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Journal of the European Ceramic Society 24 (2004) 1551–1555

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Ferroelectric and ferromagnetic properties of $0.2BiFeO_3$–$0.2RFeO_3$–$0.6ATiO_3$ (R = Pr, Nd and A = Ba, Pb) and $0.8BiFeO_3$–$0.2BaTiO_3$

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Abstract

Crystal structure, ferromagnetic and electric polarizations have been characterized for attaining the ferroelectromagnetic materials in the ternary and binary solid solutions consisting of ferroelectric and antiferromagnetic end members: $BiFeO_3$(BF), $PrFeO_3$(PF), $NdFeO_3$(NF), $BaTiO_3$(BT),and $PbTiO_3$(PT). The XRD and neutron diffraction data collected in the temperature range 10–300 K have been analyzed by the Rietveld refinement method. Every prepared sample shows weak ferromagnetization with a maximum remanent magnetization $M_r = 0.5$ emu/g in the $0.8BiFeO_3$–$0.2BaTiO_3$. The 0.2BF–0.2NF–0.6PT(0.0075 mol Ta_2O_5), 0.8BF–0.2BT, and 0.2BF–0.2PF–0.6PT(0.0075 mol Ta_2O_5) having the noncentrosymmetric structure *I4cm* ($a = b \fallingdotseq 0.54$ nm, $c \fallingdotseq 0.78$ nm) show a ferroelectricity with remanent polarization $Pr = 1.2$–$3\ \mu C/cm^2$.

Keywords: Ferroelectric properties; Magnetic properties; Perovskites; Powders-solid state reactions; X-ray methods

1. Introduction

Search for the ferroelectromagnetic materials showing ferromagnetism and ferroelectricity simultaneously in the same phase had begun in the 1950s with the substitution of magnetic ions in the perovskite B-site, such as $Pb(Fe,W)O_3$–$Pb(Mg,W)O_3$,$Pb(Co,W)O_3$, and $Pb(Fe,Ta)O_3$.[1–3] Until now only a few compounds have been reported to exhibit both ferroelectricity and ferromagnetism simultaneously. They include nickel iodine boracite $Ni_3B_7O_{13}Br$,[4] $Pb_2(Co,W)O_6$,[2] and $BiMnO_3$.[5] The most conclusive way of proving this coexistence is to measure the P–E (polarization–electric field) and M–H (magnetization–magnetic field) hysteresis curves. However, in any cases of the previously reported compounds, only either the P–E or the M–H curve has been reported at the same temperature. Other indirect properties, such as optical birefringence or pyroelectric measurement results, had been suggested as supplemental evidence. Recently Santos et al.[5] reported simultaneously the P–E and M–H curves of the thin film and bulk $BiMnO_3$ synthesized under high pressure. However, the electric polarization values were of the order of 10^{-9} C/cm^2, which was too small to be ascribed as the ferroelectric material.

Generally, ferroelectricity is not compatible with ferromagnetism since ferroelectric material is an insulator while ferromagnets are electrically conductive due to the high density of energy states near the Fermi level due to the 3d orbital in the transition metal ions.[1] Hence, the chances for the occurrence of a ferroelectric and ferromagnetic material is very low.

Hill[1] theoretically considered the scarcity and difficulty of attaining ferromagnetic ferroelectricity in the same phase. He suggested that the $6s^2$ lone pair in the A-site of Bi^{3+} can cause ferroelectric structural distortion similar to the case of the $6s^2$ electron pair in $PbZrO_3$ and $Pb(Zr,Ti)O_3$. In this case the Bi^{3+} or Pb^{2+} ions are essential for attaining the ferroelectric distortion of the crystal structure.

In this study we explored solid solutions of ternary and binary systems consisting of ferroelectric and/or weak ferromagnetic end members which are insulators: $PrFeO_3$, $BiFeO_3$, $NdFeO_3$, $BaTiO_3$, and $PbTiO_3$. The former three perovskites, $PrFeO_3$, $BiFeO_3$, and $NdFeO_3$

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doi:10.1016/S0955-2219(03)00557-0

are weak ferromagnetic insulators with canted antiferromagnetic ordering.[6,7] The latter two compounds are well known ferroelectrics. The effect of the Ta_2O_5 dopant on the physical properties was also investigated.

2. Experimental

Ceramic solid solution samples of $BiFeO_3$–$0.2RFeO_3$–$0.6ATiO_3$ (R = Pr, Nd, A = Pb, Ba) and $0.2BiFeO_3$–$0.2PrFeO_3$–$0.6Pb(Zr_{0.53}Ti_{0.47})O_3 + wTa_2O_5$ ($w = 0$, 0.0075 mol) have been prepared from the perovskite end members, BF($BiFeO_3$), NF($NdFeO_3$), PF($PrFeO_3$), BT($BaTiO_3$), PT($PbTiO_3$), and PZT[$Pb(Zr_{0.53}Ti_{0.47})O_3$]. Hysteresis curves of P–E and M–H at RT (room temperature) have been measured using a RT66A ferroelectric tester of Radiant Technologies and VSM (vibrating sample magnetometer), respectively. The X-ray diffraction data were obtained at room temperature using a MacScience M18XHF diffractometer. Neutron diffraction data were obtained in the temperature range 10–300 K using a HRPD diffractometer at HANARO in KAERI (Korea Atomic Energy Research Institute). The neutrons from the HANARO reactor were monochromatized by a vertically focusing composite Ge-monochromator to a wavelength of 1.8348 Å.

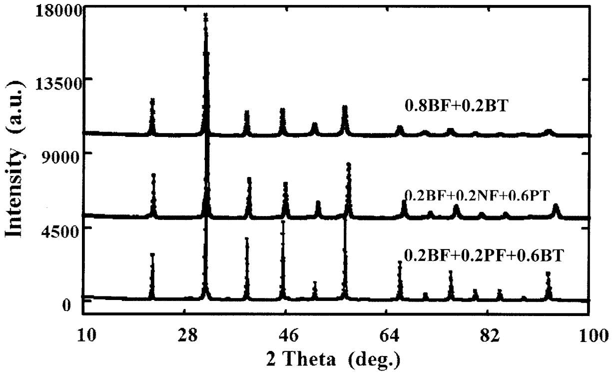

Fig. 1. XRD patterns of 0.8BF + 0.2BT, 0.2BF + 0.2NF + 0.6PT + $0.0075Ta_2O_5$, and 0.2BF + 0.2PF + 0.6BT at RT.

3. Results and discussion

The XRD patterns of the 0.8BF–0.2BT, 0.2BF–0.2NF–0.6PT, and 0.2BF–0.2NF–0.6BT are shown in Fig. 1. Neutron diffraction patterns of the 0.2BF–0.2PF–0.6BT and 0.2BF–0.2NF–0.6PT + $0.0075Ta_2O_5$ at the temperature range 10–300 K are shown in Figs. 2 and 3 respectively. Both the centrosymmetric (*P4/mmm, Pm3m*) and noncentrosymmetric (*P4mm, I4cm*) space groups have been tested by the Rietveld least squares method. The refined lattice parameters and '*R*'-values are summarized in Table 1. For the 0.2BF–0.2PF–0.6BT sample the simple cubic *Pm3m* structure ($a = b = c = 0.39758$ nm) produced the lowest '*R*'-values both for the XRD and neutron data. The non-centrosymmetric tetragonal model *P4mm* resulted in divergence of '*R*'-values during the refinement for the neutron data. In the case of the 0.2BF–0.2PF–0.6BT sample the *I4cm* model also showed a fluctuation in the *R*-value during the refinement.

The refinement of XRD data of the 0.2BF–0.2NF–0.6PT resulted in nearly the same '*R*'-values for both the cubic *Pm3m* and the tetragonal *I4cm* ($a = b = 0.5627$ nm, $c = 0.79637$ nm). However, the neutron data produced better '*R*'-values for the *I4cm* than the *Pm3m*. This difference is ascribed to the same additional reflection observed in the neutron data as in Fig. 3, which can be indexed only by the *I4cm* model. The refinement results of XRD data of 0.8BF–0.2BT show that the *I4cm* model produces better '*R*'-values than the *Pm3m* as shown in Table 1.

In Figs. 2 and 3 the reflections indicated by the arrows typically appear in the G-type antiferromagnetic ordered compounds such as $PrFeO_3$ and $GdFeO_3$.[6] Refined profiles of 0.2BF–0.2NF–0.6BT (10 K) in Fig. 4 clearly shows that this antiferromagnetic reflection is

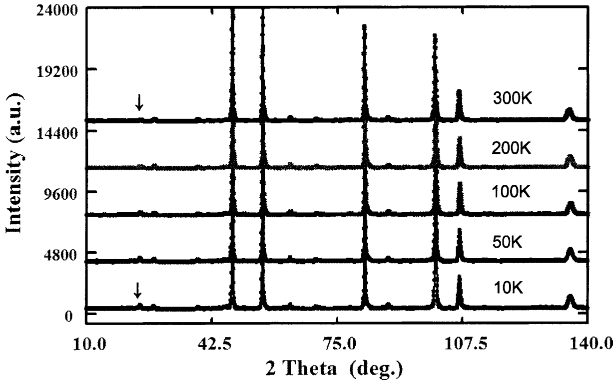

Fig. 2. Neutron diffraction patterns of 0.2BF + 0.2PF + 0.6BT at 10–300 K.

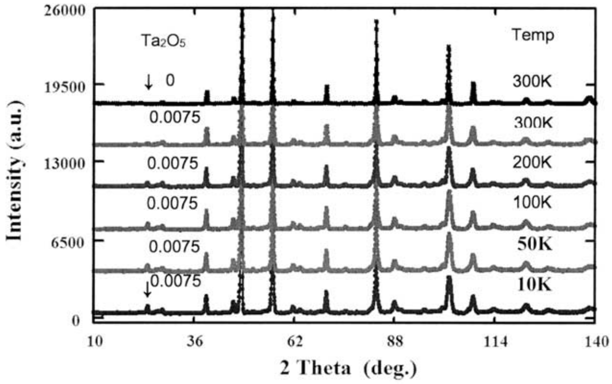

Fig. 3. Neutron diffraction patterns of 0.2BF + 0.2NF + 0.6PT ($Ta_2O_5 = 0$, 0.0075 mol) at 10–300 K.

not from the crystal structure. The intensity of this magnetic ordering peak increases with lowering the diffraction temperature. Interestingly this anti-ferromagnetic reflection is absent in the undoped 0.2BF–0.2NF–0.6PT (300 K) while with the 0.075-mol doping this reflection occurs at a low intensity.

The M–H hysteresis curves of 0.2BF–0.2PF–0.6PZT (0, 0.0075 mol Ta_2O_5) are compared to that of the previously reported 0.2BF–0.2PF–6PT[8] in Fig. 5. The 0.2BF–0.2PF–6PZT shows a larger M_r value, of 0.15 emu/g, than the 0.2BF–0.2PF–0.6PT, and after Ta_2O_5 doping (0.0075 mol) the M_r decreases to 0.05 emu/g. The M–H curves of 0.2BF–0.2NF–6PT (0, 0.0075 mol Ta_2O_5), 0.2BF–0.2PF–0.6BT, and 0.8BF–0.2BT are shown in Fig. 6. The binary solid solution 0.8BF–0.2BT showed the largest M_r value (0.5 emu/g). The Ta_2O_5 doping in the 0.2BF–0.2NF–0.6PT did not result in any significant change in magnetization value.

Ferroelectric hysteresis curves can be obtained from the three samples shown in Figs. 7 and 8. The others were electrically conductive so that P–E curves could not be measured. The 0.0075 mol Ta_2O_5 doping in the 0.2BF–0.2NF–0.6PT and 0.2BF–0.2PF–0.6PZT resulted in an electrically insulating property. The increase of resistivity by Ta_2O_5 doping had been commonly known in other PZT and BT-based ferroelectric materials, in which donor levels are produced in the energy band and compensate acceptor charge carriers by the pentavalent ions. The polarization Pr values of these Ta_2O_5 doped samples are in the range 1.0–1.2 μC/cm^2. The 0.8BF–0.2BT also showed a ferroelectric polarization with Pr value of 1.2 μC/cm^2.

Table 1
Refined lattice parameters and '*R*'-values using XRD and neutron diffraction data

Data type	Composition	0.2BF–0.2PF–0.6BT		0.2BF–0.2NF–0.6PT		0.8BF–0.2BT	
	S.G.	*Pm3m*	*I4cm*	*Pm3m*	*I4cm*	*Pm3m*	*I4cm*
XRD	*a*	0.39758(2)	[a]	0.39330(2)	0.55636(6)	0.39757(6)	0.56192(10)
	b	0.39758(2)	[a]	0.39330(2)	0.55636(6)	0.39757(6)	0.56192(10)
	c (nm)	0.39758(2)	[a]	0.39330(2)	0.78622(12)	0.39757(6)	0.79588(19)
	χ^2	5.0	[a]	4.57	4.59	3.27	2.93
	Rp, Rwp (%)	10.4, 15.8	[a]	9.84, 13.3	9.73, 13.3	9.84, 13.1	9.12, 12.4
	Rb, Rf (%)	3.98, 2.73	[a]	4.85, 3.51	4.38, 3.94	9.26, 6.15	6.96, 5.09
Neuton	*a*	0.39799(2)	0.56271(5)	0.39346(3)	0.55628(4)	–	
	b	0.39799(2)	0.56271(5)	0.39346(3)	0.55628(4)		
	c (nm)	0.39799(2)	0.79637(12)	0.39346(3)	0.78735(9)		
	χ^2	3.33	3.50	5.81	2.60		
	Rp, Rwp (%)	5.81, 7.86	5.91, 8.05	6.72, 10.1	5.36, 6.78		
	Rb, Rf (%)	3.36, 6.18	4.56, 8.96	7.52, 9.56	5.37, 5.39		

[a] Fluctuation in *R*-values.

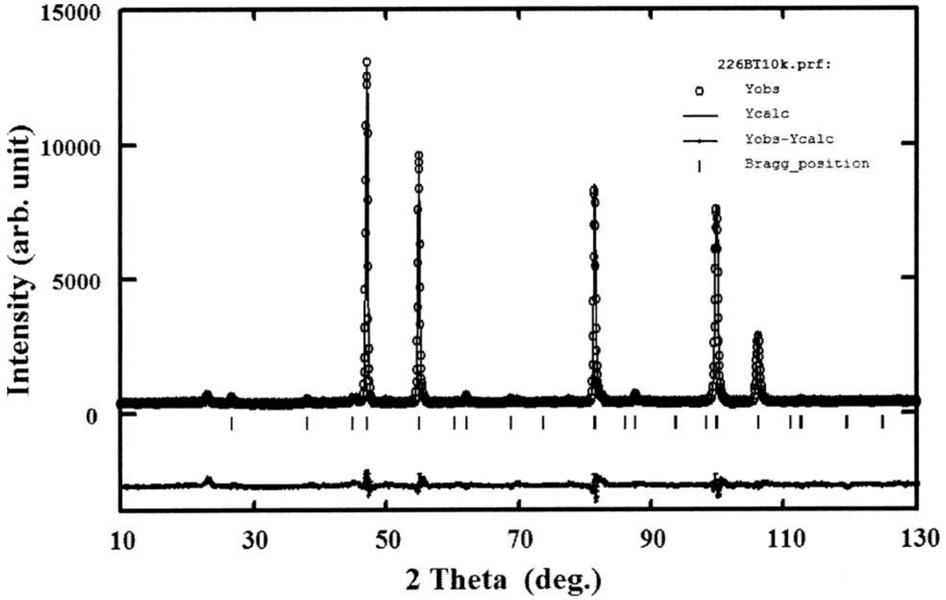

Fig. 4. Refined neutron diffraction profiles of 0.2BF + 0.2PF + 0.6BT (10 K) using the *I4cm* model.

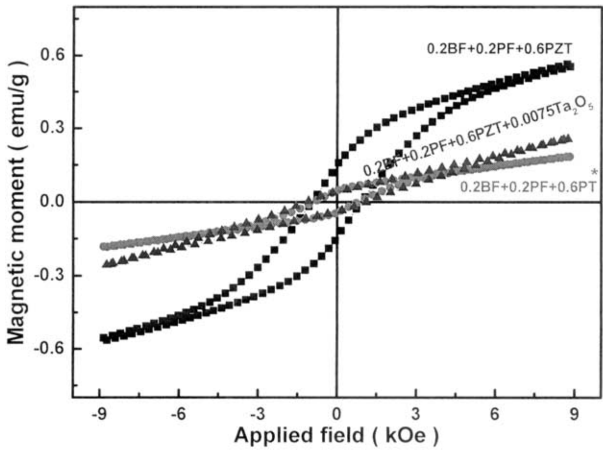

Fig. 5. M–H curves of 0.2BF–0.2PF–0.6PZT ($Ta_2O_5 = 0$, 0.0075 mol) and 0.2BF–0.2PF–0.6PT (*Ref. 8).

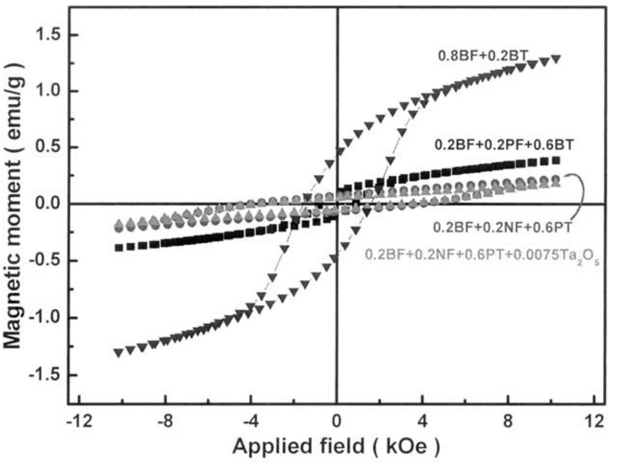

Fig. 6. M–H curves of 0.8BF–0.2BT, 0.2BF–0.2PF–0.6BT, and 0.2BF–0.2NF–0.6PT ($Ta_2O_5 = 0$, 0.0075 mol).

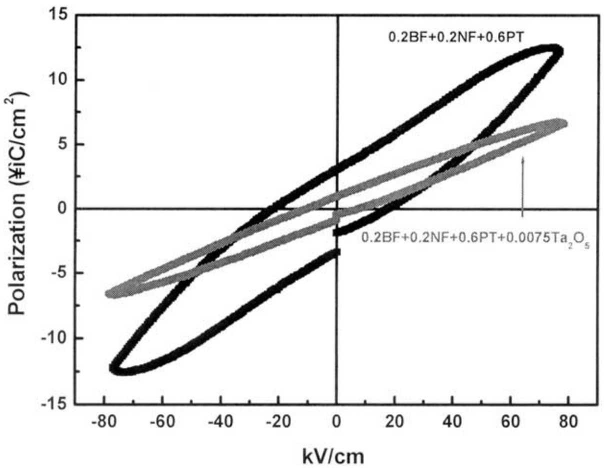

Fig. 7. P–E curves of 0.2BF–0.2NF–0.6PT and 0.2BF–0.2NF–0.6PT (0.0075 mol Ta_2O_5) at RT.

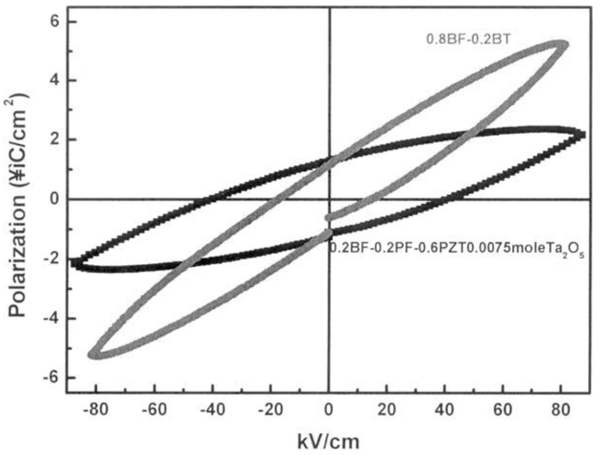

Fig. 8. P–E curves of 0.2BF–0.2PF–0.6PZT (0.0075 mol Ta_2O_5) and 0.8BF–0.2BT at 300 K.

These samples showing ferroelectric polarization have the noncentrosymmetric tetragonal structure *I4cm* consistently with the crystal structural aspects. Spontaneous magnetization observed in this study is very small, which might indicate an antiferromagnetic nature. Dzialoshinskii[9] had proposed a thermodynamic theory for the weak ferromagnetism seen in some antiferromagnets. In this theory, weak ferromagnetism is strongly dependent on the crystal structure of the antiferromagnets: cubic and triclinic symmetries cannot have weak ferromagnetism. The crystal structure analysis in this study show that 0.2BF–0.2PF–0.6BT has the cubic *Pm3m* structure and the other two systems, 0.2BF–0.2NF–0.6PT and 0.8BF–0.2PT have the tetragonal *I4cm* structure.

The spontaneous magnetization in this study is observed in both types of crystal structure. Hence Dzialoshinskii's consideration is inconsistent with our results. Furthermore, even the antiferromagnetic ordering is absent in 0.2BF–0.2NF–0.6PT: this sample still shows spontaneous magnetization. Hence antiferromagnetic ordering is not a necessary condition for the weak ferromagnetism seen in our systems. For further understanding of magnetic ferroelectricity, material cases and theoretical considerations need to be collected.

4. Conclusion

Some ternary and binary solid solution systems consisting of ferroelectric and antiferromagnetic end members have been synthesized and characterized for their magnetic and dielectric properties in relation to their crystal structures. The crystal structure of 0.2BF–0.2PF–0.6BT is the cubic *Pm3m* ($a = b = c = 0.3975$ nm at 300 K) in the temperature range 10–300 K. The others have the tetragonal *I4cm* ($a = b \fallingdotseq 0.56$, $c \fallingdotseq 0.79$ nm). Every sample shows weak ferromagnetism and the 0.8BF–0.2BT has the largest with $M_r = 0.5$ emu/g. Only the three samples, 0.0075 mol Ta_2O_5-doped 0.2BF–0.2NF–0.6PT, 0.8BF–0.2BT, and 0.0075 mol Ta_2O_5-doped 0.2BF–0.2PF–0.6PT show the ferroelectric polarization with Pr values of 1.2–3 μC/cm^2. The crystal structure analysis results are consistent with the ferroelectric polarization. The spontaneous magnetization was observed even in the 0.2BF–0.2NF–0.6PT not having the antiferromagnetic ordering. Antiferromagnetic ordering is not an essential feature for the occurrence of ferromagnetism in the solid solutions used in this study.

Acknowledgements

This work was supported by grant no. M2-0202-00-0053 from KISTEP (Korea Institute of Science and Technology Evaluation and Planning).

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