Journal of Magnetics 14(3), 117-119 (2009) DOI: 10.4283/JMAG.2009.14.3.117

Structural and Magnetic Properties of $LaFeO_3$-$BaTiO_3$ Solid Solutions

E. Venkata Ramana, O-Ung Kwon, Jin I Kim, and C. U. Jung*

Department of Physics, Hankuk University of Foreign Studies, Kyugki-do 449-791, Korea

(Received 10 August 2009, Received in final form 28 August 2009, Accepted 2 September 2009)

Polycrystalline samples of $LaFeO_3$-$BaTiO_3$ were synthesized to examine the structural and magnetic behavior. X-ray diffraction confirmed that the ceramics had tetragonal symmetry with less tetragonal strain (c/a) than $BaTiO_3$. The magnetic hysteresis measured at room temperature suggested that the magnetic nature deviates from that of the parent $LaFeO_3$, which has antiferromagentic with a G-type spin structure. Improved magnetic behavior of the solid solution compound might be due to the increase in the canting angle of the spin. The presence of oxygen vacancies and fluctuating Fe valence, arising from the substitution of Ba^{2+} and Ti^{4+} at the A- and B-sites of the lattice, might contribute to bulk magnetization. The temperature dependent magnetization indicated that magnetization was higher at low temperatures and showed a decreasing trend with increasing temperature to room temperature. The magnetic transition temperature of these samples was 665 K and 743 K for the mixed system and $LaFeO_3$, respectively.

Keywords : ferroelectric materials, ceramics, magnetic materials

1. Introduction

Multiferroics with simultaneous ferroelectric, ferroelastic and (anti)ferromagnetic order, are potential future materials for applications in non-volatile memory and spintronics [1, 2]. Coupling of the electrical and magnetic ordering can allow manipulation of the magnetic state by an electric field or vice versa, facilitating the tunability of multifunctional devices [2]. $BiFeO_3$ is a potential multiferroic memory material. In the bulk, $BiFeO_3$ has a rhombohedral structure exhibiting antiferromagnetism with a Neel temperature (T_N) of 640 K and ferroelectricity up to 1,100 K [3]. Cross-coupling between two order parameters has been demonstrated in several $BiFeO_3$ based solid solutions [4, 5]. Recently, several other materials, such as $RMnO_3$, RMn_2O_5 (R: rare earths), $Ni_3V_2O_8$, delafossite $CuFeO_2$, $CoCr_2O_4$, $MnWO_4$, and hexa-ferrite $(Ba,Sr)_2Zn_2Fe_{12}O_{22}$, have been reported to exhibit multiferroic properties [6].

This study examined the solid solution system of $LaFeO_3$-$BaTiO_3$. $LaFeO_3$ (LFO) belongs to a family of rare-earth orthoferrites, crystallizing with an orthorhombic structure of space group, *pbnm* [6, 7]. It is antiferromagentic (AFM) with T_N~740 K and the AFM axis oriented along the crystallographic a-axis [7]. On the other hand, $BaTiO_3$ (BTO) is a classical ferroelectric material with a tetragonal crystal structure (*P4/mmm*) at room temperature. Thin films of $BaTiO_3$ were reported to exhibit a large remanent ferroelectric polarization up to 70 $\mu C/cm^2$ with a coercive field of 25 kV/cm [8]. In view of the ferroelectric and insulating magnetic behavior of LFO and BTO, (1-x)$LaFeO_3$-x$BaTiO_3$ ceramics were synthesized to examine their physical properties. This paper describes the results on the structural and magnetic behavior of these ceramics.

2. Experimental

Ceramic samples of $LaFeO_3$ $BaTiO_3$ and $(Ba_{0.5}La_{0.5})$-$(Ti_{0.5}Fe_{0.5})O_3$ (LBTF) were synthesized by a conventional solid state reaction method [9, 10]. Starting raw materials (Aldrich, Purity 99.99%) of La_2CO_3, $BaCO_3$, TiO_2 and Fe_2O_3 were mixed thoroughly and ground in an agate mortar. The powders were calcined at 900°C and 1200°C for 24 hours with intermediate grinding. Finally, the powder was pressed into discs and sintered at 1300-1400 °C for 6 hours. X-ray diffraction (XRD) was performed using a Rigaku (Miniflex) diffractometer with Cu-K_α radiation. The magnetic properties were measured using a vibrating sample magnetometer (VSM, Lakeshore-7300) over the temperature range, 10-300 K, in a field of 5 kOe.

*Corresponding author: Tel: +82-31-330-4952
Fax: +82-31-330-4566, e-mail: cu-jung@hufs.ac.kr

High temperature magnetization was also measured over the range, 300-800 K.

3. Results and Discussion

Fig. 1 shows the XRD θ-2θ patterns of LFO, LBTF and BTO along with those of the end compounds of LFO and BTO. All samples were formed as a pure phase without impurities within the range of experimental error. Table 1 lists the lattice parameters calculated from these patterns. The data suggests that the LBTF and BTO samples have a tetragonal structure while LFO is formed as the orthorhombic phase. The calculated tolerance factor increased from 0.961 (LFO) to 1.062 (BTO). The simultaneous substitution of atoms with different ionic radii at the A-and B-sites of the $BaTiO_3$, such as La^{3+} (1.38 Å) for Ba^{2+} (1.61 Å) and Fe^{3+}(0.645 Å) for Ti^{4+}(0.605 Å) [11], resulted in a decrease in volume.

Fig. 2 presents the magnetic hysteresis for LBTF. The data appears to show no tendency for saturation within the range of the present field (7 kOe). The nature of the *M-H* hysteresis curve deviates from that of pristine LFO, which was reported to be antiferromagentic and appears to be a weak ferromagnetic type [12]. The inset in Fig. 2 also shows the *M-H* curve measured at various temperatures. The remanent magnetization and coercive field increases at low temperatures. The reason for the increase in magnetization was attributed to oxygen vacancies and the fluctuating Fe^{3+} valence. $LaFeO_3$ exhibits antiferromagentism with G-type spin structure [7] that is similar to the well known multiferroic material $BiFeO_3$ [3, 11]. When this is combined with the $BaTiO_3$ in solid solution form, Fe^{3+} and Ti^{4+} occupy the B-sites of the lattice, which may result in the creation of oxygen vacancies to maintain charge neutrality. Simultaneously, A-site substitution with Ba^{2+} can cause a distortion in the structure and alter the bond angle of Fe-O-Fe affecting the change in the overall magnetization similar to the observation reported by Wang *et al.* [13] in the case of Ba-doped $BiFeO_3$. Thus, the net magnetization may arise due to lattice defects, oxygen vacancies, and magnetic anisotropy. Overall, the magnetization might be due to the canting of spin, as observed in the case of pure and doped $BiFeO_3$ [12]. Further experiments will be needed to reveal the origin of magnetization.

Temperature dependent magnetization (*M-T*) for LBTF was measured in both the zero field cooled (ZFC) and field cooled (FC) sequences at a fixed magnetic field of 5

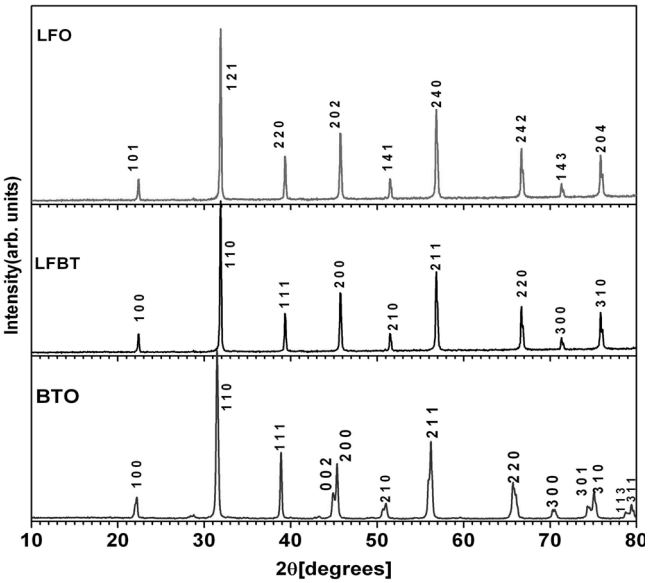

Fig. 1. X-ray θ-2θ scan of LFO, BTF and BTO.

Table 1. Structural parameters of LFO, LFBT, and BTO.

Sample	Lattice parameter (Å)			c/a	t
	a	b	c		
LFO	5.563±0.003	5.549±0.006	7.860±0.005	1.413	0.961
LFBT	3.953±0.007	3.953±0.007	3.948±0.002	0.999	1.009
BTO	3.991±0.005	3.991±0.005	4.032±0.004	1.010	1.062

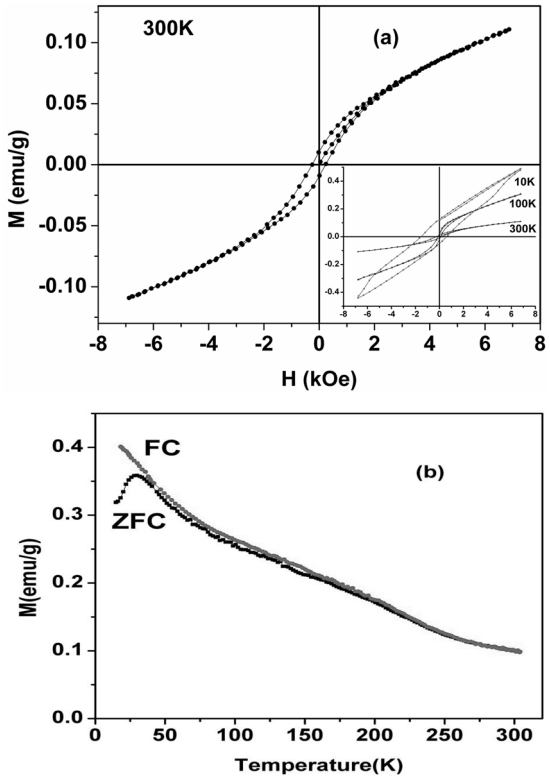

Fig. 2. (a) Magnetic hysteresis loops of LBTF. Inset: *M-H* data at various temperatures is shown for comparison. (b) *M-T* data of LBTF.

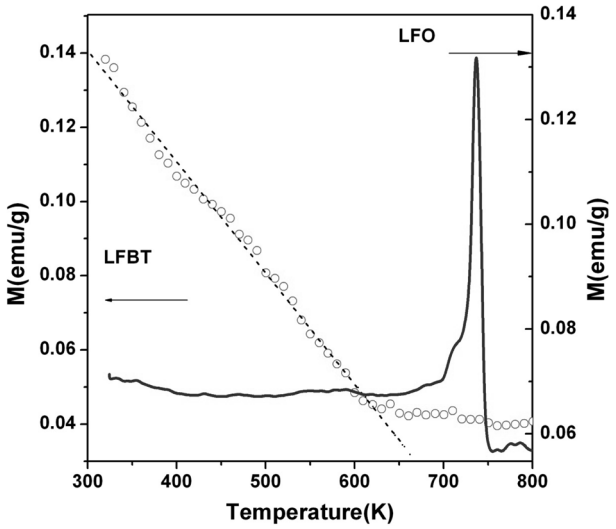

Fig. 3. Magnetization data at higher temperatures for LBTF and LFO. The dotted line indicates the linear fitting.

kOe, as shown in Fig. 2b. The magnetization in both ZFC and FC modes, which increased with decreasing temperature, was slightly higher in FC mode than in ZFC, and showed a small hump at approximately 40 K in ZFC mode. The contribution of Fe in the total magnetization was 4.5×10^{-3} μ_B/Fe at 10 K (5.7×10^{-3} μ_B/Fe for FC).

The magnetic transition temperature of LBTF was estimated by measuring the magnetization as a function of temperature over the range, 300-800 K, in a magnetic field of 5 kOe. Fig. 3 shows that the magnetization decreases linearly with increasing temperature, reaching a minimum value above which the temperature induces no significant change in magnetization. From an extension of the linear fit of this data, the magnetic transition temperature was determined and the corresponding temperature for LBTF was ~665 K. A similar magnetic transition was reported for the $LaFeO_3$-$PbTiO_3$ system at approximately 640 K [14]. Magnetic hysteresis measured at 700 K clearly shows typical paramagnetic behavior. For comparison, the magnetization of LFO was measured over this temperature range and is presented in Fig. 3. The magnetic transition temperature obtained for LFO was 743 K, which is closer to the value reported in the literature (750 K) [7]. The addition of BTO to LFO in solid solution form resulted in a decrease in the magnetic transition temperature.

The aim of this study was to establish the magnetic and ferroelectric nature of LBTF ceramics. Unfortunately, the P-E curve measured at low frequency for LBTF showed poorly developed ferroelectricity with a large leakage current (data not shown). Experiments to improve the ferroelectricity through a compositional change are currently underway.

4. Conclusions

Single phase $(Ba_{0.5}La_{0.5})$ $(Ti_{0.5}Fe_{0.5})O_3$ ceramic samples with a tetragonal unit cell were synthesized using a ceramic route. The addition of $BaTiO_3$ to $LaFeO_3$ resulted in a decrease in unit cell volume. The magnetic hysteresis deviated from that observed for antiferromagentic $LaFeO_3$. The resulting magnetization might be due to the canting of spin. The M-T data at low temperatures exhibited higher magnetization while a change in the magnetic state was observed at 665 K.

Acknowledgment

This research was supported by Basic Science Research Program Through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (No. 20090066917 and KRF-2008-314-C00126). This work was supported by Hankuk University of Foreign Studies Research Fund of 2008.

References

[1] W. Eerenstein, N. D. Mathur, and J. F. Scott, Nature **442**, 759 (2006).
[2] M. Bibes and A. Barthélémy, Nature Mater. **7**, 425 (2008).
[3] D. Lebeugle, D. Colson, A. Forget, M. Viret, P. Bonville, J. F. Marucco, and S. Fusil, Phys. Rev. B **76**, 024116 (2007).
[4] V. R. Palkar, D. C. Kundaliya, S. K. Malik, and S. Bhattacharya, Phys. Rev. B. **69**, 212102 (2004).
[5] E. Venkata Ramana, B. V. B. Saradhi, S. V. Suryanarayana and T. Bhima Sankaram, Ferroelectrics **324**, 55 (2005).
[6] S.-W. Cheong and M. Mostovoy, Nature Mater. **6**, 13 (2007) and references therein.
[7] J. B. Goodenough and J. M. Longo, Landolt-Bornstein, New Series, edited by K.-H. Hellwedge and A. M. Hellwedge (Springer, Berlin), Group III, vol. 4, part a, Chap. 3, p.126, (1970).
[8] K. J. Choi, M. Biegalski, Y. L. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y. B. Chen, X. Q. Pan, V. Gopalan, L.-Q. Chen, D. G. Schlom, and C. B. Eom, Science **306**, 1005 (2004).
[9] J. I. Kim and C. U. Jung, J. Magnetics **13**, 57 (2008).
[10] Y. J. Chang, J. I. Kim, and C. U. Jung, J. Magnetics **13**, 61 (2008).
[11] R. D. Shannon, Acta. Cryst. A **32**, 751 (1976).
[12] M. Fiebig, J. Phys. D: Appl. Phys. **38**, R123 (2005).
[13] D. H. Wang, W. C. Goh, M. Ning, and C. K. Ong, Appl. Phys. Lett. **88**, 212907 (2006).
[14] A. Singh and R. Chatterjee, Appl. Phys. Lett. **93**, 182908 (2008).