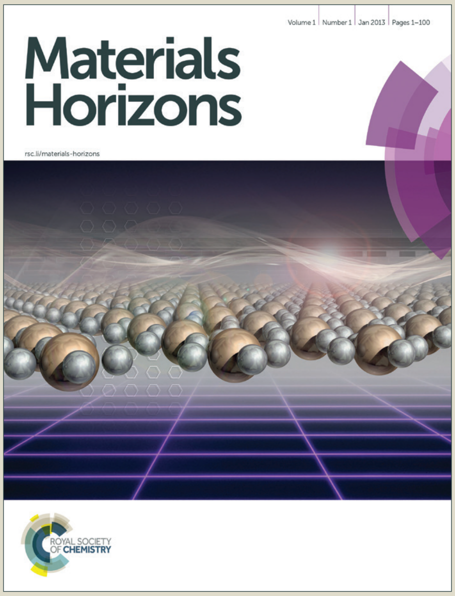
Materials Horizons

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

rsc.li/materials-horizons

Conceptual Insights

Bismuth ferrite ($BiFeO_3$) has been almost the only "star" in the field of high temperature single phase multiferroics in the last decade. Spontaneous polarization and magnetization are naturally repelling with each other in single phase crystal, because the contradictory requirements of "d^0" rule in ferroelectrics and partially occupied d-orbital in ferromagnetism. For the first time, this work demonstrates that new single-phase material with intrinsic multiferroics and considerable magnetoelectric (ME) coupling well above room temperature (RT) can be realized by inserting magnetic layer into the ferroelectric host of Aurivillius phase materials. Our work will stimulate the design of high temperature intrinsic and single-phase multiferroic materials, and make the bunches of novel multiferroic materials ready to hand for researchers, and then push the multiferroic materials into practical applications, such as spintronic devices, high density memories, low-power sensors, etc.

Materials Horizons

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

Communications

Low Magnetic Field Response Single-Phase Multiferroics under High Temperature

Jianlin Wang, [a] **Zhengping Fu,** [a,b,c] **Ranran Peng,** [a,c] **Min Liu,** [a,c] **Shujie Sun,** [a] **Haoliang Huang,** [a] **Lin Li,** [a] **Randy J. Knize** [d] **and Yalin Lu** [a,b,c,d] *****

Received (in XXX, XXX) Xth XXXXXXXXX 2014, Accepted Xth XXXXXXXXX 2014
DOI: 10.1039/b000000x

A single-phase material with a coexistence of ferroelectricity and ferromagnetism at the room temperature (RT) is hardly available in nowadays, and it is really rare for such a material further with an intrinsic and low magnetic field response magnetoelectric (ME) coupling at the temperature higher than RT. In this communication, a new single-phase Aurivillius compound, $SrBi_5Fe_{0.5}Co_{0.5}Ti_4O_{18}$ was found to exhibit a plausible intrinsic ME coupling. Remarkably, it appears at a high temperature of 100 ℃, surpassing any single-phase multiferroic materials currently under investigation. With a magnetocapacitance effect detectable at 100℃ and under a low response magnetic field, a RT functioning device was demonstrated to convert the external magnetic field variation directly into an electric voltage output. Availability of such a single-phase material with an intrinsic and low magnetic field response multiferroics at high temperature is important to fundamental physics understanding and to potential applications in sensing, memory, quantum controlling, etc.

Developing bulk multiferroic materials in the single-phase format, other than using the intensively investigated multiferroic composites artificially stacked together with ferroelectric (FE) and ferromagnetic (FM) materials, represent a new trend in recent years.[1-3] The criteria to evaluate a potential single-phase multiferroic material includes: 1) large FE and FM properties; 2) high FE and FM transition temperatures (much higher than the room temperature (RT)); and 3) strongly correlated magnetoelectric (ME) coupling occurring also at high temperatures, together with an ability to be driven by an as low as possible external electric or magnetic field, in order to ensure an improved operation stability at RT. To date, many single-phase materials, including $BiFeO_3$,[4,5] $TbMnO_3$,[6,7] $HoMnO_3$,[8,9] and CuO,[10] have been studied. However, none of them are able to simultaneously meet all above three criteria, and the majority of them indeed possesses FE and FM orderings at low temperatures (much lower than the RT). Specifically, none of them so far shows a detectable yet a low field responsive ME coupling at RT. For example, bulk $BiFeO_3$, having T_c ～1103 K, T_N ～643 K, and a plausible coupling, unfortunately, has a large leakage and the unwanted canted *G*-type antiferromagnetic (AFM) at RT.[4,11,12] In the effort to battle with such challenges, that to meet the strong RT ME coupling criteria would be the highest privilege.

Magnetic-layer-insertion (MLI, a phenomenological word to describe the method) into the layered bismuth Aurivillius materials,[13] normally appeared as ferroelectrics in the past, and may produce potential single-phase multiferroic materials.[14] It is actually a large family of oxides with a general formula of $Bi_2M_{n-1}R_nO_{3n+3}$ (*M*=Bi, Pb, Sr, etc., *R*=Ti, Ta, Fe, etc. and *n*, the number of perovskite slabs). Implementation of the MLI requires a careful selection of the host and the insertion materials, in order to form a single-phase structure. For the former, a material with good FE performance, low leakage, and stable yet tolerable structure would be preferred. While for the latter, good FM performance and the potential to be congruent with various magnetic dopants would be the key. In this work we considered a single-phase $SrBi_4Ti_4O_{15}$ (SBTi) Aurivillius material, by inserting $SrTiO_3$ into a well-known $Bi_4Ti_3O_{12}$ (BiT). SBTi was then formed with much improved FE performances, overcoming BiT's long suffering from "fatigue".[15] SBTi was found with a large saturated remanent polarization[16] (P_r) of 29 μC/cm^2 and a strong "fatigue" resistance comparable to that of the well-known FE $SrBi_2Ta_2O_9$ (SBT).[17] In considering the insertion material, on the other hand, $BiFe_{(1-x)}Co_xO_3$, which is congruent with doping Co and experiences an enhancement in magnetization when comparing to $BiFeO_3$, will be the initial choice.[18] We initially selected the half Co^{3+} substituted $BiFeO_3$, pseudo-cubic $BiFe_{0.5}Co_{0.5}O_3$ (BFCO-0.5), for the insertion. Therefore, via further inserting BFCO-0.5 into SBTi, a new single-phase multiferroic material, $SrBi_5Fe_{0.5}Co_{0.5}Ti_4O_{18}$ (SBFCT), was finally obtained. The new material shows a negligible leakage and significantly promoted FE and FM responses well above the RT. Most remarkably, both FE and FM responses are strongly correlated inside the single-phase structure, resulting in an intrinsic yet a low field response ME coupling, even at the high temperature of ~100 ℃. With this new material, a stable magnetic field controlled device was demonstrated, which functions well at RT and under a low magnetic field.

Figure 1 shows a schematic of the MLI approach applied to create SBFCT. BFCO-0.5 is a simple perovskite with Fe^{3+} and Co^{3+} randomly occupying *B*-sites to form BO_6 octahedrons. SBTi and SBFCT are of the Aurivillius structure with four and five slabs of BO_6 octahedrons sandwiched by two $Bi_2O_2^{2+}$ fluorite-like layers, respectively. The new SBFCT was obtained by inserting BFCO-0.5 into SBTi with two steps of calcinations (see Supporting Information). Three images in the middle in Figure 1 show Bi (and Sr) atoms in both SBTi (top) and SBFCT (bottom), indicating three/four Bi (or Sr) layers (corresponding to four/five

BO$_6$ octahedron slabs) sandwiched by two $Bi_2O_2^{2+}$ layers, and the perovskite structure of BFCO-0.5 (middle), disclosed by the high-angle annular dark-field (HAADF) images in an aberration-corrected scanning transmission electron microscopy (STEM). The resulting lattice parameters are 40.96 Å for c_{SBTi} and 49.21 Å for c_{SBFCT}, which are highly consistent with values from XRD Rietveld refinement,[19] which are 40.95 Å[16] for c_{SBTi} and 49.184 Å for c_{SBFCT} (See Figure S2). The above results support a successful insertion, resulting in a pure single-phase SBFCT. It is worth to note that the center perovskite layer of the SBFCT in brown in Figure 1 is a phenomenological description of the MLI method. In fact, Fe or Co occupied octahedrons may distribute disorderly inside the sandwiched five perovskite layers. Unfortunately, an accurate experimental determination of the distribution is difficult. For example, the Rietveld refinements should appear less sensitive to the ordering of Ti, Fe and Co cations, due to that the X-ray scattering powers of them are all similar.

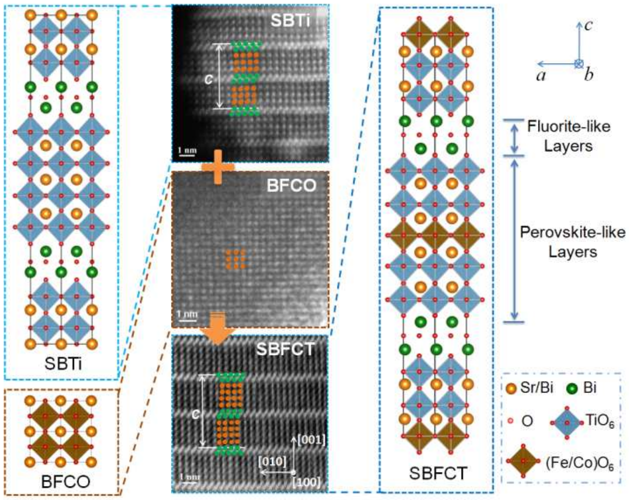


Figure 1. Schematic of the MLI approach and HAADF-STEM images. Top-left indicates the 4-layered SBTi ferroelectric host, bottom-left indicates BFCO-0.5 with a simple perovskite structure as the insertion, and then right indicates a simple schematic drawing of the final after-insertion 5-layered SBFCT new material (In reality, Fe or Co occupied octahedrons may distribute disorderly inside the sandwiched five perovskite layers). In the middle are real atomic images for SBTi, BFCO-0.5 and SBFCT, respectively.

Temperature dependencies of zero-field-cooled (ZFC) and field-cooled (FC) magnetizations at a magnetic field of 500 Oe for SBFCT are shown in Figure 2a. The FM Curie temperature (T_{CM}), defined by the peak of the differentiation $-dM/dT$, is about 436 K. The ZFC curve also shows a peak near 330 K and a separation from the FC curve, indicating the appearance of a spin glass-like behavior.[20] Temperature dependences of dielectric constant at different test frequencies of 1, 10, 100 and 1000 kHz were shown in Figure 2b. Its FE Curie temperature, T_{CE}, is 859 K, which becomes higher than that of the host SBTi (795 K) (Figure S3). Significance of the above observations is that both FE and FM transition temperatures are above the RT, which makes the new SBFCT attractive for future device development. To be justified for potential devices in terms of their working stability and reliability at RT, it is reasonable to select a high working temperature of 373K for further tests of the new SBFCT material.

Figure 2c shows a FM hysteresis loop of SBFCT with a saturated magnetic moment (M_s) of ~2.6 emu/g, a remanent moment (M_r) of ~0.62 emu/g and a coercive field (H_c) of ~92 Oe at 373 K. Compared to the host SBTi which is weak diamagnetic (Figure S4a), the resulting SBFCT becomes FM after the BFCO-0.5 insertion. The enhanced magnetization can be ascribed to the spin canting of Fe- and Co-based sublattices via the Dzyaloshinskii-Moriya interaction.[21,22] The X-ray photoelectron spectroscopy measurement also indicates an enhanced interaction strength between Co-O bond (see Figure S5), which contributes to the total magnetic moment.

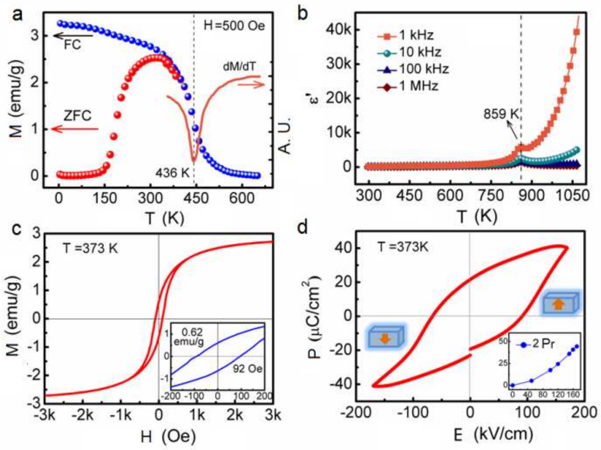


Figure 2. FM and FE properties of SBFCT. (a) Temperature dependences of ZFC and FC magnetization at 500 Oe. (b) Temperature dependences of dielectric constant at 1, 10, 100 and 1000 kHz. (c) *M-H* loop at a high temperature of 373 K. The inset shows an enlarged central region. (d) *P-E* loop also at 373 K. The inset shows the electric field dependence of remanent polarization.

In order to eliminate any possible contributions from other FM secondary phase impurities,[23] we separately synthesized two impurity FM phases most commonly occurring in the layered Aurivillius materials, BFCO-0.5 and $CoFe_2O_4$. The magnetic thermogravimetric analysis (MTGA) technique[24] was used to determine their T_{CM}. The measured T_{CM} for SBFCT is 440.8 K, which is quite close to the above *M-T* measurement (~436 K). T_{CM}s for $CoFe_2O_4$ and BFCO-0.5 are 720.5 and 744.8 K (Figure S6), respectively, which do not appear inside the SBFCT tests and are also very far away from that of the SBFCT too. Therefore, it is reasonable to exclude the two impurities as the contribution sources of the measured ferromagnetism, indicating an intrinsic magnetization to SBFCT.

Polarization versus electric field (*P-E*) hysteresis of SBFCT at 373 K is shown in Figure 2d. It has a $2P_r$ of 44.5 μC/cm^2 and a coercive electric field ($2E_c$) of 156 kV/cm at an electric field of 170 kV/cm, indicating an excellent FE performances after the BFCO-0.5 insertion into SBTi (the $2P_r$ increases from 4.18 μC/cm^2 (SBTi) to 24.2 μC/cm^2 at 100 kV/cm) (Figure S7). This enhancement may correlate to the insertion-induced structural distortion and to the measured high resistivity of ~1×10^{13} ohm·cm of SBFCT at RT (Figure S9), which is about four orders higher than that in Co-doped $BiFeO_3$ (<10^9 ohm·cm at RT[25]). Fatigue test showed almost no degradation of polarization after 10^9 cycles of up-and-down switches at the frequency of 1 kHz and under an electric field of 150 kV (Figure S8c).

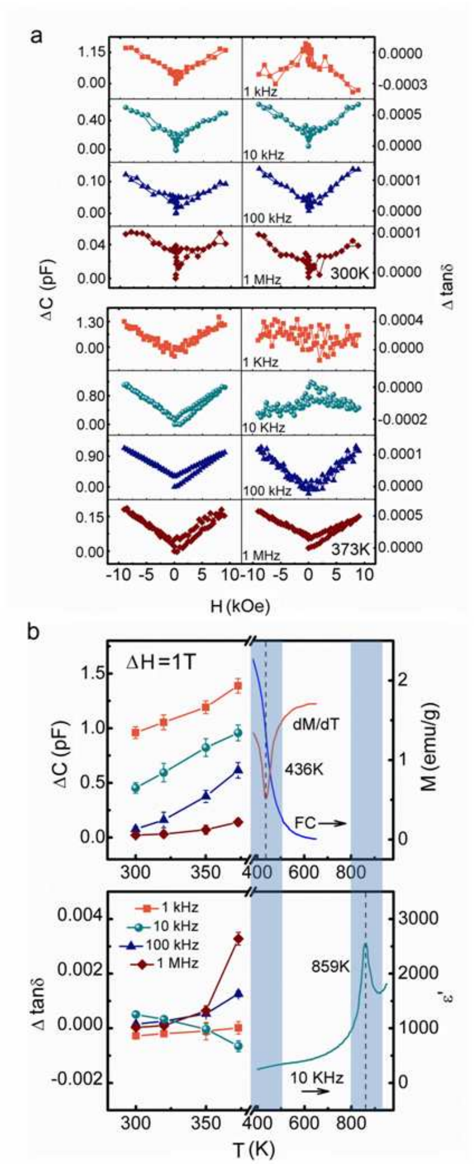


Figure 3. Magneto-capacitance (MC) tests in SBFCT. (a) Magnetic field strength dependences of both dielectric constant and loss at 1, 10, 100 and 1000 kHz at RT and 373K, respectively. (b) The insets show the temperature dependences of capacitance and loss changes between 0 T and 1T. Both FM and FE transition temperatures were also given by the FC measurement (top) and the dielectric constant measurement (bottom), respectively, which was used to indicate that the measured strong MC effect is far away from the transitions.

Magneto-capacitance (MC) measurement was performed to assess the ME coupling.[26,27] The magnetic field dependences of dielectric constant and loss, tested at temperatures of 300 K and 373 K, respectively, are shown in Figure 3a. Changes of both recorded magnetic capacitance and loss are quite similar to that of the superlattice model.[28] We have applied the Maxwell-Wagner (M-W) leaky capacitor model to our sample (see Supporting Information), and the result indicates that the layer-structured SBFCT is indeed similar to a 'natural' superlattice.[29] The "cutoff" phenomenon around 1 MHz was also observed, confirming the existence of an intrinsic ME coupling.[27,28] This strong ME coupling may relate to the superlattice-like structure in which many interfaces, disorderly distributed Fe and Co ions and distorted octahedrons. X. Zhai *et al*. reported that the magnetism in epitaxial $(LaMnO_{3+\delta})_N/(SrTiO_3)_N$ superlattices have a strong relationship with the interfacial octahedral rotation.[30] This rotation or distortion may further correlate to the ferroelectricity, which may explain the observed intrinsic ME coupling in this work.

In the past, large MC effect was usually observed at or near the transition temperatures, such as in $SeCuO_3$ and $TeCuO_3$ compounds at their FM (T_{CM}=25 K) and AFM (T_N=9 K) transition temperatures,[31] in $YFe_{1-x}Mn_xO_3$ at its spin-reorientation temperature,[32] and in $Bi_{4.2}K_{0.8}Fe_2O_{9+\delta}$ at its FE (T_{CE}=270 K) transition temperature.[33] Here the measured MC phenomenon occurs at a wide temperature range from RT to over 373 K, which is also far away from its FM (T_{CM}~436 K) and FE (T_{CE}~859 K) transition temperatures, as shown in Figure 3b. This indicates a distinct yet stable MC effect, which will be substantially important for actual device development.

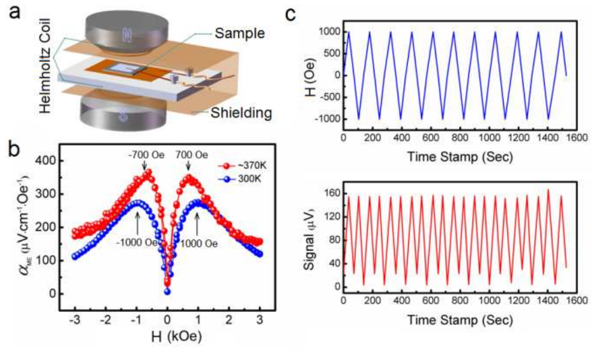


Figure 4. A ME prototype device. (a) Schematic of the ME device under tunable DC and AC magnetic fields. (b) Plots of the measured ME coefficient versus the magnetic field strength *H* at RT and 373K, respectively. (c) Voltage outputs (lower) when worked as a magnetic field sensor in the triangular wave input (upper).

Using the new SBFCT, a prototype ME device, using a dynamic technique to directly convert a magnetic signal to an electric voltage output, was fabricated.[34] Figure 4a shows a schematic of the device when it works under both tunable DC and AC magnetic fields. Inside the device, an electrically poled SBFCT as the core sensing component generates the electric potential by the interaction with an applied oscillating magnetic field. Figure 4b shows the plot of the ME coupling coefficient α_{ME} versus the DC field (H). It reaches ~270 $\mu V\cdot cm^{-1}\cdot Oe^{-1}$ at a low DC field of 1000 Oe at RT and ~350 $\mu V\cdot cm^{-1}\cdot Oe^{-1}$ at a low DC field of 700 Oe at 373K, the later is about 5 times larger than the value (64 $\mu V\cdot cm^{-1}\cdot Oe^{-1}$) measured from $BiFeO_3$ at RT.[35] This sharp "M-type" curve is similar to those from the previously developed laminated composite multiferroics.[36] Figure 4c shows the effect of the induced voltage output under a periodic magnetic field in the format of the triangular wave mode. The output instantly and reliably responds to the low input magnetic field. In a low magnetic field (< 100 Oe), noticeable ME signal output can still be instantly detected.

Conclusions

In summary, a new single-phase and intrinsic multiferroic SBFCT material, which functions well under the high temperature (373 K) and under a low magnetic field, was developed. With this new material, a ME prototype device was made, which showed an excellent low field and reliable high temperature responses. The availability of the new material is important for basic physics researches and for future device development.

Acknowledgments

This work was supported by the National Basic Research Program of China (973 Program, 2012CB922000). Dr. Lu appreciates the support for the device design and test from Quantum Design in China.

Notes and references

[a] CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, P. R. China.
[b] Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, P. R. China.
[c] Synergetic Innovation Center of Quantum Information & Quantum Physics, University of Science and Technology of China, Hefei 230026, P. R. China.
[d] Laser and Optics Research Center, Department of Physics, United States Air Force Academy, Colorado 80840, USA; E-mail: yllu@ustc.edu.cn

† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/b000000x/

1 J. Ma, J. Hu, Z. Li and C.-W. Nan, *Adv. Mater.* 2011, **23**, 1062.
2 N. A. Spaldin and M. Fiebig, *Science* 2005, **309**, 391.
3 N. A. Spaldin, S.-W. Cheong and R. Ramesh, *Phys. Today* 2010, **63**, 38.
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* 2003, **299**, 1719.
5 T. Ito, T. Ushiyama, Y. Yanagisawa, R. Kumai and Y. Tomioka, *Cryst. Growth Des.* 2011, **11**, 5139.
6 T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima and Y. Tokura, *Nature* 2003, **426**, 55.
7 S.-W. Cheong and M. Mostovoy, *Nature Mater.* 2007, **6**, 13.
8 T. Lottermosera and M. Fiebig, *Phys. Rev. B* 2004, **70**, 220407.
9 I. A. Sergienko, C. Sen and E. Dagotto, *Phys. Rev. Lett.* 2006, **97**, 227204.
10 T. Kimura, Y. Sekio, H. Nakamura and T. Siegrist, *Nature Mater.* 2008, **7**, 291.
11 G. Catalan and J. F. Scott, *Adv. Mater.* 2009, **21**, 1.
12 A. K. Pradhan, K. Zhang, D. Hunter, J. B. Dadson, G. B. Loutts, P. Bhattacharya, R. Katiyar, J. Zhang, D. J. Sellmyer, U. N. Roy, Y. Cui and A. Burger, *J. Appl. Phys.* 2005, **97**, 093903.
13 B. Aurivillius, *Arki Kemi* 1949, **1**, 463.
14 N. A. Lomanova, M. I. Morozov, V. L. Ugolkov and V. V. Gusarov, *Inorg. Mater.* 2006, **42**, 189.
15 B. H. Park, B. S. Kang, S. D. Bu, T. W. Noh, J. Lee and W. Jo, *Nature* 1999, **401**, 682.
16 H. Irie and M. Miyayama, *Appl. Phys. Lett.* 2001, **79**, 251.
17 C. A-Paz de Araujo, J. D. Cuchiaro, L. D. McMillan, M. C. Scott and J. F. Scott, *Nature* 1995, **374**, 627.
18 H. Naganuma, S. Yasui, K. Nishida, T. Iijima, H. Funakubo and S. Okamura, *J. Appl. Phys.* 2011, **109**, 07D917.
19 G. Will, *Powder Diffraction: The Rietveld Method and the Two-Stage Method*, Springer, Berlin, GER 2006.
20 X. Mao, W. Wang, X. Chen and Y. Lu, *Appl. Phys. Lett.* 2009, **95**, 082901.
21 J. Yang, W. Tong, Z. Liu, X. B. Zhu, J. M. Dai, W. H. Song, Z. R. Yang and Y. P. Sun, *Phys. Rev. B* 2012, **86**, 104410.
22 I. A. Sergienko and E. Dagotto, *Phys. Rev. B* 2006, **73**, 094434.
23 L. Keeney, T. Maity, M. Schmidt, A. Amann, N. Deepak, N. Petkov, S. Roy, M. E. Pemble and P. W. Whatmore, *J. Am. Ceram. Soc.* 2013, **96**, 2339.
24 R. L. Blaine and P. G. Fair, *Thermochimica Acta* 1983, **67**, 233.
25 S. Yasui, M. Nakajima, H. Naganuma, S. Okamura, K. Nishida, T. Yamamoto, T. Iijima, M. Azuma, H. Morioka, K. Saito, M. Ishikawa, T. Yamada and H. Funakubo, *J. Appl. Phys.* 2009, **105**, 061620.
26 T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima and Y. Tokura, *Nature* 2003, **426**, 55.
27 H. M. Jang, J. H. Park, S. Ryu and S. R. Shannigrahi, *Appl. Phys. Lett.* 2008, **93**, 252904.
28 G. Catalan, *Appl. Phys. Lett.* 2006, **88**, 102902.
29 P. Ghosez and J.-M. Triscone, *Nature Mater.* 2011, **10**, 269.
30 X. Zhai, L. Cheng, Y. Liu, C. M. Schleputz, S. Dong, H. Li, X. Zhang, S. Chu, L. Zheng, J. Zhang, A. Zhao, H. Hong, A. Bhattacharya, J. N. Eckstein and C. Zeng, *Nature Comm.* 2014, **5**, 4283.
31 G. Lawes, A. P. Ramirez, C. M. Varma and M. A. Subramanian, *Phys. Rev.Lett.* 2003, **91**, 257208.
32 P. Mandal, V. S. Bhadram, Y. Sundarayya, C. Narayana, A. Sundaresan and C. N. R. Rao, *Phys. Rev. Lett.* 2011, **107**, 137202.
33 S.-N. Dong, Y.-P. Yao, J.-Q. Li, Y.-J. Song, Y.-K. Liu and X.-G. Li, *Sci. Rep.* 2013, **3**, 1.
34 M. M. Kumar, A. srinivas, S. V. Suryanarayana, G. S. Kumar and T. Bhimasankaram, *Bull. Mater. Sci.* 1998, **21**, 251.
35 S. V. Suryanarayana, *Bull. Mater. Sci.* 1994, **17**, 1259.
36 J. Ma, J. Hu, Z. Li and C.-W. Nan, *Adv. Mater.* 2011, **23**, 1062.