Ho and Ti co-doped $BiFeO_3$ multiferroic ceramics with enhanced magnetization and ultrahigh electrical resistivity*

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$Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$ and $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ ceramics were prepared and compared to reveal the effects of Ho and Ti codoping in $BiFeO_3$. X-ray diffraction indicated that both ceramics had a high rhombohedral perovskite phase content, and microstructural analyses showed that the grains of the $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ ceramics were much smaller than those of $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$. An electrical resistivity of more than 1×10^{14} Ω·cm at room temperature, and a magnetic hysteresis loop with a remnant magnetization $2M_r$ of ∼ 0.485 emu/g were obtained for $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$; both were much higher than those of $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$. Changes in the defect subsystem of $BiFeO_3$ induced by Fe-deficiency and (Ho,Ti) codoping are proposed as being responsible for the improvement in the properties.

Keywords: $BiFeO_3$, multiferroics, magnetism, resistivity

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1. Introduction

Although a relatively large number of ferroelectric and ferromagnetic materials exist, single-phased mutiferroics, namely, simultaneous spin and electric dipole ordering in the same phase, are extremely rare in nature. So far, $BiFeO_3$ is the only natural material that shows multiferroic behavior above room temperature,[1,2] so it has been the subject of a huge number of theoretical studies and practical applications. In view of the applications, however, the properties of $BiFeO_3$ have to be improved in at least two important aspects. On the one hand, $BiFeO_3$ usually displays quite a low electrical resistivity,[3] which masks the performance of the electric dipole ordering. On the other, the net magnetization of $BiFeO_3$ is too small for magnetoelectric applications.[4] Pure $BiFeO_3$ is G-type antiferromagnetic, which means that the spins are not exactly antiparallel and a nonzero remnant magnetization can exist. However, the antiferromagnetically ordered sublattices are modulated by a long-wave superstructure, which prevents the presence of possible nonzero remnant magnetization.[5,6] Through extensive investigations in the past decade, remarkable progress has been achieved towards understanding and even solving these problems.

Many studies have shown that lanthanide substitution for Bi is an effective way to suppress the spin modulation and enhance the magnetic properties of $BiFeO_3$.[7–10] Due to the size difference between Bi^{3+} and lanthanide ions, the crystal lattice of $BiFeO_3$ is influenced by the substitution in a similar way as pressure.[2] Recently, some very attractive magnetization enhancements have been reported for Ho-doped $BiFeO_3$: Wu *et al.* observed a remnant magnetization $2M_r$ of 0.406 emu/g for $Bi_{0.9}Ho_{0.1}FeO_3$ powder,[11] while Pradhan *et al.* prepared $BiHo_{0.1}Fe_{1.1}O_3$ ceramics with a remnant magnetization $2M_r$ of 0.216 emu/g.[12] Ho-doping also seems helpful in decreasing the content of the impurity phases formed in $BiFeO_3$ sintering, and the $BiHo_{0.1}Fe_{1.1}O_3$ ceramics they prepared were almost free of impurity phases. However, the ceramics exhibited a rather high dielectric loss, about 0.95 at 100 Hz, indicating that the ceramics were still electrically leaky. It is well known that Ti substitution for Fe can greatly reduce the leakage current of $BiFeO_3$.[13–15] In particular, we have recently achieved an ultrahigh electrical resistivity, more than 1×10^{14} Ω·cm at room temperature, for nonstoichiometric $BiFe_{0.9}Ti_{0.05}O_3$.[16] Hence, there is promise in simultaneously improving the electrical and magnetic properties of $BiFeO_3$ through the codoping of lanthanide and titanium. As a matter of fact, some interesting results have already been reported for the codoping of Dy and Ti, La and Ti in $BiFeO_3$.[17–19] To our knowledge, however, there have been no reports until now on the codoping of Ho and Ti in $BiFeO_3$. Herein, we have conducted such an investigation and have successfully fabricated $BiFeO_3$ ceramics with both a much enhanced magnetization and ultrahigh electrical resistivity.

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2. Experimental procedure

High-purity powders of Bi_2O_3, Fe_2O_3, Ho_2O_3, and TiO_2 were carefully weighed and mixed according to two nominal compositions of $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$ and $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$. The mixed powders were ball-milled for 12 h using deionized water as the medium and then dehydrated in an oven at 200 °C for 6 h. The dried powders were granulated and uniaxially pressed into pellets 12 mm in diameter and 1 mm thick at a pressure of 7 MPa. Finally, the pellets were sintered for 2 h at 850 °C for $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$ and at 855 °C for $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$, respectively, and furnace-cooled to room temperature. It should be pointed out that for each composition, a series of sintering temperatures was tested, and these two sintering temperatures were found to be optimal in yielding high perovskite phase content and possibly high electrical resistivity for these two compositions, respectively. Silver electrodes were fired on the surfaces of the sintered samples for electrical measurements. The crystal structure and phase identification were examined by X-ray diffraction (XRD) on an X-ray diffractometer (Brucker D8 Discover) using Cu K_α radiation, and the J–E characteristics were measured using a Keithley electrometer/ high-resistance meter (6517A). The voltage was swept from −30 V to 30 V in increments of 1 V, and the delay time for every increment was 2 s. The dielectric constant and dielectric loss were measured using an impedance analyzer (Agilent 4294A), and the polarization versus electric field characteristics were obtained through a ferroelectric tester (Precision Premier Workstation Radiant Technology, USA). Magnetic measurement was conducted using a physical properties measurement system (Quantum Design PPMS-9).

3. Results and discussion

Figure 1 shows the XRD patterns taken on the surface of the $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$ and $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ ceramics. It is clear that both samples have a high rhombohedral perovskite phase purity, and $Bi_2Fe_4O_9$ was identified as the main impurity phase. It is interesting to note that there are some noticeable differences among the perovskite phases for these two compositions. For $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$, the peaks of (104) and (110) are clearly split, which was also observed in the rhombohedral $BiFeO_3$ with 10% Ho-doping prepared by some other groups.[12,20] On the contrary, this peak splitting almost cannot be observed for $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$. This merging of (104)/(110) peaks was also commonly observed for Ti-doped $BiFeO_3$ prepared by other researchers,[13–15] and it seems that the substitution of Ti for Fe has the tendency to merge the (104)/(110) peaks in the XRD pattern of $BiFeO_3$. In spite of the modification in crystal structure, these previous investigations indicate that Ti-doped $BiFeO_3$ is still ferroelectric.

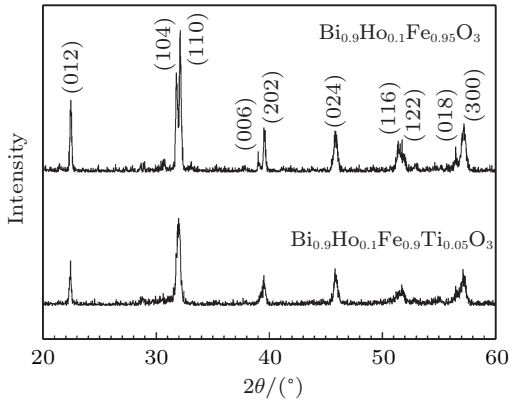


Fig. 1. X-ray diffraction patterns taken on the surfaces of $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$ and $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ ceramics sintered at 850 °C and 855 °C, respectively.

The sintering shrinkage in diameter was greater than 10% for these two compositions. Figure 2 shows the scanning electron microscopy (SEM) images taken on the surface of the samples. It can be seen that both samples had a relatively dense microstructure, while their grain size and morphology were considerably different. The $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$ sample consisted of uneven grains with diameters in the range of 1–5 μm. On the contrary, the grains of $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ were much more uniform and the grain size was decreased to less than 1 μm. It is well known that it is a great challenge to achieve high perovskite phase purity with a dense microstructure for $BiFeO_3$ ceramics through conventional sintering. Wang *et al.* successfully prepared $BiFeO_3$ ceramics with high perovskite phase purity through a rapid liquid phase sintering technique,[21] however, the ceramics had a relatively porous microstructure.[22] Obviously, Ho-doping, especially together with Ti-doping, can dramatically improve the sintering of $BiFeO_3$ ceramics.

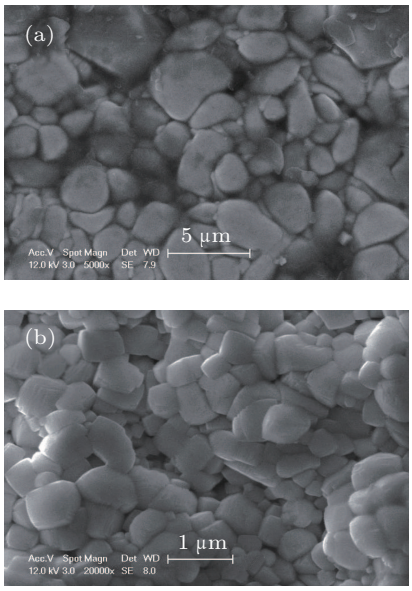


Fig. 2. SEM images taken on the surfaces of (a) $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$ ceramics sintered at 850 °C, (b) $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ ceramics sintered at 855 °C.

A remarkable difference was observed in the *E*–*J* characteristics of these two ceramics. As shown in Fig. 3, the leakage current density of $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ was decreased by about six orders of magnitude from that of $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$. Like the $BiFe_{0.9}Ti_{0.05}O_3$ ceramics we prepared before, the $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ ceramics prepared in this study also exhibited an ultrahigh electrical resistivity, over 1×10^{14} Ω·cm at room temperature. Although the influence from the difference in grain size between these two kinds of ceramics should be considered, this dramatic difference in leakage current density by about six orders of magnitude between these two compositions should have mainly resulted from some other factors. As $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$ was also Fe-deficient, while its electrical resistivity was much lower, this result further proves our previous suggestion that the ultrahigh electrical resistivity is a combined effect of Ti-substitution and Fe-deficiency in $BiFeO_3$. This mechanism was discussed in detail in our previous paper.[16] Accordingly, the $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ ceramics had a very low dielectric loss, about 0.02 at 100 Hz, as shown in Fig. 4, which is similar to that of the $BiFe_{0.9}Ti_{0.05}O_3$ ceramics we prepared previously with ultrahigh electrical resistivity. In contrast, the $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$ ceramics had a much higher dielectric loss, about 0.95 at 100 Hz, which is similar to that of the $BiHo_{0.1}Fe_{1.1}O_3$ ceramics prepared by Pradhan *et al.* Both the dielectric constant and dielectric loss of the $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ ceramics also showed a much lower dispersion over the frequency range of 10^2–10^6 Hz than those of the $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$ ceramics. The polarization hysteresis (*P*–*E*) loop obtained for the $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$ ceramics is unsaturated with rounded corners (not shown), which indicates a significant conductive loss and a high leakage current. A much improved polarization hysteresis loop is observed for the $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ ceramics with a saturation polarization P_S of 1.5 μC/cm^2 and a remanent polarization P_r of 0.4 μC/cm^2, as shown in Fig. 5. Both its P_S and P_r are larger than those of the $BiFe_{0.9}Ti_{0.05}O_3$ ceramics with ultrahigh electrical resistivity that we prepared before under similar conditions,[16] respectively. Therefore, the electrical and ferroelectric properties of Ho-doped $BiFeO_3$ ceramics have been dramatically improved through the codoping of Ti.

For the $Bi_{0.9}Ho_{0.1}FeO_3$ ceramics prepared by Jeon *et al.*, a peculiar double hysteresis loop-like magnetization-magnetic field curve with a remnant magnetization $2M_r$ of about 0.056 emu/g was observed. As shown in Fig. 6, the magnetization-magnetic field curve of the $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$ ceramics in this study was also like a double hysteresis loop with a remnant magnetization $2M_r$ of about 0.086 emu/g, which can be clearly seen from the inset of Fig. 6. It should be pointed out, however, that the remnant magnetization of these two ceramic samples was much smaller than that of the $Bi_{0.9}Ho_{0.1}FeO_3$ powder prepared by Wu *et al.*,[11] whose $2M_r$ was 0.406 emu/g at room temperature. The powder was synthesized at 600 °C, while these two ceramic samples were both sintered at 850 °C. As the defect subsystem of $BiFeO_3$ is sensitive to temperature, the defect subsystems formed at these two temperatures (600 °C and 850 °C) should be quite different and thus possibly be responsible for the difference in the observed remnant magnetization, though the

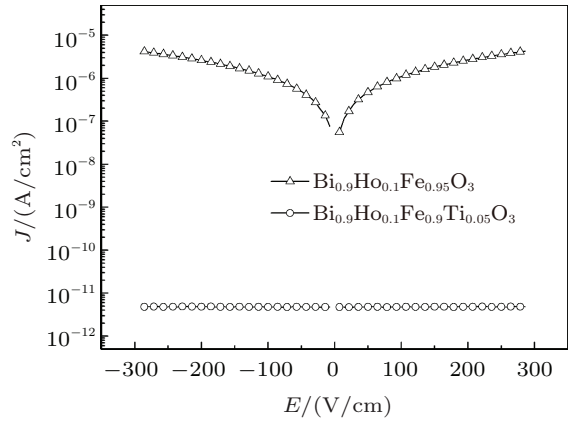


Fig. 3. The *J*–*E* characteristics measured for the $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$ and $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ ceramics sintered at 850 °C and 855 °C, respectively.

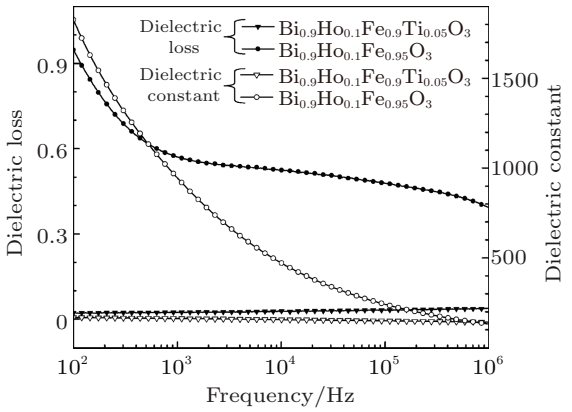


Fig. 4. The dielectric properties over 10^2–10^6 Hz measured for the $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$ and $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ ceramics sintered at 850 °C and 855 °C, respectively.

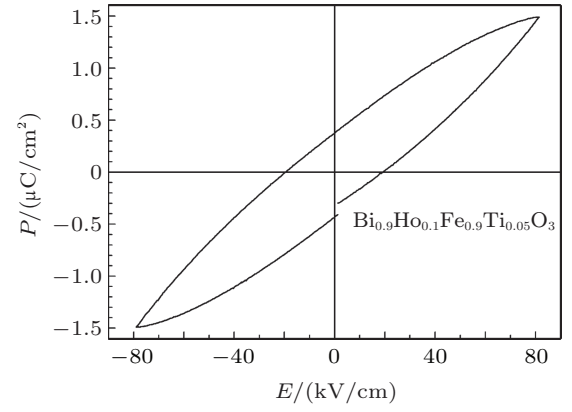


Fig. 5. The polarization hysteresis *P*–*E* loop of the $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ ceramics sintered at 855 °C.

mechanism is not clear in detail. At the same time, there were also some considerable differences in the magnetization-magnetic field curve between the $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$ and $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ ceramics prepared in this study. Compared with that of $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$, the hysteresis loop of $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ had a much larger area with a remnant magnetization $2M_r$ of about 0.485 emu/g, which was similar to the remnant magnetization of the $Bi_{0.9}Ho_{0.1}FeO_3$ powder synthesized at 600 °C. Ti substitution for Fe, which can be expressed as $Ti_{Fe}^{\bullet}$, is a positively charged point defect in the lattice of $BiFeO_3$ and should have important impacts on the defect subsystem of $BiFeO_3$. If the remnant magnetization of $BiFeO_3$ is sensitive to the defect subsystem in $BiFeO_3$, it seems that a small amount of $Ti_{Fe}^{\bullet}$ is helpful in maintaining the remnant magnetization to relatively high temperatures in Ho-doped $BiFeO_3$.

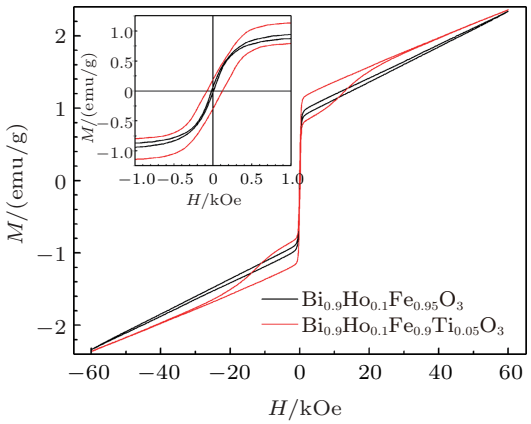


Fig. 6. (color online) The magnetic hysteresis *M*–*H* loops of the $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$ and $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ ceramics sintered at 850 °C and 855 °C, respectively. The inset shows enlarged loops at low magnetic fields.

4. Conclusion

We successfully conducted a comparison between $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$ and $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ to study the codoping effects of Ho and Ti on $BiFeO_3$. Noticeable differences were observed in both the X-ray diffraction and microstructure analyses between these two compositions. Compared with $Bi_{0.9}Ho_{0.1}Fe_{0.95}O_3$ ceramics, $Bi_{0.9}Ho_{0.1}Fe_{0.9}Ti_{0.05}O_3$ ceramics show a higher electrical resistivity by about six orders of magnitude, and a magnetic hysteresis loop of a much larger area with a remnant magnetization comparable to that of $Bi_{0.9}Ho_{0.1}FeO_3$ powder synthesized at a relatively low temperature. These results demonstrate that the multiferroic properties of $BiFeO_3$ ceramics are sensitive to the defect subsystem of $BiFeO_3$ and the coexistence of $Ti_{Fe}^{\bullet}$, and that $V_{Fe}^{'''}$ is helpful in achieving good electrical and magnetic properties in $BiFeO_3$.

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