Research Article

Effects of Ba and Ti co-doping on BiFeO$_3$ multiferroic ceramics optimized through two-step doping

Sheng ZHU[a], Yanhong GU[b], Yao XIONG[a], Xi ZHOU[a], Yong LIU[a],
Yu WANG[c], Wanping CHEN[a,*]

[a]*Key Laboratory of Artificial Micro- and Nano-structures of Ministry of Education, School of Physics and Technology, Wuhan University, Wuhan, Hubei 430072, China*
[b]*School of Physics and Electronic Information, Luoyang Normal College, Luoyang, Henan 471022, China*
[c]*School of Materials Science and Engineering, Nanchang University, Nanchang, Jiangxi 330031, China*

Abstract: Ceramics of Bi$_{0.9}$Ba$_{0.1}$Fe$_{0.925}$Ti$_x$O$_3$ (x = 0.0625, 0.08125, 0.0875, and 0.11) were prepared according to two doping strategies: one is called single-step doping in which Ba and Ti were doped together in calcination, while the other one is called two-step doping in which Ba and Ti were doped in calcination and sintering, respectively. Compared with samples prepared with single-step doping, those prepared with two-step doping have obviously different XRD patterns and small grains, and are dramatically improved in dielectric loss, resistivity, and remnant magnetization. A low dielectric loss of 0.05 at 10^3 Hz, a high resistivity of 4×10^{12} Ω·cm, and a large remnant magnetization of 1.5 emu/g, have been obtained simultaneously for Bi$_{0.9}$Ba$_{0.1}$Fe$_{0.925}$Ti$_{0.11}$O$_3$ prepared with two-step doping. The contrast between these two doping strategies clearly reveals the importance of establishing a proper doping strategy when two or more elements are co-doped to BiFeO$_3$.

Keywords: BiFeO$_3$; doping; multiferroic; nonstoichiometric

1 Introduction

As the only multiferroic material with both spontaneous polarization and magnetic orderings above room temperature [1,2], BiFeO$_3$ has attracted extensive attention and has been intensively studied in the past decade. However, before it can be actually applied as a multiferroic material, BiFeO$_3$ has to be significantly improved in a few important aspects, including enhancing its macroscopic magnetic properties and decreasing its relatively high leakage current [3]. Through extensive investigations, some outstanding progresses have been achieved with regards to these aspects [4,5].

The substitution of some elements for Bi and/or Fe has been proven crucial for improving the multiferroic properties of BiFeO$_3$ [6–8]. An ultrahigh resistivity, over 10^{14} Ω·cm, has been obtained for BiFeO$_3$ through a small substitution of Ti for Fe [9], and the magnetic properties of BiFeO$_3$ have been obviously enhanced through the substitution for Bi by about a dozen of elements [10–13], most of which are rare earth (RE) elements. As a non-RE element, Ba has also been found effective for enhancing the magnetic properties of BiFeO$_3$ through its substitution for Bi [11]. Ba^{2+} is non-magnetic and its effect on the magnetic properties of BiFeO$_3$ appears especially appealing. On the other hand, though the magnetic properties and the resistivity of BiFeO$_3$ can be dramatically improved through the

* Corresponding author.
E-mail: wpchen@whu.edu.cn

substitution of some elements for Bi and Fe respectively, they have not been able to be effectively improved simultaneously through the substitution of any single element for Bi or Fe. Co-doping of two or more elements to $BiFeO_3$ simultaneously thus seems inevitable for most applications of $BiFeO_3$. As a matter of fact, a large number of investigations have already been conducted on $BiFeO_3$ co-doped with various element combinations [14–16], including Ba and Ti, and some very promising results have been obtained. In this paper, we will report a surprising finding revealed for the co-doping of Ba and Ti to $BiFeO_3$. Through a well-designed comparison, the doping sequence of Ba and Ti has been found to play a vital role in optimizing the multiferroic properties of $BiFeO_3$. To our knowledge, the doping sequence has been quite neglected up to date when two or more elements are co-doped to $BiFeO_3$.

2   Experimental procedures

Two kinds of doping strategies for the co-doping of Ba and Ti to $BiFeO_3$ were adopted. In the first one, powders of Bi_2O_3, $BaCO_3$, Fe_2O_3, and TiO_2 were carefully weighed and mixed according to the compositions of $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_xO_3$ ($x = 0.0625$, 0.08125, 0.0875, and 0.11). The formula of $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_xO_3$ is nonstoichiometric and is only nominal due to the possible formation of some secondary phases. As Ba and Ti were doped together in one step, we name this doping strategy as single-step doping. After being ball-milled for 4 h using deionized water as medium and dehydrated in an oven at 120 ℃ for 24 h, the mixed powders were calcined in air at 800 ℃ for 2 h. Then the calcined powders were ball-milled and dehydrated again, and pressed by applying a pressure of 8 MPa to form pellets of 12 mm in diameter and 1 mm thick. In the second doping strategy, powders of Bi_2O_3, $BaCO_3$, and Fe_2O_3 were weighed and mixed according to the composition of $Bi_{0.9}Ba_{0.1}Fe_{0.925}O_3$. After being ball-milled and dehydrated, the mixed powders were calcined in air at 800 ℃ for 2 h. Then TiO_2 was added to the calcined powders according to a series of compositions of $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_xO_3$ ($x = 0.0625$, 0.08125, 0.0875, and 0.11). After being ball-milled and dehydrated, the mixed powders were pressed into pellets under conditions described above. As Ba and Ti were doped separately in two steps, this doping strategy is named as two-step doping. The pressed pellets prepared through these two kinds of doping strategies were finally sintered in air for 2 h at a series of temperatures, and furnace-cooled to room temperature. Silver electrodes were fired on the two major surfaces of the sintered samples for electrical measurements.

An X-ray diffractometer (Brucker D8) with Cu Kα radiation was used for crystal structure analysis. Dielectric measurement was obtained using an impedance analyzer (Agilent 4294A). *I–V* characteristics of the samples were recorded through a Keithley (6517A) electrometer/high-resistance meter. Magnetization hysteresis (*M–H*) loops were measured using a physical property measurement system (Quantum Design PPMS-9). All measurements and analyses were conducted at room temperature.

3   Results and discussion

Every kind of pressed pellets has been sintered at a series of temperatures, and a specific sintering temperature was chosen for them to maximize the electrical resistivity, respectively. Only those samples sintered at their respective specific temperatures were studied and analyzed in detail, as discussed in the following.

According to the X-ray diffraction (XRD) patterns taken on the surfaces of the sintered pellets, all samples have a dominant content of rhombohedral perovskite phase, with some representative ones shown in Fig. 1. The content of those common impurity phases, including $Bi_{46}Fe_2O_{72}$ corresponding to the weak peak at 30.84° and $Bi_2Fe_4O_9$ corresponding to the weak peak at

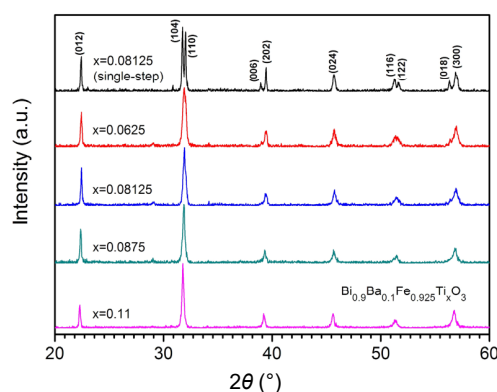**Fig. 1**   XRD patterns taken on the surfaces of $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_{0.08125}O_3$ prepared with single-step doping and sintered at 850 ℃, and $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_xO_3$ ($x = 0.0625$, 0.08125, 0.0875, and 0.11) prepared with two-step doping and sintered at 880 ℃.

$29.01°$, is very small. It is very interesting to point out that, for all the samples prepared with single-step doping, the (104) and (110) peaks of the perovskite phase are clearly split, which has also been observed in those previous investigations on the co-doping of Ba and Ti with single-step doping [17]. On the contrary, this splitting cannot be observed for those samples prepared with two-step doping. This difference of splitting/merging of (104) and (110) peaks of the perovskite phase has also been noted among Ti-doped $BiFeO_3$ in some previous works [4–6], and some subtle lattice differences in the perovskite phase have been suggested. So these two different doping sequences of Ba and Ti may have resulted in some slight differences in the lattice of the perovskite phase.

Another obvious difference in grain growth of sintering has also been observed for these two different doping sequences of Ba and Ti. Figure 2 shows five representative micrographs taken on the surfaces of samples whose XRD patterns are shown in Fig. 1. Besides more clear edges are observed for the grains in the samples prepared with two-step doping, the biggest difference should be that the grains of the samples prepared with single-step doping are much bigger than those with two-step doping. Grain growth is affected by many factors, including vacancy diffusion for solid-state sintering [18], the amount of liquid phases for liquid-phase sintering, and impurity phases at grain-boundaries. As for the grain growth observed in this study, it is reasonable to assume that more Ti ions likely exist in the grain-boundaries in the course of sintering via two-step doping, which have thus more effectively suppressed the grain growth in sintering. Obviously, the sintering behavior of Ba and Ti co-doped $BiFeO_3$ has exhibited a strong dependence on the doping strategy.

Ba-doped $BiFeO_3$ has been very attractive for its dramatically enhanced magnetization. To improve both the ferroelectric and magnetic properties simultaneously, co-doping of Ba with some other elements to $BiFeO_3$ has been considered and investigated [19–21]. However, the results have not been so satisfactory up to date. For instance, though the leakage current and dielectric loss of Ba and Ti co-doped $BiFeO_3$ have been obviously decreased from those of Ba-doped $BiFeO_3$ [17,21], they are still too large for most multiferroic applications. In these previous investigations, Ba and some other elements have been doped together in one step, in the same way as Ba and Ti were doped according to the first doping strategy in our work. As a matter of fact, for all the compositions we have investigated, the dielectric loss and leakage current of the samples prepared with single-step doping cannot be satisfactorily decreased either. As an example, the sample of $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_{0.08125}O_3$ prepared with single-step doping shows a dielectric loss around 0.5 at 10^3 Hz, and a leakage current density around 10^{-6} A/cm^2 at 400 V/cm, as shown in Fig. 3 and Fig. 4. They are quite larger than the small values that have been obtained for Ti-doping [9,22]. So though Ba-doped $BiFeO_3$ has been well-known for its magnetic properties [11], it has been a great challenge to really decrease its dielectric loss and leakage current.

Very interestingly, for all the compositions we have investigated, the samples prepared with two-step doping exhibit a much smaller dielectric loss at 10^3 Hz, as shown in Fig. 3. Generally speaking, all samples prepared with two-step doping not only have a small dielectric loss at 10^3 Hz, both their dielectric loss and
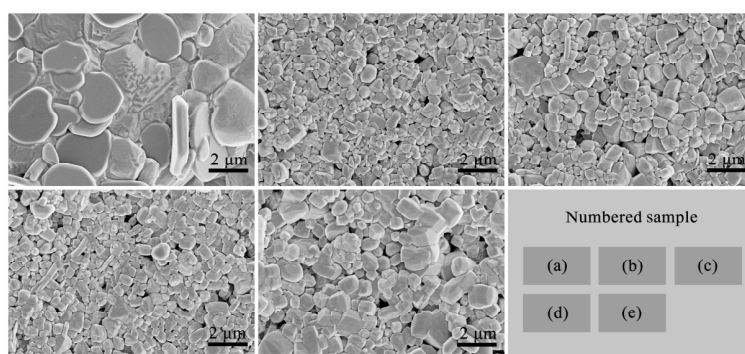

Fig. 2 SEM micrographs taken on fractured surfaces of (a) $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_{0.08125}O_3$ (single-step doping) sintered at 850 ℃, (b) $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_{0.0625}O_3$ (two-step doping) sintered at 880 ℃, (c) $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_{0.08125}O_3$ (two-step doping) sintered at 880 ℃, (d) $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_{0.0875}O_3$ (two-step doping) sintered at 880 ℃, and (e) $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_{0.11}O_3$ (two-step doping) sintered at 880 ℃.
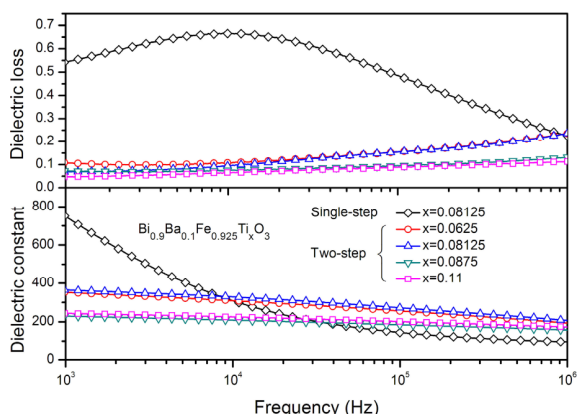
Fig. 3 Dielectric properties over 10^3 to 10^6 Hz measured at room temperature for $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_{0.08125}O_3$ (single-step doping) sintered at 850 ℃, and $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_xO_3$ (two-step doping, $x = 0.0625$, 0.08125, 0.0875, and 0.11) sintered at 880 ℃.
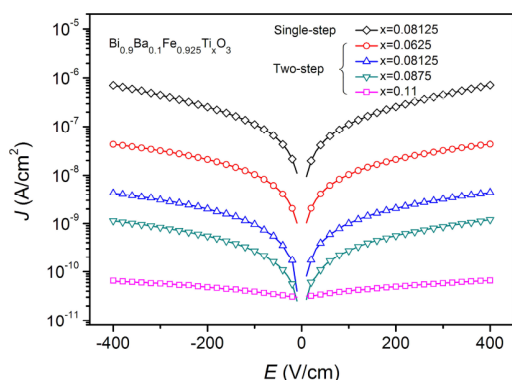
Fig. 4 Room temperature E–J characteristics measured for $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_{0.08125}O_3$ (single-step doping) sintered at 850 ℃, and $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_xO_3$ (two-step doping, $x = $ 0.0625, 0.08125, 0.0875, and 0.11) sintered at 880 ℃.

dielectric constant also show very small dispersion over the frequency range of 10^3–10^6 Hz. Obviously, this two-step doping strategy is very effective to optimize dielectric properties of Ba and Ti co-doped BiFeO$_3$. So the doping sequence of Ba and Ti plays a vital role in optimizing the dielectric properties of Ba and Ti co-doped BiFeO$_3$, which has been quite neglected in previous investigations.

Figure 4 shows the E–J characteristics obtained for the five samples whose XRD patterns are shown in Fig. 1. It can be clearly seen that for the four samples prepared with two-step doping, the leakage current density decreases steadily with increasing content of Ti. For the sample of $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_{0.11}O_3$, a high resistivity of $4{\times}10^{12}$ $\Omega{\cdot}cm$ is calculated out from its E–J characteristic. So for two-step doping, Ti-doping is indeed very effective to decrease the leakage current of

Ba-doped BiFeO$_3$, forming a sharp contrast with that for single-step doping. A tentative explanation for this contrast is that samples prepared via single-step doping may have a more complicated defect subsystem when Ba and Ti are doped together, over which Ti-doping plays a less decisive role, so relatively large leakage currents are still observed for Ba and Ti co-doped BiFeO$_3$ prepared via single-step doping. At the same time, the relatively large dielectric loss in samples prepared via single-step doping can also be explained in terms of their more complicated defect subsystem.

It is well-known that BiFeO$_3$ is canted G-type antiferromagnetic with possible nonzero remnant magnetization. However, there exists a space-modulated spin structure which does not allow a net magnetization derived in pure BiFeO$_3$. Many researches have shown that substitution for Bi with larger cations, including Ba^{2+} [8,11], can lead to effective suppression of the spiral spin structure of BiFeO$_3$, resulting in the appearance of net magnetization. In previous investigations, much enhanced magnetization has already been obtained for Ba and Ti co-doped BiFeO$_3$ [17]. Similarly, the samples prepared with single-step doping in our study also have very strong magnetization. The magnetic hysteresis M–H loop of $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_{0.08125}O_3$ prepared with single-step doping is shown in Fig. 5 as an example, which has a remnant magnetization of 1.0 emu/g. So it seems that a strong magnetization can be readily achieved in Ba and Ti co-doped BiFeO$_3$ prepared with single-step doping. To our surprise, the sample of $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_{0.08125}O_3$ prepared with two-step doping even displays a larger remnant magnetization of 1.4 emu/g, as shown in Fig. 5. It indicates that this
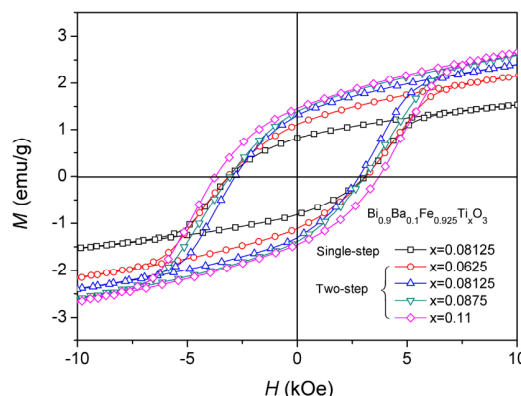

Fig. 5 Room temperature magnetic hysteresis M–H loops of $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_{0.08125}O_3$ (single-step doping) sintered at 850 ℃, and $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_xO_3$ (two-step doping, $x = $ 0.0625, 0.08125, 0.0875, and 0.11) sintered at 880 ℃.

two-step doping is important not only to improve the dielectric and electrical properties, but also to optimize the magnetic properties of Ba and Ti co-doped $BiFeO_3$. In other words, the defect subsystem in samples prepared via two-step doping is suitable to improve not only the dielectric and electrical, but also the magnetic properties of Ba and Ti co-doped $BiFeO_3$.

It should be noted that for the samples prepared with two-step doping, the remnant magnetization increases slightly with increasing content of Ti, which is 1.25, 1.4, 1.45, and 1.5 emu/g for $x = 0.0625$, 0.08125, 0.0875, and 0.11, respectively. So highly attractive overall properties, including a low dielectric loss of 0.05 at 10^3 Hz, a high resistivity of 4×10^{12} $\Omega \cdot$cm, and a large remnant magnetization of 1.5 emu/g, have been obtained simultaneously for $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_{0.11}O_3$ prepared with two-step doping. Such overall properties should be able to lay a solid foundation for the further development of $BiFeO_3$ as a single phase multiferroic material.

Co-doping of two or more elements to $BiFeO_3$ is being adopted in more and more researches focused on $BiFeO_3$. While much attention has been paid to fine stoichiometric adjustment and various special sintering processes to optimize the multiferroic properties of $BiFeO_3$, doping sequence of these co-doped elements has been quite neglected up to date. Namely, these elements have always been doped at one time together in either calcination or sintering. The contrast between Ba and Ti co-doped $BiFeO_3$ samples prepared with single-step doping, both in this investigation and in some previous investigations, and samples prepared with two-step doping clearly reveals the importance of doping sequence of Ba and Ti in optimizing the multiferrioc properties of $BiFeO_3$. So when two or more elements are co-doped to $BiFeO_3$, great attention should be paid to establish a proper doping strategy to optimize the effects of these co-doped elements.

4   Conclusions

Samples of $Bi_{0.9}Ba_{0.1}Fe_{0.925}Ti_xO_3$ ($x = 0.0625$, 0.08125, 0.0875, and 0.11) have been prepared with single-step doping and two-step doping, separately. Obvious differences in XRD pattern and grain growth have been observed between the samples prepared with these two doping strategies. Compared with those samples prepared with single-step doping, much lower dielectric loss, higher resistivity, and larger remnant

magnetization have been obtained for samples prepared with two-step doping. The contrast between the samples prepared with single-step doping and two-step doping clearly reveals the importance of establishing a proper doping strategy when two or more elements are co-doped to $BiFeO_3$.

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