Improved multiferroic properties of La-doped $0.6BiFeO_3$–$0.4SrTiO_3$ solid solution ceramics*

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The $0.6(Bi_{1-x}La_x)FeO_3$–$0.4SrTiO_3$ ($x = 0$, 0.1) multiferroic ceramics are prepared by a modified Pechini method to study the effect of substitution of $SrTiO_3$ and La in $BiFeO_3$. The X-ray diffraction patterns confirm the single phase characteristics of all the compositions each with a rhombohedral structure. The magnetic properties of the ceramics are significantly improved by a solid solution with $SrTiO_3$ and substitution of La. The values of the dielectric constant ε_r and loss tangent tan δ of all the samples decrease with increasing frequency and become constant at room temperature. The La-doped $0.6BiFeO_3$–$0.4SrTiO_3$ ceramics exhibit improved dielectric and ferroelectric properties, with higher dielectric constant enhanced remnant polarization (P_r) and lower leakage current at room temperature. Compared with a anti-ferromagnetic $BiFeO_3$ compound, the $0.6(Bi_{0.9}La_{0.1})FeO_3$–$0.4SrTiO_3$ sample shows the optimal ferromagnetism with remnant magnetization $M_r \sim 0.135$ emμ/g and ferroelectricity with $P_r \sim 5.94$ μC/cm^2 at room temperature.

Keywords: multiferroic, ferroelectric, dielectric constant, ferromagnetic

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1. Introduction

Multiferroic materials, which combine the properties of ferromagnetism (FM), ferroelectricity (FE), or ferroelasticity, have attracted more and more attention.[1] These materials demonstrate a number of attractive physical phenomena that arise from the strong coupling between the magnetic and FE order parameters.[2−5] There are several kinds of materials exhibiting multiferroic behaviours. The perovskite $BiFeO_3$ and $BiMnO_3$ are the most frequently investigated, offering ferroelectric order and spin order above room temperature. However, FE and FM are usually mutually exclusive phenomena, since FE and FM are mutually exclusive due to the d^0 electronic structure of B-site elements. As a result, single-phase multiferroic materials rarely exist.[6]

$BiFeO_3$(BFO) exhibits antiferromagnetic (AFM) ordering with high Néel temperature ($T_N = 640$ K) and FE behavior ($T_{CE} = 1103$ K) with spatially modulated spin structure. The FE in BFO is believed to be caused by the $6s^2$ lone pair electrons of Bi^{3+}, while the magnetism is thought to originate from the partially filled d-orbital of Fe. However, as for BFO bulk ceramics, research work is still being greatly hindered by the easy formation of second phases during synthesis and the low resistivity of the sample. To realize the multiferroic functionality based on BFO, it is desirable to use various preparation methods to improve the magnetic and dielectric properties.

This problem could be solved by applying a high magnetic field, doping with chemical substitutions or using a solid solution with ferroelectrics. Several groups have reported on BFO solid solution systems prepared using $BaTiO_3$, $PbTiO_3$, $PbFe_{0.5}Nb_{0.5}O_3$, $DyFeO_3$, etc.[7−12] Moreover, it was found that some rare earth ions substituted at the Bi site in bulk BFO can reduce the leakage current and Curie temperature, improving the dielectric and magnetic properties.[13−15] Although solid solutions with ferroelectrics and substitution make the formation of single-phase $BiFeO_3$ more stable, the magnetic properties at room temperature are still weak and conductivity is not reduced significantly.

In this paper, we report on the results of our studies on $0.6(Bi_{1-x}La_x)FeO_3$–$0.4SrTiO_3$ ($x = 0$, 0.1) (denoted as BFST for $x = 0$, and BLFST for $x = 0.1$) solid solutions. The structural, ferroelectric, dielec-

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tric, and magnetic properties of BFST-x are presented. This material simultaneously exhibits FM and FE at room temperature.

2. Experimental procedure

A solid solution with stoichiometric compositions $0.6(Bi_{1-x}La_x)FeO_3$–$0.4SrTiO_3$ (x = 0, 0.1) (denoted as BFST and BLFST) were synthesized using the modified Pechini method. First, raw materials of 99.9% purity $Bi(NO_3)_3{\cdot}5H_2O$, $Sr(NO_3)_2{\cdot}4H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, lanthanum nitrate hexahydrate $La(NO_3)\cdot 6H_2O$, butyl titanate and citric acid were dissolved in distilled water, with 5% excess bismuth nitrate to compensate bismuth loss during the sintering process. The solutions were adjusted to a pH value of 7–8 by adding ammonia, and the mixtures were dried at 150 °C to form gels. After that, the obtained gels were burned and then the precursory powders were calcined at 500 °C for 5 h. Finally, the powders were ground in an agate bowl for about 2 h, pressed into disks. The disks were sintered at 900 °C for 2 h, and then subsequently quenched to room temperature to minimize the bismuth evaporation. To measure the electrical properties, electrodes with a silver paste were applied to both surfaces.

The crystal structure of the samples was investigated by X-ray diffraction (XRD). Magnetic measurements were carried out using a commercial physical property measurement system (Quantum Design). Polarization versus the electric field (P–E) loop at room temperature was measured using a commercial FE test system (Premier II, Radiant Technologies). The dielectric properties of the ceramics were obtained with a precision impedance analyzer (6500B, WK, UK), with an ac voltage of 500 mA.

3. Results and discussion

XRD patterns reveal that all the samples show the coexistence of a perovskite morphotropic phase without any observable impurity phases (e.g., Fe_2O_3, Bi_2O_3, $Bi_2Fe_4O_9$, etc.). As can be seen in Fig. 1, there are several twin peaks in the XRD pattern of BFO viz [104] and [110], [006] and [202], [116] and [112], [018] and [214], and finally the twin peaks merge together to form a single peak in BFST and BLFST samples. It can be concluded that the BFST samples are of the pseudocubic phase, as we previously reported,[16] and the doping of La does not affect the lattice symmetry. With a solid solution with $SrTiO_3$ and substitution of La, all the peak positions undergo a shift toward a higher angle. This reveals a continual reduction in the lattice constant and also indicates that the unit cell is contracted with the substitution of Ti^{4+} ion (0.605 Å, 1 Å=0.1 nm), which has a smaller radius than Fe^{3+} ion (0.64 Å).

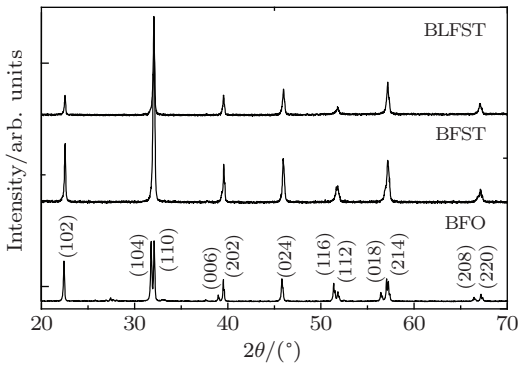


Fig. 1. The XRD patterns of $0.6(Bi_{1-x}La_x)FeO_3$–$0.4SrTiO_3$ (x = 0, 0.1) solid solutions compared with pure BFO ceramics.

The magnetization hysteresis (M–H) loops at 300 K and 10 K for all the samples are shown in Fig. 2. The pure BFO sample exhibits a linear magnetization dependence of the magnetic field, which is consistent with the early reported results.[17] A slim magnetic loop with nonzero M_r for the BFST sample is observed, reflecting the presence of a weak FM at room temperature. Additionally, La doping induces a significant increase in magnetization. The values of the coercive field (H_C) are 0.99 kOe (1 Oe=79.5775 A/m) and 2.99 kOe for BFST and BLFST at room temperature, and 1.8 kOe and 3.2 kOe for BFST and BLFST at 10 K, respectively. The corresponding values of M_r are 0.091 emμ/g and 0.135 emμ/g for BFST and BLFST at room temperature, suggesting the ferromagnetic interactions increasing with the increase of La doping.

The BFO is known to be an AFM with a G-type magnetic structure. Since the spin order in a BFO ceramic is spatially modulated, it has no macroscopic magnetization at room temperature. If the spatially modulated spin order is suppressed by chemical substitutions, the latent magnetization will be released. The MH loops of BFST and BLFST samples evidently show that the AFM nature in BFO evolves into a weak FM. A transition from the spinoidal structure of pure BFO to the homogeneous FM state in BFO-based compounds induced by doping with nonmagnetic ions was reported in Refs. [18] and [19] and it was explained by changes in the bond angle of Fe–O–Fe caused by the distortion, besides the changes of the statistical distribution of Fe^{3+}/Fe^{2+} as result of the charge compensation.

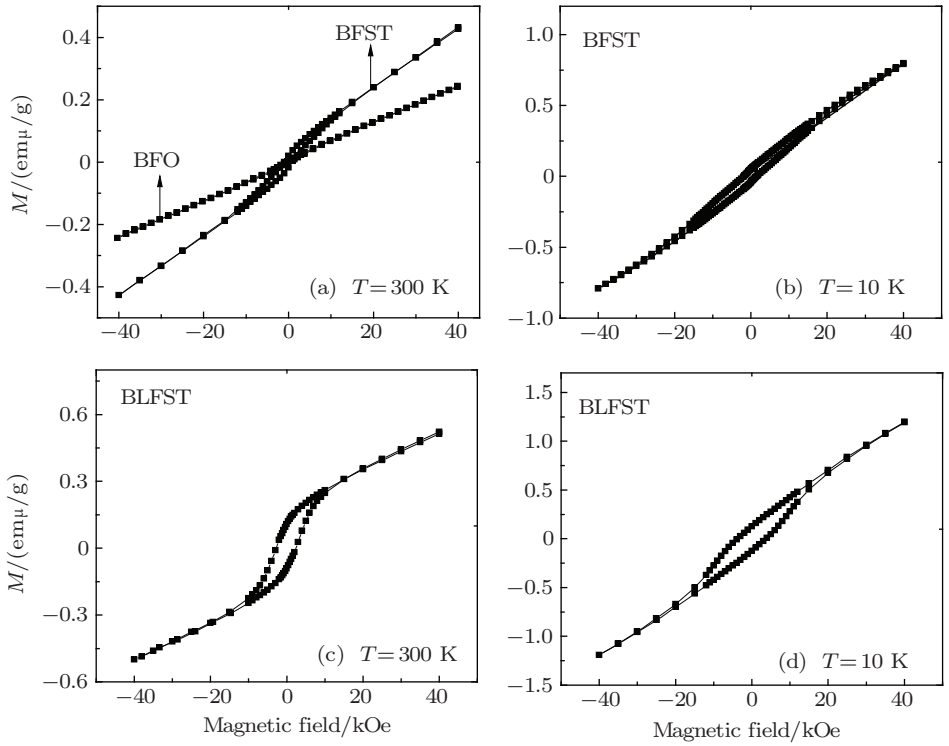


Fig. 2. (colour online) Magnetization hysteresis loops of $0.6(Bi_{1-x}La_x)FeO_3$–$0.4SrTiO_3$ (x = 0, 0.1) solid solutions at 300 K and 10 K, 1 Oe=79.5775 A/m.

Figure 3 shows the P–E loops of the BFO, BFST, and BLFST ceramics. BFO bulk ceramics usually exhibit strong conductive features. As shown in Fig. 3(a), the P–E loop of BFO bulk ceramics exhibits a rounded corner with an applied field of 20 kV/cm, and will break down as the field further increases. The low resistivity of the BFO maybe originates mainly from charge defects such as bismuth vacancies and oxygen vacancies (VO^{2+}) which comes mainly from Bi volatility and the transition from Fe^{3+} to Fe^{2+}. Compared with the ferroelectric properties of the BFO, our samples are significantly improved by a solid solution with $SrTiO_3$ and substitution of La, with large P_r observed, owing to the different breakdown fields. The maximum polarization (P_m) and the P_r increase from $P_m = 0.42$ μC/cm^2 and $P_r = 0.34$ μC/cm^2 for $x = 0$ to $P_m = 14.71$ μC/cm^2 and $P_r = 8.98$ μC/cm^2 for BFST, $P_m = 12.72$ μC/cm^2 and $P_r = 5.94$ μC/cm^2 for BFLST respectively. Although the P_r value decreases with the further additional increase of 10% La, the BLSFT samples do not break down with the maximum electric field of 150 kV/cm, indicating that the electric resistance is greatly improved by means of alio-valent ionic substitution of La. The P–E hysteresis curve of BFST appears very leaky, and the ferroelectricity of the BLFST sample is evident from the typical ferroelectric hysteresis loop without a notable conductivity effect. The enhancement of ferroelectricity on La-doping should be attributed to the decreasing of the oxygen vacancy concentration and the weakening of the defect mobility which contributes to domain pinning.[20] This result demonstrates that the leakage currents are greatly reduced due to the addition of La ions.

In addition, the dielectric properties of all samples are investigated. Figure 4 exhibits the variations of relative ε_r and tan δ of BFST and BLFST ceramics with frequency. It is observed that the dielectric constants of BFST and BLFST samples are much increased from 75 for pure BFO (not shown here) to 146 for BFST and 346 for BLFST at 1 kHz. The dielectric constant ε_r of BFST shows frequency-independence in the whole frequency range. However for the BLFST sample, the value of the dielectric constant is high at a low frequency and decreases with frequency increasing from 100 Hz to 100 kHz and then becomes constant at high frequency. This is a normal behaviour of ferroelectrics or dielectrics that may be understood in terms of space charge relaxation.[21,22] As the space charges are able to fellow the frequency of the applied field at a low frequency while at a high frequency they may not have time to build up and undergo relaxation. These improvements of dielectric properties in BLFST ceramics can be ascribed to the substitution of La for Bi, which reduces the oxygen vacancies in the ceramics, resulting in a decrease of the contribution of space

charge polarization.[23]

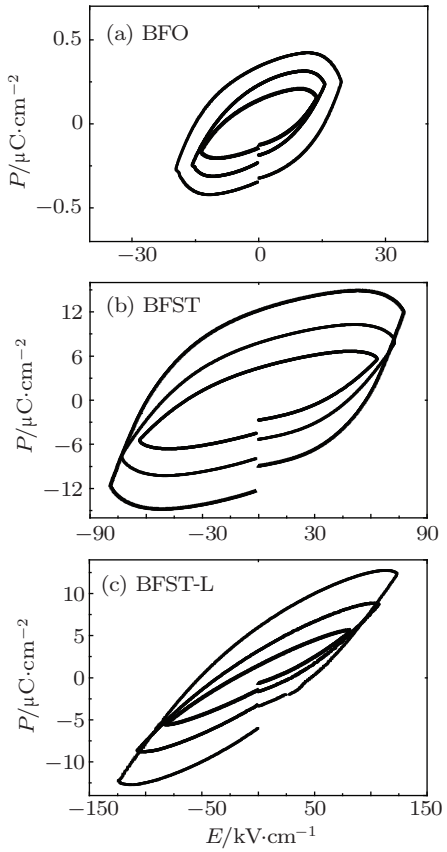


Fig. 3. Polarization hysteresis loops of $0.6(Bi_{1-x}La_x)FeO_3$–$0.4SrTiO_3$ ($x = 0$, 0.1) solid solutions at room temperature.

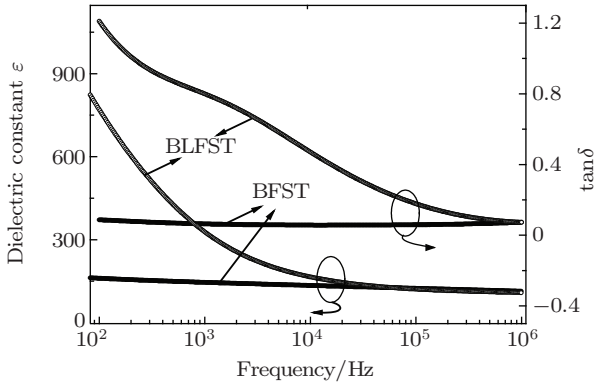


Fig. 4. Frequency dependences of relative dielectric constant ε_r and loss tangent tan δ for the $0.6(Bi_{1-x}La_x)FeO_3$–$0.4SrTiO_3$ ($x = 0$, 0.1) solid solutions at room temperature.

4. Conclusion

In the present study, the $0.6BiFeO_3$–$0.4SrTiO_3$ and $0.6(Bi_{0.9}La_{0.1})FeO_3$–$0.4SrTiO_3$ solid solution ceramics are synthesized by a modified Pechini method. And in this paper, the X-ray, dielectric and magnetic properties of all samples are presented. Both FM and FE properties at room temperature are much improved by a solid solution with $SrTiO_3$ and substitution of La. The La-doped $0.6BiFeO_3$–$0.4SrTiO_3$ ceramic exhibits improved dielectric and FE properties, with a higher dielectric constant enhanced P_r and lower leakage current at room temperature. The improved multiferroic properties are considered to result from the reduced leakage current and the collapse of the AFM spin structure in the sample.

References

[1] Spaldin N A and Fiebig M 2005 *Science* **309** 391

[2] Fiebig M 2005 *J. Phys.* D **38** 123

[3] Wang J, Neaton J B, Zheng H, Nagarajan V, Ogale S B, Liu B, Vinhjand D, Vaithyanathan V, Schlom D G, Waghmare U V, Spaldin N A, Rabe K M, Wuttig M and Ramesh R 2003 *Science* **299** 1719

[4] Zhong C G, Jiang Q, Fang J H and Ge C W 2009 *Acta Phys. Sin.* **58** 3491 (in Chinese)

[5] Bi K, Wu W and Wang Y G 2011 *Chin. Phys.* B **20** 067503

[6] Hill N A. 2000 *J. Phys. Chem.* B **104** 6694

[7] Sahoo M P K and Choudhary R N P 2012 *Mater. Lett.* **67** 308

[8] Anar S, Vibhav P, Kotnala R K and Dhananjai P 2008 *Phys. Rev. Lett.* **101** 247602

[9] Anjum G, Mollah S, Shukla D K and Ravi Kumar 2010 *Mater. Lett.* **64** 2003

[10] Zhu H W, Jiang P, Wang S L, Mao L F and Tang W H 2010 *Acta Phys. Sin.* **59** 5710 (in Chinese)

[11] Gu J J, Liu L H, Qi Y K, Xu Q, Zhang H M and Sun H Y 2011 *Acta Phys. Sin.* **60** 067701 (in Chinese)

[12] Felicia P G, Adelina I, Petronel P, Nicoleta L, Marius D, Dumitru L and Liliana M 2010 *J. Alloys Compd.* **506** 862

[13] Neeraj K, Neeraj P, Bhasker G, Neelam S, Kishan H and Awana V P S 2010 *J. Alloys Compd.* **501** 29

[14] Singh K, Kotnala R K and Singh M 2008 *Appl. Phys. Lett.* **93** 212902

[15] Bhushan B, Basumallick A, Vasanthacharya N Y, Kumar S and Das D 2010 *Solid State Sci.* **12** 1063

[16] Ma Z Z, Tian Z M, Li J Q, Wang C H, Huo S X, Duan H N and Yuan S L 2011 *Solid State Sci.* **13** 2196

[17] Jia D C, Xu J H, Ke H, Wang W and Zhou Y 2009 *J. Eur. Ceram. Soc.* **29** 3099

[18] Zhang Y J, Zhang H G, Yin J H, Zhang H W, Chen J L, Wang W Q and Wu G H 2010 *J. Magn. Magn. Mater.* **322** 2251

[19] Park T J, Papaefthymiou C C, Viescas A J, Lee Y J, Zhou H J and Wong S S 2010 *Phys. Rev.* B **82** 024431

[20] Pandit P, Satapathy S, Gupta P K and Sathe V G 2009 *J. Appl. Phys.* **106** 114105

[21] Jyoti R S and Ran C N R 2007 *Solid State Sci.* **9** 950

[22] Wang C H, Liu Z F, Tian Z M and Yuan S L 2011 *Mater. Sci. Eng.* B **176** 1243

[23] Zhu W M, Su L W, Ye Z G and Ren W 2009 *Appl. Phys. Lett.* **94** 142908