

Magnetic Ordering in $(1-x)\text{BaTiO}_3-x\text{LaFeO}_3$ Solid Solutions

R. Rajagukguk, D. G. Shin, and B. W. Lee*

Department of Physics, Hankuk University of Foreign Studies, Yongin, Gyeonggi-do 499-791, Korea

(Received 18 February 2011, Received in final form 16 March 2011, Accepted 16 March 2011)

Solid solutions between BaTiO_3 and LaFeO_3 have been prepared through a solid state reaction method. The X-ray diffraction results reveal that $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Fe}_x\text{O}_3$ ($0.1 \leq x \leq 0.7$) compounds have a cubic structure, whereas the parent material BaTiO_3 has a tetragonal structure. The magnetization measurements indicate that the materials have a magnetic ordering at room temperature and the magnetic properties of the solid solutions depending on the doping amount of LaFeO_3 . The origin of magnetic behaviors is believed to be from Fe^{3+} ions.

Keywords : barium titanate, LaFeO_3 , ferromagnetic, perovskite

1. Introduction

Perovskites have been matters of interest to many scientists due to their unique properties and a wide range of potential applications. The valence of A and B ions affects the crystal structure and the physical properties of the materials. Many $\text{A}^{2+}\text{B}^{4+}\text{O}^{2-}$ type perovskites are insulators possessing a cubic or tetragonal structure. BaTiO_3 (BTO) is known to be a classical ferroelectric material with a reasonably low Curie temperature (T_c) = 120 °C. It is crystallized in a tetragonal structure at room temperature and also has large piezoelectric, elastic and dielectric constants [1]. On comparison, $\text{A}^{3+}\text{B}^{3+}\text{O}^{2-}$ type perovskites are mostly semiconductors or magnetic materials possessing an orthorhombic structure. For instance, LaFeO_3 (LFO) is a member of the rare earth orthoferrites, which has an orthorhombic structure at room temperature and an antiferromagnetic ordering below 740 K [2]. Polycrystalline samples of donor doped BTO show the resistivity anomaly at the T_c , which is known as PTCR (positive temperature coefficient of resistance) effect [3]. The dielectric constant and the conductivity of La doped BTO increase as La amount increases [4]. In contrast, Fe doped BTO was reported to have a ferromagnetic ordering with large leakage current [5]. Simultaneous substitution of A and B ions in ABO_3 perovskite is expected to have common properties to the two original perovskites. Li *et al.* proved that the whole range solid solutions $(1-x)\text{BaTiO}_3-$

$x\text{LaFeO}_3$ (BLTF) between BTO and LFO compounds can be formed [6]. The introduction of La^{3+} ion into Ba^{2+} site causes a decrease in the number of covalence bonds; moreover Fe^{3+} ion substitution into Ti^{4+} site leads to the limitation of displacement in octahedron. Although these effects cause the ferroelectric transition point to decrease, the tunability and the dielectric constant at room temperature of the solid solution compounds increase. Another interesting point of such solid solution is that the magnetic LFO compound introduced into a ferroelectric BTO compound can induce a magnetic moment without destroying the ferroelectric properties. However, to our knowledge, the study of magnetic properties for BLTF materials in a wide range of x has not been reported yet. In this work, we investigate the effect of simultaneous replacement of the Ba^{2+} and Ti^{4+} ions with the La^{3+} and Fe^{3+} ions, on the magnetic properties of BLTF by conducting dc magnetization and hysteresis experiments.

2. Experiments

Polycrystalline samples of BLTF have been prepared by a standard solid-state reaction method. The starting materials were BaCO_3 , La_2O_3 , TiO_2 , and Fe_2O_3 with purity of > 99.9%. The materials were weighed according to the stoichiometric ratio, which were then mixed, ground, and heated in air at 900 °C first and then 1200 °C for 24 h with intermediate grinding. The resultant powders were reground and pressed into pellets. These pellets were sintered at 1350 °C for 6 h in air and then cooled to room temperature. Powder X-ray diffraction (XRD) was carried out using Rigaku diffractometer

*Corresponding author: Tel: +82-31-330-4362
Fax: +82-31-330-4566, e-mail: bwlee@hufs.ac.kr

Miniflex with $\text{Cu-K}\alpha$ radiation. The lattice constants were calculated using the least square method. The magnetization (σ) was measured by a vibrating sample magnetometer (Lakeshore, model 7300) over the temperature range of 10-800 K in a field of 5 kOe. The isothermal magnetization was measured at various temperatures while sweeping the magnetic field within ± 7 kOe.

3. Results and Discussion

Fig. 1 shows the XRD patterns for polycrystalline BTO and BLTF samples at room temperature. It appears as a single phase without the sign of impurities within the boundary of experimental error. The data suggest that the crystal structure of BLTF samples belongs to a cubic system at room temperature, while BTO sample has a tetragonal structure. Fig. 2 contains the lattice parameters a and c of BLTF samples. It indicates that the structure changes from tetragonal to cubic at approximately 10% LFO, which is consistent with the reported result [6]. For $x < 0.05$, the composition remained as tetragonal and the lattice parameter a slightly increased [6]. The introduction of La^{3+} ion and Fe^{3+} ion affects the c/a ratio. The lattice parameter c decreases more rapidly than the increase of the lattice parameter a , and eventually c and a become equal. Since the ionic radius of La^{3+} ion is smaller than that of Ba^{2+} ion and the ionic radius of Fe^{3+} ion in the low spin state is smaller than that of Ti^{4+} ion, the introduction of La^{3+} ion and Fe^{3+} ion in the low spin state can not explain the increase in lattice parameter a . Therefore, we expect the Fe^{3+} ion would be in the high spin state.

Fig. 3 shows the magnetic hysteresis (M-H) for BLTF samples at room temperature. The samples exhibit different

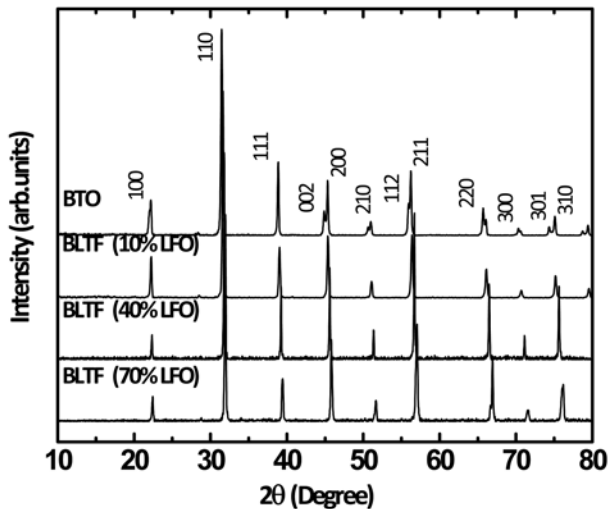


Fig. 1. Powder x-ray diffraction (XRD) patterns for polycrystalline $(1-x)\text{BaTiO}_3\text{-}x\text{LaFeO}_3$.

magnetic behaviors as the doping amount increases. Samples ($0.1 \leq x \leq 0.2$) display a weak magnetic behavior and samples ($0.3 \leq x \leq 0.7$) apparently show hysteresis, indicating ferromagnetic ordering at room temperature. Mori suggested that the $\text{Fe}^{4+}\text{-O}^{2-}\text{-Fe}^{4+}$ interaction is ferromagnetic, while the $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{4+}$ and $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$ interactions are anti-ferromagnetic [7]. However, it is also argued that ferromagnetism comes from the statistical distribution of Fe^{3+} and Ti^{4+} ions in the octahedral sites [8].

Moreover, the magnetization does not reach saturation even in the magnetic field up to ± 7 kOe. A linear paramagnetic behavior is superimposed upon hysteresis. It reveals that the M-H curves consist of a magnetic hysteresis loop and a linear paramagnetic component. The saturation magnetization (M_s) is presented in Fig. 4. The M_s of samples for $x = 0.3$ tends to increase drastically with x .

In order to find the transition point of these BLTF samples, the temperature dependent magnetization mea-

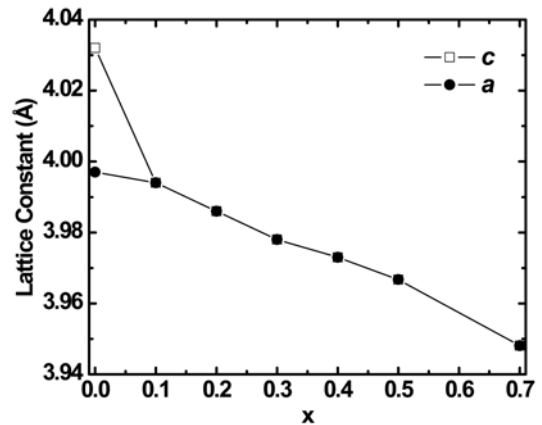


Fig. 2. Lattice parameters of $(1-x)\text{BaTiO}_3\text{-}x\text{LaFeO}_3$.

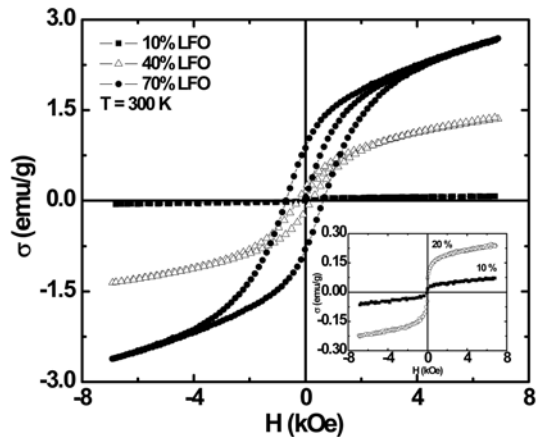


Fig. 3. Magnetic hysteresis (M-H) of $(1-x)\text{BaTiO}_3\text{-}x\text{LaFeO}_3$ measured at 300 K.

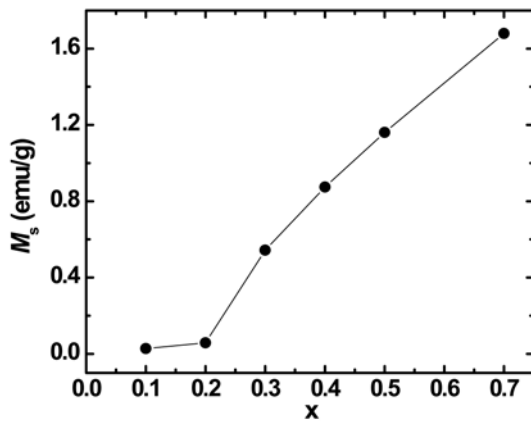


Fig. 4. Saturation magnetization (M_s) for $(1-x)\text{BaTiO}_3-x\text{LaFeO}_3$.

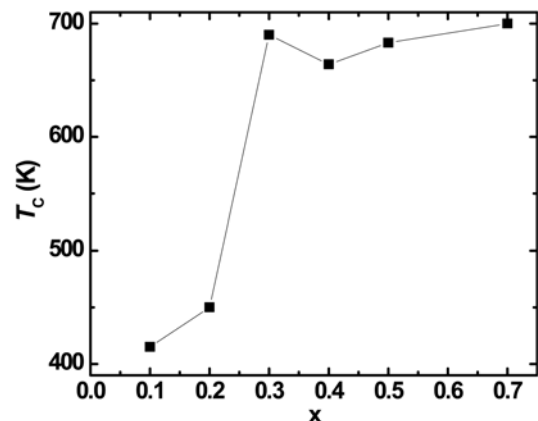


Fig. 6. The transition point of $(1-x)\text{BaTiO}_3-x\text{LaFeO}_3$.

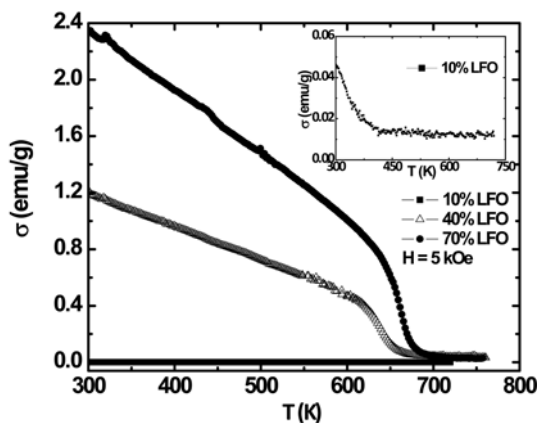


Fig. 5. Temperature dependent magnetization $\sigma(T)$ for $(1-x)\text{BaTiO}_3-x\text{LaFeO}_3$ at high temperature, measured with external field of $H = 5$ kOe.

measurements were conducted. Fig. 5 presents the temperature dependent magnetization $\sigma(T)$ for the samples with $x = 0.1, 0.4$ and 0.7 . The figure reveals that samples with $x = 0.4$ and 0.7 show sharp drop in magnetization with increasing temperature near the transition point, indicating a ferromagnetic nature. The results suggest the transition temperature of samples is in the region of 650-700 K measured in the external field of $H = 5$ kOe. The inset of Fig. 5 shows $\sigma(T)$ for $x = 0.1$. The data for $x = 0.1$ do not show any sharp drop in magnetization with increasing temperature. The corresponding doping amount dependence of transition temperature (T_c) is presented in Fig. 6, exhibiting a rise in T_c with an increasing x . The T_c was determined from the linear extension of the experimental data. It indicates the magnetization source is from Fe^{3+} ion in octahedral site. Similar results have been reported on BTO doped with Fe ion [5]. Song *et al.* [9] also predicted that the Fe ion in $(1-x)\text{LaFeO}_3-x\text{SrTiO}_3$ is Fe^{3+} in its high spin state.

4. Conclusion

Solid solutions can be formed between BaTiO_3 and LaFeO_3 by a solid state reaction. All the samples exist as a single phase and are crystallized in a cubic structure at room temperature. The lattice parameter and the volume decrease as increasing x . Magnetization measurements suggest samples have a magnetic ordering at room temperature depending on the amount of x . The origin of magnetism is believed to be from Fe^{3+} ion in the high spin state in octahedral site.

Acknowledgments

This work was supported by Hankuk University of Foreign Studies Research Fund of 2010.

References

- [1] W. J. Merz, Phys. Rev. **75**, 687 (1945).
- [2] B. Ita, P. Murugavel, V. Ponnambalan, and A. R. Raju, J. Chem. Sci. **115**, 519 (2003).
- [3] B. Huybrechts, K. Ishizaki, and M. Tanaka, J. Mater. Sci. **30**, 2463 (1995).
- [4] D. S. Jung, H. Y. Koo, H. C. Jang, and Y. C. Kang, Met. Mater. Int. **15**, 809 (2009).
- [5] F. Lin, D. Jiang, K. Ma, and W. Shi, J. Magn. Magn. Mater. **320**, 691 (2008).
- [6] D. Li and M. A. Subramanian, Solid State Sci. **2**, 507 (2000).
- [7] S. Mori, J. Phys. Soc. Jpn. **28**, 44 (1970).
- [8] G. A. Gehring, Ferroelectrics **161**, 275 (1994).
- [9] Y. W. Song, Y. Ma, H. Xiong, Y. Q. Jia, M. L. Liu, and M. Z. Jin, Mater. Chem. Phys. **78**, 660 (2003).