Synthesis and characterization of an n = 6 Aurivillius phase incorporating magnetically active manganese, Bi 7 (Mn , Ti) 6 O 21

M. A. Zurbuchen, R. S. Freitas, M. J. Wilson, P. Schiffer, M. Roeckerath, J. Schubert, M. D. Biegalski, G. H. Mehta, D. J. Comstock, J. H. Lee, Y. Jia, and D. G. Schlom

Synthesis and characterization of an *n*=6 Aurivillius phase incorporating magnetically active manganese, Bi$_7$(Mn,Ti)$_6$O$_{21}$

M. A. Zurbuchen[a)]
Electronics and Photonics Laboratory, The Aerospace Corporation, El Segundo, California 90245

R. S. Freitas,[b)] M. J. Wilson, and P. Schiffer
Department of Physics, Pennsylvania State University, University Park, Pennsylvania 16802
and Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802

M. Roeckerath and J. Schubert
IBN 1-IT, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany and CNI, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

M. D. Biegalski
Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

G. H. Mehta, D. J. Comstock, J. H. Lee, Y. Jia, and D. G. Schlom
Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802-5005

Epitaxial films of Bi$_7$Mn$_{3.75}$Ti$_{2.25}$O$_{21}$ were prepared to yield a previously unsynthesized material. The superlattice phase is produced by incorporating the magnetoelectric BiMnO$_3$ into the perovskite substructure of the ferroelectric Bi$_4$Ti$_3$O$_{12}$, a strategy which is hoped to yield previously undiscovered multiferroic materials. X-ray diffraction and transmission electron microscopy (TEM) confirm synthesis of an epitaxial *n*=6 Aurivillius phase. Magnetization measurements show ferromagnetic behavior with a Curie point of 55 K, but electronic polarization measurements show no remanent polarization. Rutherford backscattering spectrometry indicates a channeling minimum χ_{min} of 22%, consistent with the high density of out-of-phase domain boundaries observed by TEM. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2756163]

Multiferroic materials exhibit simultaneously two or more of ferroelectricity, magnetism, or ferroelasticity.[1] Magnetoelectric materials [exhibiting both ferroelectric and ferromagnetic (or ferrimagnetic) behaviors] are of particular interest because they hold the potential to control switching of electric polarization via magnetic fields and magnetization via electric fields. Such materials could enable spintronics, magnetic sensors with fewer wires and high sensitivity, and various types of memories and actuators. The physics of such systems is the focus of intense study because the nature of the physical interaction between the order parameters is not thoroughly understood.

Few electric-magnetic (magnetoelectric) materials are known, particularly that are stable at atmospheric pressure.[2,3] So far, these are limited to systems which exhibit weak ferroelectricity or weak ferromagnetism. The resulting magnetoelectric coefficients are also weak.[3–7]

In this letter, we describe the synthesis and characterization of an *n*=6 Aurivillius phase incorporating magnetically active manganese, Bi$_4$(Mn,Ti)$_6$O$_{21}$. This phase is a composite of the ferroelectric phase Bi$_4$Ti$_3$O$_{12}$ and the ferromagnetic phase BiMnO$_3$. The phase was confirmed by x-ray diffraction (XRD) and transmission electron microscopy (TEM). Crystalline quality was also characterized by Rutherford backscattering spectrometry (RBS). Magnetization behavior was studied as a function of field and temperature.

A composite approach to fabricating two-phase ferroelectric-magnetic composite heterostructures[8] has been demonstrated, and refining the scale to the atomic level is useful for both maximizing elastic coupling and exploring its spatial limits. Macroscale, 3-3 bulk composites[9] have mechanical stability issues and exhibit poor coupling.[10] Micro scale tape cast structures avoid mechanical issues and exhibit stronger coupling,[11] but granular orientation effects likely still reduce coupling. Nanoscale thin film structures have been the most effective in producing multiferroic composites. Although a 2-2 composite (stack of films on a substrate)[9] is convenient for electrical characterization, a nonferroic substrate will clamp the response.[12] A solution is to use a ferroic substrate,[13] but limited selection of substrate materials is problematic. Another solution is to use a 3-1 composite system to maximize out-of-plane mechanical coupling, for example, BaTiO$_3$−CoFe$_2$O$_4$.[14] The ultimate level is at the atomic or unit-cell scale, beyond the reach of most physical or phase separation approaches, so natural multiferroics, single-phase materials that can incorporate substructures of both types must be found.

Layered perovskite oxide materials are excellent candidates for the potential synthesis of natural multiferroic materials—nanocomposites at the atomic scale. One approach is to choose a ferroelectric host and to incorporate a magnetically active species. The Aurivillius layered perovskites[15] are chosen because most are ferroelectric,[16] and recently large-celled Aurivillius phases have been stabilized via charge-mediated growth, making them accessible. The phases are members of a homologous series of Bi-

a)Electronic mail: mark.a.zurbuchen@aero.org and mark_z@mac.com
b)Also at: Instituto de Física, Universidade de São Paulo, C.P. 66318, São Paulo, São Paulo 05315-970, Brazil.

layered oxides, consisting of $Bi_2O_2^{2+}$ layers alternating with $nABO_3$ perovskite units, described by the formula $Bi_2O_2(A_{n-1}B_nO_{3n+1})$. Typical high-$n$ Aurivillius phases are ferroelectric, such as the $n=3$ $Bi_4Ti_3O_{12}$ (Ref. [15]) or the $n=7$ $Sr_4Bi_4Ti_7O_{24}$. Bismuth also occupies the A sites.

The high-n Aurivillius phases cannot be synthesized in bulk form due to small differences in formation energy between related members, or because their free energy is higher than that of a multiphase mixture with the same overall composition. Co-deposition growth of an epitaxial film as we report here using pulsed laser deposition (PLD) can provide the driving force to stabilize a single homologous series member via epitaxial stabilization.[17]

A magnetically active cation that fits into the lattice, while existing in a magnetic oxidation state is needed. Aurivillius structures will accommodate B-site cations from 0.58 to 0.645 Å in radius.[18] Among the magnetically active transition elements, the B-site cation that best fits both criteria is Mn^{3+} ($r_{VI}=0.58$ Å).[19] Fe^{3+} will fit, but $BiFeO_3$ is antiferromagnetic,[19,20] and others [Mn^{2+} ($r_{VI}=0.67$ Å), Co^{3+} ($r_{VI}=0.545$ Å), Ni^{3+} ($r_{VI}=0.56$ Å)] (Ref. [21]) do not fit.

Bulk synthesis of a manganese-containing Aurivillius phase, $Bi_2Sr_{1.4}La_{0.6}Nb_2MnO_{12}$, was recently reported,[22] in which the manganese would have an average charge of $Mn^{3.4+}$, perhaps the lower limit of manganese accommodation in the structure. It exhibited spin-glass magnetic behavior on cooling, but was not ferroelectric. An earlier report of $Bi_2Sr_2Nb_2MnO_{12}$ remains unconfirmed,[23] and contained a significant proportion of perovskite impurity phases.[22] Such a composition, with Mn^{4+}, would in any case not be expected to be ferromagnetic. We believe that it is necessary to select a composition compatible with a large proportion of Mn^{3+} in order to synthesize a multiferroic Aurivillius phase. Single crystals or epitaxial films are desirable for study of multiferroic properties, but neither form of any Aurivillius phase containing manganese has been reported.

The interaction of strain with the substrate and the ferroic order parameters of such a film remains unknown. Layered perovskite oxides are known to exhibit magnetostrictive behavior.[24,25] But some show no ferroelectric strain.[26]

Films were synthesized by PLD from 99.99%+ pure single targets, with 10-80% excess bismuth using a KrF excimer laser, $\lambda=248$ nm, under $p_{O_2+O_3}=90$ mTorr at $600-800$ °C with a radiatively heated substrate holder[27] onto (001) $SrTiO_3$ and were quenched to avoid decomposition. We performed magnetization measurements using a Quantum Design superconducting quantum interference device magnetometer with the magnetic field parallel to the sample plane. In-plane electronic polarization measurements were taken at 77 K with interdigitated electrodes on an aix-ACCT ferroelectric tester. Chemical composition and structural perfection were investigated by RBS and channeling using 1.4 MeV He^+-ions.

As-grown films are phase pure and epitaxial, with c perpendicular to the substrate surface, as shown by the θ-2θ XRD scan in Fig. 1. The full width at half maximum (FWHM) of the rocking curve ω scan of the 00$\underline{28}$ peak and the ϕ scan of (not shown) the 111$\underline{4}$ peak taken at $2\theta=33.1°$ and $\chi=46.0°$ are 0.10° and 0.13°, respectively. RBS results are consistent with a Bi:Mn:Ti ratio of 28:18:9. This, indicates that the films have composition of $Bi_7Mn_{3.75}Ti_{2.25}O_{21}$. The c-axis lattice parameter, calculated by a regression fit of θ-2θ peak positions is 56.0 ± 0.1 Å, and
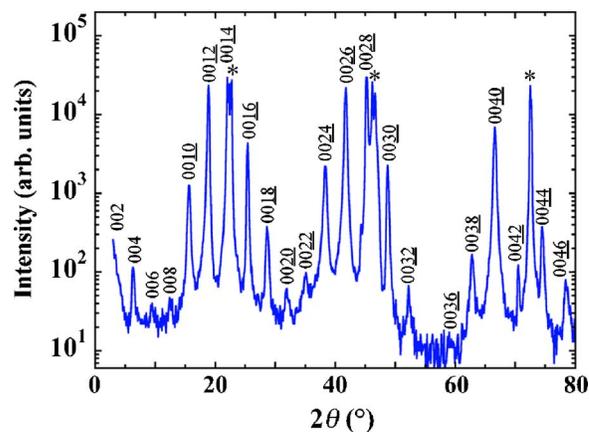
FIG. 1. (Color online) θ-2θ x-ray diffraction scan of the (001) $Bi_7Mn_{3.75}Ti_{2.25}O_{21}/(001)$ $SrTiO_3$ film, in which the $SrTiO_3$ substrate peaks are marked by asterisks. The film is phase pure and epitaxial, with a low mosaic of 0.10° FWHM out of plane and 0.13° FWHM in-plane (not shown).

$a=b=3.76\pm0.05$ Å based on a tetragonal prototype.

TEM is necessary for structure confirmation of large-period superlattice phases such as this, which are difficult to discern from intergrowths of multiple shorter-period members by XRD alone.[28,29] The cross-section electron diffraction pattern and lattice image in Figs. 2(a) and 2(b), from the same sample shown in Fig. 1, provide confirmation of synthesis of the $n=6$ Aurivillius phase. The film is free of intergrowths of other-n Aurivillius phases, but has a high density of out-of-phase boundaries[29] (OPBs) oriented at $\approx55°$ from [001]. These are visible in the cross-sectional TEM image in Fig. 2(c) and lead to the streaking of spots in the electron diffraction pattern in Fig. 2(b). Measurements confirm the c-axis lattice parameter obtained by XRD, at 54.3 ± 2.7 and
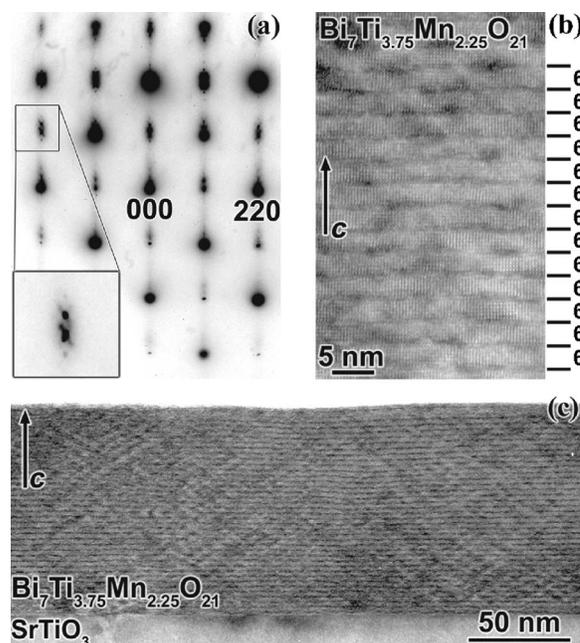
FIG. 2. TEM images taken from a cross section of the same $Bi_7Mn_{3.75}Ti_{2.25}O_{21}$ film shown in Fig. 1. The electron diffraction pattern in (a) and the lattice image in (b) confirm synthesis of an $n=6$ Aurivillius phase. The number of perovskite layers n observed between Bi_2O_2 layers is indicated at the right of the lattice image. (c) Bright-field TEM image of the full film thickness, showing an absence of intergrowths, but a high density of OPBs.
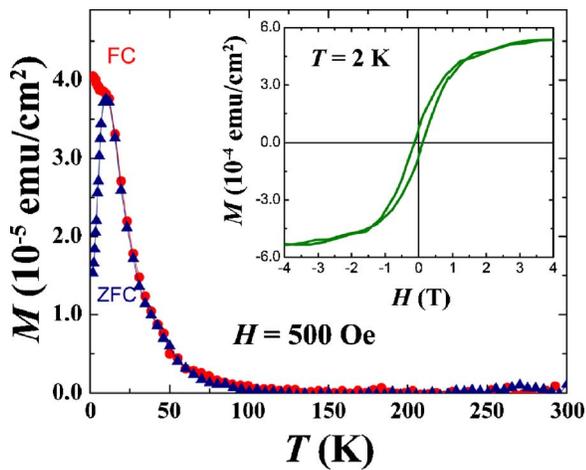
FIG. 3. (Color online) Temperature dependence of the magnetization at H = 50 Oe. The inset shows the field dependence of the magnetization at T = 2 K.

55.4±2.8 Å, by substrate-calibrated electron diffraction and high-resolution TEM, respectively. Although OPBs quench ferroelectricity,[26] the effects of OPBs on ferromagnetic superlattices are unknown.

The results of magnetic characterization are shown in Fig. 3. The sample appears to be ferromagnetic with a Curie point (T_C) of approximately 55 K. Measurements of $M(H)$ show typical ferromagnetic behavior below T_C, with a coercive field of approximately 1200 Oe at 2 K. The differences between field-cooled and zero-field-cooled data are probably attributable to domain effects, but could also indicate the presence of some glassiness in the sample. The T_C is significantly lower than that of bulk $BiMnO_3$, 105 K.[30] This is likely due to the reduced dimensionality of the $BiMnO_3$ perovskite sheets in these natural superlattices.

Electronic polarization data showed a primarily linear response to 200 kV/cm in applied field, with some slight curvature which cannot unequivocally be attributed to ferroelectric behavior and is more likely due to leakage and slight nonlinearity in the dielectric response. Although ferroelectric behavior could not be confirmed in this material, the synthesis route enables the exploration of a number of materials of the Aurivillius type, which are typically ferroelectric.[16]

RBS measurements indicate a Mn concentration of 5.36×10^{16} Mn at./cm^2 and a minimum channeling yield (χ_{min}) of 22%. Saturated value of the magnetization works out to be $1.15 \mu_B$ per manganese, in comparison to the $3.8 \mu_B$ predicted for the average manganese valence of $Mn^{3.2+}$, based on the cation stoichiometry and the low tolerance of oxygen vacancies in Aurivillius phases.[31,32] This suggests that a substantial fraction of the Mn ions are not participating in the ferromagnetic state, perhaps due to antiferromagnetic ordering which might be expected for a perovskite-based superlattice layered along the [001] of the perovskite subcell, considering the d orbital geometry.[33] The high structural disorder, in the form of OPBs,[29] might also contribute to frustration of magnetic ordering.

In conclusion, we report natural superlattices as a route to nanocompositing heteroferroic materials. Using single-target PLD, we have synthesized an epitaxial Aurivillius phase containing manganese, $Bi_7Mn_{3.75}Ti_{2.25}O_{21}$. The material is ferromagnetic, but ferroelectric behavior has not been conclusively observed. A discrepancy exists between the predicted and observed magnetization per manganese atom.

[1]N. A. Hill, Annu. Rev. Mater. Res. **32**, 1 (2002).
[2]A. F. M. dos Santos, A. K. Cheetham, W. Tian, X. Q. Pan, Y. Jia, N. J. Murphy, J. Lettieri, and D. G. Schlom, Appl. Phys. Lett. **84**, 91 (2004).
[3]H. Schmid, Ferroelectrics **162**, 317 (1994).
[4]J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, Science **299**, 1719 (2003).
[5]J. Dho, C. W. Leung, J. L. MacManus-Driscoll, and M. G. Blamire, J. Cryst. Growth **267**, 548 (2004).
[6]T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Nature (London) **426**, 55 (2003).
[7]N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha, and S.-W. Cheong, Nature (London) **429**, 392 (2004).
[8]J. Van Suchtelen, Philips Res. Rep. **27**, 28 (1972).
[9]R. E. Newnham, D. P. Skinner, and L. E. Cross, Mater. Res. Bull. **13**, 525 (1978).
[10]J. Van den Boomgard and R. A. J. Born, J. Mater. Sci. **13**, 1538 (1978).
[11]G. Srinivasan, E. T. Rasmussen, A. A. Bush, K. E. Kamentsev, V. F. Mescheryakov, and Y. K. Fetisov, Appl. Phys. A: Mater. Sci. Process. **78**, 721 (2004).
[12]K. Lefki and G. J. M. Dormans, J. Appl. Phys. **76**, 1764 (1994).
[13]M. A. Zurbuchen, S. Saha, T. Wu, J. Mitchell, and S. K. Streiffer, Appl. Phys. Lett. **87**, 232908 (2005).
[14]H. Zheng, J. Wang, S. E. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S. R. Schinde, S. B. Ogale, F. Bai, D. Viehland, Y. Jia, D. G. Schlom, M. Wuttig, A. Roytburd, and R. Ramesh, Science **303**, 661 (2004).
[15]B. Aurivillius, Ark. Kemi **1**, 463 (1950); **1**, 499 (1950); **2**, 519 (1951); **5**, 39 (1953).
[16]E. C. Subbarao, J. Phys. Chem. Solids **23**, 665 (1962).
[17]O. Y. Gorbenko, S. V. Samoilenkov, I. E. Graboy, and A. R. Kaul, Chem. Mater. **14**, 4026 (2002).
[18]R. A. Armstrong and R. E. Newnham, Mater. Res. Bull. **7**, 1025 (1972).
[19]A. Snedden, C. H. Hervoches, and P. Lightfoot, Phys. Rev. B **67**, 092102 (2003).
[20]I. G. Ismailzide, V. I. Nesterenko, F. A. Mirishli, and P. G. Rustamov, Kristallografiya **12**, 400 (1967) [Sov. Phys. Crystallogr.].
[21]R. D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **32**, 751 (1976).
[22]E. E. McCabe and C. Greaves, J. Mater. Chem. **15**, 177 (2005).
[23]W. J. Yu, Y. I. Kim, D. H. Ha, J. H. Lee, Y. K. Park, S. Seong, and N. H. Hur, Solid State Commun. **111**, 705 (1999).
[24]J. F. Mitchell, D. N. Argyriou, J. D. Jorgensen, D. G. Hinks, C. D. Potter, and S. D. Bader, Phys. Rev. B **55**, 63 (1997).
[25]M. Medarde, J. F. Mitchell, J. E. Millburn, S. Short, and J. D. Jorgensen, Phys. Rev. Lett. **83**, 1223 (1999).
[26]M. A. Zurbuchen, G. Asayama, D. G. Schlom, and S. K. Streiffer, Phys. Rev. Lett. **88**, 107601 (2002).
[27]J. C. Clark, J.-P. Maria, K. J. Hubbard, and D. G. Schlom, Rev. Sci. Instrum. **68**, 2538 (1997).
[28]J. L. Hutchison, J. S. Anderson, and C. N. R. Rao, Proc. R. Soc. London, Ser. A **355**, 301 (1977).
[29]M. A. Zurbuchen, W. Tian, X. Q. Pan, D. Fong, S. K. Streiffer, M. E. Hawley, J. Lettieri, Y. Jia, G. Asayama, S. J. Fulk, D. J. Comstock, S. Knapp, A. H. Carim, and D. G. Schlom, J. Mater. Res. **22**, 1439 (2007).
[30]T. Atou, H. Chiba, K. Ohayama, Y. Yamaguchi, and Y. Syono, J. Solid State Chem. **145**, 639 (1999).
[31]R. A. Armstrong and R. E. Newnham, Mater. Res. Bull. **7**, 1025 (1972).
[32]A. Snedden, S. M. Blake, and P. Lightfoot, Solid State Ionics **156**, 439 (2003).
[33]N. Spaldin (private communication).