Investigation of BiFeO$_3$-BaTiO$_3$ lead-free piezoelectric ceramics with nonstoichiometric bismuth

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Received: 28 Jun 2023  First Decision: 22 Aug 2023 Revised: 23 Aug 2023 Accepted: 25 Aug 2023 Published: 19 Sep 2023

Abstract
BiFeO$_3$-BaTiO$_3$ (BF-BT)-based lead-free ceramics are promising piezoelectric materials exhibiting high Curie temperatures and excellent electrochemical properties. In this study, 0.70Bi$_{1+x}$FeO$_3$-0.30BaTiO$_3$ (B$_{1+x}$F-BT, $x = -0.01$, 0.00, 0.01, 0.02, 0.03, 0.04) lead-free piezoelectric ceramics were successfully fabricated via the conventional solid-phase reaction process. Crystallographic structure, microstructure, dielectric, impedance, ferroelectric, and piezoelectric properties among different compositions were comprehensively investigated. The X-ray diffraction analysis confirmed that all compositions exhibited a typical perovskite structure with a cubic-rhombohedral phase mixture. The grain size of ceramics tends to increase as the Bi$_2$O$_3$ content rises. In particular, the backscattered electron images and energy dispersive analysis revealed prominent core-shell microstructure within grains. Notably, the BF-BT ceramic containing 1% excess Bi displayed the maximum $d_{33}$ ~217 pC/N and $d_{33}'$ ~243 pm/V accompanied by a high Curie temperature of 515 °C. The findings demonstrate the potential feasibility of BF-BT ceramics in the field of lead-free piezoelectric ceramics.

Keywords: Piezoelectric ceramics, lead-free, BF-BT, bismuth, nonstoichiometric
INTRODUCTION

Piezoelectric ceramics are extensively employed in electronic devices, such as sensors, actuators, filters, ultrasonic devices, etc., which are realized through the mutual conversion between mechanical and electrical energies\(^{1-3}\). Over decades, Pb\((\text{Zr}_{x}\text{Ti}_{1-x})\)O\(_3\)-based piezoelectric ceramics have been used dominantly in commercial devices. However, the toxicity of lead (Pb) can cause irreversible damage to human health and the environment, which promotes research hotspots on lead-free materials\(^{4-6}\). Among the lead-free materials, (K,Na)NbO\(_3\) (KNN)-based and Bi\(_{1/2}\)Na\(_{1/2}\)TiO\(_3\) (BNT)-based piezoelectric ceramics are considered to be promising candidates for lead-based piezoelectric ceramics\(^{7-10}\). Despite the high piezoelectric coefficient \((d_{33} > 500 \text{ pC/N})\), KNN ceramics suffer from certain drawbacks, such as the K and Na volatilization, unstable phase structures near room temperature, and low Curie temperatures \((T_C) \sim 200 \text{ °C}\)\(^{1,11-13}\). BNT-based ceramics used to exhibit high \(T_C\), but the volatilization of Bi and Na elements leads to unstable chemical compositions and a high coercive field; consequently, superior polarization is difficult to achieve\(^{14-17}\).

In recent years, BiFeO\(_3\)-xBaTiO\(_3\) (BF-xBT) piezoelectric ceramics have emerged as competitive candidates in lead-free materials\(^{2,18-20}\). As a kind of multiferroic material, BF has a rhombohedral phase perovskite structure (ABO\(_3\)), which has attracted significant attention because of its high \(T_C (830 \text{ °C})\) and excellent spontaneous polarization \((P_s = 90-100 \mu \text{C/cm}^2)\)\(^{21,22}\). Recent studies of BF single crystal\(^{23-25}\), polycrystalline thin film\(^{26-29}\), and epitaxial thin film\(^{30-34}\) have also been conducted, which has given researchers additional ideas for exploring and application. However, the synthesis of pure BF is usually accompanied by the generation of impurities, where excess Fe\(_2\)O\(_3\) exceeding 5 mol \% leads to the formation of pyrochlore Bi\(_2\)Fe\(_4\)O\(_9\) and gamma-Fe\(_2\)O\(_3\)\(^{35}\). Additionally, the volatilization of Bi and the valence reduction of Fe\(^{3+}\) to Fe\(^{2+}\) at high temperatures cause high leakage currents, resulting in challenges for practical applications\(^{36-38}\). BT is a traditional ferroelectric material exhibiting a tetragonal phase structure at room temperature and possesses a low \(T_C\) of \(\sim 120 \text{ °C}\)\(^{39}\). It has been found that the sintering of BF-xBT solid solution can effectively suppress the generation of secondary or impurity phases and reduce the leakage current. Specifically, a morphotropic phase boundary (MPB) can be constructed when \(x\) approaches 0.30 ~ 0.35, which contributes to enhanced dielectric, piezoelectric, and ferroelectric properties while maintaining a high \(T_C\)\(^{40-42}\).

However, one of the notable disadvantages in BF-xBT-based piezoelectric ceramics is the Bi\(_2\)O\(_3\) volatilization during the sintering process, resulting in poor electrical resistivity and piezoelectric performance. The volatilization of Bi\(_2\)O\(_3\) can be described by the following defect Equation (1)\(^{43}\)

\[
2\text{Bi}^{3+} + 3\text{O}^2^- \rightarrow \text{Bi}_2\text{O}_3\uparrow + 2\text{V}_{\text{Bi}}^{2+} + 3\text{V}_\text{O}^{2+}
\]

The volatilization of Bi\(_2\)O\(_3\) leads to the generation of Bi vacancies \((\text{V}_{\text{Bi}}^{3-})\) and O vacancies \((\text{V}_\text{O}^{2+})\) within the ceramics. Various strategies have been attempted to solve the problem. One of the most common strategies is using nonstoichiometric (excess) Bi to compensate for the loss of Bi during high-temperature sintering, as listed in Table 1.

In this study, a series of 0.70Bi\(_2\)O\(_3\)-xFeO\(_{0.30}\)BT \((x = -0.01, 0, 0.01, 0.02, 0.03, 0.04)\) ceramics were fabricated using the conventional solid-state reaction method. The influence of Bi\(_2\)O\(_3\) compensation on the phase structure, microstructure, dielectric, ferroelectric, and piezoelectric properties of ceramics are systematically investigated.
Table 1. Summary of ferroelectric and piezoelectric properties of BF-BT system piezoelectric ceramics with excess Bi$_2$O$_3$

<table>
<thead>
<tr>
<th>Composition</th>
<th>$d_{33}$ ($\mu$C/N)</th>
<th>$P_r$ ($\mu$C/cm$^2$)</th>
<th>$T_c$ (°C)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.70B$_{1-x}$F-0.30BT</td>
<td>183 pC/N</td>
<td>21.38</td>
<td>480</td>
<td>[44]</td>
</tr>
<tr>
<td>0.69B$_{1-x}$F-0.31BT</td>
<td>207 pC/N</td>
<td>-</td>
<td>-</td>
<td>[45]</td>
</tr>
<tr>
<td>0.70B$_{1-x}$F-0.30BT</td>
<td>211 pm/V</td>
<td>19.6</td>
<td>421</td>
<td>[46]</td>
</tr>
<tr>
<td>0.65B$_{1-x}$F-0.35BT</td>
<td>270 pm/V</td>
<td>27.61</td>
<td>432</td>
<td>[47]</td>
</tr>
<tr>
<td>0.70B$_{1-x}$F-0.30BT</td>
<td>214 pC/N</td>
<td>19.61</td>
<td>528</td>
<td>[48]</td>
</tr>
<tr>
<td>0.54B$_{1-x}$F-0.36BT-0.10BZ</td>
<td>197 pC/N</td>
<td>20</td>
<td>445</td>
<td>[49]</td>
</tr>
<tr>
<td>0.70B$_{1-x}$FMT-0.30BT</td>
<td>198 pC/N</td>
<td>-</td>
<td>497</td>
<td>[50]</td>
</tr>
<tr>
<td>0.70B$_{1-x}$F-0.30BT</td>
<td>180 pC/N</td>
<td>-</td>
<td>506</td>
<td>[43]</td>
</tr>
<tr>
<td>0.75B$_{1-x}$F-0.25BT</td>
<td>114 pC/N</td>
<td>34.4</td>
<td>508</td>
<td>[51]</td>
</tr>
<tr>
<td>0.71B$_{1-x}$F-0.29BT</td>
<td>142 pC/N</td>
<td>-</td>
<td>452</td>
<td>[52]</td>
</tr>
</tbody>
</table>

MATERIALS AND METHODS

0.70Bi$_{1-x}$FeO$_{3-x}$-0.30BaTiO$_3$ (B$_{1-x}$F-BT, $x$ = -0.01, 0.00, 0.01, 0.02, 0.03, 0.04) piezoelectric ceramics were fabricated using a solid-state reaction process. Bi$_2$O$_3$ (99%, Sinopharm, China), Fe$_2$O$_3$ (99.9%, Aladdin, China), BaCO$_3$ (99%, Sinopharm, China), and TiO$_2$ (98%, Sinopharm, China) powders were employed as raw materials. All powders were weighed according to stoichiometric ratios and ball-milled for 24 h using zirconia balls in ethanol. The mixed slurry was dried and calcined at 750 °C in a sealed alumina crucible for 2 h, followed by a secondary ball-milling process for 12 h. The calcined powder was mixed with a 10 wt% polyvinyl alcohol (PVA) binder, and the green pellets with a diameter of 10 mm were formed under a pressure of 127 MPa. The green pellets were kept at 600 °C for 2 h to burn out PVA and then sintered into ceramics at 1,010 °C for 3 h to obtain ceramics. Silver paste was sintered on parallel ceramic surfaces to form electrodes for electrical measurements.

The crystal structure and morphology were probed by the X-ray powder diffraction (XRD, D8 Advance X, Bruker, Germany) with Cu-K$_\alpha$ radiation and the scanning electron microscope (SEM, Apreo 2, Thermo Scientific, United States) equipped with an energy-dispersive spectroscopy (EDS) detector, respectively. The dielectric and impedance properties were measured via a precision LCR meter (E4980A, Agilent Technologies, United States) connected to a high-temperature dielectric test system (DMS-1000, Balab Technology, China). The ferroelectric hysteresis (PE) loops and field-induced strain (SE) curves were collected by a ferroelectric tester station (PK-10E, PolyK Technologies, United States). The piezoelectric coefficient ($d_{33}$) is recorded by a quasi-static $d_{33}$ meter (SA1303A, PolyK Technology, United States).

RESULTS AND DISCUSSION

The XRD results reveal that all B$_{1-x}$F-BT compositions exhibit a perovskite structure with a phase mixture consisting of cubic ($Pm\bar{3}m$) and rhombohedral ($R3c$) phases, as shown in Figure 1A. The impurity of Bi$_2$Fe$_{1-x}$O$_{4-x}$ is a common occurrence in the BF-BT system$^{[27]}$, is appeared when $x \geq 0.03$. The enlarged (111) and (200) peaks show insignificant peak shifts with varying Bi$_2$O$_3$ content. The refined results for each component are displayed in Figure 1B and Table 2. The cubic phase gradually decreases as the Bi$_2$O$_3$ content increases and tends to stabilize at $x \geq 0.01$, according to this Table. This demonstrates that the phase structure changes from the Bi$_2$O$_3$-deficient to the Bi$_2$O$_3$-excess tends to change from the cubic phase to the rhombohedral phase, while the excess Bi$_2$O$_3$ phase structure has little effect, which is also reflected in the lattice parameter.
Table 2. The rietveld refinement data of the observed XRD patterns for B\textsubscript{1+x}F-BT ceramics

<table>
<thead>
<tr>
<th>x</th>
<th>Phase fraction (%)</th>
<th>Rhombohedral (R3c)</th>
<th>Cubic (Pm\textsuperscript{3}m)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å\textsuperscript{3})</th>
<th>a (Å)</th>
<th>V (Å\textsuperscript{3})</th>
<th>Rwp</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.01</td>
<td>38</td>
<td>62</td>
<td>5.6454</td>
<td>13.839</td>
<td>381.781</td>
<td>3.9991</td>
<td>63.948</td>
<td>8.0</td>
<td>1.41</td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>54</td>
<td>46</td>
<td>5.6437</td>
<td>13.8376</td>
<td>381.704</td>
<td>3.9991</td>
<td>63.958</td>
<td>9.3</td>
<td>1.73</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>66</td>
<td>34</td>
<td>5.6393</td>
<td>13.8590</td>
<td>381.689</td>
<td>4.0045</td>
<td>64.281</td>
<td>8.8</td>
<td>1.49</td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>65</td>
<td>35</td>
<td>5.6396</td>
<td>13.8614</td>
<td>381.805</td>
<td>4.0084</td>
<td>64.407</td>
<td>8.6</td>
<td>1.52</td>
<td></td>
</tr>
<tr>
<td>0.03</td>
<td>77</td>
<td>23</td>
<td>5.6389</td>
<td>13.8669</td>
<td>381.854</td>
<td>4.0063</td>
<td>64.303</td>
<td>9.5</td>
<td>1.74</td>
<td></td>
</tr>
<tr>
<td>0.04</td>
<td>74</td>
<td>26</td>
<td>5.6389</td>
<td>13.8654</td>
<td>381.812</td>
<td>4.0075</td>
<td>64.363</td>
<td>9.2</td>
<td>1.67</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. (A) XRD patterns of the B\textsubscript{1+x}F-BT ceramics, (B) the Rietveld refinement results for x = 0.01.

Figure 2 shows the surface morphology of the B\textsubscript{1+x}F-BT ceramics in different compositions. The ceramic surface exhibits a compact morphology with clear grain boundaries and seldom pores. The calculated relative density is higher than 95% for all compositions [Supplementary Figure 1], which is consistent with the observations from SEM results. Statistical analysis of the grain size distributions reveals that the grains tend to increase with enriching the Bi\textsubscript{2}O\textsubscript{3} content. The ceramic grain size increases from 4.01 μm of x = -0.01 to 9.62 μm of x = 0.04. It is evident that the excess Bi\textsubscript{2}O\textsubscript{3} not only compensates for volatilization but also acts as a sintering aid promoting grain growth, which is consistent with the literature\cite{46,47}.

Figure 3 shows the backscattered electron (BSE) images of the polished surface of B\textsubscript{1+x}F-BT ceramics with the corresponding elemental mapping results by EDS. A BSE image is used to see the dark and bright contrast, showing the light and heavy element distributions to evidence the core-shell structure in grains, and EDS helps further identify the exact elements in the core and shell regions. The images reveal a non-uniform distribution of elements inside the ceramic, leading to a distinct core-shell microstructure, which is caused by immiscibility of the dominantly ionicley bonded BT and covalently bonded BF phases and the microscopic segregation of elements that forms during the slow cooling process of sintering\cite{3,53-56}. Murakami et al. synthesized the 0.05BiScO\textsubscript{3}-(0.95-x)BaTiO\textsubscript{3}-xBiFeO\textsubscript{3} ceramics without a discernible core-shell microstructure\cite{53}; it is proven that the BF-BT lattice can be replaced by dopants in the narrow range of the ionic radius ($R_{\text{Sc}^3+}$: 0.745; $R_{\text{Ti}^4+}$: 0.605; $R_{\text{Fe}^3+}$: 0.645 Å)/electronegativity ($E_{\text{Sc}^3+}$: 1.3; $E_{\text{Ti}^4+}$: 1.5; $E_{\text{Fe}^3+}$: 1.8) difference so as to prevent phase separation during slow cooling processes. Notably, there is a noticeable contrast between light and dark regions in Figure 3. The core, enriched with Bi and Fe, appears brighter, while the shell, enriched with Ba and Ti, appears relatively darker. In addition, the BSE images of x = -0.01 and x = 0.03 and the distribution of EDS elements are shown in Supplementary Figure 2 and Supplementary Figure 3.
Figure 2. SEM images and grain size distribution in $B_{1-x}F-BT$ ceramics with $x =$ (A) -0.01, (B) 0.00, (C) 0.01, (D) 0.02, (E) 0.03, and (F) 0.04.

Figure 3. BSE images of $B_{1-x}F-BT$ ceramics: $x =$ (A) -0.01, (B) 0.00, (C) 0.01, (D) 0.02, (E) 0.03, (F) 0.04, and EDS elemental mapping results (G) Bi, (H) Fe, (I) Ba, (J) Ti, and (K) O. (L) the scanned points in a core and a shell region and scanned line, EDS data of points and line scan on the core-shell in $B_{1.01}F-BT$ ceramic.
Figure 4A presents the temperature-dependent behavior of relative permittivity ($\varepsilon_r$) and dielectric loss (tan\(\delta\)) at 10 kHz. It reveals that as the Bi\(_2\)O\(_3\) content increases, the dielectric peak becomes narrower, and the maximum relative dielectric constant ($\varepsilon_r$) gradually increases, indicating a reduction of diffuse behavior. It is evident from the spectra that the dielectric peaks of the ceramics exhibit asymmetry, which is related to the presence of a core-shell structure within the ceramic grains. As plotted in Figure 4A, the tan\(\delta\) of ceramics exhibits an abrupt increase around the $T_m$ (temperature exhibiting the maximum $\varepsilon_r$), suggesting that there is a transition from the diffuse ferroelectric to the paraelectric phase [Figure 4B]. Figure 4C illustrates the relaxation factor ($\gamma$) calculated at 10 kHz, which demonstrates that the value of $\gamma$ decreases as the $x$ content increases, ranging from $\gamma = 1.79$ at $x = -0.01$ to $\gamma = 1.27$ at $x = 0.04$. Figure 4D displays the variation of $\Delta T_m$ between 1 kHz and 1 MHz for each component in the temperature spectrum. It is evident that $\Delta T_m$ tends to decrease with increasing $x$ content, which reveals that the ferroelectricity of the ceramic becomes more prominent, aligning with the decreasing $\gamma$ depicted in Figure 4C.

The complex impedance ($Z$) plots of Bi\(_{1-x}\)F-BT ceramics at 400 °C are shown in Figure 5A, where $Z'$ and $Z''$ represent the real part and imaginary part of $Z$, respectively. At 400 °C, the total impedance initially increases from 36.5 k\(\Omega\)-cm at $x = -0.01$ to 44.4 k\(\Omega\)-cm at $x = 0.01$ and then decreases with incorporating more Bi\(_2\)O\(_3\) content, which indicates that the composition of $x = 0.01$ is the most electrically resistive. The $Z'$ and $M'/\varepsilon_0$ plots of $x = 0.01$ at 300 °C are plotted in Figure 5B, illustrating the electrical heterogeneity associated with various conductive components. Three peaks are found in the plots corresponding to the three conductive components. $Z'$ exhibits a single peak related to the grain boundary response (component 1), while $M'/\varepsilon_0$ shows a strong peak in the low-frequency region and a weak peak in the high-frequency region, which is ascribed to the electrical heterogeneity from the core-shell structure. In this study, the strong peak represents the shell response (component 2), whereas the weaker peak is considered as the core response (component 3). The resistance ($R$) and capacitance ($C$) of all conductive components at 325 °C were calculated based on the peaks of $Z''$ and $M'/\varepsilon_0$ [Table 3]. The $R$ values of components 1 and 2 reach the maximum in the composition of $x = 0.01$. However, the $R$ value of component 3 did not change significantly with the increase of Bi\(_2\)O\(_3\) content. Additionally, the resistance of components 1 and 2 is two orders of magnitude higher than that of component 3, which matches the frequency of the peaks of the three components in Figure 5B. It is worth noting that component 3 exhibits a capacitance that is an order of magnitude higher than components 1 and 2, indicating the formation of an electrically conducting core and a nonconductive shell. Figure 5C shows the Arrhenius plots of the grain shell, core, and boundary, and the calculated activation energy calculated by fitting is shown in Figure 5D. The activation energy of the shell (1.06-1.14 eV) is generally lower than that of the core (1.15-1.28 eV) and grain boundary (1.09-1.16 eV).

Figure 6A illustrates the PE loops of the Bi\(_{1-x}\)F-BT ceramics at 60 kV/cm under a frequency of 1 Hz, and the corresponding $P_r$ and $E_c$ are plotted in Figure 6B. The PE loops show typical ferroelectric features without observations of leakage characteristics at high field amplitudes. However, when $x = -0.01, 0.00$, the loops demonstrate the phenomenon of leakage conduction, resulting in relatively high values of $P_r$ and $E_c$, which is mainly attributed to the formation of Bi and O vacancies caused by the Bi\(_2\)O\(_3\) volatilization\(^{[40]}\). When $x \geq 0.01$, the leakage conductivity of BF-BT is significantly reduced, leading to stable values of $P_r$ and $E_c$. The electric SE loops of ceramics measured at 60 kV/cm are shown in Figure 6C. It can be seen that the strain value increases as $x$ increases from -0.01 to 0.01, reaching a maximum value of 0.146% at $x = 0.01$, and then the strain value decreases. The strains are calculated by averaging the positive strains obtained at ±60 kV/cm and used for deriving the $d_{33}$ values, as plotted in Figure 6D. Notably, the highest $d_{33} = 243$ pm/V and $d_{33} = 217$ pC/N are achieved at $x = 0.01$, evidencing that the suitable amount of compensation of Bi\(_2\)O\(_3\) is effective in improving the piezoelectric properties of the BF-BT ceramics. In addition, the inset image of Figure 6D depicts the temperature dependence of $d_{33}$ for $x = 0.01$. It demonstrates that the $d_{33}$ value has a
Table 3. The values of $R$ and $C$ for each component at 325 °C derived based on the $Z''$ and $M''/\varepsilon_0$ peak values for $-0.01 \leq x \leq 0.04$

<table>
<thead>
<tr>
<th>Composition</th>
<th>Component 1 (grain boundary)</th>
<th>Component 2 (shell)</th>
<th>Component 3 (core)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R = 2 Z''$ (kΩ·cm)</td>
<td>$C = 1/(4\pi fZ''')$ (F cm$^2$)</td>
<td>$R = M''/\varepsilon_0 fZ''$ (kΩ·cm)</td>
</tr>
<tr>
<td>-0.01 (325 °C)</td>
<td>346</td>
<td>$5.73 \times 10^{-10}$</td>
<td>281</td>
</tr>
<tr>
<td>0.00 (325 °C)</td>
<td>393</td>
<td>$6.07 \times 10^{-10}$</td>
<td>315</td>
</tr>
<tr>
<td>0.01 (325 °C)</td>
<td>474</td>
<td>$3.48 \times 10^{-10}$</td>
<td>378</td>
</tr>
<tr>
<td>0.02 (325 °C)</td>
<td>438</td>
<td>$5.45 \times 10^{-10}$</td>
<td>329</td>
</tr>
<tr>
<td>0.03 (325 °C)</td>
<td>314</td>
<td>$5.25 \times 10^{-10}$</td>
<td>230</td>
</tr>
<tr>
<td>0.04 (325 °C)</td>
<td>334</td>
<td>$5.41 \times 10^{-10}$</td>
<td>245</td>
</tr>
</tbody>
</table>

Figure 4. Temperature-dependent $\varepsilon_r$ and $\tan\delta$ of (A) $-0.01 \leq x \leq 0.04$ measured at 10 kHz, (B) the $T_m$ at 10 kHz, (C) the relaxation coefficient $\gamma$ at 10 kHz, (D) the $\Delta T_m$ from 1 kHz to 1 MHz for the $B_0^+$xF-BT ceramics.

great temperature sensitivity and decreases above 300 °C as a result of the gradual depolarization at high temperatures.

CONCLUSIONS

In this work, a series of 0.70$B_0^+$xF-0.30BT-based lead-free piezoelectric ceramics were systematically studied. The addition of Bi$_2$O$_3$ to 0.70BF-BT ceramics plays a crucial role in compensating for the volatilization of Bi elements during high-temperature sintering, leading to enhanced dielectric and piezoelectric performance. The phase structure of the ceramics is barely influenced while varying the Bi$_2$O$_3$ content, where all compositions exhibit a typical perovskite structure with a rhombohedral-cubic phase mixture. The microscopy results indicate an increasing trend of grain size as more Bi$_2$O$_3$ content is incorporated into the composition. The BSE images and element mappings reveal core-shell microstructures in the ceramics, which are attributed to the segregation of elements during the sintering process. Moreover, the higher Bi$_2$O$_3$,
Figure 5. (A) Temperature-dependent $Z'$ plots for $B_{1+x}F$-BT ceramics at 400 °C, (B) Combined $Z'$ and $M'/\varepsilon_0$ spectroscopic plots at 300 °C for $x = 0.01$, (C) Arrhenius plots and (D) the activation energy for the $B_{1+x}F$-BT ceramics.

Figure 6. Ferroelectric properties of (A) $PE$ loops at 60 kV/cm and associated (B) $P_r$ and $E_c$ of the $B_{1+x}F$-BT ceramics. (C) $SE$ loops at 60 kV/cm and (D) $d_{33}$ and $d_{33}'$ as a function of $x$ concentration for the $B_{1+x}F$-BT ceramics; the inset image shows the temperature dependence of $d_{33}$ for $x = 0.01$. 
content leads to narrower dielectric peaks, higher maximum $\varepsilon_r$, and diminished relaxation factor, indicating a deteriorated relaxor behavior. The ferroelectric properties of the ceramics, as demonstrated by $PE$ loops, show that the excess of Bi$_2$O$_3$ helps improve the leakage conductivity while stabilizing the $P_r$ and $E_C$. The piezoelectric properties of the ceramics are optimized at $x = 0.01$ with $d_{33} \sim 217$ pC/N and $d_{33}^* \sim 243$ pm/V, but it has a great temperature sensitivity. The nonstoichiometric optimization of the Bi$_2$O$_3$ content in BF-BT was investigated in this work. The findings can be utilized as a foundation for further research into the BF-BT system.

DECLARATIONS

Authors’ contributions
Synthesis and testing of materials, data collection, original manuscript writing: Qin H
Validation and original manuscript revision: Zhao J
Data analysis: Chen X, Li H
Data reduction: Wang S
Chart design: Du Y
Validation: Zhou H
Revision: Li P
Reviewing and editing: Wang D

Availability of data and materials
According to reasonable requirements, all of the data examined in this research can be obtained from the correspondents.

Financial support and sponsorship
This work is supported by the Science, Technology and Innovation Committee of Shenzhen Municipality (Grant No. JCYJ20220531095802005 and No. RCBS20210706092341001).

Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

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