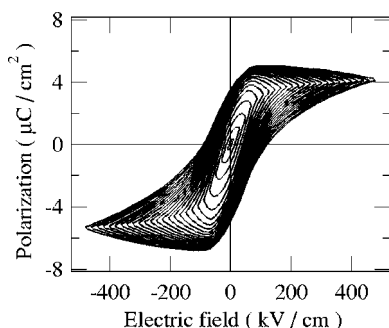


FIG. 6. Ferroelectric  $P$ - $E$  hysteresis loops of BNMO thin film measured at 7 K under 5 kHz frequency.

to show some interplay between the ferromagnetic and ferroelectric interactions. Thus, the coupling between ferromagnetic and ferroelectric interactions seems to exist in BNMO, but it seems to be quite small.

Finally, we discuss some interesting differences between our multiferroic thin film and a bulk BNMO sample synthesized under high pressure.<sup>13</sup> The bulk sample showed significant distortion with a monoclinic structure, and the noncentrosymmetric  $C_2$  arrangement of the constituent ions produced spontaneous ferroelectric polarization along the  $b$  axis. In contrast, our epitaxial BNMO thin film showed a simple tetragonal perovskite structure due to the constraining effect of the perovskite-structure substrate. If the essential crystal structure of our thin film is similar to that of bulk, the polarization vector should be along the (1 1 1) direction of the simple perovskite structure, and thus the observed ferroelectric polarization should be a projection along the out-of-plane direction. Since the polarization calculated from the refined bulk crystal structure was about  $20 \mu\text{C}/\text{cm}^2$ , the observed small polarization (about  $5 \mu\text{C}/\text{cm}^2$ ) of the film might be due to the projection. Another explanation for the observed ferroelectric polarization is that the epitaxial film has completely different structural distortion from that of the bulk. For example,  $\text{PbTiO}_3$ -type ionic displacements in the tetragonal structure may occur in the epitaxial thin film, and thus produce ferroelectric polarization along the out-of-plane direction. Although its crystal structure is rather different from the bulk, the ordered rock-salt-type arrangement of  $\text{Ni}^{2+}$  and  $\text{Mn}^{4+}$  ions, i.e., a double-perovskite structure, is realized in our thin film. However, the ferromagnetic transition temperature of about 100 K is rather low compared with

the 140 K of the bulk material. The slight difference in the crystal structure due to the epitaxial constraining effect should decrease the ferromagnetic transition temperature through changes in bond lengths and angles between the magnetic and oxygen atoms.

In conclusion, we synthesized epitaxial thin film of BNMO with an ordered double-perovskite structure on  $\text{SrTiO}_3$  substrate by means of the PLD. The magnetization measurement revealed ferromagnetic ordering of  $\text{Ni}^{2+}$  and  $\text{Mn}^{4+}$  spins below 100 K. Ferroelectric hysteresis with a saturated polarization of about  $5 \mu\text{C}/\text{cm}^2$  was confirmed. A coupling between the ferromagnetic and ferroelectric interactions in BNMO appears to exist, but it seems to be quite small.

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