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Abstract

$\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ ceramics with $x=0, 0.1, 0.2,$ and 0.3 have been synthesized by solid state reaction, starting from metal oxides. A series of structure transformations is found to depend upon the doping level. Below 10% La doping, $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ maintains the rhombohedral structure of BiFeO_3 . However, for $\text{Bi}_{0.8}\text{La}_{0.2}\text{FeO}_3$ and $\text{Bi}_{0.7}\text{La}_{0.3}\text{FeO}_3$, the structures change to the orthorhombic and tetragonal, respectively. La doping significantly reduces electric leakage and leads to successful observation of electrical polarization hysteresis loops. Doping with La also enhances the ferromagnetic moment, due to the broken cycloid spin structure caused by the changes in the crystalline structure.

Keywords

Structure, ferroelectric, properties, magnetic, properties, doped, bismuth, ferrite

Disciplines

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Structure, ferroelectric properties, and magnetic properties of the La-doped bismuth ferrite

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I. INTRODUCTION

Multiferroic [magnetolectric (ME)] materials have simultaneous ferroelectric and magnetic orders, which enables a coupling interaction between them. This coupling interaction, also called the ME effect, produces various possibilities for the realization of mutual control and detection of electrical polarization and magnetism.^{1,2} As a potential candidate for practical application among the limited choices offered by the single phase multiferroic materials, BiFeO_3 has been attracting enormous attention, due to its multiferroic properties at room temperature (Curie temperature, $T_C=1103$ K, Néel temperature, $T_N=643$ K).³⁻⁶ However, BiFeO_3 is antiferromagnetic and ordered with a G -type spin configuration along the $[111]_c$ or $[001]_h$ directions in its pseudocubic or rhombohedral structure, while having a superimposed incommensurate cycloid spin structure with a periodicity of 620 \AA along the $[110]_h$ axis at room temperature, which cancels the macroscopic magnetization and inhibits observation of the linear ME effect. Doping has been proved to be effective in suppressing this cycloid structure and enhancing the magnetic moment of BiFeO_3 . For example, La substitution for Bi can improve the magnetic moment in BiFeO_3 .⁷ Yet, our knowledge of the doping effect of La in BiFeO_3 is very limited and deficient. A systematic study of the La doping effect on the structure and on the ferroelectric, dielectric, and magnetic properties of BiFeO_3 could be of some value and has not been previously conducted.

II. EXPERIMENTS

$\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ ceramics with $x=0, 0.1, 0.2,$ and 0.3 were fabricated by a traditional solid state reaction. The starting materials were Bi_2O_3 , La_2O_3 , and Fe_3O_4 , all with a purity of 99.9% and all from Aldrich. These oxide materials were weighed out according to the molecular mole ratio, mixed,

pressed into pellets, and subsequently sintered at 1073 K for 3 h. The ceramics was crushed, ground, pressed into pellets, and sintered again at 1273 K for 1 h. The obtained ceramic pellets had a diameter of 0.98 cm and a thickness of 1.1 mm.

The structures of the obtained samples were examined on a Philips 1700 x-ray diffraction (XRD) machine using $\text{Cu } K\alpha$ radiation. The ceramic samples were electroded with postfire silver paste. Temperature dependent dielectric measurements were carried out on a HP4298 LCR meter. Ferroelectric hysteresis loops (P - E loop) were measured using an aixACCT 200 ferroelectric tester. Magnetic property measurements were conducted on a Quantum Design magnetic properties measurement system.

III. RESULTS AND DISCUSSION

The undoped and 10% La doped BiFeO_3 crystallize in a rhombohedrally distorted perovskite structure at room temperature (shown in Fig. 1). However, extra peaks were ob-

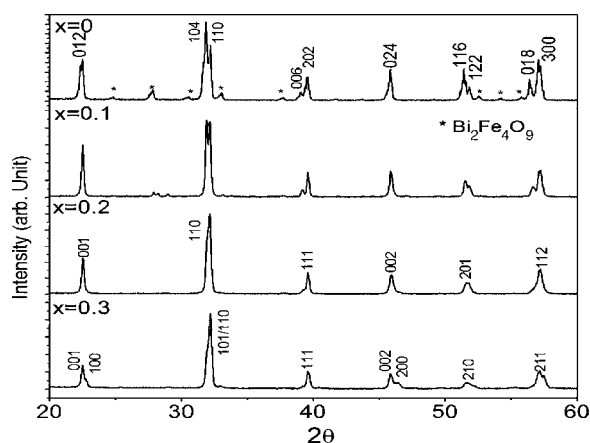


FIG. 1. X-ray diffraction patterns of $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ ($x=0, 0.1, 0.2,$ and 0.3). For the $x=0$ sample, diffraction peaks are labelled for $R3c$ symmetry. For the $x=0.2$ sample, diffraction peaks are indexed as $C222$ symmetry. For the $x=0.3$ sample, diffraction peaks are indexed as $P4mm$ symmetry.

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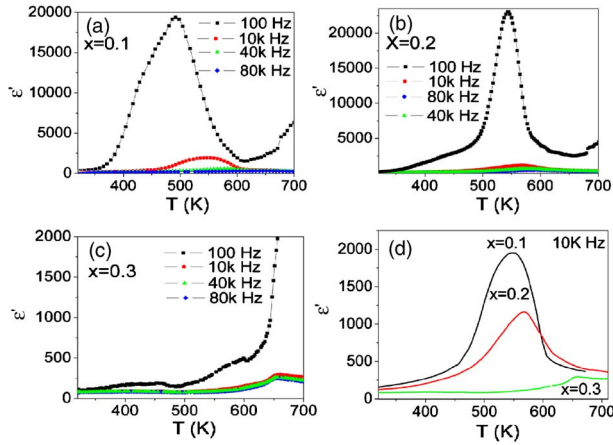


FIG. 2. (Color online) Temperature dependence of the real part of the relative dielectric constant of $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ samples with (a) $x=0.1$, (b) $x=0.2$, and (c) $x=0.3$. (d) Comparison of the temperature dependence of the dielectric constant of $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ samples with $x=0.1$, 0.2 and 0.3 at 10 kHz.

served in the XRD patterns of these two samples, which are identified from the impurity phase, $\text{Bi}_2\text{Fe}_4\text{O}_9$. It should be noted that the diffraction intensity from the impurity in the sample with $x=0.1$ is weaker than in the undoped one, while no observable impurity peaks are observed in the XRD patterns of the samples with $x=0.2$ and $x=0.3$. This means that doping with La hinders the formation of a second phase. In comparison with the $x=0.1$ sample, which retains the structure of BiFeO_3 , the sample with $x=0.2$ shows a change to $C222$ orthorhombic symmetry, as evidenced by the merging, in the $x=0.2$ sample pattern, into one peak of the split diffraction peaks around $2\theta=32^\circ$ and $2\theta=51^\circ$ in the patterns of the $x=0$ and 0.1 samples. With increasing La doping levels in BiFeO_3 up to 30%, the system symmetry transforms to $P4mm$, as evidenced by the separation of the a - and c -axis parameter lengths through splitting of the diffraction peaks around $2\theta=22^\circ$ and 45° .

In Figs. 2(a)–2(c), the temperature dependence of the dielectric constant of samples with $x=0.1$, 0.2, and 0.3 is presented at 100 Hz, 10 kHz, 40 kHz, and 80 kHz. For the sample with $x=0.1$, a very abnormal diffuse dielectric pattern, containing an extremely high dielectric constant peak (on the order of 10^4), is observed in the $\epsilon' - T$ curve around 491 K during the heating process, and the peak temperature increases significantly with increasing measurement frequency, reflecting a strong frequency dispersion feature. A similar phenomenon is observed for the samples with $x=0.2$ and 0.3. Figure 2(d) shows the temperature dependence of the real part of the dielectric constant of the samples with $x=0.1$, 0.2, and 0.3 at 10 kHz up to 700 K. The dielectric constants of these samples with $x=0.1$, 0.2, and 0.3 are 157, 128, and 81 at room temperature, respectively. The positions of the abnormal peak for the samples with $x=0.1$, 0.2, and 0.3 are 547, 567, and 655 K, respectively. Increasing La content is accompanied by an obviously decreased abnormal intensity and shifting of the abnormal peak position.

It is well known that BiFeO_3 experiences an antiferromagnetic transition at 643 K and a ferroelectric transition at 1103 K. The peak temperatures of the observed abnormal dielectric peaks are much lower than the ferroelectric transi-

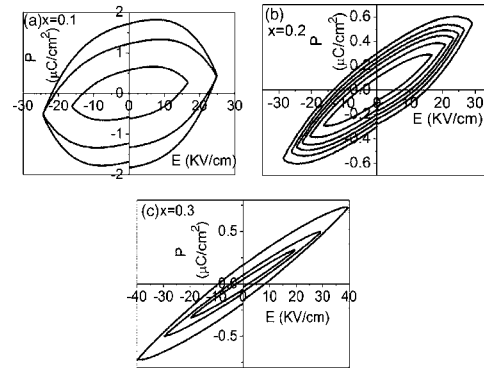


FIG. 3. P - E loops of the $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ ceramics measured at room temperature and 20 Hz.

tion temperature. They should be related to the antiferromagnetic transition. BiFeO_3 has its antiferromagnetic axis oriented along the $[110]_c$ and its electric polarization directed along one of the equivalent $[111]_c$ directions. The ferroelectric transition and accompanying distortions reduce the symmetry from cubic to rhombohedral, and therefore the ferroelectricity is accompanied by ferroelastic strain resulting from distortion of the lattice. Switching of the polarization is accompanied by switching of the ferroelastic domain state.⁸ The orientation of the antiferromagnetic sublattice magnetization is coupled to the ferroelastic strain state in BiFeO_3 , which should always be perpendicular to the ferroelectric polarization. Therefore, electric polarization switching will lead to a reorientation of the antiferromagnetic ordered spins. Conversely, a transition from the spin disordered state to the spin ordered antiferromagnetic state will affect the ferroelastic domain state and eventually disturb the ordered electric dipoles. As a result, abnormal dielectric behavior is observed around T_N . The intensity and wide temperature range of the abnormal dielectric peak means that the coupling is strong and diffusive. The same coupling has been observed in undoped BiFeO_3 .⁹ This strong coupling between electrical polarization and spin is essential for a real multiferroic system. It should be noted that a small amount of La doping in BiFeO_3 decreases its T_N , and dropping of T_N is very sensitive to the La concentration.

P - E loops of $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ samples were measured at room temperature and 20 Hz, as shown in Fig. 3. The P - E loop of BiFeO_3 was measured as a circle (not shown), which means the sample has serious electrical leakage. The P - E loop of the $\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$ sample is still rounded in shape, but much improved in comparison with that of the undoped BiFeO_3 . With increasing La doping level in BiFeO_3 , the P - E loops became more and more typical, which means the electrical leakage was greatly reduced. We were unable to obtain the exact value of the saturated polarization, due to electrical penetration before full switching could occur.

Though La doped BiFeO_3 solid solutions formed with other perovskites have been studied, and enhancement of electrical polarization and magnetic moment were observed in such solid solution systems, significant inhibition of electrical leakage has not been reported in single phase BiFeO_3 .¹⁰ We propose that La improves the formation of pure BiFeO_3 phase and inhibits the formation of a second

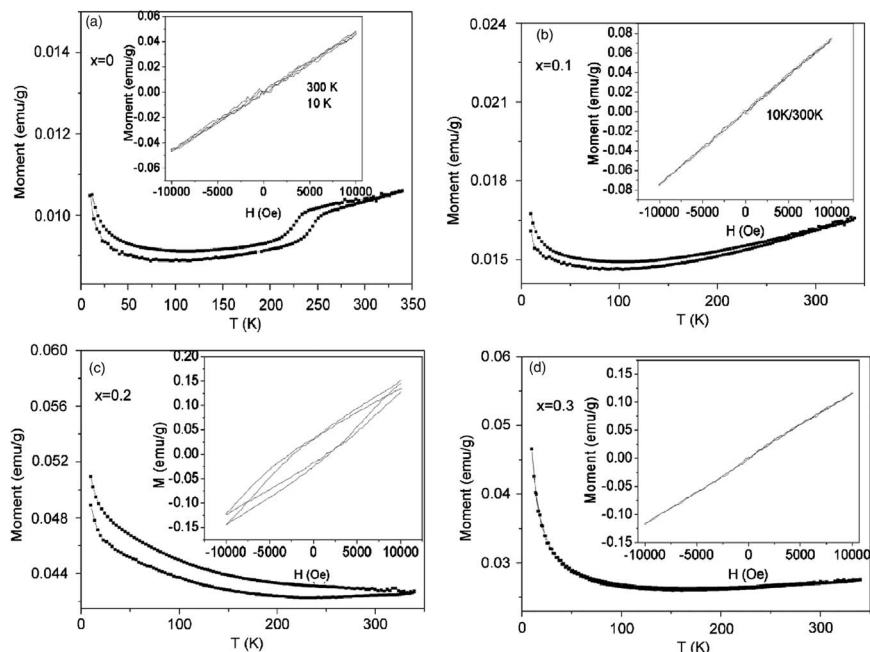


FIG. 4. FC-ZFC magnetization curves of $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ ($x=0, 0.1, 0.2,$ and 0.3). The inset in each plot is the M - H loop measured at 300 K.

phase, as shown by the XRD results. The formation of a second phase, such as $\text{Bi}_2\text{Fe}_4\text{O}_9$, will result in charge unbalance in the specimen. As a result, a large amount of defects will be generated. These defects, such as oxygen vacancies and variant valence ions, will increase the conductivity of the samples.

Figure 4 shows the field cooled and zero field cooled (FC-ZFC) magnetization curves of $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ with x from 0 to 0.3. The inset in each figure is the M - H loop at 300 K. The magnetic moment of the samples is greatly improved with increasing La doping content in BiFeO_3 . For example, the magnetic moment of BiFeO_3 measured at 2000 Oe in this experiment is 0.01 emu/g at room temperature, while the values are ~ 0.016 and ~ 0.042 emu/g for $\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$ and $\text{Bi}_{0.8}\text{La}_{0.2}\text{FeO}_3$, respectively. The magnetic moment of $\text{Bi}_{0.7}\text{La}_{0.3}\text{FeO}_3$ deviates from this trend and decreases to ~ 0.027 emu/g. Similar ferromagnetic moment enhancement has been observed previously.⁷ We believe that La doping in $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ destroys the cycloid spin structure which hinders the observation of any linear magnetoelectric effect in pure BiFeO_3 , releases the latent magnetization locked within this structure, and enhances the magnetic moment. To compare the intensity of the improvement, the 10% La doping does not improve the magnetic moment too much, while a drastic improvement is found with 20% La doping. As a result, magnetization hysteresis is observed for 20% La doped BiFeO_3 . This is in accordance with the change in the crystallization structure caused by La doping: 10% La doping does change the structure of BiFeO_3 , while 20% doping changes the structure to C222. As a result, the canting of the antiferromagnetic ordered spins and the cycloid spin structure will both be modified. The 30% La doping changes the structure of BiFeO_3 to $P4mm$, which is close to the pseudocubic structure of undoped BiFeO_3 . So the cycloid spin structure and the canting of the antiferromagnetically ordered spins are not strongly modified, resulting in only a small improvement in the magnetization.

A magnetization decrease is observed around 260 K in undoped BiFeO_3 , which can be attributed to the $\text{Bi}_2\text{Fe}_4\text{O}_9$ impurity phase. $\text{Bi}_2\text{Fe}_4\text{O}_9$ is paramagnetic at room temperature and undergoes a transition to an antiferromagnetic state near 264 K. This transition is not observed in other samples. This result is in accordance with the XRD results: only in undoped BiFeO_3 is $\text{Bi}_2\text{Fe}_4\text{O}_9$ obviously detected.

In summary, the doping of La into BiFeO_3 causes structural changes and improves its crystallization into a single phase. As a result of these changes and this improvement, both the ferroelectric properties and the ferromagnetic properties are significantly enhanced. It is regarded that La doped BiFeO_3 , or more complicated doped BiFeO_3 based on La doping, will have great potential for practical application.

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