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ORIGINAL PAPER

# Effects of Europium Substitution on the Microstructure and Electric Properties of Bismuth Ferrite Ceramics

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**Abstract** $Bi_{1-x}Eu_xFeO_3$ ($x = 0.00$–$0.15$) ceramics were synthesized by solid state reaction method with rapid liquid phase sintering process at different europium content and the microstructure and electrical properties of the samples were investigated. X-ray diffraction (XRD) studies show that europium substitution has changed the structure of $BiFeO_3$ from rhombohedral R3c to orthorhombic Pnma and decreased the impurity phase. Raman spectra results also conform that a structure transition occurs at about $x = 0.20$, and indicate that the Eu substitution at Bi site can obviously affect the Bi–O bond. Impedance analyzer measurements show that both dielectric constant and dielectric loss are strongly dependent on the Eu content. The dielectric constant of the $Bi_{1-x}Eu_xFeO_3$ increases with increasing Eu content from 0.00 to 0.20, then decreases with increasing Eu content from 0.20 to 0.30. The dielectric constant measured at 100 Hz is 542.0 for the $x = 0.20$ sample, which is about 8.5 times as big as that for unsubsitituted $BiFeO_3$. The dielectric loss can be effectively decreased by the substitution of Eu for Bi. In addition, the leakage current measurements show that the substitution of Eu can effectively reduce the leakage current density of $BiFeO_3$.

**Keywords** $Bi_{1-x}Eu_xFeO_3$ · Solid state reaction · Microstructure · Electric properties

## 1 Introduction

Multiferroic materials exhibit simultaneous presence of (anti)ferroelectricity, (anti)ferromagnetism and ferroelasticity in the same phase. In recent years, great attention has been paid to the multiferroic materials due to they not only have potential applications in ferromagnetic and ferroelectric devices, but also have the ability to couple the electric and the magnetic polarization in these materials which offers an extra degree of freedom in the design and application of new functional sensors, information storages devices, etc. [1, 2]. Besides the potential applications, the fundamental physics of multiferroic materials is also interesting and fascinating [3, 4]. However, there are very few single phase multiferroic materials, especially room temperature single phase multiferroic materials [1–4]. Among those single phase multiferroic materials, $BiFeO_3$ (BFO) is the most interesting and widely studied materials due to it exhibiting ferroelectric and antiferromagnetic orders at room temperature (the Neel temperature is about 643 K, the Curie temperature is about 1103 K) [2, 3].

The material of $BiFeO_3$ has a rhombohedrally distorted perovskite structure with the space group R3c, its ferroelectric order originated from the stereochemical activity of the Bi lone electron pair, while antiferromagnetic order was mainly attributed to the partially filled 3d orbitals of the $Fe^{3+}$ ions cause G-type antiferromagnetic order [2, 5]. In current research and applications, the major problems are needed to be overcame in $BiFeO_3$ ceramics are their high leakage current and the low magnetic properties [2, 5]. The high leakage current in BFO is due to the presence of impurity phases, oxygen vacancies, defects, variable valence of Fe ions ($Fe^{3+}$ to $Fe^{2+}$) [2, 3]. The magnetic properties of BFO is low, because the cycloid-type spatial spin modulation and superimposed on G-type antiferromagnetic spin ordering, cancels out any possible net magnetization [6]. It has been shown that ion substitution is an effective method to decrease the leakage current and improve the magnetic properties of BFO ceramics [2, 6]. For examples, Bi-site

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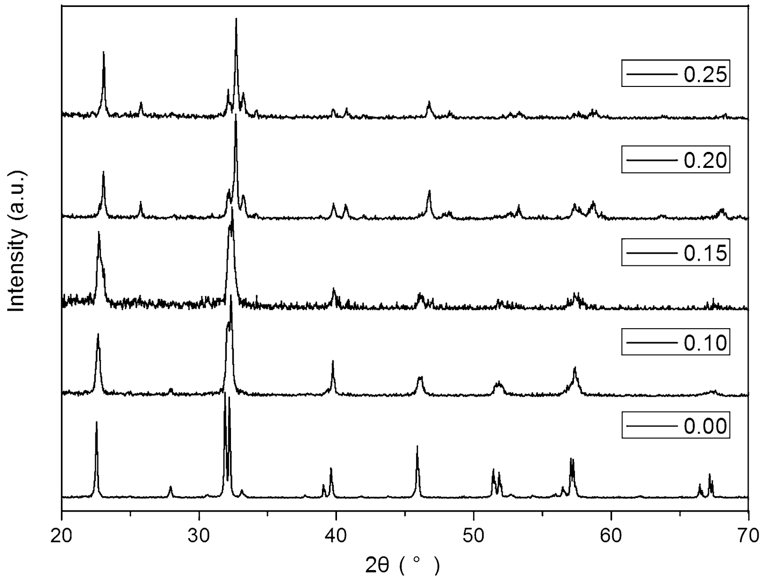


**Fig. 1** XRD patterns of $Bi_{1-x}Eu_xFeO_3$ ceramics at room temperature

substitution with La, Nd atoms and Fe-site substitution with Cr, Mn, Ti atoms et al. can suppress generation of impurity phases and suppress the spin structure modulation to release the latent weak ferromagnetic moment, improving the ferroelectric properties and magnetic properties to some extent [2, 3, 6]. In our previous work [7], the effects of Gd substitution on the crystal structure, ferroelectricity and ferromagnetism of $BiFeO_3$ ceramics synthesized by conventional solid-state reaction method have been studied. In this study, the influences of Eu substitution on the microstructure, electric properties of $BiFeO_3$ ceramics are systemically investigated.

## 2 Experimental

$Bi_{1-x}Eu_xFeO_3$ ceramics were prepared by solid state reaction method with rapid liquid phase sintering process. High purity powders of $Bi_2O_3$ (99.99%), $Eu_2O_3$ (99.99%), and $Fe_2O_3$ (99.99%) were used as starting materials. The powders were carefully weighed in stoichiometric proportions (3% bismuth excess to compensate the Bi loss) and ground thoroughly in an agate mortar for 6 h using ethanol as a medium. The mixed powders were dehydrated at 150 °C for 12 h and dry pressed into small discs with 11 mm in diameter and 1.6 mm in thickness at 16 MPa pressure. The disks were directly put into a furnace quickly sintered at 850–880 °C for 20 min followed with subsequently quenched to room temperature by taking them out of the furnace immediately, and the accuracy of the furnace is ±1 °C. The polished flat surfaces were coated with silver paste and dried at 550 °C for 30 min before taking electrical measurements.

The structures of samples were studied by Bruke D8 X-ray diffraction (XRD) with Cu–$K_\alpha$ radiation. Raman measurements were carried out at room temperature using a Renishaw inVia spectrometer, and the excitation source was the 514.5 nm line of an $Ar^+$ laser with 200 mW output. The power of the laser spot on the sample was less than 20 mW to prevent laser heating damages. The dielectric measurements were carried out in the frequency range (100 Hz–1 MHz) using an impedance analyzer (HP 4194 A). The leakage current measurements were measured by a RT 6000 ferroelectric tester at room temperature.

## 3 Results and Discussion

Figure 1 shows the XRD patterns of $Bi_{1-x}Eu_xFeO_3$ ceramics at room temperature. XRD peak intensity ratios observed in the above XRD pattern suggest polycrystalline behavior with good crystallinity. A rhombohedral perovskite structure with the space group R3c can be indexed in the pattern of the unsubsitituted $BiFeO_3$ [1–3]. A small amount of impurity phases, such as $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{39}$, is also detected in this ceramics [1, 8]. The impurity phases decrease with increasing Eu content and almost disappear when $x \geq 0.2$. The diffraction peaks in the pattern of $Bi_{0.9}Eu_{0.1}FeO_3$ and $Bi_{0.85}Eu_{0.15}FeO_3$ ceramics shift slightly toward high angle compared with those of $BiFeO_3$ ceramic, indicating that the $Bi_{0.85}Eu_{0.15}FeO_3$ ceramic maintains the same rhombohedral R3c structure as that of BFO ceramic but with a slight lattice distortion due to the Eu substitution for Bi. However, when $x \geq 0.2$, all the peaks match up to the orthorhombic structure with Pnma space group, this suggests that a structural transition from rhombohedral R3c to orthorhombic Pnma occurs at $x = 0.20$ [6, 9]. This transition is probably resulted from the smaller ionic radii of $Eu^{3+}$ (1.07 Å) than that of $Bi^{3+}$ (1.17 Å) [3].

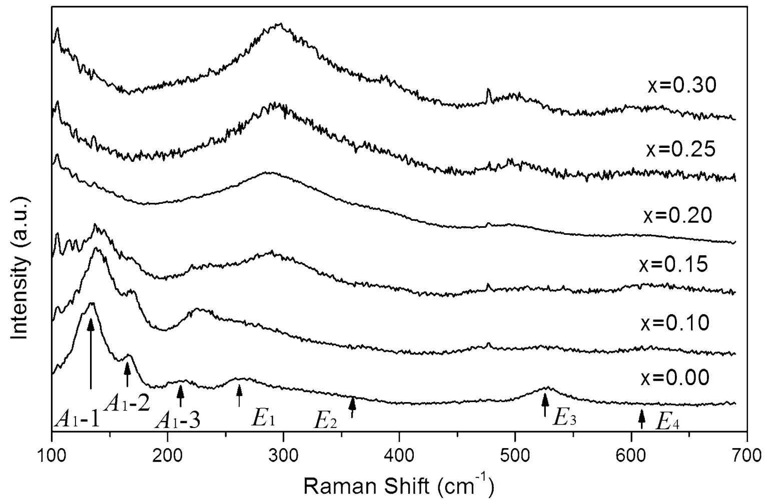


**Fig. 2** Raman spectra of $Bi_{1-x}Eu_xFeO_3$ samples measured at room temperature

Raman spectroscopy is suitable for investigating the material microscopic properties such as structure-property relations, local information due to the coherence length and time scale of the phonons, vibrational state of the imperfect material, dynamic behavior of phonons in relation to phase transitions, crystal symmetry, etc. [10]. It has been reported that the Raman active modes of the distorted rhombohedral perovskite $BiFeO_3$ (with a space group of R3c) can be summarized as:

$\Gamma = 4A_1 + 9E$ [11, 12].

The $A_1$ and $E$ modes are both Raman and IR (infra-red) active. And it has been reported that there are only several Raman active modes can be observed between 100 and 700 $cm^{-1}$ at room temperature due to the scattering intensities of some active modes is so weak as to be observed [12].

Figure 2 presents the Raman spectra of $Bi_{1-x}Eu_xFeO_3$ samples measured at room temperature, where the scanning scope is in the range of 100–700 $cm^{-1}$. It can be seen seven fundamental Raman modes in the spectrum of unsubstituted $BiFeO_3$ sample, the first three peaks at 135, 165, and 213 $cm^{-1}$ are $A_1$ modes, recorded as $A_1$-1, $A_1$-2, $A_1$-3, respectively. And the remaining four peaks at 261, 359, 526, and 605 $cm^{-1}$ are the $E$ modes of $BiFeO_3$, assigned to be $E$-1, $E$-2, $E$-3 and $E$-4, respectively [11, 12]. The mode frequencies are in good agreement with other reports [11, 12]. The intensities of $A$ modes are greater than $E$ modes in the present study.

Since Raman scattering spectra are sensitive to atomic displacements, the evolvement of Raman normal modes with increasing $x$ can provide valuable information about ionic substitution, phase transitions and electric polarization [11, 12]. It has been found that the motions of the Bi–O bounds contribute mostly to the low-frequency Raman spectrum between 70 and 300 $cm^{-1}$ [11]. Therefore, the $A_1$-1, $A_1$-2, $A_1$-3, $E$-1 modes in our experiment should be dominated by the Bi–O covalent bonds which supposedly believed to be responsible for the ferroelectric nature of the bismuth ferrite samples. From Fig. 2, it can be seen that when $x$ increases from 0.00 to 0.15, the $A_1$-1, $A_1$-2 and $A_1$-3 modes shifted to higher mode frequencies, the mode intensity had a continuous and slow change. In the $Bi_{1-x}Eu_xFeO_3$ samples, with the replacement of $Eu^{3+}$ for $Bi^{3+}$, a part of Bi–O bonds were replaced by Eu–O bonds and the stereochemical activity of the Bi lone electron pair was changed. The $Eu^{3+}$ ion with smaller size and lighter mass replaced for $Bi^{3+}$ ion may cause a decline of the stereochemical activity of the Bi lone electron pair and change the Bi–O bonds, and then affect the polarization of the samples [3, 11]. And the presence of the $A$-site ion disorder commonly brings a continuous and slow change for mode intensity [11]. The most important feature in the Raman spectra is the sudden disappearance of $A_1$-2 mode, when $x = 0.20$. This phenomena indicate that a phase transition occurs at about $x = 0.20$ in $Bi_{1-x}Eu_xFeO_3$ ceramic [11]. This is consistent with the XRD results.

In order to investigate the effect of Eu substitution on the dielectric constant and dielectric loss of the $Bi_{1-x}Eu_xFeO_3$ ceramics, the variations of dielectric constant and dielectric loss of $Bi_{1-x}Eu_xFeO_3$ ceramics at room temperature measured at selected frequencies versus Eu content $x$ have been plotted in Figs. 3 and 4 respectively. It can be seen from Fig. 3 that the dielectric constant increases dramatically with increasing Eu content from 0.00 to 0.20, then decreases with increasing Eu content from 0.20 to 0.30. Especially, the dielectric constant measured at 100 Hz reaches a maximum value of 542.0 when $x = 0.20$, 8.5 times as big as that for unsubsitituted $BiFeO_3$(63.4); and the dielectric constant measured at 5 kHz reaches a maximum value of 146.0 when $x = 0.20$, 3.4 times as big as that for unsubsitituted $BiFeO_3$(43.2). This dielectric behavior of $Bi_{1-x}Eu_xFeO_3$ ceramics might be understood in terms of oxygen vacancy

**Fig. 3** The variations of dielectric constant of $Bi_{1-x}Eu_xFeO_3$ ceramics versus Eu content $x$ measured at selected frequencies

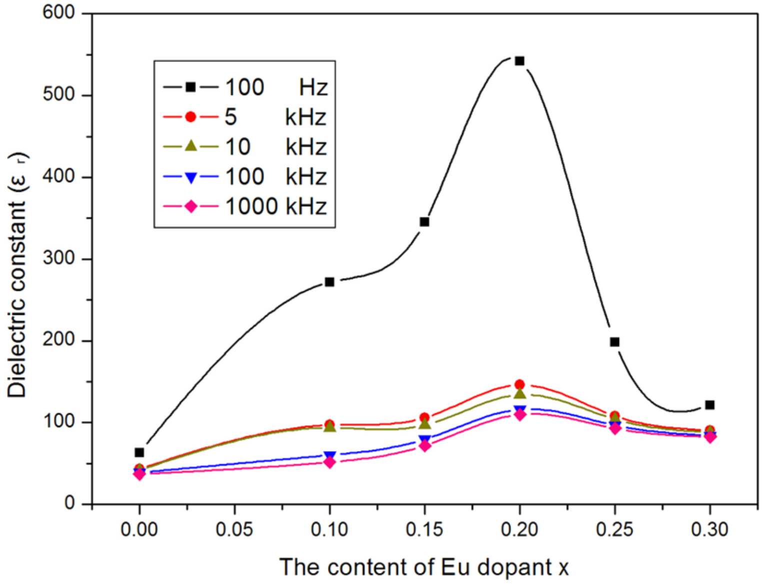
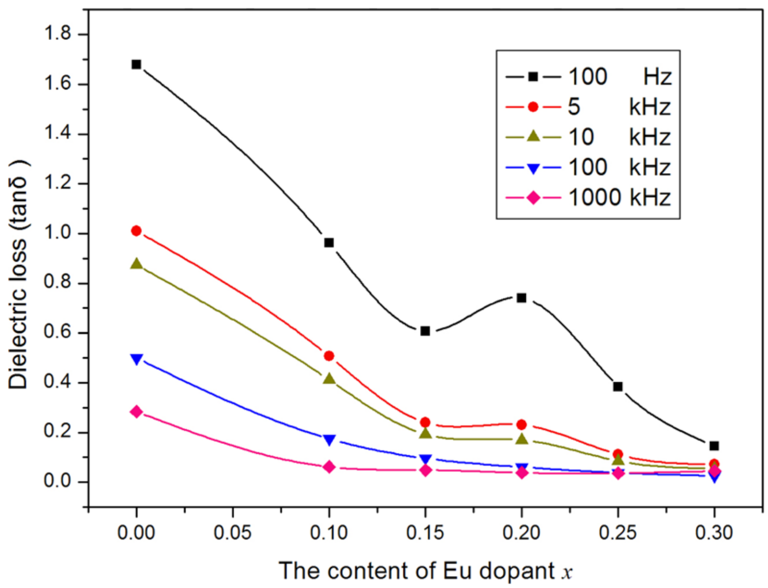


**Fig. 4** The variations of dielectric loss of $Bi_{1-x}Eu_xFeO_3$ ceramics versus Eu content $x$ measured at selected frequencies



and the displacement of $Fe^{3+}$ ions. Due to the volatilization of Bi during sintering process, there are always some oxygen vacancies in pure $BiFeO_3$, which results in relatively high conductivity and small dielectric constant $\varepsilon$. The substitution of more stable $Eu^{3+}$ for $Bi^{3+}$ in a certain range would stabilize the perovskite structure of $BiFeO_3$, and hence reduce the density of oxygen vacancies and subsequently increases the dielectric constant. Further increase in Eu content ($x = 0.20$–$0.30$) would result in a unit cell volume contraction because the ionic radius of $Eu^{3+}$ is smaller than that of $Bi^{3+}$ [3]. The free volume available for the displacement of $Fe^{3+}$ ions in the Fe–O oxygen octahedral becomes smaller and this would lead to a decrease in dielectric polarization. From Fig. 3 it can be also seen that the dependence of dielectric constant of samples with Eu content $x = 0.10, 0.15, 0.20$ and $0.25$ on the frequency is obviously, but the dielectric constant of samples with $x = 0.30$ is almost independent of frequency. The result is useful for the practical application of this material. The dielectric loss of $Bi_{1-x}Eu_xFeO_3$ ceramics as a function of Eu content is shown in Fig. 4. The dielectric loss $\tan\delta$ decreases significantly after being doped by $Eu_2O_3$, and the minimum dielectric loss is reached when Eu content is 0.3. The dielectric loss $\tan\delta$ for the samples with $x = 0.10, 0.15, 0.20, 0.25$ and 0.30 at 5 kHz is about 0.507, 0.240, 0.231, 0.112 and 0.072 respectively, which reduced by 49.8%, 76.2%, 77.1%, 88.9% and 99.3% when compared with that of the unsubstitutied $BiFeO_3$ sample (1.010). Furthermore, the dielectric loss in samples with $x = 0.25$ and 0.30 has a relatively small frequency dependence.

**Fig. 5** The dielectric constant of the $Bi_{1-x}Eu_xFeO_3$ ($x = 0.00$–$0.30$) as a function of frequency

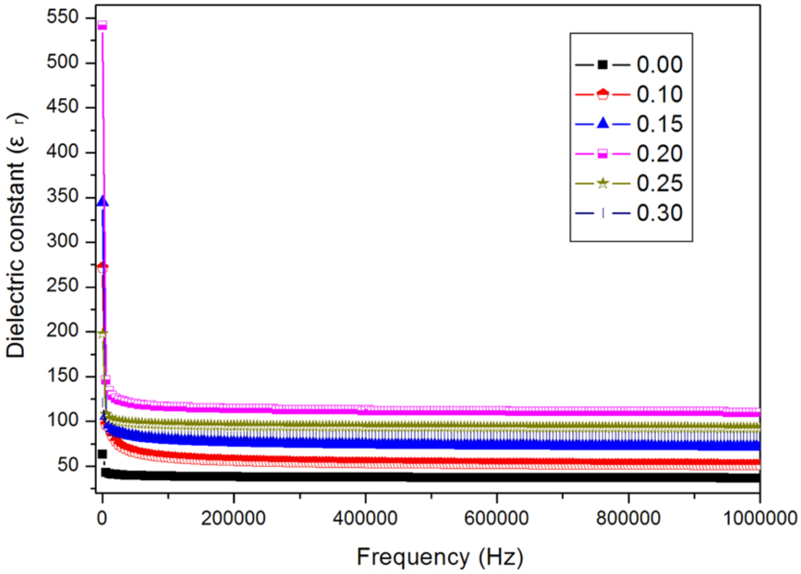


**Fig. 6** The dielectric loss of the $Bi_{1-x}Eu_xFeO_3$ ($x = 0.00$–$0.30$) as a function of frequency

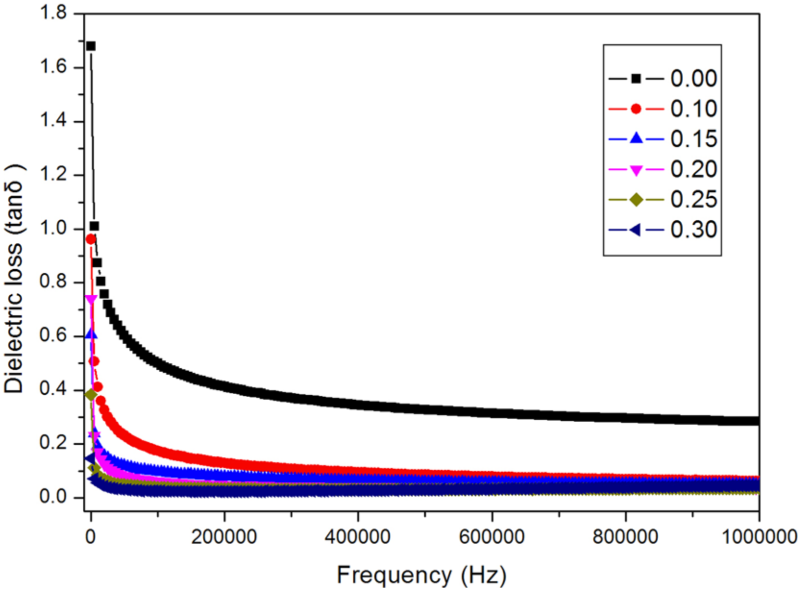


Figure 5 shows the dielectric constant of the $Bi_{1-x}Eu_xFeO_3$ ($x = 0.00$–$0.30$) as a function of frequency at room temperature. From Fig. 5, it can be seen that the dielectric constant of all the samples decreases with increasing frequency from 100 Hz to 1 MHz. This observation can be explained by the phenomenon of dipole relaxation process, the dipoles are able to follow the frequency of the applied field at low frequencies, while they are incapable of following the frequency of the applied field at high frequencies [3]. It is obvious that the dielectric constant of unsubstituted $BiFeO_3$ is lower than that of the Eu-substituted $BiFeO_3$ in the measured range of 100 Hz–1 MHz, it means that the dielectric property of $BiFeO_3$ can be improved greatly after being doped with Eu, which reaches a maximum at a Eu content $x = 0.20$. For all the samples investigated, the curves display smooth plateaus in a broad frequency range of 5 kHz–1 MHz, this suggests the dielectric constant of the samples has a small frequency dependence, especially in the higher frequency scope. Figure 6 shows the dielectric loss ($\tan\delta$) as a function of the frequency for $Bi_{1-x}Eu_xFeO_3$ ceramics. The frequency dependences of dielectric loss is similar to the dielectric constant, the dielectric loss also decreases smoothly with increasing the frequency. All the Eu-substituted $BiFeO_3$ samples have a smaller dielectric loss than that of unsubstituted $BiFeO_3$. It can be observed that the dielectric loss is quite stable over the entire frequency range investigated, particularly in the frequency range between 50 kHz and 1 MHz.

In order to get more insight into the electrical properties, the leakage current measurements were carried out.

**Fig. 7** Leakage current as a function of applied electrical field in $Bi_{1-x}Eu_xFeO_3$ ceramics

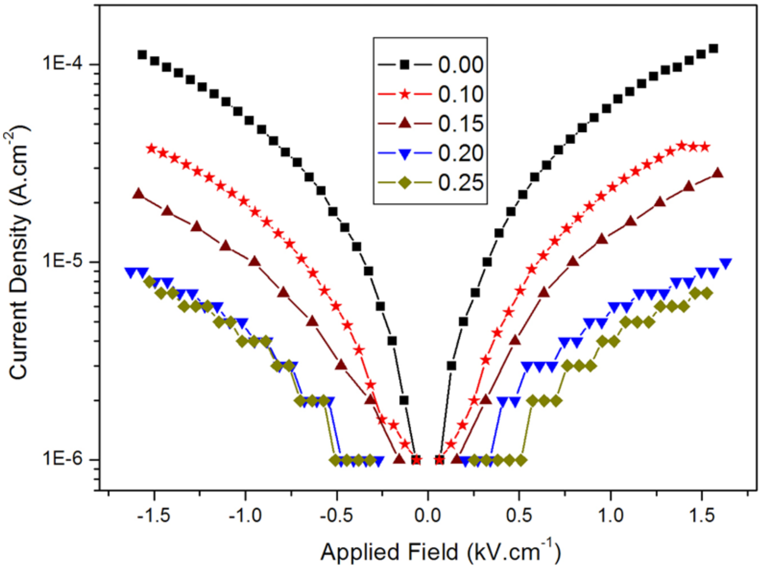


Figure 7 exhibits the dependence of the leakage current density ($J$) of the $Bi_{1-x}Eu_xFeO_3$ ceramics on the applied electric field ($E$). It can be seen from Fig. 7 that the leakage current increases with increasing the electric field, all the $J$–$E$ curves have good symmetry under positive and negative electric fields. The $BiFeO_3$ ceramic exhibits a relatively high leakage current density, while the Eu-substituted $BiFeO_3$ ceramics have lower leakage current densities. Under an applied electric field of 1.5 kV/cm, the leakage current density of $BiFeO_3$, $Bi_{0.9}Eu_{0.1}FeO_3$, $Bi_{0.85}Eu_{0.15}FeO_3$, $Bi_{0.8}Eu_{0.2}FeO_3$ and $Bi_{0.75}Eu_{0.25}FeO_3$ is $1.1 \times 10^{-4}$ $A{\cdot}cm^{-2}$, $3.8 \times 10^{-5}$ $A{\cdot}cm^{-2}$, $2.6 \times 10^{-5}$ $A{\cdot}cm^{-2}$, $9 \times 10^{-6}$ $A{\cdot}cm^{-2}$ and $7 \times 10^{-6}$ $A{\cdot}cm^{-2}$, respectively. This indicates that the leakage current decreases monotonically with the increase of the Eu content. Therefore, it is clear that the substitution of Eu for Bi can effectively reduce the leakage current density of the $BiFeO_3$ ceramics, which is consistent with the results of dielectric loss discussed above. It is believed that the high leakage current in $BiFeO_3$-base materials is caused by oxygen vacancies and iron ions with different valences ($Fe^{3+}$ and $Fe^{2+}$) via the formation of shallow energy centers [13]. Since the strength of Eu–O bond ($557 \pm 13$ kJ/mol) is higher than that of Bi–O bond ($343 \pm 6$ kJ/mol) [14], the substitution of Eu for Bi in the A site can stabilize the perovskite structure, decrease the volatilization of Bi, lower the concentration of oxygen vacancies and the amounts of $Fe^{2+}$. Therefore, the substitution $Eu^{3+}$ for $Bi^{3+}$ can significantly decrease the leakage current density in the $BiFeO_3$ ceramics.

## 4 Conclusions

$Bi_{1-x}Eu_xFeO_3$ ceramics with varying $x$ from 0.00 to 0.30 were prepared using solid state reaction method with rapid liquid phase sintering process. The effect of Eu substitution on the microstructure and electric behaviors of the $BiFeO_3$ was investigated.

1. The measurements of XRD and Raman spectra reveal that a structure transition occurs at about $x = 0.20$. The Eu substitution can suppress the impurity phase and influence the Bi–O bonds in the samples.

2. Dielectric measurements show that the dielectric constant, dielectric loss and their frequency responses can be changed dramatically by substitution of Eu for Bi. Both dielectric constant and dielectric loss of $Bi_{1-x}Eu_xFeO_3$ ceramics decrease with increasing frequency between 100 Hz and 1 MHz. The value of dielectric constant increases with increasing Eu content from 0.00 to 0.20, while decrease when Eu content exceeds 0.20. The dielectric loss decreases with increasing Eu content.

3. Leakage current measurements show that the substitution of Eu can effectively reduce the leakage current density of $BiFeO_3$.

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