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Influence of diamagnetic Pb doping on the crystal structure and multiferroic properties of the BiFeO₃ perovskite

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Structural, magnetic, and electrical properties of Bi_{1-x}Pb_xFeO₃ ($x=0, 0.1, 0.2$, and 0.3) polycrystalline prepared by solid solution route were studied. The crystal structure data obtained from x-ray diffraction indicate that the solid solution Bi_{1-x}Pb_xFeO₃ successively transforms from rhombohedral to pseudocubic symmetry with an increase in the Pb concentration. The observed weak ferromagnetism and ferroelectricity at room temperature indicated the multiferroic nature of Pb-doped BiFeO₃ compounds. The magnetoelectric coupling was estimated by the changes in the dielectric constant with an external magnetic field. It was found that the value of magnetodielectric effect have a maximum of 0.4% for Bi_{0.7}Pb_{0.3}FeO₃ ceramic under a magnetic field of 12 kOe at room temperature. © 2009 American Institute of Physics. [DOI: 10.1063/1.3079770]

I. INTRODUCTION

As one of the most promising multiferroic materials, BiFeO₃ (BFO) is known to be the only material that is both ferroelectric ($T_C \sim 1103$ K) and antiferromagnetic ($T_N \sim 643$ K) at room temperature (RT), which appears to have the best potential applications.^{1,2} However, low resistivity and weak ferromagnetism in bulk BFO have been obstacles for further applications.³ Low resistivity mainly results from the valence fluctuation of Fe ions and the existence of second phases,⁴ which can be suppressed by optimizing the fabricating process or forming BFO-based solid solution.⁵⁻⁸ Recently, Lebeugle *et al.* reported a large polarization in excess of 100 $\mu\text{C}/\text{cm}^2$ in highly pure BFO single crystals.⁶ Moreover, the electric-field-induced spin flip was also observed at RT.⁷ Recently, Zhu *et al.*⁸ studied the structural and magnetic properties of BFO_{1-x}(PbTiO₃)_x solid solutions. A morphotropic phase boundary region observed in this system reveals the coexistence of multiple phases, which seems to affect the magnetic properties.

On the other hand, BFO is an antiferromagnet with a spatially modulated spin structure,³ which does not allow net magnetization and also inhibits observation of the linear magnetoelectric (ME) effect. Several groups are involved in improving the multiferroic properties of BFO with various A and B site substitutions.^{5,9-12} Among all these reports, doping at the A site with diamagnetic ions such as La,⁵ Ca,⁹ Ba,¹⁰ and Pb¹¹ can effectively suppress the spin cycloid. Enhanced multiferroic properties in Ba-doped BFO samples have been reported by Wang *et al.*¹⁰ Recently, Khomchenko *et al.*^{11,12} studied the effect of diamagnetic Ca, Sr, Pb, and Ba substitutions on the multiferroic properties of the BFO ceramic.

The weak ferromagnetic found in Bi_{1-x}A_xFeO₃ ($A=\text{Pb}, \text{Ba}; x=0.2, 0.3$) compounds showed that doping of BFO with the bigger ionic radius ions may be a promising way for preparing multiferroic materials. In the present work, we report on the sintering, crystal structure, and multiferroic properties of Bi_{1-x}Pb_xFeO₃ (BPFO) ceramics systematically.

II. EXPERIMENT

BPFO ($x=0, 0.1, 0.2$, and 0.3) ceramics were prepared by the rapid liquid phase sintering method.⁵ Starting materials were high purity powders of Bi₂O₃, Fe₂O₃, and PbO.

The crystal structure was determined by x-ray diffraction (XRD) measurement. Magnetic property measurements were carried out by using the physical properties measurement system of Quantum Design. Ferroelectric properties were measured with RT6000 test system. The dielectric properties were measured using an impedance analyzer.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the XRD patterns of BPFO ceramics. It can be seen that all the samples exhibit single-phase characteristics. The pure BFO crystallize in arhombohedrally distorted structure, which is obtained by an antiphase tilt of the adjacent FeO₆ octahedra and a displacement of the Fe³⁺ and Bi³⁺ cations from their centrosymmetric position along [111] axes.¹³ The weak reflection near $2\theta=37.65^\circ$ is a superlattice peak resulting from the doubling of the unit cell due to the antiphase rotations of FeO₆ octahedra. From the evolution of the XRD patterns, it can be seen that the doubly split peaks of BFO merge partially to form a broadened peak with Pb doping increase, as shown in the enlarged XRD patterns in the 2θ ranges of $38^\circ\text{--}40^\circ$ and $66^\circ\text{--}68^\circ$ [Figs. 1(b) and 1(c)], indicating a structural transition in BPFO solid solutions as Pb content increases. Furthermore, the relative intensity of

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FIG. 1. XRD patterns of BPFO ceramics: (a) 2θ from 20° to 60° ; (b) 2θ near 39° ; (c) 2θ near 67° .

superlattice reflections decreased with increasing Pb content. Since the intensity of the superstructure reflections is qualitatively related to the amplitude of rotation of the octahedra in antiphase, the decrease in the observed intensity as Pb doping increases indicates that the amplitude of tilt of rhombohedrally distortion reduces. In general, the amplitude of rotation of O octahedra is known to decrease as the average perovskite tolerance factor (t) increases.¹⁴ The decrease in the antiphase rotation angle of the FeO_6 octahedra about the pseudocubic $[111]$ axes in BFO with the increase in coupled substitution of Pb^{2+} and Ti^{4+} in BFO was indeed observed by transmission electron microscopy.¹⁴ Since the Pb^{2+} has a larger ionic radius than that for Bi^{3+} , the tolerance factor (t) of BPFO ceramics increases as Pb doping increases; the amplitude of rotation decreases, and the intensity of the superlattice reflections reduces. For $x=0.3$, the XRD data show that the (006) peak and (202) peak combine into a single (111) peak; the (208) peak and (220) peak combine into a single (220); the superlattice peak near $2\theta=37.65^\circ$ cannot be observed. These results indicate that this composition has pseudocubic symmetry with very small rhombohedral distortion. That is to say, the solid solution of the BPFO system changes the crystal symmetry from rhombohedral to pseudocubic at $x=0.3$.

The magnetization hysteresis (M - H) loops of BPFO ceramics are shown in Fig. 2. It is evident that the antiferromagnetism nature in BFO evolves into weak ferromagnetism with a small remanent magnetization in Pb-doped BFO ceramics. The Pb^{2+} substitution seems to induce oxygen vacancies or/and Fe^{4+} for charge compensation. Khomchenko *et al.* studied the models of the defects' formation in $\text{Bi}_{1-x}\text{A}_x\text{FeO}_3$ (Pb, Ca, and Ba) compounds with Mössbauer spectroscopy measurements. They found that no indication of the presence of Fe^{4+} was detected and A^{2+} substitution results in oxygen vacancies.¹² Taking into account that the same conclusions were made for $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_3$ ($x \leq 0.1$) (Ref. 9) and $\text{Bi}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x \leq 0.67$) (Ref. 15) solid solutions, one can argue that the formation of oxygen vacancies is a general mechanism of charge compensation in the case of A^{2+} substitution in $\text{Bi}_{1-x}\text{A}_x\text{FeO}_3$. The influence of oxygen vacancies on the ME properties of BFO has been studied using first principles density functional theory calculations

FIG. 2. Field dependence of magnetization for the BPFO ceramics measured at room temperature. The inset represents the Pb composition dependent remanent magnetization.

by Ederer *et al.*¹⁶ They proposed that the canting of the magnetic moments was not significantly affected by the presence of oxygen vacancies and no increase in the macroscopic magnetization due to oxygen vacancies could be found.

On the other hand, the structural transition in BPFO compounds might destruct the inhomogeneous spin structure as to the spin cycloid of BFO correlative to its $R3c$ structure. The measured remanent magnetization (M_r) values as a function of x are plotted in the inset of Fig. 2. It can be seen that the M_r value increases with increasing x , whereas it is found that the M_r values of BPFO with $x \leq 0.2$ are significantly less than that of $x=0.3$ compound. This is in accordance with the change in the crystal structure caused by Pb doping. When the doping content is below 0.2, the Pb substitution can only suppress but cannot destroy the spin cycloid structure completely and results in a limited increase in M_r . However, as $x=0.3$, the transformation from the rhombohedral symmetry in BFO to pseudocubic symmetry leads to the collapse of the spatial spin structure. Therefore, the latent magnetization locked within the cycloid will be released and a significant increased M_r is observed.

Figure 3 shows the room temperature ferroelectric hysteresis loops (P - E) of BPFO. For pure BFO sample, a weak polarization of $0.2 \mu\text{C}/\text{cm}^2$ was observed under an applied field of 10 kV/cm. This implies that the sample is highly conductive at RT and only partial reversal of the polarization takes place, which is known to be attributed to the variable oxidation states of Fe ions. Due to the relatively large leakage current, only low field electric hysteresis loops were obtained for Pb-doped BFO compounds.

Figure 4 illustrates the frequency (f) dependence of relative dielectric constant (ϵ) and loss tangent ($\tan \delta$) for the BPFO samples at RT. All the samples show decreasing trends in both of them with increasing frequency. Pb-doped BFO possesses a larger ϵ from 81 for pure BFO to 165 for $x=0.3$ Pb-doping content at 1 kHz.

The coupling between electric and magnetic dipoles in BPFO was investigated by measuring the variation in the dielectric constant with the applied magnetic field. Here the magnetodielectric (MD) effect is defined as $[\epsilon(H) - \epsilon(0)]/\epsilon(0)$. The RT value of MD for $x=0.2$ and $x=0.3$

FIG. 3. Polarization–electric field (P - E) hysteresis loops of the BPFO ceramics measured at room temperature.

measured at 3 kHz under varying magnetic fields is shown in the inset of Fig. 4. The dielectric constant increases with the applied magnetic field; the values of MD effect are 0.3% and 0.4% for $x=0.2$ and $x=0.3$ under a magnetic field of 12 kOe,

FIG. 4. Frequency dependence of the dielectric constant and dielectric loss for the BPFO ceramics at room temperature. The inset shows the magnetic-field-induced change in dielectric constant of $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_3$ and $\text{Bi}_{0.7}\text{Pb}_{0.3}\text{FeO}_3$ measured at room temperature.

respectively. Palkar *et al.* thought that such behavior originated from the coupling between the magnetic and ferroelectric domains, which is similar to the magnetoelectric composites.¹⁷

IV. CONCLUSIONS

In summary, the ME system BFO is studied with Pb doping. XRD showed that the rhombohedral structure evolves toward a pseudocubic symmetry as Pb doping increases. The structural phase transition destructs the space-modulated spin structure and results in improved magnetic properties. The change in the dielectric constant with applied magnetic field suggests that magnetoelectric coupling exists in this compound.

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