Available online at www.sciencedirect.com

Journal of the European Ceramic Society 29 (2009) 1183–1187

www.elsevier.com/locate/jeurceramsoc

Technical note

Enhanced ferroelectric properties of Ce-substituted $BiFeO_3$ thin films on $LaNiO_3$/Si substrates prepared by sol–gel process

Xiuzhang Wang[a,b], Hongri Liu[a,b,*], Bowu Yan[c]

[a] *Hubei Key Laboratory of Bioanalytical Technique, Hubei Normal University, Huangshi 435002, China*
[b] *Department of Physics, Hubei Normal University, Huangshi 435002, China*
[c] *School of Computer Science, Huangshi Institute of Technology, Huangshi 435003, China*

Received 27 May 2008; received in revised form 8 August 2008; accepted 12 August 2008

Abstract

The effects of Ce substitution on the structural and electrical properties of multiferroic $BiFeO_3$ thin films grown on $LaNiO_3$/Si(1 0 0) substrates by a sol–gel process have been reported. X-ray diffraction data confirmed the substitutions of Ce into the Bi site with the elimination of all secondary phases under a substitution ratio $x = 15\%$. The dielectric constants of the films increased from 90 to ~260 below 100 kHz with 5% molar Ce substitution and the films showed enhanced dielectric behavior. We observed a substantial increase in the remnant polarization (P_r) with Ce substitution and obtained a maximum value of ~71 μC/cm^2 by 5% molar Ce incorporation. The leakage current behavior at room temperature of the films was studied and it was found that the leakage current density decreased from 10^{-6} to 10^{-8} A/cm^2 for 5% molar Ce-substituted films under a field 150 kV/cm. The reduction of dc leakage current of Ce-substituted films is explained on the basis of relative phase stability and improved microstructure of the material.

Keywords: X-ray methods; Ferroclectric properties; Dielectric properties; $Bi_{1-x}Ce_xFeO_3$ thin film; Sol–gel processes

1. Introduction

Magnetoelectric multiferroics, being a class of materials that have electric, magnetic, and structural order parameters in the same phase, have attracted considerable interests for their simultaneous ferroelectricity, ferromagnetism and ferroelasticity.[1–4] Recently, ferroelectromagnetism is extensively studied because of the potential to provide a wide range of applications, including the emerging field of spintronics, memory,[3] and data-storage media.[4] $BiFeO_3$ (BFO) crystallizes in a rhombohedrally distorted perovskite structure with both ferroelectric ($T_c \sim 830\,°C$) and antiferromagnetic ($T_N \sim 370\,°C$) characteristics.[2,3] The specific characteristics, such as a simple crystal structure, a high Curie temperature (electrical), and a high Néel temperature (magnetic), are advantageous for research and various applications.

However, it is well known that BFO suffers from high leakage currents, which in turn lead to a unsaturated *P–E* hysteresis loop at room temperature if care were not taken on the control of the processing parameters such as the oxygen pressure during the pulsed laser deposition process and the annealing temperatures.[5,6] The leakage problem is more severe for BFO films prepared on Pt/Ti/SiO_2/Si substrates using the chemical solution deposition methods. Although the leakage current of BFO films can be reduced by doping high valence ions such as Ti^{4+} and Nb^{5+}, saturated ferroelectric hysteresis loops are still not be able to be observed in $BiFe_{1-x}Ti_xO_3$ and $BiFe_{1-x}Nb_xO_3$ films.[7,8] Recently, Singh et al. have reported that the leakage current density of BFO films can be decreased by doping Mn^{3+} ions at Fe^{3+} sites.[9] Furthermore, a well saturated hysteresis loop with a P_r value of 100 μC/cm^2 can be observed in a 5% Mn-doped BFO film at room temperature. The enhancement of the ferroelectric properties can also be found in Cr-doped $BiFeO_3$ films.[10] This suggests that isovalent ion substitution is more effective not only in reducing the leakage current but also in improving the ferroelectric properties of BFO films compared to the substitution using high valence ions. According to Uchida

---

[*] Corresponding author at: Hubei Key Laboratory of Bioanalytical Technique, Hubei Normal University, Huangshi 435002, China. Tel.: +86 714 6571339.
E-mail address: lhr1229@126.com (H. Liu).

0955-2219/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2008.08.016

and Singh, it seems to that BFO films doped with lanthanides (such as La and Nd) exhibit lower values of $P_r \sim 50\,\mu C/cm^2$ in comparison with those doped with Mn or Cr for the same doping content,[11,12] while Hu reported larger P_r values of about $80\,\mu C/cm^2$ by Gd substitution.

As a rare earth element, few attentions have been paid to Ce doping effects on BFO thin films. In the present work, we report the effect of Ce substitution on the crystalline structure and electric properties to BFO thin films. Moreover, $LaNiO_3$ is a type of excellent perovskite structural conductive oxide and was extensively used as under electrode to prepare ferroelectric film. Preferentially oriented ferroelectric film can be easily obtained on it.[13] In our work, nitrate salt of Bi, Fe, and Ce were used as starting materials and Ce-substituted BFO films were deposited on $LaNiO_3$/Si substrates by sol–gel process and substantially enhanced ferroelectric and dielectric property was observed.

2. Experimental procedure

The $Bi_{1-x}Ce_xFeO_3$ (BCFO) films were prepared on $LaNiO_3$/Si(1 0 0) substrates by the sol–gel process. The preparation method of $LaNiO_3$/Si(1 0 0) (see Ref. 14). Before spin coating the $LaNiO_3$/Si(1 0 0) substrates were cleaned by ultrasonication in alcohol and acetone repeatedly. The BCFO precursor solutions were prepared using bismuth nitrate [$Bi(NO_3)_3{\cdot}5H_2O$], iron nitrate [$Fe(NO_3)_3{\cdot}9H_2O$] and cerium nitrate [$Ce(NO_3)_3{\cdot}6H_2O$] as starting materials. Bismuth nitrate, cerium nitrate and ion nitrate were mixed with a proper molar ratio and dissolved at room temperature in 2-methoxyethanol and stirred for 30 min. The molar percent ratios of Ce were determined according to the composition formula of BCFO, in which $x = 0.00$ (pure BFO), 0.05, 0.10 and 0.15. The molar ratios of Bi to Ce are 1:0, 95:5, 9:1 and 8.5:1.5, respectively. Then sufficient acetic anhydride was added to dehydrate and ethanolamine was added to adjust the viscosity under constant stirring. The concentration of the stock solutions was adjusted to 0.3 M by adding 2-methoxyethanol. The above processes were performed in an ambient atmosphere at room temperature. The depositions were carried out by spin coating at 4000 rpm for 15 s. The as deposited wet films were pre-annealed at 350 °C for 3 min and followed by an annealing at 500 °C in air for 4 min. The above procedures were repeated several times to obtain the desired thickness.

The structure of the films was analysed by XRD. The XRD patterns were recorded with an X-ray diffractometer with Cu Kα radiation. The morphology was analyzed by scanning electron microscopy. For electrical measurements, Au dots of $0.1\,mm^2$ were deposited through a mask on the films by evaporation. Before measuring, the films were annealed at 300 °C for 20 min to get full contact with the electrodes. The dielectric property was measured with a HP 4294A LCR meter. Ferroelectric hysteresis loops and leakage current density were obtained using a precision work station (Radiant Technology).

3. Result and discussion

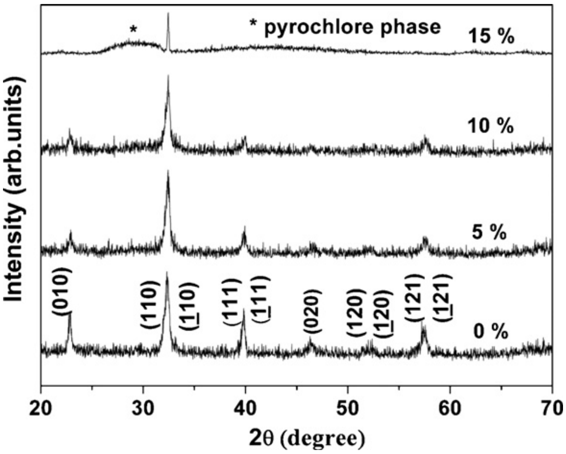

Fig. 1. XRD patterns of a $BiFeO_3$ film and $Bi_{1-x}Ce_xFeO_3$ ($x = 0$–0.15) thin films.

Fig. 1 shows the XRD patterns of the BCFO films on $LaNiO_3$/Si(1 0 0) substrates annealed at 500 °C in air. The effect of Ce substitution on the structure of BCFO thin films was analyzed in the range of 0–15 mol%. From which we can see that all films are fully crystallized since intense peaks can be observed. BCFO thin films with $x = 0$–0.10 have been identified as polycrystalline perovskite structure without secondary phases, while in the film with $x = 0.15$, pyrochlore phase can be observed. Furthermore, the (1 0 1) peak corresponding to perovskite structure shift slightly towards the small angle and it is originated from the Ce. A site substitution since the radius of Ce^{3+} is a little larger than that of Bi^{3+}.

Surface morphologies of BCFO films with different Ce contents ranging from 0% to 15 mol% are shown in Fig. 2(a)–(d). It is clear that the surfaces of the films with $x = 0$ and 0.05 are smooth and the average grain sizes are about 100 and 50 nm, respectively. Therefore by the Ce substitution, the average grain size was reduced. As for the films with $x = 0.10$ and 0.15, the grain size is reduced further and non-crystal phase can be observed in the film with $x = 0.15$ and it is accord with the XRD results. Moreover, their surfaces are coarser.

Fig. 3 shows the leakage currents density as a function of electric field measured at room temperature. For the case of BFO film, the leakage current density increases rapidly with the increasing of electric field before it gets breakdown at about 150 kV/cm. The leakage current density is about $2.0 \times 10^{-6}\,A/cm^2$ at 150 kV/cm. While for the case of BCFO films with $x = 0.05$–0.15, the leakage are lower than $2 \times 10^{-6}\,A/cm^2$ under a higher field of 300 kV/cm. Further more, the leakage current density vs. electric field curves show well symmetry. It can be seen that the doping of Ce can reduce the leakage current of BFO thin film in the whole electric field region. Similar phenomenon has been observed in Mn-doped BFO films.[9] Among all BCFO films, BCFO film with $x = 0.05$ shows the lowest leakage current, which is more than two orders of magnitude lower than that of the BFO film before breakdown. Interestingly, the leakage current does not decrease monotonically with the increase of the Ce content, although it has been demonstrated that doping of lanthanides can suppress the formation of oxygen vacancies in ferroelectric films.[15] The physics buried in these phenomena is still unclear so far. Based on the

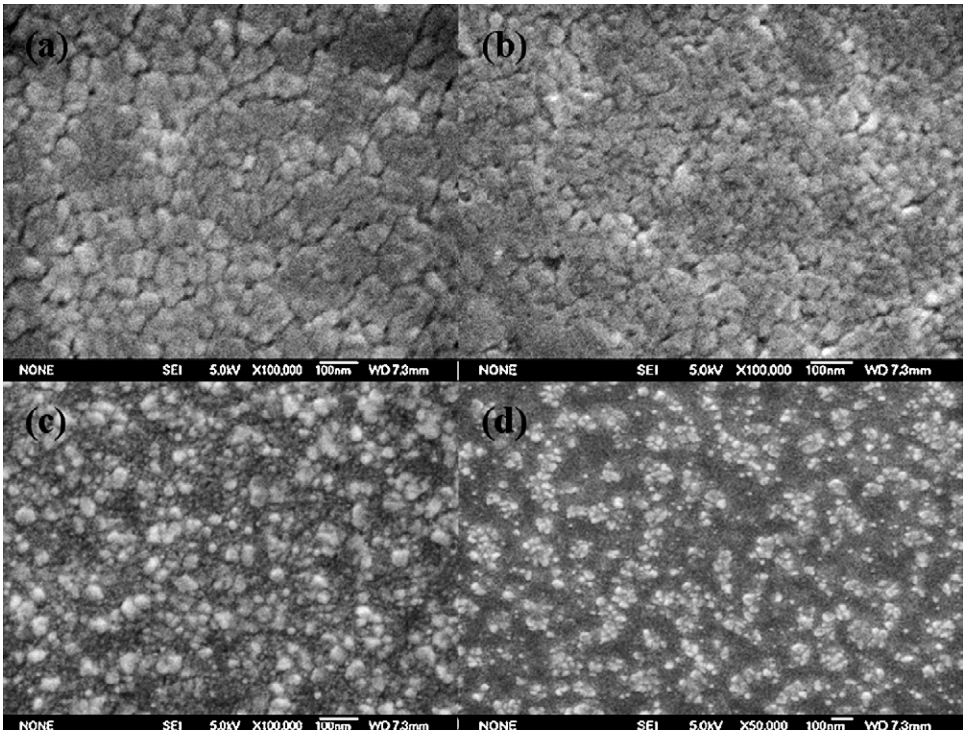

Fig. 2. SEM images of a $BiFeO_3$ film and $Bi_{1-x}Ce_xFeO_3$ ($x = 0$–0.15) films.

SEM results, it can be concluded that the smaller grain size should be another origins responsible for the lower leakage currents density for BCFO thin films compared to that of the undoped one.

Fig. 4 shows the *P–E* hysteresis loops of the BCFO films with Ce content of 0, 5, 10, and 15 molar percentages measured at room temperature. All loops were obtained under a measuring frequency of 1 kHz. The pure BFO thin film exhibits a poor *P–E* hysteresis loop, which has been typically observed from conductive ferroelectrics and it get breakdown with increased bias electric field due to a large leakage current. In contrast, the 5% Ce substitution BCFO thin film shows well-saturated hysteresis characteristics with a large remanent polarization (P_r) of 71 $\mu C/cm^2$ and a coercive field (E_c) of 103 kV/cm at a maximum applied electric field of 245 kV/cm. The 10% Ce-substituted BFO thin film shows well-saturated hysteresis characteristics with a large P_r of 47 $\mu C/cm^2$ and a E_c of 118 kV/cm at the same applied field to the 5% Ce-substituted BCFO film. The Ce-substituted BCFO film annealed at 500 °C exhibits a decreased remanent polarization and increased coercive field with increasing Ce content. The ferroelectric properties with Ce substitution in BCFO may be related to two main factors: one is the increased rattling space of the oxygen octahedron due to larger Ce atom, and the other is the decreased grain size with increased Ce contents, since the strength of polarization is strongly related to the grain size.[16] It has been found that the polarizability in perovskites (ABO_3) is partially related with the sizes of A and B cations. In general, a large A cation results in an increase in polarizability, since the large A cation leads to "a larger rattling space" available for B cation by increasing the size of the oxy-

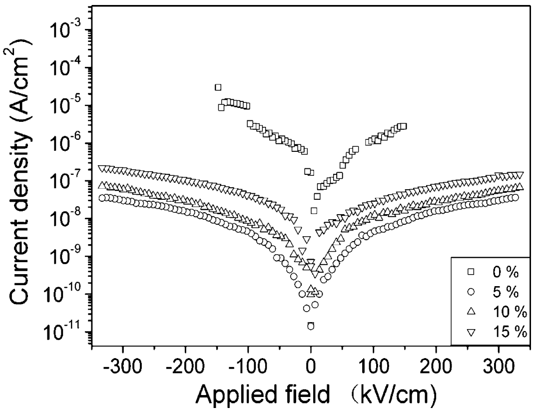

Fig. 3. Leakage currents as a function of electric field for a $BiFeO_3$ film and $Bi_{1-x}Ce_xFeO_3$ ($x = 0.0$–0.15) thin films.

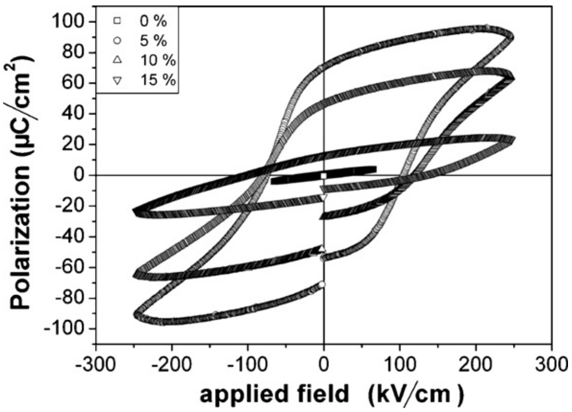

Fig. 4. Room temperature *P–E* hysteresis loops for a $BiFeO_3$ film and $Bi_{1-x}Ce_xFeO_3$ ($x = 0$–0.15) thin films.

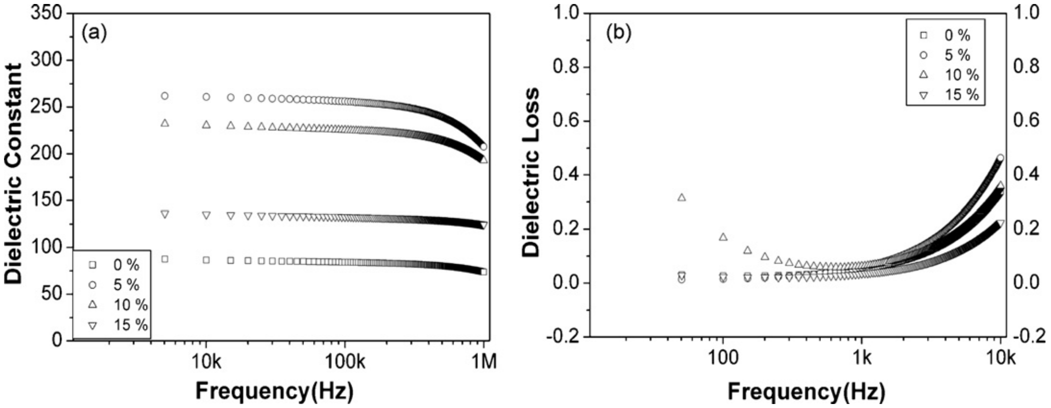

Fig. 5. Frequency relations of $Bi_{1-x}Ce_xFeO_3$ films. (a) Dielectric constant; (b) dielectric loss.

gen octahedron. The increased remanent polarization of BCFO films with Ce content up to 5 mol% could be explained by the substitution of larger Ce (1.19 Å) ions for a part of Bi (1.03 Å) ions in BCFO, even though grain sizes were decreased resulting a reduced polarization. In the case of 10 mol% Ce-substituted BCFO film, the decreased volume fraction of dielectric polarization with decreasing grain size could have predominant affect on the remanent polarization. However, the exact mechanism for the improved ferroelectric property of 5 mol% Ce-substituted BCFO film is not completely understood at this moment, which should be investigated further.

We also studied the dielectric property of the BCFO films. Fig. 5 shows the dielectric constant and dielectric loss vs. frequency relations. The measuring frequency ranges from 5 kHz to 1 MHz. It is easy to see from Fig. 5(a) that all films indicate small dielectric dispersion at low frequency since at which the dielectric constants decrease slightly with the frequency for all films. It means that the films has good interface between the BCFO film and $LaNiO_3$ bottom electrodes. Moreover, the film with $x = 0.05$ show the largest dielectric constant while with the increasing of x, the dielectric constant decreases at the same frequency. The results are accord with the ferroelectricity results and it means that by 5% Ce substitution, the ferroelectric property of the BCFO film was enhanced since the dielectric constant is mainly from the ferroelectric polarization in ferroelectrics.

The dielectric loss is shown in Fig. 5(b), at low frequency, the dielectric loss decreases with frequency and it caused from the contribution of space charge. All films have low dielectric loss in the whole frequency range and the dielectric loss increases drastically above 100 kHz. The results are similar to the result that has been reported in our previous work.[17] While at high frequency, the BFO film has the least dielectric loss. The relative large dielectric loss of 5 and 10% Ce-substituted BFO film may be related to dipole resonance. Therefore new polarization mechanisms have been introduced by the Ce substitution.

4. Conclusions

$Bi_{1-x}Ce_xFeO_3$ (BCFO) films with $x = 0$, 0.05, 0.10 and 0.15 were prepared by a sol–gel method followed by annealing at 500 °C under air. It was confirmed that the films deposited on $LaNiO_3$/Si(1 0 0) substrates with $x < 0.15$ consist of a single phase with dense and smooth surface. A noticeable improvement of hysteresis loops with better squareness than that of BFO film was obtained for the 5 molar percent Ce-substituted BCFO film. The remanent polarization and the coercive field were 71 μC/cm^2 and 103 kV/cm under a maximum applied field of 245 kV/cm, respectively. The leakage-current density of a 5 molar percent Ce-substituted BFO thin film was significantly decreased. Under 300 kV/cm, the leakage-current density is 2.2×10^{-7} A/cm^2. Moreover, the dielectric constant for the film with $x = 0.05$ are found substantially enhanced. These results demonstrated that Ce substitution could be a simple and effective method to obtain a film with a large ferroelectricity.

Acknowledgement

The work is supported by the Young People Program of Hubei Province Education Committee under Grant No. Q200722002.

References

1. Hill, N. A., Why are there so few magnetic ferroelectrics? *J. Phys. Chem. B*, 2000, **104**, 6694–6709.
2. Wang, J., Neaton, J. B., Zheng, H., Nagarajan, V., Ogale, S. B., Liu, B. *et al.*, Epitaxial $BiFeO_3$ multiferroic thin film heterostructures. *Science*, 2003, **299**, 1719–1722.
3. Yang, S. Y., Zavaliche, F., Mohaddes-Ardabili, L., Vaithyanathan, V., Schlom, D. G., Lee, Y. J. *et al.*, Influence of La doping in multiferroic properties of $BiFeO_3$ thin films. *Appl. Phys. Lett.*, 2005, **87**(102903), 1–3.
4. Fiebig, M., Lottermoser, T., Frohlich, D., Golsev, A. V. and Pisarev, R. V., Observation of coupled magnetic and electric domains. *Nature*, 2002, **419**, 818–820.
5. Dho, J., Qi, X., Kim, H., MacManus-Driscoll, J. L. and Blamire, M. G., Large electric polarization and exchange bias in multiferroic $BiFeO_3$. *Adv. Mater.*, 2006, **18**, 1445–1448.
6. Simões, A. Z., Gonzalez, A. H. M., Cavalcante, L. S., Riccardi, C. S., Longo, E. and Varela, J. A., Ferroelectric characteristics of $BiFeO_3$ thin films prepared via a simple chemical solution deposition. *J. Appl. Phys.*, 2007, **101**(074108), 1–4.
7. Qi, X., Dho, J., Tomov, R., Blamire, M. G. and MacManus-Driscoll, J. L., Greatly reduced leakage current and conduction mechanism in aliovalent-ion-doped $BiFeO_3$. *Appl. Phys. Lett.*, 2005, **86**, 062903–062905.

8. Chung, C. F., Lin, J. P. and Wu, J. M., Influence of Mn and Nb dopants on electric properties of chemical-solution-deposited $BiFeO_3$ films. *Appl. Phys. Lett.*, 2006, **88**(242909), 1–3.
9. Singh, S. K., Ishiwara, H. and Maruyama, K., Room temperature ferroelectric properties of Mn-substituted $BiFeO_3$ thin films deposited on Pt electrodes using chemical solution deposition. *Appl. Phys. Lett.*, 2006, **88**(262908), 1–3.
10. Kim, J. K., Kim, S. S., Kim, W., Bhalla, A. S. and Guo, R., Enhanced ferroelectric properties of Cr-doped $BiFeO_3$ thin films grown by chemical solution deposition. *Appl. Phys. Lett.*, 2006, **88**(132901), 1–3.
11. Uchida, H., Ueno, R., Funakubo, H. and Koda, S., Crystal structure and ferroelectric properties of rare-earth substituted $BiFeO_3$ thin films. *J. Appl. Phys.*, 2006, **100**(014106), 1–3.
12. Singh, S. K., Maruyama, K. and Ishiwara, H., The influence of La-substitution on the micro-structure and ferroelectric properties of chemical-solution-deposited $BiFeO_3$ thin films. *J. Phys. D: Appl. Phys.*, 2007, **40**, 2705–2709.
13. Meng, X. J., Cheng, J. G., Sun, J. L., Ye, H. J., Guo, S. L. and Chu, J. H., Growth of (1 0 0)-oriented $LaNiO_3$ thin films directly on Si substrates by a simple metalorganic decomposition technique for the highly oriented PZT thin films. *J. Cryst. Growth*, 2000, **220**, 100–104.
14. Bao, D., Yao, X., Wakiya, N., Shinozaki, K. and Mizutani, N., Structural, dielectric, and ferroelectric properties of $PbTiO_3$ thin films by a simple sol–gel technique. *Mater. Sci. Eng. B*, 2002, **94**, 269–274.
15. Park, B. H., Kang, B. S., Bu, S. D., Noh, T. W., Lee, J. and Jo, W., Lanthanum-substituted bismuth titanate for use in non-volatile memories. *Nature*, 1999, **401**, 682–684.
16. Cole, M. W. and Geyer, R. G., The dependence of dielectric properties on compositional variation for tunable device applications. *Mech. Mater.*, 2004, **36**, 1017–1026.
17. Liu, H. R., Liu, Z. L., Li, X. L., Li, X. A. and Yao, K. L., $Bi_{1-x}La_xFeO_3$ films on $LaNiO_3$ bottom electrode by the sol–gel process. *J. Phys. D: Appl. Phys.*, 2007, **40**, 242–248.