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Effect of A and B-site substitution with Pb, La and Ti on phase stabilization and multiferroic properties of BiFeO₃

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ABSTRACT

The work presents a comparative study of the effects of divalent (Pb), trivalent (La) and tetravalent (Ti) substituents on the multiferroic properties of BiFeO₃ (BFO). Both A and B-sites were substituted to obtain the compositions i.e. (Bi₁₋ₓLaₓPb₀.₁₋ₓLaₓ₁₋₎₀₀₂)₀₁₋₅₀₀₂O₃ (x = 0, 0.1, 0.2 and 0.3, 0.05, 0.1, 0.15). Each of the substituent was particularly chosen i.e. Pb was chosen to keep the lone pair character which is the similar case as Bi ion. Additionally isovalent La was chosen to achieve single phase by reducing Bi volatilization. Both these ions, on substitution, stabilized the crystal structure and suppressed the formation of extra phases which are unavoidable in pure BFO. All the Ti substituted and Bi₀.₈LaₓFeO₃ compositions exhibited rhombohedral perovskite (R3c) phase, while Bi₀.₈PbₓFeO₃ and Bi₀.₈LaₓPbₓFeO₃ exhibited cubic phase. Mössbauer measurements revealed that impurity phase in case of compositions with divalent and trivalent substituents, disappeared completely when Ti substituted Fe. For all the compositions Fe ions were found in +3 state. High temperature dielectric properties showed that all the compositions were ferroelectric with paraelectric transition lying well above the room temperature. Weak ferromagnetism was found in Ti substituted compositions where coercivity was found to increase as the Ti concentration increases. All the BFO samples substituted with Pb, exhibited a dielectric anomaly in the temperature range, 100 °C ≤ T ≤ 250 °C. A systematic reduction in the intensity of the dielectric anomaly peak was observed as a function of Ti concentration which indicates that the anomaly is related to the conductivity and is element specific. However, Mössbauer data revealed absence of Fe²⁺ state, which ensured that it was not related with the presence of Fe²⁺ ions. Saturation polarization was found to increase as Ti concentration increased from 0% to 10%.

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1. Introduction

Materials possessing more than one ferroic orders (ferroelectric and ferromagnetic or ferroelastic) simultaneously are called multiferroic. Strong magnetoelectric coupling can be used to manufacture devices to meet the present and future needs, such as high-speed memories with magnetically and electrically addressable states, magnetically tunable tunnel-junctions, filters, sensors, and transducers [1,2]. From the last few decades (BiFeO₃) BFO has attracted the focus of researchers because it is the only single phase material which is multiferroic at room temperature. BFO has high Curie (Tc ~ 830 °C) and Néel temperatures (Tn ~ 367 °C) [3]. BFO has perovskite structure (space group R3c) at room temperature, with rhombohedral distortion along [1 1 1] direction [4]. The temperature variation introduces consecutive structural phase transitions from the ferroelectric α-phase (rhombohedral space group R3c with a = 5.6 Å, c = 13.9 Å and γ = 120°) to two para-electric phases. First, the process leads to the orthorhombic β-phase (space group Pbnm) with a = 5.613 Å, b = 5.647 Å, and c = 7.971 Å) between 820 °C and 830 °C and then in the range 925–933 °C, to the cubic γ-phase (space group Pm-3m with a = 3.992 Å), which decomposes above 960 °C. Pure BFO is ferroelectric and G-type antiferromagnetic, having
noncollinear spins and has a spiral spin structure of wavelength \( \sim 62 \text{ nm} \). The ferroelectric behavior comes from Bi 6s lone pair electrons while the magnetic behavior arises mainly from the partially filled d-orbital electrons in Fe [4,5]. Structure of BFO is different from other perovskites in the sense that the A-site is occupied by trivalent Bi\(^{3+}\) cations, whereas most of the perovskites possess divalent rare earth cations on A-site. Typical rare earth cations have partially filled f-shells which are spatially placed nearer to the core region and are protected by outer shells of inert 5s and 5p orbitals. This is the reason that rare earth ions are non-reactive and cannot make stable chemical bonds with oxygen ions in its neighborhood. Contrary to rare earth cations, Bi\(^{3+}\) cations have 6s electrons in the valence shell, making possible magnetic behavior in terms of spatial positions and electron energy bands, which may either produce covalent bonds with oxygen ions (Bi 6s–O 2p) or make 6s lone pairs. This 6s lone pair introduces magnetic ordering in BFO [5,6]. Lone-pair driven mechanism is used for simultaneous existence of magnetism and ferroelectricity [7], where the A-site drives the displacement and the incompletely filled "d" shell on the B-site contributes to the magnetism. Examples include BiFeO\(_3\) [8], BiMnO\(_3\) and PbVO\(_3\) [7].

However, there are some critical issues with BFO. The leakage current is too high which hinders the potentially excellent ferroelectric properties of this material. The leakage current arises due to impurity phase, multiple valent state of Fe ions and oxygen vacancies [9]. Moreover, the spiral spin-modulated magnetic structure of BFO having a wavelength of \(~ 62 \text{ nm}\) makes it anti-ferromagnetic rather than ferromagnetic which leads to the absence of macroscopic magnetization which in turn weakens the magnetoelectric coupling. Furthermore, the appearances of secondary phases like Bi\(_2\)Fe\(_2\)O\(_6\), Bi\(_2\)Fe\(_2\)O\(_9\), Bi\(_2\)O\(_3\) and Fe\(_2\)O\(_3\) is another big issue. There is an ongoing effort from researchers to address these issues and some issues have been resolved by the use of suitable processing techniques and by introducing suitable dopants at both A and B-sites [10–12]. For example, the Bi\(^{3+}\) volatilization can be controlled by replacing a small amount of Bi\(^{3+}\) cations with some other suitable non-volatile cations. The substitution is also critical to optimize the synthesis conditions to obtain single phase compositions. Doping of trivalent cations, like Lanthanides (La\(^{3+}\), Nd\(^{3+}\), Gd\(^{3+}\), Pr\(^{3+}\), Sm\(^{3+}\)) [13–17] and divalent cations like (Sr\(^{2+}\), Pb\(^{2+}\) and Ba\(^{2+}\)) for bismuth have good response to obtain pure phases. Structural transitions have also been reported with such dopants, leading to enhanced multiferroic properties [18].

In the present work, we report a detailed study of the effect of co-doping on structural, dielectric and magnetic properties of BFO. Here A-site was doped with La\(^{3+}\) and Pb\(^{2+}\) to stabilize the perovskite crystal structure and to control the bismuth volatilization. It has been suggested that La\(^{3+}\) substitution stabilizes the perovskite structure and reduces formation of oxygen vacancies. Moreover, it is the key to replace Bi\(^{3+}\) with Pb\(^{2+}\) to keep concentration of lone pair ions up to certain value; hence Pb\(^{2+}\) was specifically chosen. But presence of Pb\(^{2+}\) ions lead to the formation of oxygen vacancies due to the charge compensation, since the oxidation state of Pb\(^{2+}\) is lower compared to Bi\(^{3+}\). Therefore Fe\(^{3+}\) is substituted with higher valency Ti\(^{4+}\) cations to suppress oxygen vacancies and to improve the resistivity. Here one of the goals is to look in to the magnetism in BFO. Generation of weak ferromagnetic response in Ti substituted samples showed stabilization of the antiferromagnetic spin spiral structure. Consistently polarization has been seen to increase with Ti concentration which showed enhancement of resistivity with a corresponding decrease in the leakage current.

### 2. Experimental section

The samples BiFeO\(_3\) (BFO), Bi\(_{0.9}La_{0.1}Fe_{0.95}Ti_{0.05}O_3\) (LP(10)-T0), Bi\(_{0.9}La_{0.1}Fe_{0.95}Ti_{0.05}La_{0.1}O_3\) (LP(10)-T5), Bi\(_{0.9}La_{0.1}Fe_{0.95}Ti_{0.05}Pb_{0.1}O_3\) (LP(10)-T10), Bi\(_{0.9}La_{0.1}Fe_{0.95}Ti_{0.05}Pb_{0.1}La_{0.1}O_3\) (LP(10)-T15), Bi\(_{0.9}Pb_{0.1}Fe_{0.95}O_3\) (P(20)) and Bi\(_{0.9}La_{0.1}Fe_{0.95}O_3\) (L(20)) were prepared by solid state reaction method. Selection of calcination and sintering conditions to obtain single phase compositions. Doping of trivalent ions up to certain value; hence Pb\(^{2+}\) was specifically chosen. But presence of Pb\(^{2+}\) ions lead to the formation of oxygen vacancies due to the charge compensation, since the oxidation state of Pb\(^{2+}\) is lower compared to Bi\(^{3+}\). Therefore Fe\(^{3+}\) is substituted with higher valency Ti\(^{4+}\) cations to suppress oxygen vacancies and to improve the resistivity. Here one of the goals is to look in to the magnetism in BFO. Generation of weak ferromagnetic response in Ti substituted samples showed stabilization of the antiferromagnetic spin spiral structure. Consistently polarization has been seen to increase with Ti concentration which showed enhancement of resistivity with a corresponding decrease in the leakage current.

### 3. Results and discussion

Fig. 1(a) shows the X-ray diffraction (XRD) patterns for the compositions (Bi\(_{1-x}\),La\(_{x}\),Pb\(_{x}\),Fe\(_{1-x}\),Ti\(_{x}\))\(_2\)O\(_3\) (x = 0, 0.1 and 0.20, and z = 0, 0.05, 0.1 and 0.15) measured at room temperature. XRD confirmed the distorted rhombohedral perovskite structure for pure BFO with space group R3c. Some low intensity diffraction peaks of impurity phase (Bi\(_{2}\)Fe\(_2\)O\(_6\) at 2\(\theta\) = 27.8°, 27.44° and 32.858°) were also observed in the XRD pattern of pure BFO. The occurrence
of this phase is unavoidable during the kinetics of BFO formation due to Bi volatization. The occurrence of this phase is very common in BFO and is widely reported in literature [19,20]. Some authors also reported the presence of other phases such as FeO, and Bi$_2$FeO$_3$ [21,22]. The achievement of single phases for samples doped with La$^{3+}$ and Pb$^{2+}$ indicates that these dopants suppress the formation of secondary phases. For the co-doped compositions, single phase structure was obtained up to 10% Ti substitution. Co-doped sample with 15% Ti exhibits an extra low intensity diffraction peak of La$_2$Ti$_2$O$_7$ (PCPDF # 70-1690). Therefore for the co-doped system, the saturation level for Ti doping occurs somewhere between 10% and 15% concentrations. However, it is important to point that intensity associated with La$_2$Ti$_2$O$_7$ is very low even for highest Ti concentration. Thus substitution of A and B-site in BFO with these dopants yields single phases and suppress the formation of the secondary phase.

To further highlight the effect of La$^{3+}$, Pb$^{2+}$, and Ti$^{4+}$ substitution on the structure of BFO, XRD patterns in the range 30–34° are shown in Fig. 1(b). Two clearly well-separated diffraction peaks, (104) and (110), in the vicinity of 2θ = 32° were found to merge into a single peak (1 1 0) for P(20) sample. However, for L(20) sample, no change in diffraction peaks related to (104) and (110) planes were observed as shown in Fig. 1(b). This reflects that Pb$^{2+}$ doping has a tendency to transform the structure from rhombohedral (R3c) to cubic (Pm-3m), while La$^{3+}$ doping has no effect on the structure. This might be due to the reason that, the effective ionic radii of La$^{3+}$ (1.03 Å) and Bi$^{3+}$ (1.03 Å) are nearly equal while that of Pb$^{2+}$ (1.19 Å) is larger. In addition to the ionic radii, same oxidation states of La and Bi might also play an important role to keep the crystal structure of the sample unchanged. For the compositions where B-site is not doped while the A-site is co-doped with Pb and La, crystal structure was mostly cubic with a shoulder visible at higher 2θ which indicates that both rhombohedral and cubic phases co-exist for this composition, (see Fig. 1(b)). With the introduction of Ti at B-site, the tendency of crystal structure to exhibit rhombohedral phase is increased.

4. Mössbauer measurements

Fig. 2 shows the room temperature Mössbauer spectra of all compositions. The Mössbauer parameters extracted from the best fits are given in Table 1. Mössbauer spectra of pure BFO show both sextet and a singlet. Sextet corresponds to pure BFO phase and indicates the presence of magnetic ordering in the system, while the singlet corresponds to the impurity phase (Bi$_{25}$O$_{40}$) which shows that the impurity phase does not exhibit long range order at room temperature [23]. The sextet having hyperfine field ($H_{hf}$) of about 500 kOe is considered as originating from the iron ions located on sites with octahedral symmetry. The isomer shift ($\delta$) of both spectra (sextet and singlet) correspond to Fe$^{3+}$ state and the value of the quadruple splitting ($\Delta$) is nearly equal to zero, indicating the presence of cubic symmetry. Relative area under the singlet peak indicates that the impurity phase of about 20% of the total phase. The presence of this impurity phase is also evident from the XRD pattern for this sample. However, contribution of the impurity phase decreases to 10% for both LP(10)-T0 and P(20) compositions. The impurity phase disappears completely when Ti substitutes Fe. The decrease in the percentage of the impurity phase shows that these dopants stabilize the structure. We note that the values of isomer shift, $\delta$, are reported to be in the range of 0.6–1.7 mm/s for Fe$^{3+}$, 0.05–0.5 mm/s for Fe$^{2+}$ and ~0.15 to 0.05 for Fe$^{4+}$ [24], whereas values of $\delta$ for all samples obtained in our case lie in the range between 0.35 and 0.40. The measured $\delta$ values indicate the presence of all iron ions in Fe$^{3+}$ state.

Moreover, value of $H_{hf}$ decreases from 501 to 484 kOe as the Ti content increases from 0% to 15% at Fe-site. This is consistent with the fact that Ti is a non-magnetic ion which reduces the strength of the internal magnetic field (see Table 2).

![Image](https://via.placeholder.com/400)

**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spectrum</th>
<th>$H_{hf}$ (kOe)</th>
<th>$\Delta$ (mm/s)</th>
<th>$\delta$ (mm/s)</th>
<th>Relative area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BFO</td>
<td>Sextet</td>
<td>502</td>
<td>0.22</td>
<td>0.35</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>Singlet</td>
<td></td>
<td>0.00</td>
<td>0.17</td>
<td>20</td>
</tr>
<tr>
<td>LP(10)-T0</td>
<td>Sextet</td>
<td>501</td>
<td>-0.11</td>
<td>0.35</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>Singlet</td>
<td></td>
<td>0.00</td>
<td>0.17</td>
<td>10</td>
</tr>
<tr>
<td>LP(10)-T5</td>
<td>Sextet</td>
<td>495</td>
<td>-0.08</td>
<td>0.39</td>
<td>100</td>
</tr>
<tr>
<td>LP(10)-T10</td>
<td>Sextet</td>
<td>489</td>
<td>-0.11</td>
<td>0.39</td>
<td>100</td>
</tr>
<tr>
<td>LP(10)-T15</td>
<td>Sextet</td>
<td>484</td>
<td>0.02</td>
<td>0.40</td>
<td>100</td>
</tr>
<tr>
<td>P(20)</td>
<td>Sextet</td>
<td>500</td>
<td>-0.08</td>
<td>0.38</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>Singlet</td>
<td>0.00</td>
<td>0.10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>L(20)</td>
<td>Sextet</td>
<td>503</td>
<td>0.00</td>
<td>0.39</td>
<td>100</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>Sample’s name</th>
<th>$P_s$ ($\mu$C/cm$^2$)</th>
<th>$P_t$ ($\mu$C/cm$^2$)</th>
<th>$E_c$ (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BFO</td>
<td>1.5</td>
<td>0.125</td>
<td>0.87</td>
</tr>
<tr>
<td>L(20)</td>
<td>1.53</td>
<td>0.89</td>
<td>5.31</td>
</tr>
<tr>
<td>P(20)</td>
<td>1.3</td>
<td>0.6</td>
<td>4.457</td>
</tr>
<tr>
<td>LP(10)-T0</td>
<td>0.55</td>
<td>0.255</td>
<td>5.375</td>
</tr>
<tr>
<td>LP(10)-T5</td>
<td>1.027</td>
<td>0.5</td>
<td>4.8</td>
</tr>
<tr>
<td>LP(10)-T10</td>
<td>1.612</td>
<td>0.64</td>
<td>2.76</td>
</tr>
<tr>
<td>LP(10)-T15</td>
<td>1.001</td>
<td>0.431</td>
<td>3.4</td>
</tr>
</tbody>
</table>
5. Dielectric properties

The temperature dependence of dielectric constant ($\varepsilon$) and loss tangent ($\tan \delta$) of all compositions were measured at 10 kHz and are shown in Fig. 3. In the case of pure BFO, nearly an invariant behavior for in-phase part of dielectric constant ($\varepsilon$) and $\tan \delta$ in the low-temperature region was observed as shown in Fig. 3(a). While in the higher temperature regime ($T > 250^\circ C$), the values of both these parameters increased significantly with rise in temperature. Steady increase in the $\varepsilon$ with temperature in the region $T < T_C$ is described in terms of the response of an anharmonic solid [25,26]. However, rapid increase in $\varepsilon$ as the sample approached phase transition, as in the present case, is also attributed to the thermal activation of dipoles over orientational barriers [26]. Thermal activation effects have commonly been observed in all the compositions. However, in-phase part exhibits an anomalous feature, specifically for the case of Pb$^{2+}$ doped compositions. In compositions where Bi-site is substituted with Pb, anomalous peak has been observed as shown in Fig. 3(b)–(f). Consistently, $\tan \delta$ in some compositions also exhibited variation in the similar temperature region where the anomalous peak appears in the in-phase part. In contrary, there is no trace of such response in the La substituted BFO, i.e. L(20). This shows that this peak is actually related to the presence of Pb$^{2+}$ ions, occupying the A-site. Polomska et al. [27] attributed this anomaly to a transient interaction of oxygen ion vacancies with the Fe$^{3+}$/Fe$^{2+}$ redox couple. Similar results have

![Graphs showing dielectric properties](image_url)
been found for Y-doped BFO, especially for Bi0.85Y0.15FeO3, showing that along with a specific dopant, the concentration of oxygen vacancies which varies with the concentration of dopant plays a key role to improve the dielectric properties and hence shows a wide peak in the in-phase part of the dielectric function \(\varepsilon(T)\) [28].

The Ti\(^{4+}\) is in higher oxidation state compared to Fe\(^{3+}\), therefore Ti substitution at B-site reduces the concentration of oxygen vacancies and hence reduces the conductivity. The intensity of anomaly is highest for LP(10)-T0 and it decreases as the Ti content increases as shown in Fig. 3(b)-(e). In general, as the Ti concentration increases, concentration of oxygen vacancies will decrease leading to decrease in concentration of Fe\(^{3+}\). Therefore Fe\(^{3+}\)/Fe\(^{3+}\) ratio will decrease and hence the associated peak will disappear from the in-phase part of the dielectric function. Hussain et al. [18] reported that for the case of divalent substitution \((Bi_{0.75}FeO_3)\) FeO\(_3\) \((A = Ba, Pb and Sr)\), dielectric anomaly was observed only for the case of Pb substitution. The absence of such an anomaly in the case of either the pure BFO or L(20) samples suggests that it is related with the specific divalent ion. Loss tangent measured for LP(10)-T0, LP(10)-T10, LP(10)-T15 and LP(20) as shown in Fig. 3(b), (d), (e) and (g) respectively, do not show any clear peak in the temperature range where the in-phase part exhibited anomalous behavior. This indicates that the dielectric anomaly is not a phase transition. On the other hand, in the loss tangent, weak peaks for the LP(10)-T5 (Fig. 3(c)) and P(20) doped compositions (Fig. 3(f)) were observed. These additional low intensity peaks in the loss tangent may arise due to the presence of small additional phases in the major phase of these compositions, as shown in XRD.

In the present studies absence of Fe\(^{2+}\) ions as confirmed by Mössbauer studies, suggests that this peak is not associated with the redox couple. This anomaly arises in the samples where A-site is doped with Pb. As Ti concentration increases, resistivity increases and peak associated with this anomaly decreases.

The reported Néel temperature of BFO is almost 370 °C and its ferroelectric Curie temperature is nearly 830 °C [3]. For all compositions, as temperature increases from the room temperature, both \(\varepsilon\) and \(\tan\delta\) increases. This is the expected behavior for the dielectric susceptibility of a ferroelectric for \(T < T_C\). As shown in Fig. 3, for all the compositions, ferroelectric \(T_C\) lies above the highest measured temperature i.e. \(T = 390^\circ\) C. We observed change in slope for \(T > 250^\circ\) C and these transitions lie in the region where Néel temperature is expected. For the un-substituted BFO, the \(T_N\) is around 370°C. Landau–Devonshire theory of phase transition predicts this type of dielectric anomaly in magnetoelectrically ordered systems and is related with the vanishing magnetic order on the electrical order [29]. As shown in the Fig. 3(a) (for BFO) \(T_N\) lies above the maximum measured temperature whereas for L(20) sample, \(T_N\) is found to be around 360°C. For the P(20) composition, instead of emergence of peak there is clear change in slope around 320°C. Néel temperature for the LP(10)-T0 lies above the 400 °C as shown in Fig. 3(b). With the increase in Ti concentration from 0% to 5%, 10% and 15%, \(T_N\) is found to be equal to 365 °C, 325 °C and 350 °C, respectively. However, there is no compositional dependent variation in \(T_N\), which is perhaps due to the fact that A-site substitution is constant. Therefore all the compositions are expected to exhibit antiferromagnetic behavior at room temperature with a possible weak ferromagnetic response which will be investigated in the next section where magnetic response will be discussed.

6. Magnetic properties

Fig. 4(a)-(d) shows the magnetic hysteresis (M-H) loops of \((Bi_{1-x},La,Pb)_x(Fe_{1-y}Ti)_3O_7\) \((x, y = 0, 0.1, 0.20 and z = 0, 0.05, 0.1 and 0.15)\) samples measured at 300 K and 75 K, for maximum applied magnetic field strength of 3 T. Magnetic hysteresis loops for pure BFO (shown in Fig. 4(a) and 4(b)) exhibit linear field dependence, which is an indication of antiferromagnetic (AFM) behavior. We did not see any ferromagnetic character in the magnetic hysteresis loops of BFO at 75 K and 300 K. In literature, there are reports where doped BFO have been shown to be ferromagnetic. For example, Hussain et al. [18] reported that for the case of divalent substitution \((Bi_{0.75}FeO_3)\) FeO\(_3\) \((A = Ba, Pb and Sr)\), M–H loops exhibited ferromagnetic hysteresis. Mainly in this system A-site was substituted with 25% of divalent substituents, which in turn increases Fe\(^{3+}\) concentration and an appreciable weakening of the spin spiral leads to a significant increase in magnetic moment. In contrary we have much lower concentration of divalent \((Pb^{2+})\) substituent which is 10% at the A-site. Even for the P(20) composition, M–H loop showed AFM behavior. Here compared to the literature, A-site is substituted with lower percentage of divalent substituent. Hence magnetic studies reveal that the concentration of Fe\(^{2+}\) ions and oxygen vacancies have much lower density to push the system to become ferromagnetic. It is also very important to point out that the oxygen vacancies should be suppressed to avoid leakage current which deteriorates the dielectric response in multiferroics. The ferromagnetic behavior has been reported in titanate thin films, where the saturation magnetization increases as the oxygen vacancy increases due to the enhanced F-center exchange interaction [30]. Hence the magnetic data presented here revealed that the choice of compositions reduces formation of oxygen vacancies and stabilizes pure phase.

Pure BFO exhibits AFM behavior due to the presence of the anti-ferromagnetic spiral spin structure [31]. We consistently observed this behavior. However, Pb doping led to similar magnetic response as shown in Fig. 4(a). On the other hand La substitution led to observation of weak Ferromagnetic (FM) character with non-zero coercivity and remanence as shown in Fig. 4(a). Consistently coercivity decreases with decrease in temperature, as evident from the loops measured at 75 K (Fig. 4(b)). Substitution of both La and Pb at A-site exhibited weak FM response. As the Ti ions were introduced to the system, magnetization at 3 T, coercivity and Remanence was found to progressively increase as function of Ti concentration, as shown in Fig. 4(c). While the loops (Fig. 4(c)) recorded at lower temperature i.e. 75 K, coercivity was found to decrease as is the case of typical FM. This shows that Ti substitution effectively suppresses the antiferromagnetic spiral spin structure resulting in the release of small net moment due to canting.

7. Ferroelectric properties

The electric field dependence of polarization i.e. \(P-E\) hysteresis loops measured at room temperature are shown in Fig. 5. Here, the maximum applied electric field is 10 kV/cm. \(P-E\) loops of BFO, L(20) and P(20) compositions are shown in Fig. 5(a) whereas the \(P-E\) loops for the LP(10)-T(x) \((x = 0, 0.05, 0.1 and 0.15)\) compositions are shown in Fig. 5(b). Recall that A-site cation \((Bi^{3+})\) of this perovskite has a 6s lone pair of electrons and 6p empty orbital. Hybridization of these orbitals induces the non-centrosymmetric distribution of the electronic cloud and makes BFO a ferroelectric. La\(^{3+}\) and Pb\(^{2+}\) doping suppress the impurity phases by controlling the Bi\(^{3+}\) volatilization; however, the loops are comparatively lossy. Similar shaped hysteresis loops are also reported in literature [19]. The lossy behavior may arise due to the lower density of the pellets [32]. The density of the pellets can be increased by annealing at higher temperatures [32,33], but the problem is that higher temperature annealing reduces Pb and Bi since both these elements are volatile and form extra phases [34–38]. Therefore, due to this volatilization issue, there is an upper limit on the annealing temperature and samples have to be annealed in optimized conditions.
to obtain the right phase. Pb and Bi volatization also introduces oxygen vacancies in the system which further degrades ferroelectric behavior.

In general, since we have different substituents, therefore it is better to compare effect of Ti variation keeping the Pb and La concentrations fixed. Saturation polarization ($P_s$), remanent polarization ($P_r$) and coercive field ($E_c$) as function of Ti concentration are plotted in Fig. 6(a)–(c). Magnitude of $P_s$ and $P_r$ increases as Ti content increases from 0% to 10%. However, there is a drop in the magnitude of $P_s$ and $P_r$ for 15% Ti composition. Gu et al. reported a significant decrease in the leakage current as Ti replaces Fe [39]. However, in ferroelectrics, it has been reported that even though for identical crystal and electronic structure, lower sintering temperatures due to higher porosity yields an order of magnitude decrease in the value of the dielectric constant and exhibits diffused phase transition [32]. We observed that the saturation polarization decrease as the Ti concentration increases from 10% to 15%, as shown in Fig. 6(a). It has been reported that Ti substitution significantly decreases the grain size [40]. Chaodan et al. [41] also studied the effect of B-site substitution with Ti on morphology of the samples. They reported that the grain size reduces by the addition of Ti. In the present study, the porosity first decreases up to 10% Ti concentration but beyond this concentration the porosity increases. One of the reasons for decrease in $P_r$ for 15% Ti doped BFO is the reduction of grain size with increasing Ti concentration due to which the sample's porosity increases. Therefore to achieve the densification of the sample, annealing temperature should be increased, which in turn results in the enhancement of the grain size. Hence our experimental studies revealed that 10% Ti composition yielded best dielectric response for the given synthesized protocol.

8. Conclusion

A composition series of $\text{Bi}_{1-x-y}\text{La}_x\text{Pb}_y\text{Fe}_{1-z}\text{Ti}_z\text{O}_3$ ($x, y = 0, 0.1, 0.2$ and $z = 0, 0.05, 0.1, 0.15$) were prepared by solid state route. These three substituents were chosen in order to investigate the effect of
oxygen vacancies, extra phases, lone pair activity and crystal structure on the multiferroic response of BFO. A-site was substituted with Pb, so as to control the Bi$_2$O$_3$ volatilization and preserve the samples major phases were cubic. Mössbauer and Ti doped BFO exhibited an anomaly for Pb doped BFO exhibited rhombohedral perovskite structure, while in Bi$_{0.9}$Pb$_{0.1}$Fe$_2$O$_3$ and Bi$_{0.95}$La$_{0.05}$Fe$_2$O$_3$ samples major phases were cubic. Mössbauer spectra revealed absence of any extra phases in the Ti substituted samples and Fe ions retained their +3 state. Progressive increase in saturation polarization indicates suppression of leakage current upto 10% of Ti. However, beyond this limit extrinsic factors such as porosity and small grain size lead to decrease in saturation polarization. In addition to that as the Ti concentration increase, monotonic increase in coercivity and remanent magnetization, revealed presence of weak ferromagnetism associated with the suppression of antiferromagnetic spiral structure.

High temperature dielectric measurements revealed that an anomaly for Pb$^{2+}$ compositions arises in the in-phase part of dielectric function in the temperature range, 100 °C < T < 250 °C. This anomaly has not been found to be associated with magnetic or structural transformations, since the anomaly was not consistently observed in tan δ, and Néel temperature lies well above the particular temperature region. Previous reports suggested that this anomaly was attributed to the oxygen vacancies interaction with Fe$^{3+}$/Fe$^{2+}$ redox couple. However, in the present case, we found, (1) absence of Fe$^{3+}$ ions in all compositions, (2) presence of anomalous peak only in the Pb doped compositions, and (3) decrease in the intensity of anomalous peak with increase in Ti concentration. Hence detailed analysis of all characterizations, suggest that anomaly arises due to the extra phase or charge transfer involving Pb ions and vanishes as the conductivity decreases with Ti substitution.

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