RAPID COMMUNICATIONS

PHYSICAL REVIEW B **67**, 180401(R) (2003)

Magnetocapacitance effect in multiferroic $BiMnO_3$

T. Kimura,[1,*] S. Kawamoto,[1] I. Yamada,[2] M. Azuma,[2,3] M. Takano,[2] and Y. Tokura[1]

[1]*Department of Applied Physics, University of Tokyo, Tokyo 113-8656, Japan*
[2]*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*
[3]*Japan Science Technology Corporation, Kawaguchi 332-0012, Japan*

(Received 27 January 2003; published 7 May 2003)

We have investigated the structural, magnetic, and electric properties of ferromagnetic $BiMnO_3$ with a highly distorted perovskite structure. At $T_E = 750–770$ K, a centrosymmetric–to–non-centrosymmetric structural transition takes place, which describes of the ferroelectricity in the system. The changes in the dielectric constant were induced by the magnetic ordering ($T_M \approx 100$ K) as well as by the application of magnetic fields near T_M. These features are attributed to the inherent coupling between the ferroelectric and ferromagnetic orders in the multiferroic system.

DOI: 10.1103/PhysRevB.67.180401 PACS number(s): 75.47.Lx, 75.80.+q, 77.80.−e

The nomenclature ‘‘multiferroics’’ has been coined for materials in which two or all three ferroic orders, ferroelectrics, ferromagnetics, and ferroelastics coexist in the same phase.[1] In the multiferroics with ferromagnetic and ferroelectric ordering simultaneously, one can expect the coupling between the magnetic and dielectric properties as well as their control by the application of magnetic and/or electric fields.[2] However, we rarely encounter such multiferroics. Most ferromagnetic oxides contain the center of symmetry and do not allow an electric polarization, whereas most of the ferroelectric oxides consist of transition-metal ions without the seed of magnetism (i.e., active *d* electrons). Hence, few multiferroics have been reported so far,[3] although a history of studies on ferroelectromagnets can be traced back to the work in 1958 by Smolenskii and co-workers.[4,5] Furthermore, with the exception of a few compounds such as some boracites[6] and magnetite,[7] most of the multiferroics reported so far are antiferromagnets without spontaneous magnetization, in which a conspicuous response to the application of magnetic fields cannot be expected.

Recently, Hill and co-workers performed band-structure calculations on a highly distorted perovskite $BiMnO_3$, and proposed that this ferromagnetic compound is expected to be ferroelectric.[8] The electronic configuration of Mn^{3+} ion in $BiMnO_3$ is $t_{2g}^3 e_g^1$ (spin quantum number $S=2$) as in a famous orbital-ordered manganite $LaMnO_3$. The ionic radius of Bi^{3+} (1.24 Å in nine-coordination) on an *A*-site is very close to that of La^{3+} (1.22 Å).[9] However, $BiMnO_3$ shows the ferromagnetism below ~ 105 K (Refs. 10 and 11) in contrast to $LaMnO_3$ having the *A*-type antiferromagnetic ground state. As for electric properties, $BiMnO_3$ is an insulator unlike double-exchange ferromagnets such as $(La,Sr)MnO_3$. Furthermore, a ferroelectric hysteresis loop has been reported in the ferromagnetic state of impure samples recently.[12] The detailed crystal structure of $BiMnO_3$ with the $6s^2$ lone pair in Bi^{3+} is monoclinic (space group; $C2$),[13] which indicates that the system has an off-center distortion responsible for the polar behavior (see the inset of Fig. 1). The $6s^2$ lone pair may play an important role in producing such a polar structure as in a ferroelectric $PbTiO_3$.[8] These studies indicate that $BiMnO_3$ is one of the rare examples of multiferroics. Another interesting feature of in $BiMnO_3$ is its orbital state of e_g electrons. The crystallographic data for the distortion of the MnO_6 octahedra[13,14] suggest that $BiMnO_3$ shows the ordering of e_g-orbital. The semiempirical estimate from the distortion of the MnO_6 octahedra infers the orbital occupation that is defined by the value of θ.[15,16] The occupied e_g-orbital wave function Ψ is taken as $\Psi = \cos(\theta/2)\phi_{3z^2-r^2} + \sin(\theta/2)\phi_{x^2-y^2}$. The $d_{3x^2-r^2}$, $d_{3y^2-r^2}$, and $d_{3z^2-r^2}$, orbital states correspond to $\theta = 120°$, $-120°$, and $0°$, respectively. The expected orbital ordering pattern of $BiMnO_3$ at room temperature[13] can be regarded as the ordered stack of θ

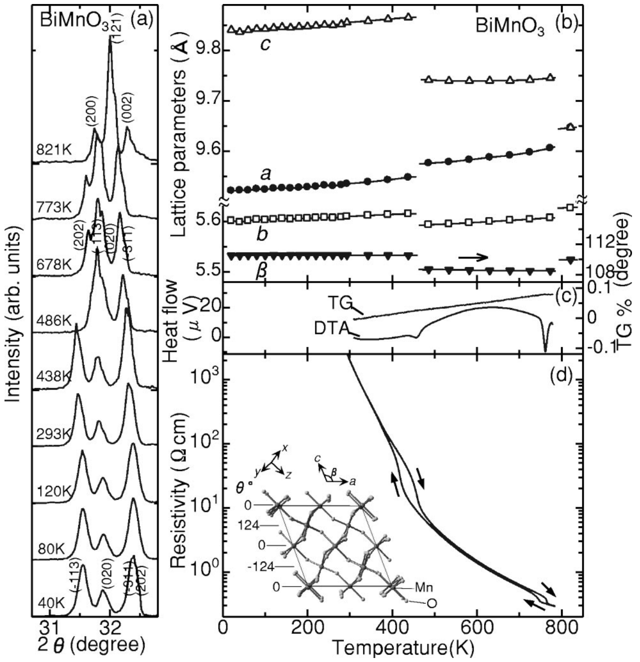

FIG. 1. Left: (a) Portion of powder x-ray diffraction data (Cu $K\alpha$) at various temperatures for $BiMnO_3$. (b) Temperature dependence of the lattice parameters of $BiMnO_3$ in the $C2$ monoclinic unit cell. The crystal structure at 835 K can be indexed by the $Pbnm$ orthorhombic structure. (c) Temperature dependence TG/DTA and (d) resistivity which showing two anomalies at 420–440 K and 750–770 K. The inset shows the crystal structure and the possible orbital ordering at room temperature.

$=0°/124°/0°/-124°/0°/\cdots$ along the c axis, as displayed in the inset of Fig. 1. The ferromagnetism of $BiMnO_3$ may be attributed to the orbital ordering that produces the three-dimensional ferromagnetic superexchange interaction of e_g electrons.[17] In this paper, we report the magnetic-order- and magnetic-field-induced change in the dielectric response of $BiMnO_3$, and discuss the coupling between the magnetic and dielectric properties in the non-centrosymmetric ferromagnet.

Polycrystalline $BiMnO_3$ samples were prepared under high pressure. A mixed powder of Bi_2O_3, Mn_2O_3, and MnO_2 with a prescribed ratio was packed into a gold capsule ($\sim$4 mm$\phi\times$6 mm), and was heated in a cubic anvil-type apparatus at 3 GPa and 700 °C for 30 min. The obtained samples were characterized by powder x-ray diffraction (XRD) measurements using Cu$K\alpha$ radiation. The Rietveld analysis[18] on the XRD pattern indicated that the samples are almost single phase of $BiMnO_3$ and can be indexed by the $C2$ monoclinic structure at room temperature. However, a small amount of impurity phases ($Bi_2O_2CO_3$ and $Bi_2Mn_4O_{10}$) were included. The magnetization and specific heat for the samples were also measured with a commerical magnetometer and a relaxation technique, respectively. For dielectric measurements, the sample was transformed into thin plates with smooth faces onto which Au electrodes were evaporated. The dielectric constant was measured at 1–100 kHz in magnetic fields using a LCR meter and a superconducting magnet. Magnetic fields H were applied parallel to the plates.

One of the requirements for ferroelectric materials is the existence of the structural phase transition from non-centrosymmetric–to–centrosymmetric structure. We performed XRD measurements over a wide temperature range to search for the phase transition. Above room temperature, the measurements were performed in a flow of 6N-purity Ar gas to prevent the oxidation of the sample. (Former XRD studies at high temperature were made in air atmosphere.[11,12,19]) Figure 1(a) displays a portion of powder XRD patterns for $BiMnO_3$ at various temperatures. In Fig. 1(b), we summarize the temperature dependence of the lattice parameters in the warming run. No significant structural phase transition has been observed below room temperature, which is consistent with the recent neutron-diffraction studies.[13,14] Above room temperature, however, successive structural changes take place. The first structural change is observed at $\sim$450 K, where the lattice parameters abruptly change. However, the crystal structure of the midtemperature phase can be indexed by the $C2$ monoclinic one, the same as that at low temperatures. On further increasing the temperature, another structural change occurs around $\sim$770 K. The high-temperature phase can be indexed by the $Pbnm$ orthorhombic structure that does not allow spontaneous polarization. To clarify the nature of these transitions, we performed measurements of thermogravimetry (TG), differential thermal analysis (DTA), and resistivity in a flow of Ar. As shown in Fig. 1(c), the DTA curve exhibits two endothermic peaks corresponding to the structural transitions. Furthermore, the resistivity also shows two anomalies in accord with the structural transitions [Fig. 1(d)]. The anomalies accompany thermal hystereses with a width more than $\sim$20 K. These observations confirm that both structural transitions have the first order nature, and indicate that the ferroelectric transition in $BiMnO_3$ is likely to occur at $T_E\approx$750–770 K in terms of crystallography.

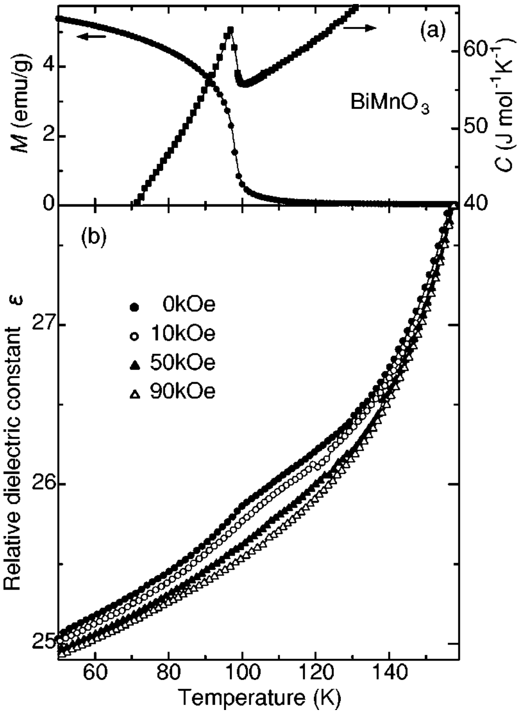

FIG. 2. Temperature dependence of (a) the magnetization at 100 Oe, the specific heat, and (b) the real part of relative dielectric constant of $BiMnO_3$ at selected magnetic fields in the vicinity of T_M.

Let us proceed to the relation between magnetic and dielectric properties. Figure 2 shows the temperature profiles of (a) the magnetization at 100 Oe, the specific heat, and (b) the relative dielectric constant ε of 100 kHz at selected magnetic fields. A steep rise of magnetization toward lower temperature and an anomaly of specific heat at $T_M\sim$100 K correspond to the onset of ferromagnetic ordering. The shape of the specific-heat anomaly together with the lack of any observable thermal hystereses describes the second order nature of the ferromagnetic transition. Remarkable features in the ε-T curves are anomalies in the vicinity of T_M. At zero field, ε decreases steeply below T_M. This suggests that the magnetic ordering suppresses the dielectric constant. A similar cusp of the ε-T curves correlated with the magnetic ordering can be observed in some ferroelectric antiferromagnets such as $BaNiF_4$ (Ref. 20) and hexagonal rare-earth manganites.[21]

In the framework of the Ginzburg-Landau theory for the second-order phase transition, Smolenskii[5,22] explained the origin of the anomaly in ε on the magnetic order of ferroelectromagnets with $T_M\ll T_E$. In a ferroelectromagnet, the thermodynamic potential Φ can be written in the form[23]

$$\Phi=\Phi_0+\alpha P^2+\frac{\beta}{2}P^4-PE+\alpha' M^2+\frac{\beta'}{2}M^4-MH + \gamma P^2M^2, \tag{1}$$

where P and M are the polarization and the magnetization, respectively. Φ, α, β, α', β', and γ are functions of temperature. The term of exchange magnetoelectric interaction of the form γP^2M^2 is allowed in any ferroelectromagnet, which gives rise to a deviation of electric susceptibility $\chi^E(T)$ below T_M from the values obtained by extrapolation into the region $T<T_M$ of $\chi^E(T)$ from the paramagnetic phase. [Here, $\chi^E(T)=(\partial^2\Phi/\partial P^2)^{-1}$.] We denote this difference as $\delta\chi^E$. When T_M and T_E are separated apart, enough, such as in the present $BiMnO_3$, we can neglect the dependence of the electric parameters on the temperature near T_M.[23] In this case, the difference of the relative dielectric constant ($\delta\varepsilon=4\pi\delta\chi^E$) below T_M will be proportional to the square of the magnetic-order parameter:

$$\delta\varepsilon \sim \gamma M^2. \tag{2}$$

The sign of $\delta\varepsilon$ depends on the sign of the constant magnetoelectric interaction γ, and can be either positive or negative. $\delta\varepsilon$ will increase in absolute magnitude as a function of temperature in proportion to square of the spontaneous magnetization. However, it is generally hard to confirm it experimentally due to the difficulty in estimating the ε value of the paramagnetic phase below T_M. For instance, in a pyroelectric and weak ferromagnetic $BaMnF_4$, there are conflicting reports about the relation between $\delta\varepsilon$ and the sublattice magnetization.[24,25]

Since the magnetic-order parameter of ferromagnets can be controlled by the application of relatively low magnetic fields near T_M, a more remarkable magnetic-field effect on the dielectric constant in the present $BiMnO_3$ is expected than in ferroelectric antiferromagnets.[26,27] As shown in Fig. 2, the application of magnetic fields induces a fairly large suppression of ε around T_M, and suppresses the anomaly in ε at T_M. The field-induced change in ε (magnetocapacitance effect) becomes maximal at T_M. To further clarify the character of the magnetocapacitance effect, we display in Figs. 3(a) and 3(b) the isothermal magnetization and magnetocapacitance ($\Delta\varepsilon(H)/\varepsilon(0)=[\varepsilon(H)-\varepsilon(0)]/\varepsilon(0)$) curves, respectively, at various temperatures. As seen in Fig. 3(a), the saturated moment is near that expected for the full Mn moment at 10 K ($\sim 3.6\mu_B$), and gradually decreases with increasing temperature. The coercive force in the $BiMnO_3$ sample is small (<200 Oe). At temperatures enough below T_M, the magnitude of magnetocapacitance is negligibly small, although the magnetization has reached $\geqslant 80\%$ of its value by 10 kOe (due to magnetic domain rotation). This suggests that the magnetic domain rotation least affects the dielectric constant at the low temperature. With increasing temperature, the magnitude of magnetocapacitance becomes larger and shows the maximum around T_M. For example, $-\Delta\varepsilon(90\text{ kOe})/\varepsilon(0)$ reaches 0.6% at 100 K. On further increasing the temperature above T_M, the magnetocapacitance again decreases.

The change in the sample dimension by the magnetic order, i.e., magnetostriction, might be considered as the origin of the observed magnetocapacitance effect. To estimate the magnitude of magnetostriction $\Delta L/L$, we also performed the striction measurements using a uniaxial strain gauge with the length of 0.2 mm, which was attached to the widest face of the specimen. Even in the vicinity of $T_M \approx 100$ K, $\Delta L/L$ both parallel and perpendicular to magnetic fields is $\sim 4\times10^{-5}$ at 70 kOe. The estimated change in the dielectric constant due to the magnetostriction is $\sim(4\times10^{-3}\%)$ (at 110 K and 70 kOe), which is two orders of magnitude smaller than the presently observed value. Therefore, the magnetostriction is not the main origin of the observed magnetocapacitance effect.

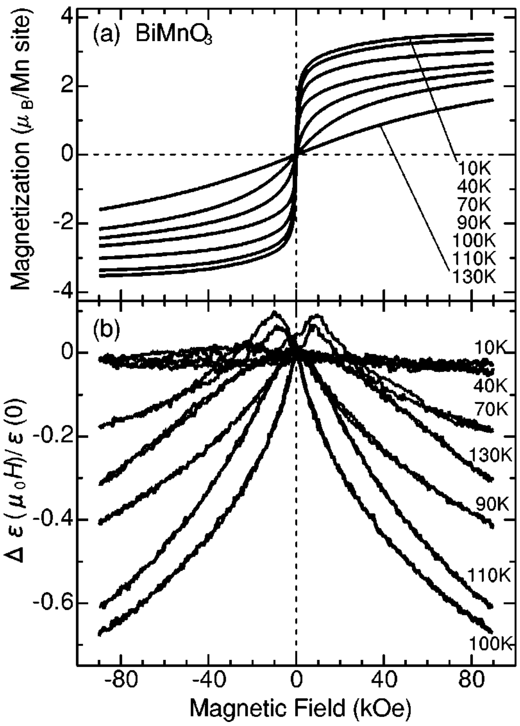

FIG. 3. Isothermal (a) magnetization and (b) field-induced change in dielectric constant as a function of a magnetic field at various temperatures of $BiMnO_3$.

To examine the effect of magnetic ordering on the dielectric constant and see the validity of Eq. (2), the data near T_M

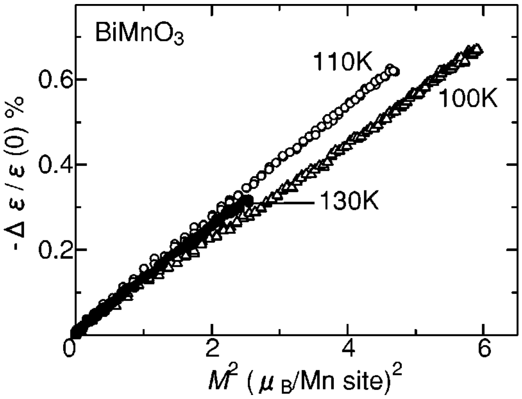

FIG. 4. Magnitude of field-induced change of dielectric constant $-\Delta\varepsilon/\varepsilon(0)$ as a function of square of magnetization M^2 at temperatures in the vicinity of T_M.

in Fig. 4 are replotted as $-\Delta\varepsilon/\varepsilon(0)$ vs M^2 in Fig. 4. It should be noted that the $\Delta\varepsilon - M^2$ data at different temperatures approximately falls onto a single line in spite of seemingly different magnetocapacitance behaviors. The M dependence of the magnetocapacitance value is thus expressed by a scaling function, $-\Delta\varepsilon/\varepsilon(0) = kM^2$ (k: constant). This implies that Eq. (2) is valid for the present non-centrosymmetric ferromagnet, $BiMnO_3$. These observed results lead to the conclusion that the origin of the magnetocapacitance is attributed to the coupling term $\gamma P^2 M^2$ in the thermodynamic potential [see Eq. (1)].

In summary, we have examined the relation between magnetocapacitance and magnetization of a non-centrosymmetric ferromagnet with orbital ordering, $BiMnO_3$. A fairly large negative magnetocapacitance effect was observed in the vicinity of the ferromagnetic transition temperature T_M. The magnitude of magnetocapacitance is well described as $-\Delta\varepsilon/\varepsilon(0) = kM^2$ near T_M. The magnetocapacitance effect can be phenomenologically interpreted in terms of a simple Ginzburg-Landa theory for the second-order phase transition of ferroelectromagnets, and is ascribed to the magnetoelectric coupling term $\gamma P^2 M^2$ in the thermodynamic potential. The observations ascertain the possible control of dielectric properties by magnetic fields in ''multiferroics.''

We thank D. I. Khomskii and N. Nagaosa for helpful discussions, H. Shintani for specific-heat measurements, and K. Otzschi for high-temperature x-ray diffraction measurements. This work was supported by Grant-in-Aids for Scientific Research from the MEXT of Japan.

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*Present address: Los Alamos National Laboratory, K774, Los Alamos, New Mexico 87545.

[1] H. Schmid, Ferroelectrics **62**, 317 (1994).

[2] H. Schmid, Ferroelectrics **221**, 9 (1999).

[3] N.A. Hill, J. Phys. Chem. B **104**, 6694 (2000).

[4] G.A. Smolenskii, A.I. Agranovskaya, S.N. Popov, and V.A. Isupov, Zh. Tekh. Fiz. **28**, 2152 (1958) [Sov. Phys. Tech. Phys. **3**, 1981 (1958)].

[5] G.A. Smolenskii and I.E. Chupis, Ups. Fiz. Nauk **137**, 415 (1982) [Sov. Phys. Usp. **25**, 475 (1982)].

[6] E. Ascher, H. Rieder, H. Schmid, and H. Stössel, J. Appl. Phys. **37**, 1404 (1966).

[7] K. Kato, S. Iida, K. Yanai, and K. Mizushima, J. Magn. Magn. Mater. **31-34**, 783 (1983).

[8] R. Seshadri and N.A. Hill, Chem. Mater. **13**, 2892 (2001).

[9] R.D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **32**, 751 (1976).

[10] V.A. Bokov, I.E. Myl'nikova, S.A. Kizhaev, M.F. Bryzhina, and N.A. Grigoryan, Fiz. Tverd. Tela (Leningrad) **7**, 2993 (1966) [Sov. Phys. Solid State **7**, 2993 (1966)].

[11] F. Sugawara, S. Iida, Y. Syono, and S. Akimoto, J. Phys. Soc. Jpn. **25**, 1553 (1968).

[12] A. Moreira dos Santos, S. Parashar, A.R. Raju, Y.S. Zhao, A.K. Cheetham, and C.N.R. Rao, Solid State Commun. **122**, 49 (2002).

[13] T. Atou, H. Chiba, K. Ohoyama, Y. Yamaguchi, and Y. Syono, J. Solid State Chem. **145**, 639 (1999).

[14] A. Moreira dos Santos, A.K. Cheetham, T. Atou, Y. Syono, Y. Yamaguchi, K. Ohoyama, H. Chiba, and C.N.R. Rao, Phys. Rev. B **66**, 064425 (2002).

[15] G. Matsumoto, J. Phys. Soc. Jpn. **29**, 606 (1970).

[16] J. Kanamori, J. Appl. Phys. **31**, 14S (1960).

[17] T. Hotta, S. Yunoki, M. Mayr, and E. Dagotto, Phys. Rev. B **60**, R15 009 (1999).

[18] F. Izumi, in *Rietveld Method*, edited by R. A. Young (Oxford University Press, Oxford, 1993), Chap. 13.

[19] H. Faqir, H. Chiba, M. Kikuchi, and Y. Syono, J. Solid State Chem. **142**, 113 (1999).

[20] A.M. Glass, M.E. Lines, M. Eibschutz, F.S.L. Hsu, and H.J. Guggenheim, Commun. Phys. (London) **2**, 103 (1977).

[21] N. Iwata and K. Kohn, J. Phys. Soc. Jpn. **67**, 3318 (1998).

[22] G.A. Smolenskii, Fiz. Tverd. Tela (Leningrad) **4**, 1095 (1962) [Sov. Phys. Solid State **4**, 807 (1962)]; A.I. Mitsek and G.A. Smolenskii *ibid.*, **4**, 2620 (1963).

[23] In reality, the ferroelectric transition is likely of to be the first order in $BiMnO_3$ as we clarified in this study, and the P^6 term in Eq. (1). However, the neglect of this term has no influence on the semiquantitative discussion on $\delta\chi^E$ near $T_M (\ll T_E)$.

[24] J.F. Scott, Phys. Rev. B **16**, 2329 (1977).

[25] D.L. Fox, D.R. Tilley, J.F. Scott, and H.J. Guggenheim, Phys. Rev. B **21**, 2926 (1980).

[26] Z.J. Huang, Y. Cao, Y.Y. Sun, Y.Y. Xue, and C.W. Chu, Phys. Rev. B **56**, 2623 (1997).

[27] In paraelectric $EuTiO_3$, the dielectric constant shows remarkable change $[\Delta\varepsilon/\varepsilon(0) \sim 7\%]$ with the magnetic ordering of Eu spins.T. Katsufuji and H. Takagi, Phys. Rev. B **64**, 054415 (2001).