Room temperature multiferroic and magnetodielectric properties in Sm and Sc co-doped BiFeO$_3$ ceramics

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Abstract
In this work, Sm and Sc co-doped Bi$_{1-x}$Sm$_x$Fe$_{1-y}$Sc$_y$O$_3$ ($x = 0.00$–$0.20$; $y = 0.03$) ceramics are fabricated by a rapid liquid phase sintering method, in order to develop single-phase multiferroics with large magnetization and polarization. X-ray diffraction and Raman spectroscopic studies reveal that the ceramics are single-phase with a structural transition from rhombohedral to orthorhombic structures near $x = 0.15$. Electric and magnetic measurement results indicate that the transition significantly enhances the multiferroic properties, which stems from the Sm/Sc doping induced collapse of space-modulated spin structure and internal structural distortion. At an optimized composition of Bi$_{0.85}$Sm$_{0.15}$Fe$_{0.97}$Sc$_{0.03}$O$_3$ ($x = 0.15$), a remanent polarization of 16.5 $\mu$C cm$^{-2}$, a magnetization 0.2020 emu g$^{-1}$, and a magnetodielectric effect of 0.46% can be obtained. These results clearly demonstrate a potential application for Sm/Sc doped BiFeO$_3$ ceramics in the field of multiferroic devices.

Keywords: BiFeO$_3$, ceramics, multiferroics, ferroelectric polarization, magnetization

I. Introduction
Multiferroic materials that simultaneously exhibit ferroelectric, ferromagnetic, and/or ferroelastic orderings have attracted much attention due to their interesting fundamental physics and their potentials for new type of device applications [1–6]. Among the reported multiferroic materials, BiFeO$_3$ (BFO) is the most well-known room temperature magnetoelectric material because of its high Curie temperature (~1103 K) and Neel temperature (~643 K) [5]. The ferroelectricity is originated from the Bi$^{3+}$ ions with its lone electron pairs (6s$^2$) displaced away from the centrosymmetric position relative to the adjacent oxygen ions. The magnetism results from the partially filled $d$ orbital of Fe$^{3+}$ ion ($d^5$) [2]. Currently, large spontaneous polarization of ~100 $\mu$C cm$^{-2}$ has been reported in films and single crystals [2, 6]. However, its ferromagnetism in macroscopic size is weak due to its G-type canted antiferromagnetic (AFM) along with a long-range cycloidal spatially modulated spiral spin structure [7]. Thus, the coupling effect between the ferroelectric and ferromagnetic orders is very weak, which limits its applications in the field of multiferroic devices.

It is worth noting that the excellent ferroelectric properties are rarely reported in BFO bulk ceramics owing to the large leakage current from many factors, e.g. second phases, charge defects and nonstoichiometry [8, 9]. In addition, the weak magnetism in BFO is also needed to be improved to satisfy the requirements for applications in multiferroic devices. To improve the ferroelectric and ferromagnetic properties simultaneously, many studies have endeavored to synthesize high quality BFO ceramics [9–21]. Substitution of A- and/or B-sites by other elements in BFO has been extensively adopted with...
the aim to suppress the spatial-modulated AFM spin ordering and stabilize ferroelectric distortion [9, 12–21]. For instance, Zhang et al [14] and Zou et al [16] reported the enhanced ferromagnetism in BFO ceramics through the substitution of Bi$^{3+}$ by La$^{3+}$, and Fe$^{3+}$ by Ti$^{4+}$ ions, respectively. However, the reports on doped BFO ceramics that exhibit large polarization and magnetization simultaneously are still rather limited.

Among various co-doped BFO systems reported, substitution of non-magnetically active Sc ion into Fe-site of pure BFO compounds is able to improve sample density and ferroelectric properties due to the stable electronic configuration of Sc$^{3+}$ ions. In addition, Sc$^{3+}$ ion could help break the spatially antiferromagnetic spin-modulated structure, hence improving the ferromagnetic properties [11, 13, 21]. On the other hand, introduction of magnetically active Sm$^{3+}$ ion into Bi-site was also reported to enhance the ferroelectric and magnetic properties of BFO by reducing the concentration of oxygen vacancies and enlarging the spins canting in the corresponding sub-lattices [12]. Therefore, one can expect that the Sm and Sc co-doping may be able to greatly enhance the ferroelectric and magnetic properties simultaneously. Furthermore, the fabrication method of rapid liquid phase sintering was proved very effective for preparing pure phase BFO ceramics with good ferroelectric properties. For instance, Chen et al [8] reported a well saturated ferroelectric loop with a large remnant polarization of 25 $\mu$C cm$^{-2}$ in pure BFO ceramics. This stimulated us to synthesise the novel single-phase Sm and Sc co-doped BFO ceramics by using rapid liquid phase sintered method and study in detail their crystalline, dielectric, ferroelectric, and magnetic properties. In this paper, we study dielectric, electric polarization, magnetization, and magneto-dielectric properties of Sm and Sc co-doped BFO ceramics. It was found that Sm and Sc co-doped BFO ceramics exhibit enhanced room temperature electric polarization, magnetization, and magnetodielectric properties, which implies potential applications in multiferroic devices.

II. Experimental details

Sm and Sc co-doped Bi$_{1−x}$Sm$_x$Fe$_{1−y}$Sc$_y$O$_3$ ($x = 0.05, 0.10, 0.15, 0.20; y = 0.03$) and non-doped BFO ($x = 0$) ceramics were prepared by a rapid liquid phase sintered method. High purity Bi$_2$O$_3$, Fe$_2$O$_3$, Sm$_2$O$_3$ and Sc$_2$O$_3$ of analytical grade were used as starting materials, which were fully mixed using planetary milling with zirconia balls in ethanol for 24h. After ball milling, the resultant powders were first granulated using 3 wt% poly vinyl alcohol (PVA) solutions and then uniaxially pressed into pellets with 11.5 mm in diameter and 1 mm in thickness by applying a pressure of 9 MPa. The disk samples were sintered by rapid liquid phase sintering process of 850 °C for 20min at a heating rate of ~100 °C s$^{-1}$ and a cooling rate of ~10 °C s$^{-1}$.

The crystalline phase of non-doped and co-doped BFO samples was determined by x-ray diffraction (XRD) (PANalytical X’Pert PRO diffractometer) with CuK$_a$ radiation. Raman spectroscopy was measured using inViaReflex micro-Raman system with 633nm Ar ion laser source in backscattering geometry. Dielectric characterizations were done by high performance frequency analyzer (Alpha-A, Novocontrol Technology) with the ac drive amplitude of 100 mV from 0.1 Hz to 2 MHz. The polarization hysteresis (P-E) loops was investigated by ferroelectric tester (Radiant Technology). The magnetic properties were carried out using a vibrating sample magnetometer incorporated into a physical properties measurement system (PPMS, Quantum Design).

III. Results and discussion

Figure 1(a) shows the XRD patterns of non-doped BFO and Bi$_{1−x}$Sm$_x$Fe$_{1−y}$Sc$_y$O$_3$ ($x = 0.05, 0.10, 0.15, 0.20; y = 0.03$) ceramics at room temperature. One can find that all the samples show good crystallinity without any second phase, indicating that the rapid liquid phase sintered method is suitable for fabricating single-phase doped BFO ceramics. With increasing Sm concentration $x$, the intensities of some diffraction peaks, e.g. (006), (116) and (018), become weak and tend to disappear, starting to appear at $x \geq 0.15$. Further detailed analysis reveals that the XRD patterns for $x < 0.15$ were a rhombohedral distorted perovskite structure (space group: R3c). Once $x \geq 0.15$, the structures become similar to that of orthorhombic SmFeO$_3$ (space group of Pbnm). It can also be seen from figure 1(b) that the sharp single peak (0 1 2) in the 20 range of 21.5°–23° red shifts with increasing $x$. At $x \geq 0.15$, a new peak in the 20 range of 21.5°–23° appears, meanwhile, the doubly splitting peaks in the 20 range of 31°–33° overlap and form broadened peaks, see figure 1(c). The observation shows a structural phase transition from R3c to Pbnm near $x = 0.15$. A similar phenomenon has also been observed previously in many rare earth doped BFO ceramics [9, 14, 15, 18].
Room temperature Raman spectra of pure BFO and Bi\textsubscript{1-x}Sm\textsubscript{x}Fe\textsubscript{1-y}Sc\textsubscript{y}O\textsubscript{3} (x = 0.05, 0.10, 0.15, 0.20; y = 0.03) ceramics at wave number ranging from 100 to 650 cm\textsuperscript{-1} are plotted in figure 2. The Raman active modes of the rhombohedral BFO with R3c structure can be given as: $\Gamma = 4A_1 + 9E$ [22, 23]. From figure 2, four $A_1$ modes and eight $E$ modes can be found for all the samples. To clearly assign the observed peaks, the peak positions for non-doped BFO ceramics, which represent the active Raman modes, can be identified by fitting the measured spectra, in which the fitted spectra are decomposed into individual Gaussian components. Four $A_1$ peaks are observed at 142 cm\textsuperscript{-1}, 174 cm\textsuperscript{-1}, 223 cm\textsuperscript{-1}, and 437 cm\textsuperscript{-1}. The remaining eight $E$ peaks at 121 cm\textsuperscript{-1}, 261 cm\textsuperscript{-1}, 282 cm\textsuperscript{-1}, 351 cm\textsuperscript{-1}, 373 cm\textsuperscript{-1}, 475 cm\textsuperscript{-1}, 529 cm\textsuperscript{-1} and 630 cm\textsuperscript{-1} are also identified in the spectra. These results are consistent with previous reports in polycrystalline BFO samples [20, 23]. With increasing x, the density of Raman active mode at 174 cm\textsuperscript{-1} first increases and then decreases, while the density at 223 cm\textsuperscript{-1} reduced monotonously. Hermet et al [24] suggested that the Bi-atoms are associated with the low frequency modes below 167 cm\textsuperscript{-1}, whereas the Fe atoms are mainly related to the modes between 152 and 262 cm\textsuperscript{-1} by using first-principles calculation analysis. In our case, the former modes are related to the stereochemical activity of Bi\textsuperscript{3+} ions, which can affect the ferroelectric polarization. The latter modes can be ascribed to a significant destabilization of the FeO6 octahedron, which affects the canting of spins in iron via octahedral rotation [16]. Furthermore, the density of Raman peak around 625 cm\textsuperscript{-1} is enhanced as increasing x. Especially, the Raman peak is shifted toward a lower wave number once x \(\geq\) 0.15, which can be ascribed to the structural transition, which is consistent with the XRD results.

Figures 3(a) and (b) display the room temperature dielectric constant ($\varepsilon_r$) and loss tangent (tan $\delta$) as a function of frequency (0.1 Hz–2 MHz) for the non-doped BFO and Bi\textsubscript{1-x}Sm\textsubscript{x}Fe\textsubscript{1-y}Sc\textsubscript{y}O\textsubscript{3} (x = 0.05, 0.10, 0.15, 0.20; y = 0.03) ceramics. It is evident that the $\varepsilon_r$ and tan $\delta$ values in all the samples show a trend of decrease with increasing frequency at the lower frequency of <100 Hz, and remain almost unchanged at higher frequencies of >100 Hz. Generally, the charged defects that come from the bismuth vacancies (V\textsubscript{B}\textsuperscript{3+}), oxygen vacancy (V\textsubscript{O}\textsuperscript{2-}), and Fe\textsuperscript{3+}/Fe\textsuperscript{2+} fluctuation induced-localized charges in the BFO ceramics are able to follow the frequency of electric field, which contribute to the high dielectric constant and loss at low frequencies [25, 26]. In our samples, the increased $\varepsilon_r$ and tan $\delta$ values at lower frequencies may result...
from these charged defects due to the Bi evaporation during sintering. In contrast, the weak dependence of $\varepsilon_r$ and tan $\delta$ on frequency implies that intrinsic electrons-domains rather than the charged defects are dominating in the characteristics of $\varepsilon_r$ and tan $\delta$ above 100 Hz. Moreover, the observed increase in $\varepsilon_r$ with increasing in Sm content at all frequencies may be attributed to a possible increase in the ferroelectric polarization dipoles. During heat treatment, the volatile nature of Bi might create defects in the system, such as $V_{Bi}^{n-}$, $V_{Bi}^{3+}$ and Fe$^{3+}$/Fe$^{2+}$ fluctuation. These defects along with Bi 6s$^2$ lone pairs contribute to the charge polarization. The improved dielectric behaviors can be attributed to the reduction of these defects and favors the formation of intrinsic Bi 6s$^2$ lone pairs in the doped BFO ceramics.

Figures 4(a)–(e) plot polarization hysteresis (P-E) loops of non-doped BFO and Bi$_{1-x}$Sm$_x$Fe$_{1-y}$Sc$_y$O$_3$ ($x = 0.05, 0.10, 0.15, 0.20; y = 0.03$) ceramics at room temperature. These loops are measured at 100 Hz with different electric bias fields. Obviously, the well-saturated ferroelectric behaviors with large remanent polarization ($P_r$) are observed. The measured $P_r$ are 10.6 $\mu$C cm$^{-2}$, 19.5 $\mu$C cm$^{-2}$, 20.8 $\mu$C cm$^{-2}$, and 16.5 $\mu$C cm$^{-2}$ for $x = 0.00, 0.05, 0.10, 0.15$, respectively, together with a weak polarization of 2.4 $\mu$C cm$^{-2}$ for $x = 0.20$. From the dependence of $P_r$ on the Sm doping concentration $x$, it can be found that $P_r$ is first increased and then decreased with increasing $x$. The improved ferroelectricity at the lower doping contents may be attributed to the enhanced stoichiometric activity of Bi$^{4+}$ ions due to Sm-substitution, as supported by Raman spectra analysis. While the degraded polarization properties at the higher doping level may be well explained by considering the effect of structural transition.

Figures 5(a)–(e) show the zero field cooled (ZFC) and field cooled (FC) magnetization curves of non-doped BFO and Bi$_{1-x}$Sm$_x$Fe$_{1-y}$Sc$_y$O$_3$ ($x = 0.05, 0.10, 0.15, 0.20; y = 0.03$) ceramics at a magnetic field of 500 Oe and a temperature range of 5–400 K. For pure BFO, see figure 5(a), the ZFC and FC magnetization values reduce with decreasing the measured temperature ranging from 50 K to 400 K, which shows conventional antiferromagnetic nature, whereas a small anomaly is seen at ~260 K, which exhibits a spin glass-like transition [27, 28]. Moreover, both ZFC and FC curves show sudden jump in magnetization below 50 K, indicating a weak ferromagnetic nature. For Sm/Sc doped BFO ceramics, see figures 5(b)–(e), both ZFC and FC curves exhibit a bump in the whole temperature range, which is similar to these reports for antiferromagnetic/ferri-ferromagnetic materials [27, 28]. With increasing $x$, the broad humps in the ZFC and FC curves are shifted towards lower temperature. Meanwhile, the magnetization is also enhanced gradually. This means that the AFM nature in doped BFO is altered with the increase of Sm doped contents due to the stronger ferri-ferromagnetic interactions.

Room temperature magnetization-magnetic field ($M$-$H$) curves of non-doped and Bi$_{1-x}$Sm$_x$Fe$_{1-y}$Sc$_y$O$_3$ ($x = 0.05, 0.10, 0.15, 0.20; y = 0.03$) ceramics are shown in figure 6. Clearly, no macroscopic magnetization can be observed in the pure BFO ceramics, which is consistent with other reports [12, 14, 16]. For the Sm/Sc doped BFO ceramics, as expected, the $M$-$H$ curves exhibit clearly nonlinear behaviors. The measured remanent magnetization values ($M_r$) are 0.0209 emu g$^{-1}$, 0.0924 emu g$^{-1}$, 0.2020 emu g$^{-1}$, and 0.2568 emu g$^{-1}$ for $x = 0.05, 0.10, 0.15, 0.20$, respectively, which are remarkable higher than that of non-doped BFO (0.0008 emu g$^{-1}$). It is accepted that the enhanced ferromagnetism in doped BFO originates from the suppression or destruction of space modulated cycloidal spin structure by doping [9, 17]. For $x < 0.15$, the ferromagnetism increases slightly with rising amount of doping, meaning that a small amount of Sm can only slightly suppress but is still not enough to destroy the spin cycloid. Once $x \geq 0.15$, a structural phase transition can be triggered, likely leading to the destruction of spin cycloids so that the
Comparably, our study on Sm/Sc doped BiFeO$_3$ ceramics reveals an interaction between polarization dipole and spin fluctuations. Actually, the multiferroic properties have been reported in the Sm only doping BiFeO$_3$ ceramics, for example Yuan et al. have reported simultaneously $P_r$ of 15.09 $\mu$C cm$^{-2}$ and $M_r$ of 0.071emu g$^{-1}$ in [12]. However, the magnetization is still weak. Comparably, our study on Sm/Sc doped BiFeO$_3$ ceramics shows better multiferroic properties, in which $M_r$ of up to 0.2020 emu g$^{-1}$ along with $P_r$ of 16.5 $\mu$C cm$^{-2}$ can be realized at the optimized composition of Bi$_{0.85}$Sm$_{0.15}$Fe$_{0.97}$Sc$_{0.03}$O$_3$ ceramics. Therefore, Sc doping should play a major role in the enhanced multiferroical properties for the Sm/Sc doped BiFeO$_3$ ceramics.

To explore the coupling between ferroelectric and magnetization in the Sm/Sc doped BFO ceramics, we measured the variation of dielectric constant under various magnetic fields for an optimized composition, i.e. Bi$_{0.85}$Sm$_{0.15}$Fe$_{0.97}$Sc$_{0.03}$O$_3$ ceramics at room temperature. The magnetodielectric effect is defined as: $MD = (\varepsilon(H) - \varepsilon(0))/\varepsilon(0) \times 100\%$. Figure 7(a) shows the dependence of MD on magnetic field at 100kHz frequency. The magnetic field induced MD shift is ~0.46\% at an applied field of 15 kOe. Similar observations were reported in other doped BFO ceramics. For example, ~0.04\% for Sc-doped BFO nanoparticles [21]; ~1.05\% for La/Zr doped BFO ceramics [30]. Generally, MD effect can be explained in the framework of the Ginzburg–Landau free energy theory for the second phase transition [31]. From the theory, one can obtain a quadratic dependence of the dielectric constant on magnetization i.e. $MD \sim \gamma M^2$. Figure 7(b) shows the variation of MD versus $M^2$. It is found that the MD effect proportional to the $M^2$. Such a linear relation between MD and $M^2$ was also observed in many magnetoelectric multiferroic materials [30, 31]. This MD effect in our samples reveals an interaction between polarization dipole and spin orders, which implies a potential application for multiferroic devices.

### IV. Conclusions

We have successfully fabricated the Sm and Sc co-doped Bi$_{1-x}$Sm$_x$Fe$_{1-y}$Sc$_y$O$_3$ ($x = 0.05, 0.10, 0.15, 0.20; y = 0.03$) ceramics by using rapid liquid phase sintered method. XRD and Raman spectra confirmed that Sm-doping induced a structural transform from rhombohedral to orthorhombic structure near at $x = 0.15$. Especially, the room temperature enhanced multiferroical properties with $P_r$ of 16.5 $\mu$C cm$^{-2}$ and $M_r$ of 0.2020 emu g$^{-1}$ were obtained at an optimized composition of Bi$_{0.85}$Sm$_{0.15}$Fe$_{0.97}$Sc$_{0.03}$O$_3$ ceramics. Furthermore, a large magnetodielectric effect of 0.46\% was observed at room temperature for the optimized composition. These results imply that the Sm/Sc doped BFO ceramics may have a potential application as multiferroic materials in the future.

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