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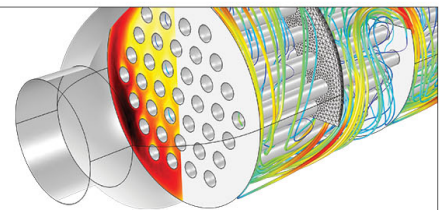
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Monoclinic M_C phase in (001) field cooled BaTiO_3 single crystals

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We report here the finding of a new phase in BaTiO_3 single crystals. High precision x-ray diffraction investigations of (001) field cooled crystals have shown the presence of a monoclinic M_C phase for temperatures below 300 K. This M_C phase is shown to be stable upon removal of the electric field. The results demonstrate the presence of structurally bridging low symmetry phases that lie between tetragonal and rhombohedral ones in this classic perovskite system: indicating a means to achieve high piezoelectricity in Pb-free systems via domain engineering. © 2009 American Institute of Physics. [DOI: 10.1063/1.3073716]

Monoclinic (M) ferroelectric phases have been reported in Pb-based perovskites with morphotropic phase boundaries (MPBs).^{1–11} These low symmetry phases are sandwiched between rhombohedral (R) and tetragonal (T) ferroelectric ones. Such structurally bridging states are believed to be important to the high piezoelectricity of Pb-based perovskites¹² and have been reported in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\%$ PbTiO_3 or $\text{PMN-}x\%$ PT ,^{4–7} $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\%$ PT or $\text{PZN-}x\%$ PT ,^{8–11} and $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ or PZT .^{1–3} Various types of monoclinic structures have been reported in these Pb-based systems including M_A/M_B and M_C , which belong to the space groups C_m and P_m , respectively. The M_A/M_B unit cells have a unique b_m axis along the [110] direction and are doubled and rotated 45° about the c -axis with respect to the pseudocubic cell. The M_A and M_B unit cells are similar except with respect to the magnitudes of the components of the polarization corresponding to the pseudocubic unit cell: for M_A , $P_x = P_y < P_z$, whereas for M_B , $P_x = P_y > P_z$. The M_C unit cell is primitive having a unique b_m axis that is oriented along the pseudocubic [010].

This monoclinic symmetry allows the polarization vector to be unconstrained within a plane rather than constricted to a particular crystallographic axis as for the higher symmetry R , T , or O (orthorhombic) phases. According to the polarization rotation theory,^{13–15} the high electromechanical properties of ferroelectric monoclinic phases are due to the rotation of the polarization vector within the symmetry allowed plane. An alternative adaptive ferroelectric phase theory has proposed that the M_C phase is a structurally heterogeneous state^{16–19} consisting of conformably miniaturized stress accommodating tetragonal nanotwins. This adaptive state is heterogeneous on the nanoscale but homogeneous on the macroscale; it cannot be resolved due to limitations of the diffraction optics. Recent transmission electron microscopy experiments have shown the presence of T nanotwins within the M_C phase of $\text{PMN-}x\%$ PT ^{20,21} for compositions close to the MPB.

Enhanced piezoelectricity in Pb-free materials is of much interest for environmental reasons. However, a suitable replacement for PZT piezoceramics remains elusive. Notable progress has been made in chemically modified

($\text{K}_{0.5}\text{Na}_{0.5}$) NbO_3 -based piezoelectric ceramics^{22–25} and in domain engineering BaTiO_3 crystals.^{26,27} BaTiO_3 is the classic perovskite and is a lead-free ferroelectric. It undergoes a sequence of ferroelectric transitions: $C \rightarrow T \rightarrow O \rightarrow R$ upon cooling with the polarization oriented in the [001], [110], and [111] directions in the T , O , and R phases, respectively. Under an electric field (E) applied along orientations that are different than that of the spontaneous polarization (P_s) directions, enhanced piezoelectricity has been reported by Wada *et al.*^{26,28} This enhancement is similar to that found in domain-engineered $\text{PMN-}x\%$ PT and $\text{PZN-}x\%$ PT crystals.¹² Interestingly, a domain size effect for piezoelectricity has been reported in BaTiO_3 crystals for $E \parallel [111]$,²⁶ where the piezoelectric coefficient notably increases with decreasing domain size. Furthermore, investigations of BaTiO_3 under $E \parallel [111]$ by polarized light microscopy have indicated the presence of monoclinic phases.²⁸ However, there have yet to be any reports of ferroelectric monoclinic phases in its sequence of phase transformations.

Here, we performed high resolution x-ray diffraction (XRD) studies on BaTiO_3 single crystals with $E \parallel [001]$ in the field-cooled or FC condition. We find that BaTiO_3 has signatures of the M_C phase on (001) FC, where the sequence of phase transformations is $C \rightarrow T \rightarrow M_C$. Furthermore, we find that the M_C phase is stable once domain engineered. The findings demonstrate the presence of structurally bridging phases in non-Pb ferroelectrics that are similar to those of $\text{PMN-}x\%$ PT and $\text{PZN-}x\%$ PT crystals: opening an approach to high piezoelectricity in Pb-free materials.

Crystals of BaTiO_3 with dimension of $3 \times 3 \times 3 \text{ mm}^3$ were obtained from Shanghai Institute of Ceramics, Chinese Academy of Sciences. All surfaces were oriented along the (100) pseudocubic faces and were polished to $0.25 \mu\text{m}$. Gold electrodes were deposited on one pair of opposite surfaces of the cube by sputtering—we designate here the electrode faces as (001). XRD studies were performed using a Philips MPD high-resolution system equipped with a two bounce hybrid monochromator, an open three-circle Eulerian cradle, and a domed hostage. A Ge (220)-cut crystal was used as an analyzer, which had a resolution of 0.0068° . The x-ray wavelength was that of $\text{Cu K}\alpha = 1.5406 \text{ \AA}$ and the x-ray generator was operated at 45 kV and 40 mA. Measurements made under zero-field cooling are designated as ZFC,

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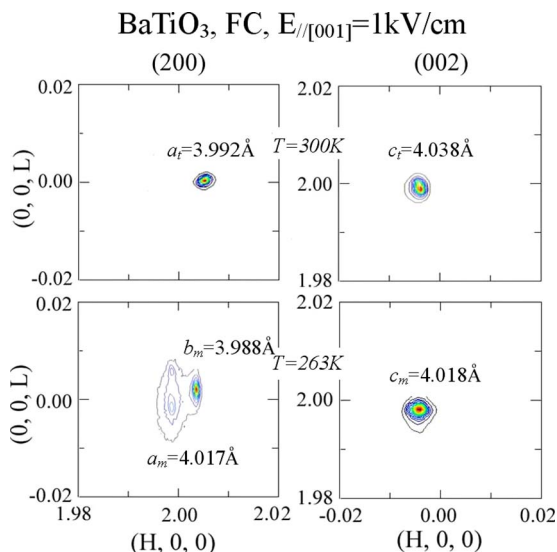


FIG. 1. (Color online) Mesh scans taken around (002) and (200) reflections of BaTiO₃ with $E=1$ kV/cm applied along the [001] at 300 and 263 K in the FC condition.

whereas those made under field cooling are designated as FC. At 450 K, the lattice constant of cubic BaTiO₃ was $a=4.011$ Å, correspondingly the reciprocal lattice unit (or 1 rlu) was $a^*=2\pi/a=1.566$ Å⁻¹. All mesh scans of BaTiO₃ shown in this study were plotted in reference to this reciprocal unit.

Upon ZFC, BaTiO₃ is known to have the sequence of phase transitions of $C \rightarrow T \rightarrow O \rightarrow R$, which occur at 393, 283, and 183 K, respectively. In the ZFC state, BaTiO₃ has a multitude of domain states with a complicated domain configuration in area or mesh scans of reciprocal space. However, application of electric field E can simplify the domain configurations, as the field can fix an axis. Figure 1 shows mesh scans taken around the (002) and (200) reflections at 300 and 263 K for (001) BaTiO₃ under $E=1$ kV/cm in the FC condition. In the tetragonal or T phase region, $E\parallel[001]$ fixes the c -axis stabilizing a single-domain T state, as can be seen in the mesh scans of Figs. 1(a) and 1(b). At 300 K, both the (200) and (002) scans exhibit a well-defined sharp contour: the (200) peak at higher H has a lattice parameter of $a_t=3.992$ Å and the (002) peak at lower L of $c_t=4.038$ Å. These data clearly demonstrate that upon cooling under $E=1$ kV/cm applied along the (001) that the system transforms from a cubic phase into a single domain tetragonal one.

Upon further cooling below room temperature under an $E\parallel(001)$ of 1 kV/cm, the crystal undergoes a secondary phase transition near the $T \rightarrow O$ phase boundary of the ZFC state. Figures 1(c) and 1(d) show mesh scans taken about the (200) and (002) at 263 K, respectively. The (200) reflection at 263 K was found to split into three peaks: two (200) peaks and a single (020) one, whereas the (002) reflection remained as a single peak. Clearly, the (200) and (002) mesh scans at 263 K have the signature of the M_C phase, similar to that previously reported for PMN- x %PT and PZN- x %PT for compositions close to the MPB. The lattice parameters of this monoclinic phase of BaTiO₃ were $(a_m, b_m, c_m; \beta_m) = (4.167$ Å, 3.988 Å, 4.168 Å; 89.8°). The limiting case of this M_C phase is the orthorhombic (O) phase, which has been known for many years in BaTiO₃.²⁹

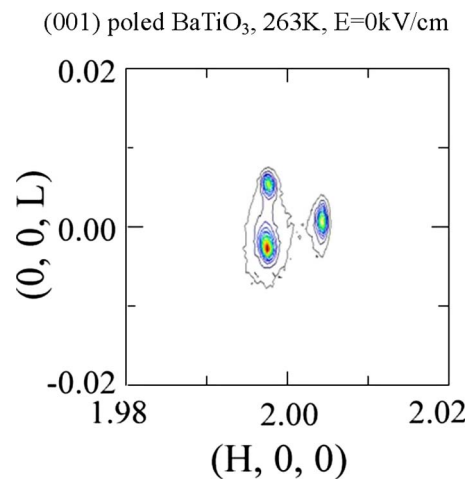


FIG. 2. (Color online) Mesh scan taken around (200) of BaTiO₃ at 263 K under an electric field of $E=0$ kV/cm after a prior FC under $E=1$ kV/cm.

Figure 2 shows a mesh scan taken about the (200) reflection at 263 K upon removal of the electric field after field cooling. This scan reveals that the signatures of the M_C phase remained after removal of field; the M_C phase is stable once induced. Our findings are exciting, demonstrating a new phase in BaTiO₃: a classic material known for over half a century that serves as the foundation of the capacitor industry. The M_C cell is primitive having a unique b_m axis that is oriented along the pseudocubic [010]. The M_C phase is a domain engineered state, which consists of four monoclinic domains. This is an important finding because domain engineered states are key to enhanced piezoelectricity in Pb-based crystals. It opens up the possibility that many classic perovskite systems may have intermediate structurally bridging phases, by which enhanced piezoelectricity can be achieved.

In Fig. 3, we show the temperature dependence of the lattice parameters for BaTiO₃ under $E=1$ kV/cm applied along the [001] direction. At 450 K, a sharp change in the lattice parameter can be seen on cooling, corresponding to the $C \rightarrow T$ transition. Below this temperature, the lattice constant $c_t(a_t)$ gradually increased (decreased) as the temperature was decreased in the tetragonal region. Near 283 K, a sharp change was found corresponding to the $T \rightarrow M_C$ trans-

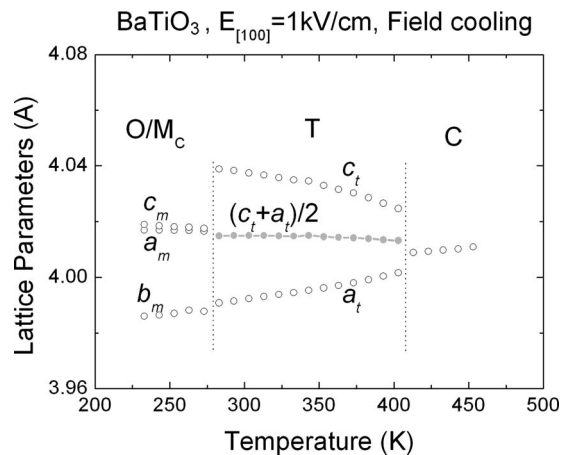


FIG. 3. Temperature dependence of lattice parameter for BaTiO₃ with $E=1$ kV/cm applied along [001].

formation where c_m was decreased with respect to c_t , a_m increased with respect to a_t , and b_m was nearly equal to a_t . The temperature dependent lattice parameters are quite similar to the corresponding one in the ZFC condition, which exhibits a $T \rightarrow O$ transition. The main difference for M_C was that $c_m > a_m$ under $E = 1$ kV/cm. This indicates that application of $E \parallel [001]$ results in a slight polarization rotation away from the $[110]$ toward the $[001]$, which is the pathway of $O \rightarrow T$, as previously reported for PZN-0.08PT.¹¹

Please note that special crystallographic relationships were followed between the T and M_C lattice parameters, as illustrated in Fig. 3. In this figure, it can be seen on crossing the $T \rightarrow M_C$ phase boundary that $a_t \approx b_m$ and $a_t + c_t \approx a_m + c_m$. Both b_m and a_t were calculated from the same (200) reflection; the continuity of these parameters demonstrates that one of the d -spacing in the unit cell of BaTiO₃ remains unchanged by the $T \rightarrow M_C$ transition. These are the same geometrically invariant conditions of the lattice parameters recently predicted by the adaptive phase theory and experimentally reported at the $T \rightarrow M_C$ transition for PMN- x PT and PZN- x PT^{16,17} crystals. This model is based on the concept that the M_C phase consists of conformably miniaturized tetragonal nanodomains with very low domain-wall energies. It is interesting to note that enhanced piezoelectricity has also recently been reported in $[111]$ field BaTiO₃ crystals, where the value of the transversal piezoelectric coefficient (d_{31}) and electromechanical coupling coefficient (k_{31}) was shown to increase dramatically with decreasing domain size.²⁴

In summary, we report a monoclinic M_C phase in BaTiO₃ crystals when FC under $E = 1$ kV/cm applied along the (001) direction. The phase transformational sequence is $C \rightarrow T \rightarrow M_C$. This monoclinic phase is stable upon removal of electric field. Our findings suggest a way by which to develop enhanced piezoelectricity in Pb-free systems via domain engineering of structurally bridging phases of low symmetry.

¹B. Noheda, D. Cox, G. Shirane, J. Gonzalo, L. E. Cross, and S. E. Park, *Appl. Phys. Lett.* **74**, 2059 (1999).

²B. Noheda, J. Gonzalo, L. C. Cross, R. Guo, S. E. Park, D. E. Cox, and G.

Shirane, *Phys. Rev. B* **61**, 8687 (2000).

³B. Noheda, D. E. Cox, G. Shirane, R. Guo, B. Jones, and L. E. Cross, *Phys. Rev. B* **63**, 014103 (2000).

⁴B. Noheda, D. E. Cox, G. Shirane, J. Gao, and Z. G. Ye, *Phys. Rev. B* **66**, 054104 (2002).

⁵J.-M. Kiat, Y. Uesu, B. Dkhil, M. Matsuda, C. Malibert, and G. Calvarin, *Phys. Rev. B* **65**, 064106 (2002).

⁶A. K. Singh and D. Pandey, *J. Phys.: Condens. Matter* **13**, L931 (2001).

⁷F. Bai, N. Wang, J. F. Li, D. Viehland, P. Gehring, G. Xu, and G. Shirane, *J. Appl. Phys.* **96**, 1620 (2004).

⁸B. Noheda, D. E. Cox, G. Shirane, S. E. Park, L. E. Cross, and Z. Zhong, *Phys. Rev. Lett.* **86**, 3891 (2001).

⁹D. La-Orautapong, B. Noheda, Z. Ye, P. M. Gehring, J. Toulouse, D. E. Cox, and G. Shirane, *Phys. Rev. B* **65**, 144101 (2002).

¹⁰B. Noheda, Z. Zhong, D. E. Cox, G. Shirane, S. E. Park, and P. Rehring, *Phys. Rev. B* **65**, 224101 (2002).

¹¹K. Ohwada, K. Hirota, P. Rehring, Y. Fujii, and G. Shirane, *Phys. Rev. B* **67**, 094111 (2003).

¹²S. E. Park and T. R. Shrout, *J. Appl. Phys.* **82**, 1804 (1997).

¹³H. Fu and R. E. Cohen, *Nature (London)* **403**, 281 (2000).

¹⁴A. Garcia and D. Vanderbilt, *Appl. Phys. Lett.* **72**, 2981 (1998).

¹⁵L. Bellaiche, A. Garcia, and D. Vanderbilt, *Phys. Rev. Lett.* **84**, 5427 (2000).

¹⁶D. Viehland, *J. Appl. Phys.* **88**, 4794 (2000).

¹⁷Y. Jin, Y. Wang, A. Khachatryan, J. Li, and D. Viehland, *Phys. Rev. Lett.* **91**, 197601 (2003).

¹⁸Y. Jin, Y. Wang, A. Khachatryan, J. Li, and D. Viehland, *J. Appl. Phys.* **94**, 3629 (2003).

¹⁹Yu. Wang, *Phys. Rev. B* **73**, 014113 (2006).

²⁰H. Wang, J. Zhu, N. Lu, A. A. Bokov, Z.-G. Ye, and X. W. Zhang, *Appl. Phys. Lett.* **89**, 042908 (2006).

²¹S. Bhattacharyya, J. Jinschek, H. Cao, Y. Wang, J. Li, and D. Viehland, *Appl. Phys. Lett.* **92**, 142904 (2008).

²²Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, and M. Nakamura, *Nature (London)* **432**, 84 (2004).

²³Y. Guo, K. Kakimono, and H. Ohsata, *Appl. Phys. Lett.* **85**, 4121 (2004).

²⁴H. Y. Park, C. W. Ahn, H. C. Song, J. H. Lee, S. Nahm, K. Uchino, and H. J. Lee, *Appl. Phys. Lett.* **89**, 062906 (2006).

²⁵R. Z. Zuo, X. S. Fang, and C. Ye, *Appl. Phys. Lett.* **90**, 092904 (2007).

²⁶S. Wada, K. Yako, H. Kakemoto, T. Tsurumi, and T. Kiguchi, *J. Appl. Phys.* **98**, 014109 (2005).

²⁷S.-E. Park, S. Wada, L. E. Cross, and T. R. Shrout, *J. Appl. Phys.* **86**, 2746 (1999).

²⁸S. Wada, S. Suzuki, T. Noma, T. Suzuki, M. Osada, M. Kakihana, S.-E. Park, L. E. Cross, and T. R. Shrout, *Jpn. J. Appl. Phys., Part 1* **38**, 5505 (1999).

²⁹F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, New York, NY, 1962).