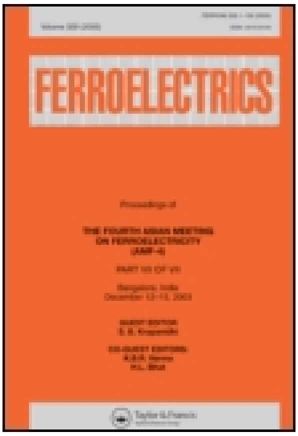
This article was downloaded by: [Xian Jiaotong University]
On: 04 September 2013, At: 07:06
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Ferroelectrics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gfer20

Ferroelectric and Ferromagnetic Properties of $0.7Bi_{1-x}Nd_x(Fe_{0.9}Cr_{0.1})O_3$-$0.1BaTiO_3$-$0.2PbTiO_3$ Solid Solutions

Xiao-Hui Liu [a] , Zhuo Xu [a] , Xiao-Yong Wei [a] & Xi Yao [a]
[a] Electronic Materials Research Laboratory, Key Laboratory of Ministry of Education, Xi'an Jiaotong University, Xi'an, 710049, China

Published online: 20 Jan 2011.

To cite this article: Xiao-Hui Liu , Zhuo Xu , Xiao-Yong Wei & Xi Yao (2010) Ferroelectric and Ferromagnetic Properties of $0.7Bi_{1-x}Nd_x(Fe_{0.9}Cr_{0.1})O_3$-$0.1BaTiO_3$-$0.2PbTiO_3$ Solid Solutions, Ferroelectrics, 410:1, 22-28, DOI: 10.1080/00150193.2010.492031

To link to this article: http://dx.doi.org/10.1080/00150193.2010.492031

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Ferroelectrics, 410:22–28, 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 0015-0193 print / 1563-5112 online
DOI: 10.1080/00150193.2010.492031

Ferroelectric and Ferromagnetic Properties of $0.7Bi_{1\text{-}x}Nd_x(Fe_{0.9}Cr_{0.1})O_3\text{-}0.1BaTiO_3\text{-}0.2PbTiO_3$ Solid Solutions

XIAO-HUI LIU,* ZHUO XU, XIAO-YONG WEI, AND XI YAO

Electronic Materials Research Laboratory, Key Laboratory of Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China

$0.7Bi_{1\text{-}x}Nd_x$ $(Fe_{0.9}Cr_{0.1})$ $O_3\text{-}0.1BaTiO_3\text{-}0.2PbTiO_3$ ($x = 0$, 0.03, 0.05, 0.07) solid solutions were prepared by the traditional ceramic process. X-ray diffraction results revealed that all samples showed pure rhombohedral perovskite structure. The addition of Nd substitutions could decrease the coercive field and electrical insulation resistivity. The P-E loops of specimens with $x = 0.03$ and 0.05 attained saturation. Piezoelectric constant d33 of the solid solutions increased firstly and then decreased, but the Magnetization of the solid solutions decreased slightly with increasing of the Nd content.

Keywords Ceramics; ferroelectric properties; Magnetically ordered materials

1. Introduction

Ferroelectromagnetic materials possess ferromagnetism and ferroelectricity simultaneously as a result of the coexistence of electric and magnetic orders. In this case, coupling between the magnetic and ferroelectric order parameters in these materials can give rise to magnetoelectric effect, which provides an additional degree of freedom in design of new functional sensor, current devices, transducers and multi-state memory devices [1, 2]. However, due to their low Néel temperature or negligible magnetoelectric effect in most ferroelectromagnetic materials, no practical application of ferroelectricity and ferromagnetism has been reported. $BiFeO_3$ (BFO) is a promising candidate as single-phase ferroelectromagnetic material because it is antiferromagnetic with a relatively high Neel temperature ($T_N = 380°C$) and ferroelectric with high $T_c = 810°C$ [3]. Unfortunately, as for bulk BFO ceramics, research work is still being hindered by the easy formation of second phase during synthesis and the low resistivity of samples. These have prevented its practical applications as piezoelectric or magnetoelectric functional components. Recent work mainly has focused on binary or ternary solid solutions of BFO with other ABO_3 perovskite materials or doping on these solid solutions. Because these perovskite materials can prevent the formation of second phases and improve sample resistivity. To date, several perovskites (such as $PbTiO_3$ and $BaTiO_3$) [4, 5] have been used to form solid solution with BFO. Although perovskite structure of these solid solutions has been found to be stable and the spontaneous magnetic moment is increased at room temperature, their ferromagnetism is weak due to the antiferromagnetic nature. Substantial work has been implemented on BFO-based materials to

---

Received August 23, 2009.

*Corresponding author. E-mail: lxhui@mail.xjtu.edu.cn improve magnetization, such as doping at A sites [6, 7] or B sites [8]. Therefore, in previous literatures about BFO-based materials, the focus was either on better ferroelectric or better ferromagnetic properties. Better ferroelectric and ferromagnetic properties simultaneously, especially, piezoelectric properties were seldom reported.

This paper was based on our foregoing work [9], Nd substituting for Bi in 0.7Bi $(Fe_{0.9}Cr_{0.1})O_3$-$0.1BaTiO_3$-$0.2PbTiO_3$ solid solution is to improve the ferroelectric and piezoelectric properties. Ferroelectric, piezoelectric, and ferromagnetic properties were investigated.

2. Experimental Procedure

$0.7Bi_{1\text{-}x}Nd_x(Fe_{0.9}Cr_{0.1})O_3$-$0.1BaTiO_3$-$0.2PbTiO_3$ (BNxFOC-BT-PT, with $x = 0, 0.03, 0.05$, and 0.07) solid solutions were fabricated by the conventional solid-state reaction method. Analytical-grade raw materials, Bi_2O_3, Fe_2O_3, Cr_2O_3, $BaCO_3$, and TiO_2, were weighed and mixed in a ball mill for 12 h, using alcohol as media. After drying, the powders were calcined at 860–960°C for 2 h in air and ball milled for another 12 h. The resultant powders were pressed into disks of 10mm in diameter and 1mm in thickness using a hardened a stainless steel die at a pressure of 400 MPa, with polyvinyl alcohol (PVA) as binder. After burning off PVA, the pellets were sintered at 1060–1120°C for 3 h in air. The specimens were polished and electroded with a postfire silver paste on both sides.

Phase compositions of the specimens were characterized by an X-ray diffraction (XRD) (Rigaku D/MAX-2400, CuK_α radiation). Microstructure of fresh fracture surfaces of sintered samples was examined by using a scanning electron microscopy (SEM) (JSM-6360). The electrical insulation resistance was tested using HP4339A-HP16339A high resistance meter. Ferroelectric hysteresis loops were characterized by using a ferroelectric test system (TF Analyzer 2000) and magnetic hysteresis loops were measured by LakeShore 7307 vibrating sample magnetometer (VSM).

3. Results and Discussion

Figure 1 shows the XRD patterns for BNxFOC-BT-PT with $x = 0, 0.03, 0.05$, and 0.07. All samples possess single phase of rhombohedral perovskite structure. In addition, diffraction peaks of the samples shift toward higher angles with increasing content of Nd. This result indicates that lattice constant of the samples decreases with increasing content of Nd, which is because the radius of Nd^{3+} is smaller than that of Bi^{3+}.

Figures 2(a)–2(d) show SEM images of BNxFOC-BT-PT for $x = 0, 0.03, 0.05$, and 0.07, respectively. These images were taken from the fresh fracture surface. It can be seen that BNxFOC-BT-PT ceramics are well densified, containing no residual porosity and second phases. The grain size of BNxFOC-BT-PT decreased slightly with increasing content of Nd. It can also be found that the fracture surfaces of BNxFOC-BT-PT with Nd substitutions look more transgranular rather along grain boundary indicating that the grain boundary has the similar strength as the inside grain. It has been known that materials fractured in the transgranular style need more energy. Therefore, the mechanical strength and toughness of BNxFOC-BT-PT with Nd substitutions can be enhanced with the increase of Nd content.

Figure 3 shows the room temperature electrical insulation resistivity of the BNxFOC-BT-PT ceramics as a function of Nd content. It can be seen that the resistivity of

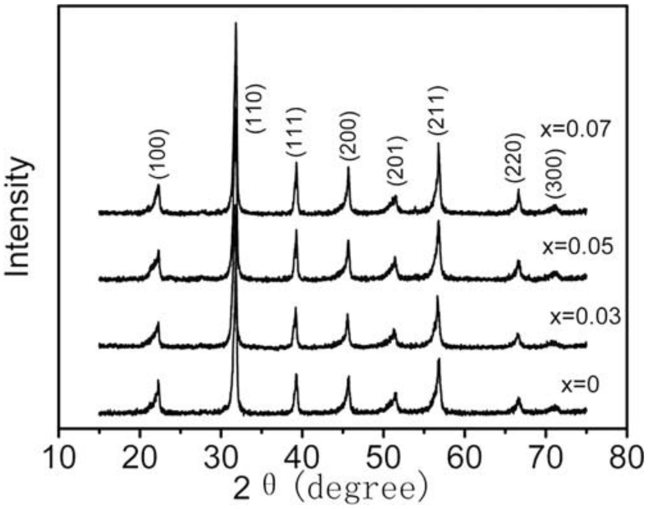


Figure 1. XRD patterns of the BNxFOC-BT-PT ceramics with different Nd contents.

BNxFOC-BT-PT decreases with the Nd content increasing. We conjectured that the Nd3+ ions substituting Pb2+ or Ba2+ ions would be occurred though Nd3+ should substitute Bi3+ mostly for their similar ion radius and valence. Therefore, the BNxFOC-BT-PT ceramics would be become "soft", decreasing electrical resistivity.

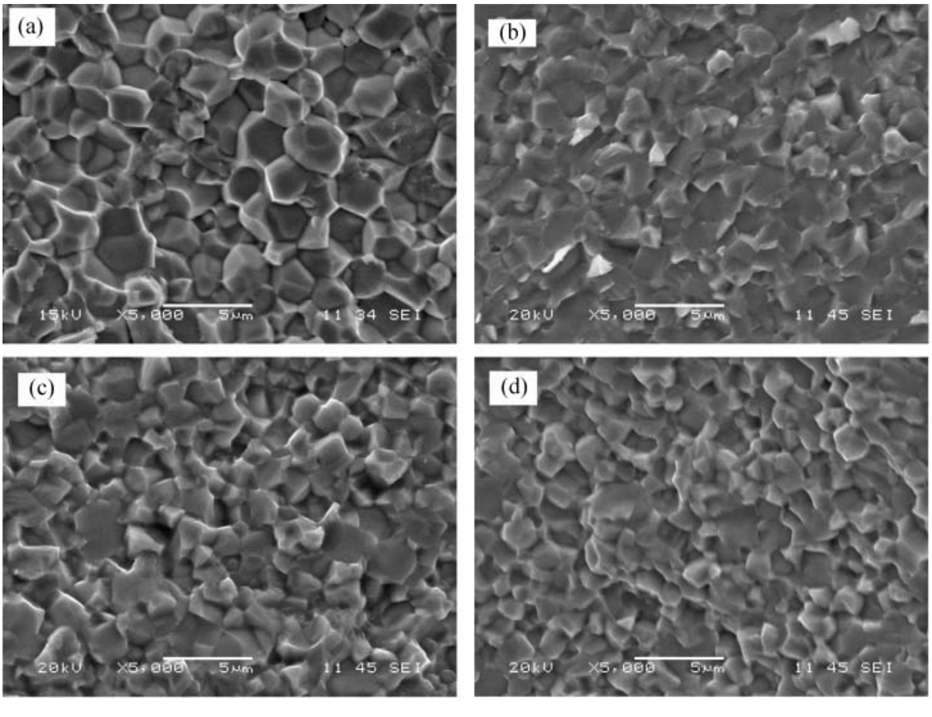


Figure 2. SEM photos of fracture surfaces of the BNxFOC-BT-PT samples with different Nd contents. (a) x = 0 (b) x = 0.03 (c) x = 0.05 (d) x = 0.07.

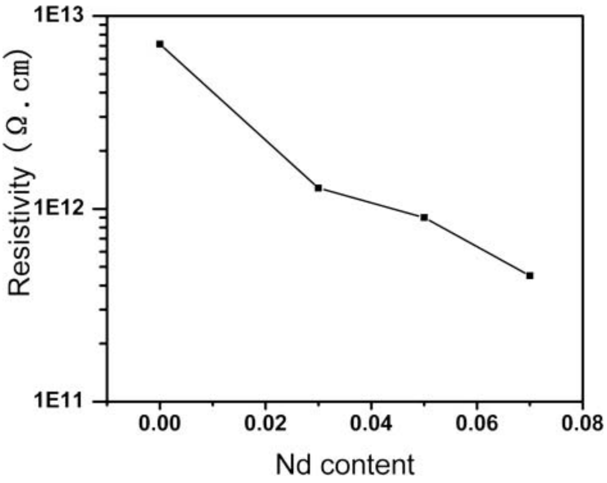


Figure 3. Electrical resistivities of BNxFOC-BT-PT ceramics with different Nd contents.

P–E curves of the BNxFOC-BT-PT samples with x = 0, 0.03, and 0.05, respectively, are shown in Fig. 4. For the sample with x = 0, *P–E* loop rounded corners, and could not reach saturation, indicating significant conductive losses and large coercive field. However, *P–E* loops of the samples with x = 0.03 and 0.05 reach saturation. We considered that the coercive field was decreased for the introduction of Nd. Therefore, the *P–E* loops with x = 0.03 and 0.05 can attain saturation though possessing of lower electrical resistivities. The specimens would be completely poled, and hence the piezoelectric properties could be characterized. The conductive losses of the specimen with x = 0.07 was too significant to allow specimens to be completely poled though lower coercive field.

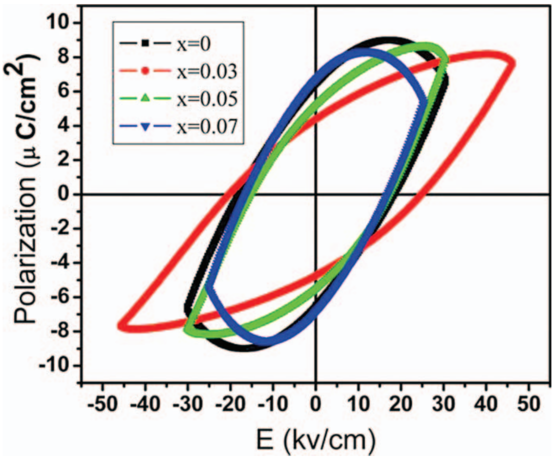


Figure 4. Ferroelectric hysteresis loops of the BNxFOC-BT-PT samples with different Nd contents. (See Color Plate III)

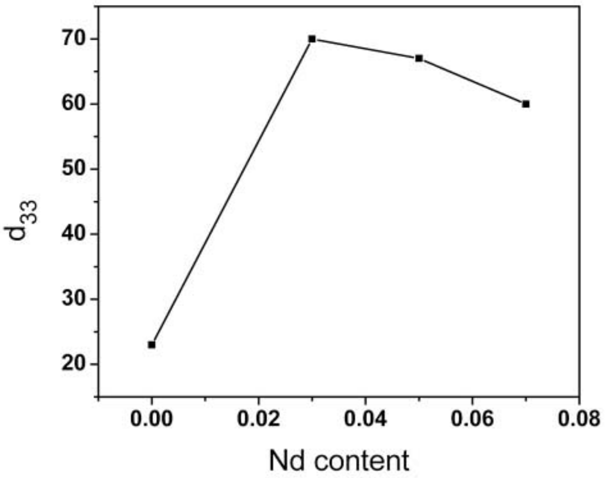


Figure 5. Piezoelectric constant of the BNxFOC-BT-PT samples with different Nd contents.

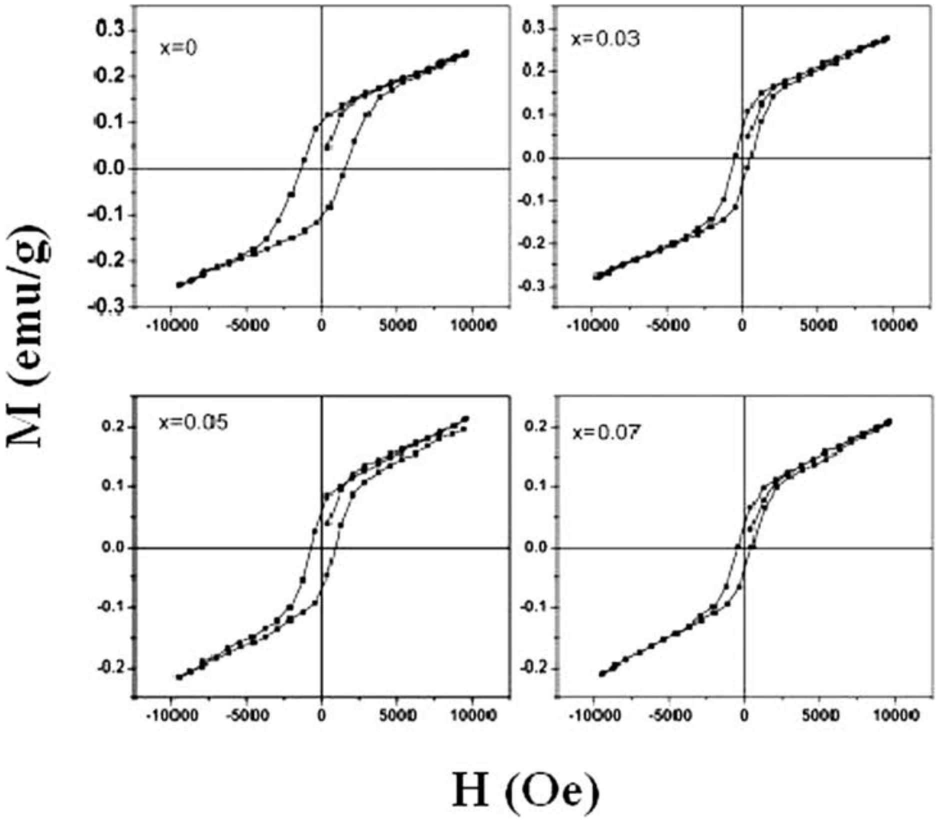


Figure 6. Magnetic hysteresis loops of the BNxFOC-BT-PT samples with different Nd contents.

For piezoelectric measurement, we polarized the samples in the silicon oil under an electric field 30 kV/cm at 120°C. The piezoelectric constant d33 was measured using a quasi-static d33 meter (Model ZJ-3, Institute of Acoustics Academic Sinica). Figure 5 shows the dependence of the piezoelectric constant d33 on the Nd contents. It can be seen that the piezoelectric constant d33 increases firstly and then decreases with increasing content of Nd. The d33 of specimen with $x = 0.03$ was the largest. That is because the specimens with $x = 0.03$ can be poled completely.

Figure 6 shows *M-H* curves of the BNxFOC-BT-PT samples with $x = 0$, 0.03, 0.05, and 0.07, respectively, measured at room temperature. The BNxFOC-BT-PT solid solutions exhibit symmetric magnetic hysteresis loops, indicating that they are magnetic ordered materials. The remanent magnetizations of BNxFOC-BT-PT for $x = 0$, 0.03, 0.05, and 0.07 was about 0.11, 0.06, 0.05, and 0.03 emu/g, respectively, showing a slight fall with the increase of Nd content. The remanent magnetizations were relatively small as compared to nominal ferromagnetic compounds. Small remanent magnetizations and unsaturated *M-H* behavior of the solid solutions indicate that they are basically antiferromagnetic with weak ferromagnetism. [10] In such a case, spontaneous magnetization *Ms* could be obtained by extrapolating the linear portion of the *M-H* curves to $H = 0$. The estimated values of *Ms* decreased with increasing x, were 0.15, 0.14, 0.09, and 0.08 emu/g, for $x = 0$, 0.03, 0.05, and 0.07, respectively. Physical properties of BFO-based solid solutions with simultaneously occurring magnetic and electric orderings are not yet understood. Remanent magnetizations observed in this investigation reveal ferromagnetism, but very weak compared to typical ferromagnetic compounds. The magnetic properties of $0.7Bi\ (Fe_{0.9}Cr_{0.1})\ O_3$-$0.1BaTiO_3$-0.2PbTiO3 were discussed in our previous report. [9]. We considered the possible reason for the slight fall in these materials systems was the local ferromagnetic ordered structure might form between Fe^{3+} ions and Cr^{3+} ions is destroyed partly.

4. Conclusions

Pure perovskite 0.7Bi1-xNdx $(Fe_{0.9}Cr_{0.1})\ O_3$-$0.1BaTiO_3$-0.2PbTiO3 ($x = 0$, 0.03, 0.05, 0.07) solid solutions were prepared by the traditional ceramic process. The addition of Nd substitutions can decrease the coercive field, and the specimens can be completely poled. The BNxFOC-BT-PT ceramics are of good ferroelectric, piezoelectric, and ferromagnetic properties simultaneously. This will become a promising candidate as single phase ferroelectromagnetic material for application of ferroelectricity, ferromagnetism, and magnetoelectricity.

Acknowledgments

This work was financially supported by the National Basic Research Program of China under Grant No 2009CB623306, the National Natural Science foundation of China under Grant No. 10976022, and the Key Science and Technology Research Project from the Ministry of Education of China under Grant No.108180.

References

1. M. Fiebig, T. Lottermoser, D. Frohlich, A. V. Goitsev, and R. V. Pisarev, Observation of coupled magnetic and electric domains. *Nature* **419**(6909), 818–820 (2002).
2. M. Fiebig, Revival of the magnetoelectric effect. *J. Phys. D.* **38**, R123 (2005).

3. M. Popa, D. Crespo, J. M. Calderon-Moreno, S. Preda, and V. Fruth, Synthesis and structural characterization of single-phase BiFeO3 powders from a polymeric precursor. *J. Am. Ceram. Soc.* **90**, 2723–2727 (2007).
4. D. I. Woodward, I. M. Reaney, A. R. West, and C. A. Randall, Crystal and domian structure of the BiFeO3-PbTiO3 solid solution. *J. Appl. Phys.* **94**(5), 3313–3318 (2003).
5. M. M. Kumar, S. Srinath, G. S. Kumar, and S. V. Suryanarayana, Spontaneous magnetic moment in BiFeO3-BaTiO3 solid solutions at low temperatures. *J. Magn. Magn. Mater.* **188**, 203–212 (1998).
6. V. R. Palkar, C. Darshan, S. K. Kundaliya, and S. Malik, Bhattacharya: Magnetoelectricity at room temperature in the Bi0.9-xTbxLa0.1FeO3 system. *Phys. Rev. B.* **6**, 212102 (2004).
7. V. L. Mathe, K. K. Patankar, R. N. Patil, and C. D. Lokhande, Synthesis and dielectric properties of Bi1-xNdxFeO3 perovskite. *J. Magn. Magn. Mater.* **270**, 380–388 (2004).
8. C. H. Yang, T. Y. Koo, and Y. H. Jeong, How to obtain magnetocapacitance effects at room temperature: The case of Mn-doped BiFeO3. *Solid State Commun.* **134**, 299–301 (2005).
9. X. H. Liu, Z. Xu, X. Y. Wei, X. Yao, and X. Yang, Dielectric and magnetic properties of 0.7BiFe1-xCrxO3–0.1BaTiO3–0.2PbTiO3 solid solutions. *J. Alloys Compd.* **480**, L41–L44 (2009).
10. J. S. Kim, Y. N. Choi, and P. W. Jang, Ferroelectric and ferromagnetic properties of $BiFeO_3$-$PrFeO_3$-$PbTiO_3$ solid solutions. *J. Appl. Phys.* **93**, 9263–9270 (2003).