Multiferroic and nanomechanical properties of Bi$_{1-x}$Y$_x$FeO$_3$ polycrystalline films (x = 0.0–0.1)

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ABSTRACT

In order to improve the multiferroic properties of BiFeO$_3$ and to clarify the Y substitution effect, we use an Nd:YAG laser to grow Bi$_{1-x}$Y$_x$FeO$_3$ (BYFO) films on glass substrates at low deposition temperatures by pulsed laser deposition (PLD). Their phase structure, microstructure, ferroelectric and magnetic characteristics, and leakage mechanism are explored. The existence of the perovskite phase in BYFO films with x = 0.00–0.10 is confirmed. The structure is transformed from rhombohedral for x = 0.00 to pseudo-cubic for x = 0.05, and an additional phase, orthorhombic, is coexisted for x = 0.10. The microstructure and surface morphology analyses demonstrate a decrease in grain size and film roughness when the Y concentration is increased. The crystalline structure and grain size dominate the hardness of 6.5–10.1 GPa, as measured by nanoindenter. We attain good ferroelectric characteristics for BYFO films with x = 0.00–0.05, where the greatest remanent polarization (2P$_r$) of 102.6 $\mu$C/cm$^2$ is achieved for x = 0.05, connected to minimizing leakage and oxygen vacancy suppression. The typical ferromagnetic behavior with increased saturation magnetization from 4.4 emu/cm$^3$ to 6.5 emu/cm$^3$ by Y substitution possibly attributed to the suppressed spiral spin structure of G-type antiferromagnetism. The mechanisms of electric conduction behavior as functions of Y content and growth temperature are also discussed.
1 Introduction

BiFeO$_3$ (BFO), an room-temperature (RT) multiferroic material, with two main ferro-ordering parameters: ferroelectricity (FE) at temperatures below 1103 K \cite{1} and antiferromagnetism (AFM) at temperatures below 643 K \cite{2}. However, due to the net magnetization from a canted spin structure, it exhibits modest magnetization at room temperature \cite{3}. The single-phase multiferroic BFO has gotten a lot of interest in the recent decade because of its excellent FE properties, multiferroic nature, possible magnetolectric (ME) coupling, and lead-free nature. These features suggest nonvolatile ferroelectric data storage, the developing field of spintronics, and ME sensors as possible applications. Due to the existence of stereochemically active Bi$^{3+}$ ions with 6 s lone pair electrons, BFO has a high FE. Li et al. \cite{4} found that epitaxial pseudo-cubic BFO(001) thin films on SrRuO$_3$/SrTiO$_3$(100) substrates by PLD have an unexpectedly significant residual polarization $2P_r = 120$ C/cm$^2$, which is one order of magnitude greater than bulk BFO ($\approx 6.1$ C/cm$^2$) \cite{5}. Large ferroelectric polarization was achieved in BFO polycrystalline, and epitaxial films \cite{6}. The intrinsic feature of BFO causes large polarization, which is further supported by the first-principles calculation \cite{7}. The magnetic nature of BFO, on the other hand, is a G-type AFM order, in which Fe$^{3+}$ ions are surrounded by six Fe$^{3+}$ ions with spin antiparallel to the core ion \cite{8}. Due to the spiral magnetic spin cycloid, BFO has weak ferromagnetic (FM) properties, hence the cross-coupling between these ferroic parameters in BFO is weak.

Although FE features are prominent, significant leakage, a tendency to fatigue \cite{9,10}, and weak FM are the key drawbacks for BFO-related devices. The use of rare-earth cations to partly replace Bi ions has been shown to be an efficient method to reduce leakage and improve magnetic characteristics \cite{11,12}. Due to the suppressed oxygen vacancies in BFO caused by A substitution, FE property increase was also observed in A-site doped BFO ceramics and films (A = Sm, La, Pr, and Ca) \cite{13,14}. Although experiments on A-site modified BFO have been reported, there is still a lack of clarification on certain aspects of rare-earth-doped BFO materials, particularly for Y-doped BFO films. For instance, Saleh-Medina et al. \cite{15} discovered that in Bi$_{1-x}$Y$_x$FeO$_3$ nanoparticles, there is a compositional driven structural alteration attributable to a rhombohedral to tetragonal phase transition for $0.1 < x < 0.2$. This matches the results of powder samples with compositions ranging from 0 to 0.15 \cite{16}. Furthermore, raising $x$ above 0.10 results in a structural change from rhombohedral R3c to orthorhombic Pn21 in $x$Y$_x$FeO$_3$ polycrystalline films \cite{17}, while Wei et al. found this transition in ceramic samples \cite{18}. Furthermore, spanning a ferroelectric-paraelectric phase transition, a structural symmetry breaking from rhombohedral R3c to orthorhombic Pnma was seen in powder samples at $x = 0.10$ \cite{19}.

However, the FE characteristics reported in previous literatures are too low; even for BYFO thin films, the greatest remanent polarization $2P_r$ is only 12 $\mu$C/cm$^2$ \cite{17}. Although the mechanisms of isovalent substitution-driven improvements in resistivity, FE, and FM are unknown, it appears that FE is mostly controlled by the average size of the A-site ion \cite{20}, rather than by the dopant nature. Y$^{3+}$ has a radius of 1.019 Å \cite{21}, which is between Dy$^{3+}$ (1.027 Å) and Ho$^{3+}$ (1.015 Å) in the same coordination. $2P_r$ is 140 $\mu$C/cm$^2$ \cite{22} for Dy doped BFO and 52 $\mu$C/cm$^2$ \cite{23} for Ho doped BFO, respectively. Therefore, $2P_r$ of 12 $\mu$C/cm$^2$ is a poor characteristic in BYFO thin films and is not consistent with that is expected.

In this work, high-quality Bi$_{1-x}$Y$_x$FeO$_3$ (BYFO) polycrystalline films on glass substrates are prepared by pulsed laser deposition (PLD) to fit with the above empirical expectation. The structural evolution, surface morphology, ferroelectric, leakage, and magnetic characteristics of BYFO films are investigated in detail. Furthermore, because most practical applications of functional devices are manufactured with thin films, it is desirable and crucial to understand the mechanical properties of the films. Accordingly, nano-mechanical properties of BYFO films are also explored.

2 Experiment

The schematic diagram of the experimental procedure for the preparation of targets and the films is shown in Fig. 1. The solid-state reaction technique was used to make Bi$_{1-x}$Y$_x$FeO$_3$ targets ($x = 0.00–0.10$). They are equimolar combinations of initial Bi$_2$O$_3$, Fe$_2$O$_3$, and Y$_2$O$_3$ powders that were then blended utilizing ball milling with 30 zirconia balls as a grinding ball. The powder combinations were
uniaxially crushed into pellets in steel dies (10 mm in diameter). The discs were sintered in air for 24 h at 800 °C, then allowed to cool naturally to room temperature (RT). BYFO films were prepared using the above targets. As a bottom electrode, a 20-nm thick Pt layer was deposited on a Corning 1737 glass substrate by sputtering with a power of 60 W in an Ar atmosphere of 10 mTorr at RT. A pulsed Nd:YAG laser deposition with a triple-frequency laser wavelength of 355 nm was used to deposit 300-nm thick BYFO films onto the Pt layer. During the BYFO deposition, a pulsed laser with a power of 2.5 mJ and a repetition rate of 5 Hz was used with a substrate temperature (T_s) of 300–500 °C and an O_2 pressure of 30 mTorr. An x-ray fluorescence analysis was used to determine the chemical composition of the BYFO thin films, which were then double-checked with an energy-dispersive x-ray spectroscopy examination. X-ray diffractometry (XRD) with copper Kα radiation was used to determine the phase, crystallographic orientations, and lattice parameters. The 2θ scan in XRD has an angular resolution of 0.02° and ranged from 20° to 55°. The scan rate was 60 s per degree. The XRD pattern is refined and structural characteristics are analyzed using the HighScore Plus program. The inorganic crystal structure database (ICSD) [24–27] was used to infer rhombohedral (space group: R3c), orthorhombic (space group: Pnma), and orthorhombic Bi_2Fe_4O_9 (space group: Pbam) structures. The surface and grain morphologies were studied using a scanning electron microscope (SEM). Sputtering was used to deposit a circular-shaped Pt layer with a diameter of 0.2 mm as a top electrode for ferroelectric measurements. The ferroelectric behavior and leakage current mechanism were studied at room temperature using the TF-2000 Analyzer FE-Module ferroelectric test system (axiACCT Co.). P–E loop was measured with an integrating capacitor by applying a triangular AC voltage at 5 kHz. X-ray photoelectron spectroscopy (XPS) is used to analyze iron ion valence distribution for the BFO and BYFO films. The magnetic behavior of BYFO films is investigated using a vibrating sample magnetometer (VSM) at RT. Piezoelectric force microscopy is used to examine the ferroelectric domain structure and piezoelectric response of BYFO films (PFM).

The hardness of BYFO films was determined using a nanoindenter with a Berkovich tip, with the applied indentation load divided by the projected contact area calculated as follows:

$$H = \frac{P_{\text{max}}}{A_p}$$

At the maximum indentation load, $P_{\text{max}}$, $A_p$ is the projected contact area between the indenter and the sample surface. The projected area $A_p$ of a perfectly sharp Berkovich indenter is given by $A_p = 24.56 h_c^2$, where $h_c$ is the true contact depth. To eliminate the substrate effect on hardness measurements, the indentation depth should never exceed 30% of the film thickness [28].
3 Results and discussion

Firstly, the structure, ferroelectric, and magnetic properties of Bi$_{1-x}$Y$_x$FeO$_3$ films at $T_s = 400$ $^\circ$C are studied. A strong Pt(111) texture with Laue fringes for Pt underlayer reveals high crystallinity and a very flat surface, as shown in Fig. 2. The use of a flat and well-crystallized Pt bottom electrode may contribute to the formation of high-quality BYFO films. Besides, according to the ICSD [24–27], the diffraction peaks in the range of 2-theta = 31–33$^\circ$ could be identified: for rhombohedra, two peaks are around 32$^\circ$; for pseudo-cubic, they are merged into one peak at 32$^\circ$; for orthorhombic, there are three peaks around 32$^\circ$. As shown in Fig. 2, BYFO has undergone two structural transitions as Y content $x$. As $x$ increased from 0 to 0.10, from the rhombohedral phase for $x = 0.00$ to the pseudo-cubic phase for $x = 0.05$, and finally to the coexistence of pseudo-cubic and orthorhombic phases for $x = 0.10$. The coexistence of the two above phases in the sample with $x = 0.10$ suggests the morphotropic phase boundary (MPB), which is in good agreement with previous literature [17]. The appearance of the orthorhombic phase could be expected to decrease the ferroelectricity of the BYFO film due to higher crystal symmetry for the orthorhombic phase. Such a complex structural transition occurs only in a narrow range of Y content $x$, presumably due to the fact that Y$^{3+}$ ions are much smaller than Bi$^{3+}$ ions [21]. BFO with Ho substitution showed a similar phenomenon [20]. Unlike Ho-doped BiFeO$_3$ films [20], the structural transition in the current BYFO films is quite smooth, and no additional impurity phase is observed inside $x = 0$–0.05, which could be due to much smaller radius for Ho$^{3+}$ ion. In addition to structural transformations with $x$, the BYFO (001) and BYFO (002) pseudo-cubic phase diffraction peaks with increasing $x$ show a clear shift toward a higher angle, indicating that the spacing for (001) and (002) planes is reduced due to smaller Y$^{3+}$ than Bi$^{3+}$ ions and hints at the entrance of Y into the pseudo-cubic phase. Furthermore, the appearance of a minor Bi$_2$Fe$_3$O$_9$ phase for $x = 0.10$ indicates that a larger Y content may make the pseudo-cubic phase of BYFO films more unstable.

The surface morphology of the BYFO films, as revealed by SEM, is depicted in Fig. 3a–c. Those three samples have a smooth and crack-free morphology. Relatively large grain size is found in Y-free film ($x = 0$). The average grain size is around 108.5 nm. With Y substitution, the grain size is greatly reduced, and the average grain size for the sample with $x = 0.05$ is about 70.6 nm. The average grain size of higher Y content ($x = 0.10$) results is around 83.5 nm. AFM results show in Fig. 2 d–f, the root-mean-square-roughness ($R_{rms}$) is diminished from 3.7 nm for $x = 0$ to 1.7, and 1.0 nm, for $x = 0.05$, and 0.10 respectively. The reduced $R_{rms}$ might be related to the above-mentioned microstructure refinement with Y-substitution.

Figure 4a shows the P-E curves of BYFO films. For three samples with $x = 0$, 0.05, and 0.10. The remanent polarization ($2P_r$) grows with increasing Y content, from 41.1 $\mu$C/cm$^2$ for $x = 0$ to 102.6 $\mu$C/cm$^2$ for $x = 0.05$, and finally lowers to 20.4 $\mu$C/cm$^2$ for $x = 0.10$, however the coercive electric field ($E_c$) decreases significantly. PFM additionally verifies the ferroelectricity and its switching. The inset in Fig. 4b shows the PFM image for BYFO film with $x = 0.05$ following a box-in-box switching with a tip bias of 10 V. After switching, a clear domain pattern suggests typical ferroelectricity in this sample, which favors applications in ferroelectric RAM. By simultaneously applying an ac modulation and a dc bias on the PFM tip, the local piezo-electrical phase response as a function of E is also measured. A sharp ferroelectric switching found in the Bi$_{0.95}$Y$_{0.05}$FeO$_3$ film, as shown in Fig. 4b, further verifies the good piezoelectric behavior caused by the ferroelectricity.

Figure 5 depicts the leakage current density (J)-electric field (E) curves of BYFO films (a). With an
increase in $x$, the leakage current shows a declining trend. The flattened interface between BYFO and Pt for $x = 0.05$ and the development of the orthorhombic phase for $x = 0.10$, respectively, are connected to the decrease in leakage current with $x$. The log($J$) versus log($E$) curves for BYFO films are plotted in Fig. 5b. The Ohmic conduction [29] and space-charge-limited conduction (SCLC) [30], which are based on the following relationships, are initially discussed to identify the dominant leakage mechanism.

$$J_{\text{Ohmic}} = nq\mu E \Rightarrow \log(J) \propto \log(E),$$  

(1)

$$J_{\text{SCLC}} = \frac{9\varepsilon E^2}{8d} \Rightarrow \log(J) \propto 2\log(E),$$  

(2)

where $\mu$ is the carrier mobility, $q$ is the electronic charge, $n$ is the carrier density, $d$ is the film thickness, and $\varepsilon$ is the dielectric constant. Each leakage behavior may be separated into many parts using these models, and the slope ($S \approx 1$ for $J_{\text{Ohmic}}, S \approx 2$ for $J_{\text{SCLC}}$) of each region can be fitted as illustrated in Fig. 5b. At a lower electric field, Ohmic conduction prevails with a slope of $S = 1.08$ for BFO, whereas SCLC conduction
with $S = 1.97$ is detected nearby. The observed slope of 1 for BYFO with $x = 0.05$ and 0.10 at a low electric field, on the other hand, indicates grain boundary limited behavior in this region [31], and subsequently transforms into Ohmic conduction at a relatively high electric field without any SCLC conduction. The SCLC conduction is linked to oxygen vacancies in BFO [32], which could be due to Bi$^{3+}$ volatilization [33]. The lack of SCLC at $x = 0.05$ and 0.10 suggests that substituting Y$^{3+}$ for Bi$^{3+}$ can prevent Bi$^{3+}$ from volatilizing.

The log($J/E$) vs $E^{1/2}$ curves for BYFO films are shown in Fig. 5c, according to the Poole–Frenkel emission (PF) model, which is defined as

$$J_{PF} = AE\exp\left( -\frac{q}{kT} \sqrt{\frac{qE}{4\pi\varepsilon_0\varepsilon_r}} \right)$$

$$\Rightarrow \log\left( \frac{J}{E} \right) \propto \sqrt{\frac{q^3}{4\pi\varepsilon_0\varepsilon_r kT}} E^3,$$

where $k$ is the Boltzmann constant, $T$ is the thermodynamic temperature, $A$ is the constant, $\varphi_T$ is the trap ionization energy height, and $\varepsilon_0$ and $\varepsilon_r$ are the free space and dynamic (or optical) dielectric permittivity, respectively. For BFO films, $\varepsilon_r$, which is related to the refractive index ($n$) in the range of $2.5 \leq n \leq 3.1$, can be used to calculate PF emission [34]. For BFO, $\varepsilon_r$ ($= n^2$) should be $6.25 \leq \varepsilon_r \leq 9.61$. $\varepsilon_r$ is assumed to be extremely close to the above-reported value for BFO due to the low content in the tested BYFO films. The slope of the linear fits was used to calculate the $\varepsilon_r$ values, which are also shown in Fig. 5c. $\varepsilon_r = 8.65$ and 9.18 for the films with $x = 0.00$ and 0.05, respectively, indicates that PF emission dominates conduction in this region E for those two samples. The field-assisted thermal ionization of trapped carriers into the conduction band of thin films appears to be a typical leakage mechanism in BFO thin films, resulting in PF emission. For $x = 0.10$, however, there was no linear relationship between log($J/E$) and the $E^{1/2}$ curve, which is possibly due to the efficient suppression of oxygen and bismuth vacancies for higher Y content.

According to the Schottky model [35], the log($J$) vs $E^{1/2}$ curves for BYFO films are shown in Fig. 5d.

$$J_{Schottky} = BT^2\exp\left( -\frac{\varphi_B - \sqrt{\frac{qE}{4\pi\varepsilon_0\varepsilon_r}}}{kT} \right)$$

$$\Rightarrow \log(f) \propto \sqrt{\frac{q^3}{4\pi\varepsilon_0\varepsilon_r kT}} E^2,$$

in which $B$ is constant, and $\varphi_B$ is the interface potential barrier. Schottky emission (SE) can also be calculated by $\varepsilon_r$, according to this model. Only for $x = 0.05$, it is a linear relationship between log($J$) and $E^{1/2}$ observed, shown in Fig. 5d, and the fitting result shows $\varepsilon_r = 6.93$. The detection of SE for $x = 0.05$ is likely due to a flat electrode-film contact, as illustrated in Fig. 2.

The log($J/E^2$) vs $1/E$ curves for BYFO films are shown in Fig. 5e, according to the Fowler–Nordheim (FN) tunneling [36], which is defined as

\[ J = \frac{A}{E^2} \exp\left( -\frac{B}{E} \right) \]
where $C$ and $D$ are constants in this equation. In general, FN tunneling was found in the presence of a strong electric field. The leaking mechanism is converted to FN tunneling at 53 kV/cm and 40 kV/cm for $x = 0.00$ and 0.05, respectively, as shown in Fig. 5e.

Figure 5f summarizes the leakage mechanisms of the BYFO films studied here. By doping Y with $x = 0.05$ and 0.10, the SCLC mechanism, which is
detrimental to ferroelectric characteristics, may be successfully controlled. The increased amount of the grain boundary limit behavior for BYFO films with $x = 0.05$ and $0.10$, according to the phenomena of grain refinement by doping Y observed in SEM. Furthermore, when $x = 0.10$, a slightly altered conduction process is observed, which might be due to the structural evolution. Otherwise, because the leakage current is greatly lowered with $x = 0.10$, the extremely low leakage current $J = 9.59 \times 10^{-7}$ A/cm$^2$ at $E = 100$ kV/cm may make it difficult to observe the leakage mechanism, such as SCLC, SE, PF, and FN.

Figure 6 shows the XPS results for Fe ions for BiFeO$_3$ and Bi$_{0.95}$Y$_{0.05}$FeO$_3$ films. Since the sample contains a Pt layer, it can accurately correspond to the $2^+ + 3^+$ peaks in the 2P orbital of Fe ions after binding energy correction by Pt ion and fitted by using the Voigt function. The fitted peak area could be calculated as the concentration of the ion valence. For BFO, in Fig. 6a, higher amount of Fe$^{2+}$ of up to 32% is found, revealing larger amount of the oxygen vacancies. In Fig. 6b, the amount of Fe$^{2+}$ is significantly reduced to 18%. The above XPS analysis indicates Y substitution could effectively suppress the oxygen vacancies.

Figure 7 shows the M-H curves of BYFO films. With increasing $x$, the saturation magnetization ($M_s$) improves from 4.4 emu/cm$^3$ for $x = 0.00$ to 4.9 emu/cm$^3$ and 6.7 emu/cm$^3$ for $x = 0.05$ and 0.10. The saturation magnetization is highly dependent on both the magnetic structure [37] and the magnetic moments. The spiral spin structure of BFO can effectively change by the crystal constant and Fe–O–Fe bond angle, resulted from the radius difference between Y$^{3+}$ and Bi$^{3+}$. BYFO films will turn into ferromagnetism if the spiral spin of the octahedral ferrite with weak antiferromagnetism in BFO is reduced with Y substitution. As a result, $M_s$ is enhanced.

Because contact loading is inevitable in manufacturing and packaging operations, it is vital to understand the mechanical properties of BYFO films for practical applications. The nanomechanical characteristics are investigated using a nano-indenter. The hardness versus depth curves of BYFO are displayed in Fig. 8. The mechanical parameter is
calculated using curves derived from the average penetration depth, which is between 60 and 80 nm. The penetration depth range was purposefully set to be deep enough to observe plastic deformation during indentation while being shallow enough to minimize problems caused by surface roughness and substrate. The analysis result shows that the hardness of the film increases from 7.0 GPa for \( x = 0.00 \) to 10.1 GPa for \( x = 0.05 \), related to the grain refinement. Because of the refined grain size and compact grain structure, the grain boundary effectively hinders dislocation motions, improving the hardness of the BYFO films. Finally, when \( x = 0.10 \), it reduces to 6.5 GPa, probably due to the appearance of the orthorhombic phase. It is consistent with past research on the substitution of Sm, La, Pr, and Gd in BFO films [20], in which the orthorhombic phase causes a decrease in hardness.

The structure and ferroelectric characteristics of BYFO films grown at various \( T_s \) with \( x = 0.05 \) are also investigated. Figure 9 shows the XRD patterns of BYFO with \( x = 0.05 \) deposited at various \( T_s \). At \( T_s = 300-450 \) °C, the films have a strong Pt(111) texture with Laue fringes, but the Laue fringes disappear at \( T_s = 500 \) °C, implying a rougher Pt surface induced due to higher \( T_s \). Except for Pt(111), no diffraction peak can be seen at \( T_s = 300 \) °C, indicating that the BYFO phase has not yet developed due to the low processing temperature. The isotropic perovskite structure can be seen at \( T_s = 350-500 \) °C. The (001) peak of the perovskite phase is found when \( T_s \) rises from 400 to 450 °C. Bi\(_2\)Fe\(_4\)O\(_9\) phase arises in addition to the BYFO phase at high \( T_s = 500 \) °C, probably due to Bi volatilization at high \( T_s \). Furthermore, both rhombohedral and pseudo cubic phases contribute to two peaks near 2\( \theta = 32.5^\circ \) and 47°: one near 2\( \theta = 32.5^\circ \) is made up of (104), and (110), and the other near 2\( \theta = 47^\circ \) is made up of (024), and (110), (002). At \( T_s = 350 \) °C, this suggests that rhombohedral and pseudo-cubic crystals coexist. When \( T_s = 400-500 \) °C, however, the pseudo-cubic crystal structure takes over.

Figure 10 shows SEM images of BYFO grown at various \( T_s \) with \( x = 0.05 \). There is no visible grain structure detected for the films made at low \( T_s = 300 \) °C, as illustrated in Fig. 9a, which is consistent with XRD results. Figure 10b–e shows the surface morphology with the crystalline grain as \( T_s \) is increased to 350–500 °C, as well as grain growth with \( T_s \). At \( T_s = 350 \) °C, the average grain size increases to 70.6 nm at \( T_s = 400 \) °C, 78.4 nm at \( T_s = 450 \) °C, and 100.8 nm at \( T_s = 500 \) °C, respectively.

Figure 11 shows a ferroelectric and leakage analysis of BYFO developed at various \( T_s \) with \( x = 0.05 \). The film deposited at \( T_s = 300 \) °C has no ferroelectric characteristic because no perovskite structure is formed due to the low manufacturing temperature. Figure 11a shows hysteresis loops with good ferroelectric characteristics for films at \( T_s = 350-500 \) °C. (d) 2\( P_r \) increases with increasing \( T_s \) from 61.3 \( \mu \)C/cm\(^2\) at \( T_s = 350 \) °C to 102.6 \( \mu \)C/cm\(^2\) at \( T_s = 400 \) °C at first, then drops to 95.2–98.6 \( \mu \)C/cm\(^2\) at \( T_s = 450-500 \) °C. The increase in 2\( P_r \), with increasing \( T_s \) from 350 to 400 °C may be due to the suppression of
rhombohedral phase and improved crystallinity, while the slight decrease in $2P_r$ with increasing $T_s$ from 400 to 500 °C may be due to a change in orientation composition of the films.

Figure 12a shows J-E curves, whereas Figs. 10b–f demonstrate the leakage mechanism examined by fitting J-E curves based on Ohmic and SCLC models, PF emission, SE, and FN tunneling, respectively. The leaking mechanisms for the aforesaid samples is also presented in Fig. 12f at varied E. The leakage current diminishes as $T_s$ rises. Reduced leakage aids for the promotion of ferroelectric characteristics. $T_s$ rises, causing grain growth, and results in a reduction in the volume of grain boundaries in the sample. The increased leakage at higher $T_s = 500$ °C is presumably related to the appearance of the secondary phase due to the volatilization of Bi ions at higher $T_s$. The only one that has been observed SCLC conduction,
which could be another evidence that the high leakage is related to the vacancies of Bi ions. At lower electric fields, the films made at $T_s = 350–400 \, ^\circ\text{C}$ exhibit grain boundary limited behavior, which could be connected to the reduced grain size observed in the SEM analysis. For $T_s = 350–400 \, ^\circ\text{C}$, the PF emission, which results from the field-assisted thermal ionization of trapped carriers into the conduction band, was seen. For $T_s = 400–450 \, ^\circ\text{C}$, the Schottky emission, which relates to a flat interface, was found. At higher $E$, for all samples, the mechanisms are converted into FN tunneling. The SE mechanism is present in samples with outstanding ferroelectric characteristics, according to the above analysis for the leaking mechanism. It reveals that SE mechanism is advantageous to ferroelectric characteristics. Furthermore, the SCLC that occurs at the maximum growth temperature causes substantial damage to the P-E loop squareness rather than the ferroelectric polarization. The grain boundary limited behavior and PF emission, on the other hand, appear in thin films with relatively small grains.

The physical parameters of BYFO bulk materials and films that have been developed up to now are listed in Table 1. Both ferroelectric ($2P_r$ less than 1 $\mu\text{C/cm}^2$) and ferromagnetic ($M_s$ less than 1.8 emu/cm$^3$) properties are very low in BYFO bulks. Intriguingly, BYFO in film form shows a considerable improvement in ferroelectric properties along with better ferromagnetic properties. Kuang reported that BYFO films made by the sol–gel method have improved $2P_r = 12 \, \mu\text{C/cm}^2$ with low magnetic characteristics. BYFO films deposited on a refined Pt(111) underlayer at a lower temperature of 400 °C show superior FE and FM properties in this study. Good FE properties is related to pseudo-cubic structure and the reduced leakage. Reduced leakage is due to suppressed oxygen vacancy, refined interface morphology, and fine microstructure. Good FM properties is related to the suppression of spiral spin structure for BFO with Y substitution. As a results, higher both $2P_r$ of 102.6 $\mu\text{C/cm}^2$ and $M_s$ of 5.0 emu/cm$^3$ are attained for Bi$_{0.95}$Y$_{0.05}$FeO$_3$ thin film. The findings in this work show that Y-substituted BFO thin films produced by PLD on a Pt electrode buffered glass substrate could be a suitable multiferroic material for applications.

4 Conclusions

We investigate the effects of Y content and substrate temperature on the structure, microstructure, multiferroic, and nanomechanical properties of BYFO thin films produced by PLD on 20-nm-thick Pt underlayer buffered glass substrates in this paper. At $T_s = 400 \, ^\circ\text{C}$, the perovskite phase in BYFO films with
$x = 0.00–0.10$ has been confirmed. A rhombohedral phase for $x = 0.00$ is transitioned to a pseudo-cubic phase for $x = 0.05$, and an extra orthorhombic phase is discovered for $x = 0.10$. As the Y content in BYFO increases, the grain size reduces. BYFO thin films have a hardness range of 6.5 to 10.1 GPa, and nanomechanical characteristics are substantially influenced by phase compositions and grain size. Furthermore, due to proper Y substitution, phase composition, microstructure, and surface shape have a significant impact on ferroelectric characteristics. Ferroelectric characteristics are increased to
Table 1 Multiferroic and nanomechanical properties of developed Bi$_{1-x}$Y$_x$FeO$_3$

| Composition          | Sample Form      | $2P_r$ (µC/cm$^2$) | $E_c$ (kV/cm) | $M_s$ (emu/cm$^3$) | $H_c$ (Oe) | Hardness (GPa) | References |
|----------------------|------------------|---------------------|---------------|-------------------|------------|----------------|------------|
| Bi$_{0.90}$Y$_{0.10}$FeO$_3$ Bulk | 1.8 | $< 100$ |
| Bi$_{0.95}$Y$_{0.05}$FeO$_3$ Bulk | 0.6 | 20 | $< 0.02$ | $< 100$ |
| Bi$_{0.95}$Y$_{0.05}$FeO$_3$ Bulk | 1.0 | 25 | |
| Bi$_{0.90}$Y$_{0.10}$FeO$_3$ Polycrystalline film | 12 | 30 | $< 0.3$ | $< 100$ |
| Bi$_{0.95}$Y$_{0.05}$FeO$_3$ Polycrystalline film | 1.1 | 200 | 1.6 | $< 100$ |
| Bi$_{0.95}$Y$_{0.05}$FeO$_3$ Polycrystalline film | 102.6 | 295 | 5.0 | 200 | 10.1 | This work |
| Bi$_{0.90}$Y$_{0.10}$FeO$_3$ Polycrystalline film | 20.4 | 240 | 6.7 | 200 | 6.2 | |

$2P_r = 41.1–102.6$ µC/cm$^2$ and $E_c$ of 248–295 kV/m for BYFO films with $x = 0.00–0.05$, probably due to suppressed leakage current caused by the suppressed oxygen vacancy, the flattened interface, and microstructure refinement. The suppression of the spiral spin structure of the octahedral ferrite causes the increased $M_s$ of 4.4–6.7 emu/cm$^3$ found in BYFO films due to Y substitution. This work suggests that Y-substituted BFO thin films on a Pt electrode buffered glass substrate deposition at a lower temperature could be a promising multiferroic material.

Data availability

Source data for figures [1–12] are provided with the paper.

Declarations

Competing interests  The authors have no relevant financial or non-financial interests to disclose.

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