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Enhancement in electrical and magnetodielectric properties of Ca- and Ba-doped $BiFeO_3$ polycrystalline ceramics

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Abstract

We carried out a comparative study on the electrical and magnetodielectric properties of polycrystalline $BiFeO_3$, $Bi_{0.9}Ca_{0.1}FeO_{2.95}$, $Bi_{0.9}Ba_{0.05}Ca_{0.05}FeO_{2.95}$, and $Bi_{0.9}Ba_{0.1}FeO_{2.95}$

ceramics. The two dielectric anomalies, near 25 K and 281 K, are observed for $BiFeO_3$. Interestingly, the anomaly near 25 K shifts towards a higher temperature above 60 K with Ca and/or Ba doping, attributed to the doping induced chemical pressure. In addition, the room temperature switchable magnetodielectric effect is witnessed for the doped $BiFeO_3$ compounds, due to the quadratic magnetoelectric coupling. This indicates the improved magnetoelectric coupling in $BiFeO_3$ with the Ca and Ba doping. This is essentially due to the enhanced magnetic ordering and reduced leakage current in $BiFeO_3$ after the doping.

KEYWORDS: multiferroics, oxides, dielectric materials/properties, electrical properties

1. INTRODUCTION

Bismuth ferrite ($BiFeO_3$) is one of the most widely studied multiferroic materials in the literature due to the coexistence of ferroelectric and magnetic ordering at room temperature (RT) and hence it is a potential material for functional electronic devices.[1-6] This material is ferroelectric below the Curie temperature, T_C = 1100 K and exhibits antiferromagnetic ordering below the Néel temperature, T_N = 643 K.[6] In fact, multiferroic materials have gained enormous attention due to their potential in microelectronic and spintronic applications,[7,8] and the possibility of controlling magnetization (M) by electric fields or polarization (P) by magnetic fields.[9-11] Particularly, the magnetoelectric (ME) coupling is one of the most important material parameters of multiferroics,[12-15] and is measured directly using a dynamic ME effect.[9,10] While magnetodielectric (MD) effect has been used as an indirect method to probe ME coupling in multiferroic systems.[15-18]

The intrinsic dielectric properties such as polarization and dielectric permittivity of $BiFeO_3$ near RT are usually hampered by its large electrical conductivity. In this respect, the frequency-dependent dielectric properties of bulk $BiFeO_3$ over the temperature range of 10–300 K were studied by Kamba *et al.*[19] They attributed an anomaly near 250 K to the Maxwell-Wagner (MW) contribution for permittivity as a result of a relaxation arising at the interfaces between grains and grain boundaries.[19,20] At low frequencies or at high temperatures, colossal dielectric constants are also reported due to an increased electrical conductivity, which leading to the MW effects.[21-23] The temperature at which

the MW relaxation begins to dominate the dielectric response depends on the sample conductivity; this could be as low as 200 K for some samples.[19]

Recently, we have investigated the effects of oxygen non-stoichiometry on the structural and dielectric properties of bulk $BiFeO_3$.[24] We found that the coupling among spin, lattice, and charge degrees of freedom persists down to low temperatures (<30 K) and furthermore these properties depend on the degree of oxygen non-stoichiometry.[24] One of the primary mechanisms that produce ME coupling in $BiFeO_3$ is the interactions between spin waves (magnons) and polarization waves (optical phonons)[25,26], which results in low-frequency magneto-optical resonances in the dielectric susceptibility[26]. These so-called electromagnetic excitations[26] (electromagnon – magnon with electric dipole activity) could be related to the dielectric anomaly below 100 K in the undoped and Ca-doped $BiFeO_3$ compounds.[24,27] We also observed the improved MD effect in polycrystalline $Bi_{0.9}Ca_{0.1}FeO_{2.95}$, presumably due to the nonlinear ME coupling.[27]

In a recent study, Ramachandran *et al.*[28] showed that both phonon (acoustic and optical) and magnon transport heat in the $BiFeO_3$-based samples using the thermal conductivity and magneto-thermal conductivity measurements. Remarkably, the dip in thermal conductivity near the low-*T* dielectric anomaly was seen for the undoped and Ca-doped $BiFeO_3$ ceramics,[24,27,28] presumably due to the phonon-magnon coupling.[28] Notably, this study revealed that the Ca doping enhances the optical phonon thermal transport, particularly optical phonon-magnon resonant contribution. These findings are essentially attributed to the chemical pressure induced by Ca that leads to an enhanced magnetic ordering and the softening of phonon modes. Very recently, Caspers *et al.*[29] also observed a dip feature near 50 K in the spectral weight of the spin cycloid resonance (SCR) peaks in stoichiometric polycrystalline $BiFeO_3$, which ascribed to the phonon-magnon coupling. Hence, in the present work, we conducted a study to compare Ca- and Ba-doped $BiFeO_3$ ceramic samples with $BiFeO_3$ using the dielectric, magnetodielectric, and leakage current measurements. This study has been done to optimize the materials properties of $BiFeO_3$-based samples for the electroceramic devices.[30-32]

2. EXPERIMENTAL PROCEDURE

Synthesis of polycrystalline $BiFeO_3$, $Bi_{0.9}Ca_{0.1}FeO_{2.95}$, $Bi_{0.9}Ba_{0.05}Ca_{0.05}FeO_{2.95}$, and $Bi_{0.9}Ba_{0.1}FeO_{2.95}$ samples was carried out using a sol-gel approach, described

elsewhere.[6,33] The obtained powder samples were sintered in air at 1123 K for 6 hours. We noticed that $Bi_{0.9}Ca_{0.1}FeO_{2.95}$ samples have a slightly lower relative density (~88%) than $BiFeO_3$ (~90%). However, Ba doping led to an improved densification (~92%).[31] Here, we have restricted the doping concentration of Ca and Ba at x = 0.1, because the Ca doping in $BiFeO_3$ ($Bi_{1-x}Ca_xFeO_3$) results in the ferroelectric-paraelectric transition at x ~0.125.[34] In addition, the doping of alkali-earth-metals in $BiFeO_3$ leads to the structural transition at higher contents ($x \geq 0.1$). Indeed, all studied samples are crystallized in the rhombohedral crystal symmetry with $R3c$ space group,[33] which is essential to seize ME coupling in the doped $BiFeO_3$.

Notably, the doping of Ca and Ba in the $BiFeO_3$ lattice has resulted in the reduction in unit cell parameters.[33] For instance, the unit cell volume of the doped samples is decreased to < 370 $Å^3$ from the value of about 374.4 $Å^3$ for $BiFeO_3$. In addition, the Fe1-O-Fe2 bond length of the doped $BiFeO_3$ samples is also decreased slightly as compared to $BiFeO_3$. Besides, we also confirmed the presence of oxygen vacancy and the valence state of Fe (3+) in the doped $BiFeO_3$ samples using X-ray photoelectron spectroscopic studies. As a result of these structural changes by the doping, the magnetic properties of the doped samples are enhanced considerably as compared to $BiFeO_3$.[33] On the other hand, the ferroelectric properties of the Ba-doped $BiFeO_3$ samples are improved than that of $BiFeO_3$. i.e., the maximum polarization of $Bi_{0.9}Ba_{0.1}FeO_{2.95}$ at an applied voltage of 4 kV is about P_{max} = 1.2 μC/cm^2, which is twice higher than that of $BiFeO_3$. Thus, the coupling between different order parameters such as spin, charge, and lattice in the doped $BiFeO_3$ (especially Ca-doped) compounds is enhanced noticeably.[24,27,28]

In the current work, we present a comparative study on the electrical and magnetodielectric properties of $BiFeO_3$-based materials with Ca and/or Ba doping at the Bi-site. The temperature-dependent dielectric constant (ε_r) and dielectric loss ($tan\delta$) of undoped and doped $BiFeO_3$ ceramic samples are measured in the temperature range of 10–350 K, using a precision LCR meter (Agilent 4284A), coupled with a physical property measurement system (PPMS, Quantum design) for controlling both temperature and magnetic field, as per needs. The dielectric measurements are performed with an applied voltage of 1 V at a frequency of 30 kHz. We also carried out the magnetodielectric and leakage current (J-V) measurements on these samples at RT using

the LCR meter and Radiant ferroelectric loop tracer, respectively. Here, it is important to note that the stability of the capacitance measurements using the Agilent 4284A LCR meter is about 0.01%. Furthermore, the precision values of the capacitance and leakage current measurements are about 0.01 fF and 10 pA, respectively.

3. RESULTS AND DISCUSSION

The temperature-dependent dielectric constant (ε_r) and dielectric loss ($tan\delta$) of the undoped and doped $BiFeO_3$ samples measured at 30 kHz are presented in Figs. 1a and 1b, respectively. We found the enhanced dielectric constant over the entire temperature range upon the doping. The dielectric loss of the Ba-doped $BiFeO_3$ is slightly smaller than $BiFeO_3$ near RT, while the dielectric loss increases for both Ca-doped and Ba-Ca co-doped samples (Fig. 1b). However, above 200 K, the observed large dielectric constant for the undoped, Ca-doped, and Ba-Ca co-doped $BiFeO_3$ samples suggests the development of an MW effect, and is associated with the increased electrical conductivity near RT.[19,20] However, the Ba-doped $BiFeO_3$ seems to display entirely intrinsic behavior over the investigated temperature range of 10–350 K.

The two dielectric anomalies near 25 K and 281 K are clearly visible for $BiFeO_3$, Fig. 1b. The low-T anomaly is attributed to a magnetic transition with magnetoelectric coupling and magnetic glassy behavior.[24,27] Interestingly, the anomaly near 25 K showed a noticeable shift towards higher temperature >60 K and broadened considerably with the doping (inset, Fig. 1b). The values of peak temperatures of the low-*T* dielectric anomaly are about 25 K, 68 K, 98 K, and 109 K for the undoped, Ca-, Ba-Ca-, and Ba-doped $BiFeO_3$ samples, respectively. At lower temperatures <100 K, the frequency-dependent dielectric constant of the Ca-doped $BiFeO_3$ samples can be fitted to a Vogel-Fulcher equation,[27] implying the glassy behavior. This is similar to the conventional relaxor ferroelectric behavior. While the undoped and Ba-doped $BiFeO_3$ samples follow an Arrhenius relation, signifying the superparaelectric behavior for these samples.[24,27] Importantly, it is noted that the dielectric relaxation time of the Ca-doped $BiFeO_3$ samples is in order of 10^{-8} s in the low-*T* region, which is higher than that of the undoped and Ba-doped samples ($\leq 10^{-10}$ s). On the other hand, the high-*T* dielectric

anomaly above 250 K is broadened for the Ca-doped and Ba-Ca co-doped samples as compared to that of $BiFeO_3$. Here, the observed high-T anomaly is due to the MW relaxation at the interfaces between grains and grain boundaries.[19] However, the high-T anomaly has vanished for the Ba-doped $BiFeO_3$, which is clearly evident in Fig. 1b. The absence of this feature can be associated with the disappearance of antiferromagnetic to spin glass transition in the Ba-doped $BiFeO_3$,[33] which confirms a link between the development of magnetic glassy behavior and the high-T dielectric anomaly.

To probe the spin-charge coupling in the undoped and doped $BiFeO_3$ samples, we studied the RT MD effect by measuring the magnetic field (H) modulated dielectric constant (ε_r) up to 80 kOe. The relative change in dielectric constant ($\Delta\varepsilon/\varepsilon = \Delta\varepsilon(H)/\varepsilon(0)$) is computed (illustrated in Fig. 2) using the relation:

$$\frac{\Delta\varepsilon(H)}{\varepsilon(0)} = \frac{\varepsilon(H)-\varepsilon(0)}{\varepsilon(0)}, \qquad (1)$$

where $\varepsilon(H)$ and $\varepsilon(0)$ are the dielectric constants with and without an applied magnetic field. We noticed that the $\Delta\varepsilon/\varepsilon$ value at a magnetic field of 80 kOe is about 1.12%, 0.22%, 0.15%, and 0.03% for $BiFeO_3$, $Bi_{0.9}Ca_{0.1}FeO_{2.95}$, $Bi_{0.9}Ba_{0.05}Ca_{0.05}FeO_{2.95}$, and $Bi_{0.9}Ba_{0.1}FeO_{2.95}$, respectively. The MD effect in $BiFeO_3$ shows a linear increase in dielectric constant with increasing H (Fig 2a) and has higher $\Delta\varepsilon/\varepsilon$ values than the doped samples. This behavior of $BiFeO_3$ is most likely due to an improper MD effect such as the MW effect and magnetoresistance;[19] but not due to the coupling between the spontaneous polarization and magnetization. This is due to fact that the linear ME effect should not occur in $BiFeO_3$ due to its cycloidal G-type antiferromagnetic structure.[19,35] Actually, the undoing of this magnetic ordering can only happen at higher fields >160 kOe.[35,36] It should also be noted here that the linear shift in dielectric constant at certain fields reflecting some background effect and is not the intrinsic property of $BiFeO_3$.

On the other hand, MD effect is changed drastically with the Ca and Ba doping in the Bi-sites of $BiFeO_3$ (Fig 2b). Notably, these materials display a distorted butterfly-like loop behavior, contrary to the linear behavior of $BiFeO_3$ (Fig. 2a). This finding implies that the MD effect in the doped $BiFeO_3$ compounds has improved considerably when compared to $BiFeO_3$ in which the intrinsic ME effect is non-traceable (or trivial). In fact,

a quadratic-type magnetodielectric coupling is expected for these ME multiferroic systems, i.e. the shift in dielectric constant proportional to the square of H in the magnetically ordered phase. Hence, the observed nonlinear MD effects in the doped $BiFeO_3$ materials can be ascribed to a bi-quadratic term in the Ginzburg-Landau free energy, P^2M^2,[27] which always allowed by the symmetry.

In general, the relative change in dielectric constant ($\Delta\varepsilon/\varepsilon$) below T_N is proportional to the magnetic order parameter, since the magnetization (M) is proportional to magnetic field (H), which can be written as

$$\frac{\Delta\varepsilon(H)}{\varepsilon(0)} = \gamma H^m. \qquad (2)$$

Here, the sign of $\Delta\varepsilon/\varepsilon$ depends on the sign of the ME interaction constant $\gamma(T)$ which can be either positive or negative depending on the nature of ME coupling, and m is the power factor. Importantly, the absolute value of $\Delta\varepsilon/\varepsilon$ will increase as the square of the spontaneous magnetization at a given temperature. However, it is hard to confirm this experimentally, mainly due to the difficulties in estimating the ε values for the paramagnetic phase below T_N. In fact, the contribution of the improper MD effect to the doped $BiFeO_3$ samples cannot be ignored entirely.[19] Yet, we have tried a nonlinear fit to the data of $\Delta\varepsilon/\varepsilon$ versus H for the doped $BiFeO_3$ samples using the Eq. 2, which is illustrated by the solid lines in Fig. 3. However, at higher magnetic fields (>44 kOe), the $\Delta\varepsilon/\varepsilon$ value tends to saturate for the doped $BiFeO_3$ samples (Fig. 3), presumably due to the tendency of saturation in magnetization at higher H.[27,33] Notably, the fitting reveals that the ME interaction constant, γ (in order of ppb) is higher for the $Bi_{0.9}Ca_{0.1}FeO_{2.95}$ sample than the Ba-doped samples, which is due to the increase in the magnetic susceptibility with the Ca doping.[33] While the value of power factor (m) is estimated to be higher (~1.3) for the $Bi_{0.9}Ba_{0.05}Ca_{0.05}FeO_{2.95}$ as compared to other doped samples (~1.2).

To further clarify these observations, we have plotted the relative change in dielectric constant ($\Delta\varepsilon/\varepsilon$) versus magnetization ($M$), as shown in Fig. 3b, using the first-quarter M-H data for the doped samples that presented in our earlier report.[33] From this graph, it is clear that the $\Delta\varepsilon/\varepsilon$ value of the doped $BiFeO_3$ samples increases with increasing M (or H), presumably due to the proper ME effect. Among these doped samples, the Ba-Ca co-

doped sample displays a better MD behavior, as it showed a gradual variation in $\Delta\varepsilon/\varepsilon$ with M over the wide range of magnetic fields, without any saturation effects at higher fields (unlike the sample $Bi_{0.9}Ca_{0.1}FeO_{2.95}$). Most importantly, the observed nonlinear and switchable MD effect in the Ca-doped $BiFeO_3$ ceramic materials can be explained by the enhancement of weak ferromagnetic moments,[33] due to the energy gain of the Dzyaloshinskii-Moriya (DM) interaction under an external magnetic field that tend to align with H.[37,38] That's why, the Ca-doped samples showed a better MD effect than the Ba-doped $BiFeO_3$, which is mainly due to the improvement in the magnetic properties of $BiFeO_3$ with Ca content.[33] This means that the applied H can increase the polarization in the doped $BiFeO_3$ samples via the DM interaction and hence the improved ME properties for the doped samples is witnessed here.

Besides, it is obvious that the presented data, $\Delta\varepsilon/\varepsilon$ versus H or M (see Figs. 2-3) of the doped $BiFeO_3$ samples display a dynamic behavior; however, the experimental error in the dielectric measurements is expected to be a static one. Hence, we propose that the observed MD effect in the doped samples is an intrinsic material behavior. Whereas $BiFeO_3$ shows a peculiar behavior (inset of Fig. 3b), e.g., the plateau features at the certain fields, likely due to the improper ME effects.[19] For example, the $\Delta\varepsilon/\varepsilon$ value increases continuously with increasing or decreasing magnetic field (see Fig. 2a), which is possibly due to the continuous relaxing of ferroic domains in $BiFeO_3$ while varying the field (i.e., its ferroic domains relatively insensitive to the applied field). This means that this sample takes unusually long time to come to a static value for a given field. Thus, the MD effect in $BiFeO_3$ is completely different from that in the doped samples.

Furthermore, in an earlier work,[33] Ramachandran *et al.* showed that both remnant magnetization (M_r) and coercive field (H_C) improved substantially for the Ca-doped $BiFeO_3$ samples as compared to $BiFeO_3$. In addition, the antiferromagnetic transition temperature (T_N) is also increased to 645 K with Ca doping ($Bi_{0.9}Ca_{0.1}FeO_{2.95}$ and $Bi_{0.9}Ba_{0.05}Ca_{0.05}FeO_{2.95}$) from 643 K of $BiFeO_3$. This is mainly credited to the induced chemical pressure by the Ca doping in $BiFeO_3$.[33] Besides, the value of magnetic susceptibility of the Ca-doped samples showed the sharp increase with lowering temperature near T_N, which is attributed to a sharp rise in the paramagnetic susceptibility at around T_N. This is essentially due to the antisymmetric spin coupling via an anisotropic

superexchange interaction.[39] As a result, a weak ferromagnetic ordering is being induced in the Ca-doped $BiFeO_3$ samples,[33] which eventually leads to the enhanced ME coupling in $BiFeO_3$ with Ca doping (see Figs. 2-3).[27,28] Besides, we also attribute the reduced leakage current behavior of these doped samples for showing the improved MD effect, which is discussed in the following.

Figure 4 illustrates the electric voltage dependence of leakage current density (*J*-*V*) for the undoped and doped $BiFeO_3$ samples at RT. The samples in disc form with about 1 mm thickness are used for this study. Under the same testing voltage, the doped $BiFeO_3$ samples have a lower leakage current density than $BiFeO_3$. At the applied voltage of 4 kV, the leakage current density of $BiFeO_3$, $Bi_{0.9}Ca_{0.1}FeO_{2.95}$, $Bi_{0.9}Ba_{0.05}Ca_{0.05}FeO_{2.95}$, and $Bi_{0.9}Ba_{0.1}FeO_{2.95}$ samples are about 8.5 x 10^{-4} A/cm^2, 1.7 x 10^{-4} A/cm^2, 5.8 x 10^{-5} A/cm^2, and 5.6 x 10^{-5} A/cm^2, respectively. The Ba-doped $BiFeO_3$ showed a lowest leakage current density among the examined samples, analogous to its dielectric loss value (Fig. 1b). In particular, its value is estimated to be about 15 times lower than $BiFeO_3$. In addition, the Ba-Ca co-doped sample showed a similar leakage current density to that of $Bi_{0.9}Ba_{0.1}FeO_{2.95}$.

The inset of Fig. 4 shows logarithmic plots of the current density (*J*) versus the electric voltage (*V*) for the studied samples. The slope of this curve in the low voltage range (or near the origin) is close to ~1, consistent with the Ohmic conduction. At the intermediate voltages (<2.0 kV), the slope of all the samples is less than 2 (inset of Fig. 4). This suggests a trap-free conduction mechanism in these samples. This observation is in agreement with space-charge-limited current conduction,[40-42] which is given by

$$J = \frac{9}{8}\varepsilon_r \varepsilon_0 \theta \mu \frac{V^n}{d^3}, \qquad (3)$$

where *V* is the applied field, *d* is the sample thickness, ε_0 is the permittivity of free space, μ is the mobility, θ is the ratio of free electrons to trapped electrons, and *n* is the power factor. The estimated value of power factor (*n*) is about 1.5, 1.3, 1.4, and 1.6 for $BiFeO_3$, $Bi_{0.9}Ca_{0.1}FeO_{2.95}$, $Bi_{0.9}Ba_{0.05}Ca_{0.05}FeO_{2.95}$, and $Bi_{0.9}Ba_{0.1}FeO_{2.95}$, respectively. At higher voltages (>1.7 kV), the value of power factor (*n*) increases to ~2 for the undoped and Ca-doped $BiFeO_3$ samples, in accordance with the steady-state space-charge-limited current conduction mechanism.[40,42]

Thus, the present study provides an approach for optimizing the electrical and magnetodielectric properties of $BiFeO_3$ by doping divalent elements, Ca and Ba. Notably, the doped $BiFeO_3$ materials showed the improved dielectric constant, together with the low dielectric loss and leakage current, as compared to $BiFeO_3$. In addition, the Ca-doped samples also have a weak ferromagnetic ordering (induced by chemical pressure) and the enhanced ferroelectric property.[33] These findings make the Ca-doped $BiFeO_3$ compounds as attractive materials for the ME coupling studies, especially Ca-Ba co-doped sample.

4. SUMMARY

We investigated the electrical and magnetodielectric properties of the $BiFeO_3$, $Bi_{0.9}Ca_{0.1}FeO_{2.95}$, $Bi_{0.9}Ba_{0.05}Ca_{0.05}FeO_{2.95}$, and $Bi_{0.9}Ba_{0.1}FeO_{2.95}$ ceramic materials to compare their material properties. An enhancement in dielectric constant over the wide temperature range is observed by the doping Ca and/or Ba into $BiFeO_3$. Notably, the dielectric anomaly near 25 K in $BiFeO_3$ is shifted towards the higher temperatures (>60 K) upon the doping in conjunction with a broadening of the respective dielectric anomaly. In addition, the switchable magnetodielectric effect for the doped $BiFeO_3$ materials at room temperature is witnessed and is attributed to the improved magnetoelectric (spin-charge) coupling after the doping. Finally, the lowest leakage current is achieved for the Ba-Ca co-doped $BiFeO_3$ among the studied materials, which makes it as a potential material for magnetoelectric applications.

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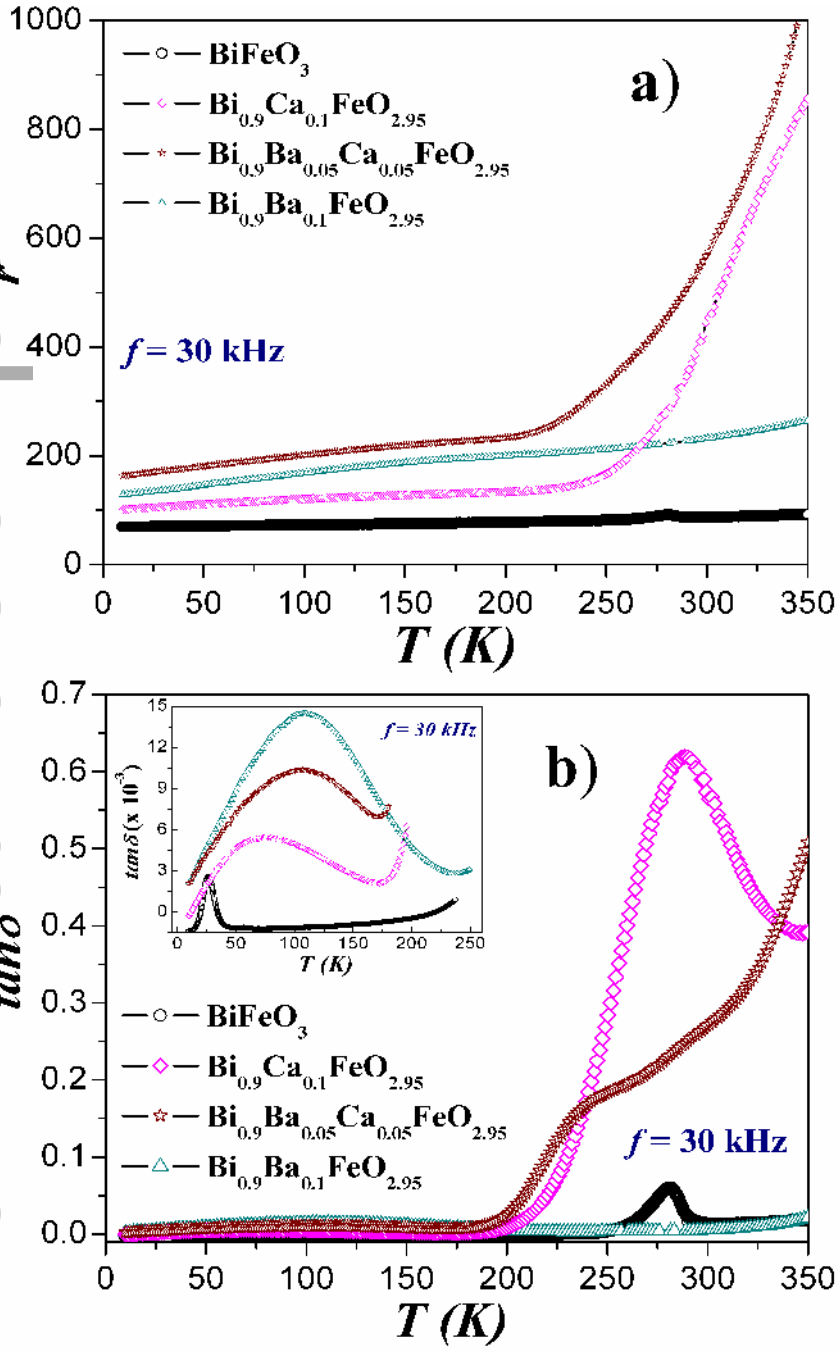
FIGURE CAPTIONS

FIGURE 1 Temperature-dependent a) dielectric constant (ε_r) and b) dielectric loss ($tan\delta$) of the undoped and doped $BiFeO_3$ samples measured at 30 kHz. Inset of Fig. 1b shows the low-temperature dielectric loss of the samples at 30 kHz.

FIGURE 2 Magnetic field dependence of relative dielectric constant of a) undoped and b) doped $BiFeO_3$ compounds at RT. The arrows in Fig. 2a illustrate the direction of an applied magnetic field.

FIGURE 3 a) The fitted data of $\Delta\varepsilon/\varepsilon$ vs H at RT for the Ca- and Ba-doped $BiFeO_3$ samples using the Eq. 2 and b) the plot of $\Delta\varepsilon/\varepsilon$ vs M for the doped $BiFeO_3$ samples at RT. Inset of Fig. 3b illustrates the plot of $\Delta\varepsilon/\varepsilon$ vs M for $BiFeO_3$.

FIGURE 4 Room temperature current density-voltage, J-V (in semi-log scale) characteristics of the undoped and doped $BiFeO_3$ samples. The inset shows logarithmic plots of J-V of the $BiFeO_3$-based samples and the solid lines represent the linear fit to the data using the Eq. 3 for the trap-free space-charge conduction mechanism.



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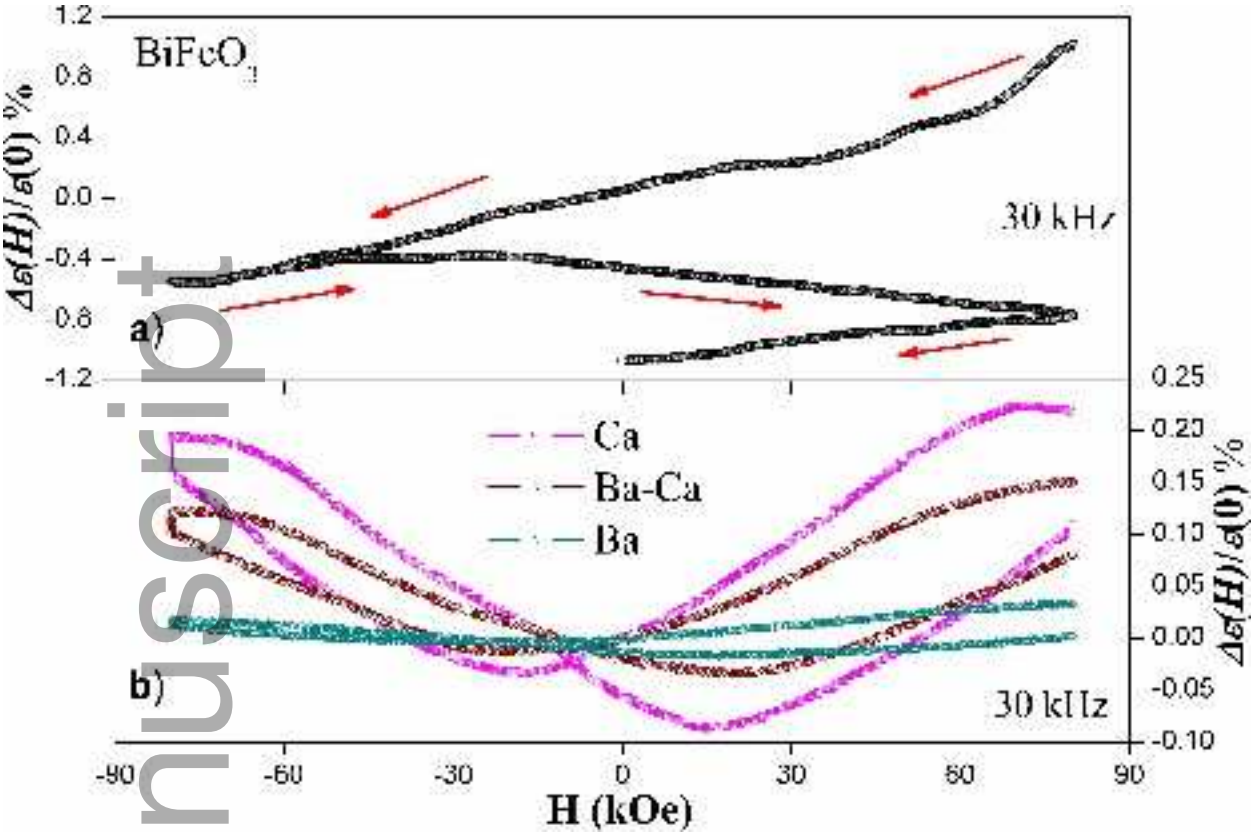

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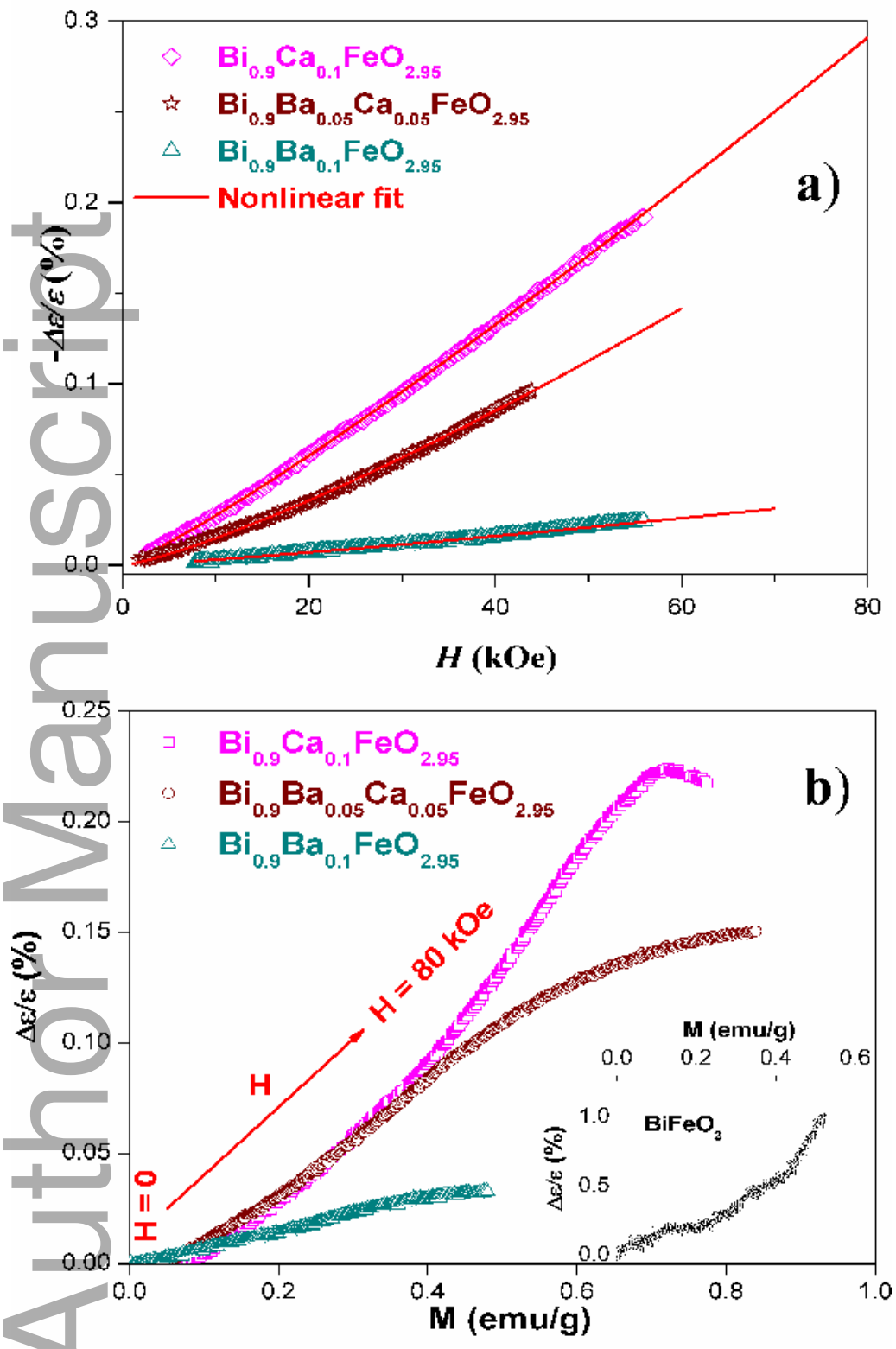

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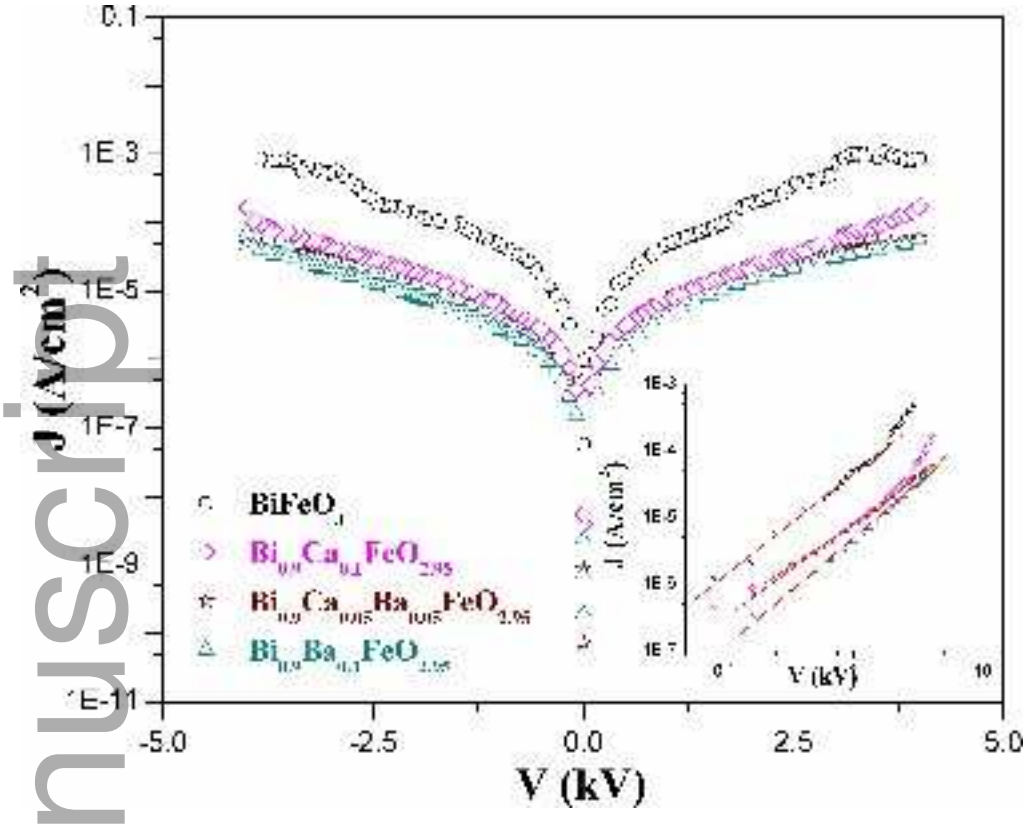

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