Effect of concentration of Nd\textsuperscript{3+} on the photoluminescence and ferroelectric properties of Bi\textsubscript{4-x}Nd\textsubscript{x}Ti\textsubscript{3}O\textsubscript{12} films

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\textbf{ABSTRACT:} Lead-free films of Bi\textsubscript{4-x}Nd\textsubscript{x}Ti\textsubscript{3}O\textsubscript{12} were deposited on Pt(111)/Ti/SiO\textsubscript{2}/Si(100) substrate via spin-coating methods. It is shown that there are no secondary phases in Bi\textsubscript{4-x}Nd\textsubscript{x}Ti\textsubscript{3}O\textsubscript{12} films and clear interfaces between the Bi\textsubscript{4-x}Nd\textsubscript{x}Ti\textsubscript{3}O\textsubscript{12} films and substrates when the films are annealed at 700 °C. And the Bi\textsubscript{4-x}Nd\textsubscript{x}Ti\textsubscript{3}O\textsubscript{12} films also exhibit a blue light emission peak at 437 nm and a yellow light emission peak at 580 nm. There are narrower band gaps, higher dielectric constant and lower dielectric loss when Nd\textsuperscript{3+} concentration varies from 0 to 0.85. And the Bi\textsubscript{3.15}Nd\textsubscript{0.85}Ti\textsubscript{3}O\textsubscript{12} film possesses the minimum of band gap energy (2.67 eV). Moreover, Bi\textsubscript{3.55}Nd\textsubscript{0.45}Ti\textsubscript{3}O\textsubscript{12} film exhibits a minimal leakage current density and a maximal remanent polarization, which is highly beneficial for the potential applications in multi-functional devices.

1 Introduction

Since the ferroelectricity in Rochelle salt crystals was discovered by French Valasek in 1920, ferroelectric materials have become a research hotspot [1] and been widely used in transducers, filters, resonators, ferroelectric memories and other fields [2-6]. Up to date, the widely used ferroelectric materials are lead-based because of their stable and excellent ferroelectric properties [7-10]. However, lead-based ferroelectric materials undesirably bring about harm to human beings and pollution to environment during the preparation and application processes. As a result, researchers have been looking for alternative lead-free high performance ferroelectric materials to rival the lead-based ferroelectrics such as PbZr\textsubscript{x}Ti\textsubscript{1-x}O\textsubscript{3} [11].

Bismuth titanate (Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12}), a typical lead-free multiferroics, has drawn widespread attention owing to its high Curie temperature and excellent fatigue...
resistance [12-14]. Unfortunately, its remnant polarization is rather low because of the evaporation of Bi$^{3+}$ in the system, which gives rise to the increase of concentration of oxygen vacancies and the deterioration of ferroelectricity [15]. Thus, more and more researchers have been trying to inhibit the evaporation of Bi$^{3+}$ through doping of rare elements in Bi$_4$Ti$_3$O$_{12}$ [16-18]. M. Chen [19] reported that the substitution of Pr$^{3+}$ for Bi$^{3+}$ will decrease the space charge density which improves ferroelectric properties of Bi$_4$Ti$_3$O$_{12}$ materials. And C. P. Cheng [20] reported that the doping of Dy$^{3+}$ will enhance the ferroelectric properties of Bi$_4$Ti$_3$O$_{12}$. U. Chon [21] and X. Y. Mao [22] pointed that the doping of Nd$^{3+}$ in Bi$_4$Ti$_3$O$_{12}$ can also enhance the ferroelectric properties. The reason is that the substitution of Nd$^{3+}$ for Bi$^{3+}$ causes obvious structural distortion along the C axis, thus resulting in a large polarization along the C axis [21, 23] besides inhibiting the evaporation of Bi$^{3+}$. Surprisingly, Bi$_4$Ti$_3$O$_{12}$ materials doped with rare earth elements possess obvious photoluminescence [24, 25]. R. Bokolia [26] reported that Er$^{3+}$-doped Bi$_4$Ti$_3$O$_{12}$ materials possess photoluminescence besides ferroelectric properties. And K. Ruan [27] pointed that Eu$^{3+}$-doped Bi$_4$Ti$_3$O$_{12}$ films possess good photoluminescent properties. Although, up to date, ferroelectric properties of Nd$^{3+}$-doped Bi$_4$Ti$_3$O$_{12}$ films have been investigated, there are few reports on investigating photoluminescence of Nd$^{3+}$-doped Bi$_4$Ti$_3$O$_{12}$ films. Therefore, it is necessary to study not only ferroelectric properties but also photoluminescence of Nd$^{3+}$-doped Bi$_4$Ti$_3$O$_{12}$ films systematically.

In this work, Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films were prepared on the substrates (Pt(111)/Ti/SiO$_2$/Si(100)) via the sol-gel and spin-coating method. And impact of the concentration of Nd$^{3+}$ in Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films on the ferroelectric properties, dielectric properties, leakage current densities and photoluminescence were investigated. Photoluminescence and ferroelectric properties were studied in detail.

2 Experimental

The Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ (when x=0, 0.25, 0.45, 0.65, 0.85) films were deposited on the Pt(111)/Ti/SiO$_2$/Si(100) substrate, and precursors were fabricated by sol-gel method. Neodymium oxide (Nd$_2$O$_3$), bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O) and tetrabutyl titanate (Ti(OC$_4$H$_9$)$_4$) were selected as starting materials. 2-methoxyethanol
(C₃H₈O₂) and acetic acid (C₂H₄O₂) were used as the solvents. Acetylacetone (C₅H₈O₂) was used to stabilize the solution. Firstly, certain proportion of Nd₂O₃ and Bi(NO₃)₃·5H₂O were dissolved in C₂H₄O₂ according to the stoichiometry of Bi₄₋ₓNdₓTi₃O₁₂. Thus, solution A was obtained. And excessive Bi(NO₃)₃·5H₂O (8 wt%) was used to compensate the loss of Bi³⁺ volatilization during annealing process. Then, Ti(OC₄H₉)₄ was dissolved in C₃H₈O₂, and a small quantity of stabilizer (C₅H₈O₂) was dripped into C₃H₈O₂. Then solution B was obtained. Then, the above two solutions (A and B) were mixed to get sol. And the sol was deposited on the substrates to get monolayered Bi₄₋ₓNdₓTi₃O₁₂ films via spin-coating technology. Subsequently, Bi₄₋ₓNdₓTi₃O₁₂ films were pre-annealed and annealed in tube furnace. At last, the above-mentioned process needs to be repeated three times to acquire four-layered Bi₄₋ₓNdₓTi₃O₁₂ films. The specific process was displayed in Fig. 1.

The phase constitutions of Bi₄₋ₓNdₓTi₃O₁₂ films were carried out by X-ray diffraction (X’Pert Pro MPD, PANalytical, Holland). The morphologies of the surface and cross-section were investigated though FESEM (SU8020, Hitachi, Japan). P-E hysteresis loops of the films were determined by Precision LC Unit (Radiant Precision LC, Radiant Technologies, USA). The leakage current densities were determined by semiconductor tester (Keithley, 4200-SCS, USA). Absorption spectrum of films were obtained by the UV spectrophotometer (Cary-5000, Agilent, USA). Photoluminescent spectrum of the films were measured via fluorescence spectrophotometer (F4500, Hitachi, Japan).

3 Results and discussion

3.1 Phase constitution

The XRD patterns of five films of Bi₄₋ₓNdₓTi₃O₁₂ were displayed in Fig. 2. As shown in Fig. 2. (a), it is obvious that the diffraction peaks of the Bi₄₋ₓNdₓTi₃O₁₂ films are composed of those from Bi₄Ti₃O₁₂ (JCPDS No.72-1019) and from Pt on the top layer of the substrates without any from impurity phases [28, 29]. It indicates that Nd³⁺ has dissolved into the crystal lattice of Bi₄Ti₃O₁₂ and pure Bi₄₋ₓNdₓTi₃O₁₂ films have been prepared [30, 31]. And the sharp peaks imply good crystallinity [26]. As
shown in Fig. 2(b), for all the five films, the diffraction peaks at about 30.0° shift slightly to a greater angle. This is mainly due to the fact that the radius of Nb$^{3+}$ (1.11 Å) is less than that of Bi$^{3+}$ (1.17 Å) [22, 32]. The replacement of Bi$^{3+}$ with Nd$^{3+}$ will lead to reduction of lattice parameters and crystal plane spacing, and thus the diffraction peaks shift to a greater angle according to Bragg equation.

### 3.2 Microstructure

The surface graphs of the films were illustrated in the Fig. 3. It is seen that, for the Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films (x being 0 and 0.25, respectively), there are obvious cracks and pores on the surfaces of these samples. However, for the other films, cracks and pores are not found. With the increase of Nd$^{3+}$ concentration, the particle sizes decrease and the relative density of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films increases.

The cross-section images of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films were shown in Fig. 4. All of the five films exhibit layered structure. The interfaces between Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films and substrates are flat. And there are no inter-layers between the films and substrates, implying that no diffusion exists between the Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films and substrates. It can be observed that the thicknesses of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films are all around 200 nm, which is higher than that of pure Bi$_4$Ti$_3$O$_{12}$ film. The difference in thicknesses for Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films with different Nd$^{3+}$ concentration is mainly due to the preparation of films by spin-coating technology.

### 3.3 Ferroelectric properties

The hysteresis loops of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films were displayed in Fig. 5. The results obtained from Fig. 5 were listed in Tab. 1. Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films seem to exhibit good ferroelectric properties. The values of remnant polarization ($P_r$) and saturated polarization ($P_s$) of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films are great than those of un-doped Bi$_4$Ti$_3$O$_{12}$ film, which indicates that doping of Nd$^{3+}$ is beneficial for the improvement of the ferroelectric properties. It is seen that, firstly, the values of $P_r$ increase to 16.86 µc·cm$^{-2}$ and then decrease gradually with increasing Nd$^{3+}$ concentration. The Bi$_{3.55}$Nd$_{0.45}$Ti$_3$O$_{12}$ film possesses the maximal value of $P_r$ (16.86 µc·cm$^{-2}$) which is greater than those of Bi$_4$Ti$_3$O$_{12}$ films in Ref. [33] (10.5µc·cm$^{-2}$) and Ref. [34] (10
\( \mu \text{c} \cdot \text{cm}^{-2} \)). And it is also significantly greater than undoped Bi\(_4\)Ti\(_3\)O\(_{12}\) films in Ref. [35] (4.8 \( \mu \text{c} \cdot \text{cm}^{-2} \)).

In addition, it is worth noting that volatilization of Bi\(^{3+}\) during annealing process inevitably brings about increased oxygen vacancies and degraded ferroelectric properties of the films [28, 30]. The doping of a small amount of Nd\(^{3+}\) will inhibit the volatilization of Bi\(^{3+}\) and reduce the concentration of oxygen vacancies, and thus increase the values of \( Pr \), as shown in Fig. 5. However, with the further increase of Nd\(^{3+}\) concentration, particle size will decrease and the values of \( Pr \) reduce correspondingly owing to the pinning effect [29, 34]. Therefore, The Bi\(_{3.55}\)Nd\(_{0.45}\)Ti\(_3\)O\(_{12}\) film possesses the maximal value of \( Pr \).

3.4 Leakage current densities

The leakage current densities of Bi\(_{4-x}\)Nd\(_x\)Ti\(_3\)O\(_{12}\) films were displayed in Fig. 6. Obviously, when the values of applied electric field (\( E \)) are below 100 KV \cdot \text{cm}^{-1}, the leakage current densities increase rapidly with increasing \( E \). However, when the values of \( E \) are greater than 100 KV \cdot \text{cm}^{-1}, the leakage current densities increase slowly and remain constant finally. Compared with the Bi\(_4\)Ti\(_3\)O\(_{12}\) film, Nd\(^{3+}\)-doped films possess lower leakage current densities, indicating that doping of Nd\(^{3+}\) is beneficial for the reduction of leakage current densities. The reason is that volatilization of Bi\(^{3+}\) during the annealing process induces higher concentration oxygen vacancies [36]. And the substitution of Nd\(^{3+}\) for Bi\(^{3+}\) inhibits the volatilization of Bi\(^{3+}\) effectively, thus reducing oxygen vacancies and leakage current densities. The data summarized from Fig. 6 were shown in Tab. 2. Among the five films, Bi\(_{3.55}\)Nd\(_{0.45}\)Ti\(_3\)O\(_{12}\) film possesses the minimum of leakage current density (1.02\( \times 10^{-6} \) A \cdot \text{cm}^{-2}), which is close to the data from Ref. [32] (2\( \times 10^{-6} \) A \cdot \text{cm}^{-2}) and lower than those from Ref. [37] (1.15\( \times 10^{-5} \) A \cdot \text{cm}^{-2}). It should be noted that leakage current density of Bi\(_{3.55}\)Nd\(_{0.45}\)Ti\(_3\)O\(_{12}\) films is about one order lower than that of Bi\(_4\)Ti\(_3\)O\(_{12}\) film (1.85\( \times 10^{-5} \) A \cdot \text{cm}^{-2}).

3.5 Dielectric properties

Variation of dielectric constant (\( \varepsilon \)) and dielectric loss (\( \tan \delta \)) with frequency was
shown in Fig. 7. As shown in Fig. 7(a), at lower frequency (<10000 Hz), the values of \( \varepsilon \) decrease rapidly with increasing frequency. Nevertheless, at higher frequency (>10000 Hz), the values of \( \varepsilon \) decrease slowly and remain nearly constant. It is clearly seen from Fig. 7(b) that, with increasing frequency, the values of \( \tan \delta \) remain nearly unchanged when frequency is smaller than 10000 Hz and increase rapidly when frequency is above 10000 Hz. At the same frequency, the values of \( \varepsilon \) increase and the values of \( \tan \delta \) decrease with the increase of Nd\(^{3+}\) concentration. This indicates that doping of Nd\(^{3+}\) can effectively enhance the dielectric properties of the films.

3.6 Photoluminescence

Excitation spectra of Bi\(_{4-x}\)Nd\(_x\)Ti\(_3\)O\(_{12}\) films were shown in Fig. 8(a). Obviously, there is a distinct excitation peak at about 294 nm, which corresponds to the energy level transition of \( ^4I_{9/2} \rightarrow ^2H_{11/2} \) [38, 39]. The emission spectra of Bi\(_{4-x}\)Nd\(_x\)Ti\(_3\)O\(_{12}\) films were illustrated in Fig. 8(b), showing that there is one blue light emission peak at 437 nm and one yellow light emission peak at 580 nm. These are attributed to the energy level transitions of \( ^4G_{9/2} \rightarrow ^4F_{9/2} \) and \( ^4G_{7/2} \rightarrow ^4F_{9/2} \), respectively [38, 39]. The wavelength of the emission peaks almost doesn’t change under different doping concentration of Nd\(^{3+}\). With increasing concentration of Nd\(^{3+}\), the emission intensities increase firstly and then decrease. The emission intensity reaches the maximum when the concentration of Nd\(^{3+}\) is equal to 0.45, which indicates quenching concentration is about 0.45. Concentration quenching mechanism is highly relevant to the critical interaction distance between neighboring activators in the host lattice [40, 41].

Next, we give an intuitive description on the luminescence mechanism of the Bi\(_{4-x}\)Nd\(_x\)Ti\(_3\)O\(_{12}\) films based on the possible partial energy level diagram of Nd\(^{3+}\), as shown in Fig. 8(c). It can be clearly seen that Nd\(^{3+}\) was excited from ground state (\( ^4I_{9/2} \)) to excited state (\( ^2H_{11/2} \)) when excited at a deep ultraviolet light (DUV, 294nm). Then, Nd\(^{3+}\) was relaxed from excited state of \( ^2H_{11/2} \) to the energy level of \( ^4G_{9/2} \) and \( ^4G_{7/2} \) via non-radiative-relaxation [39, 41]. Finally, the electronic transitions from energy level of \( ^4G_{9/2} \) and \( ^4G_{7/2} \) to the energy level of \( ^4F_{9/2} \) give rise to a blue light emission peak at 437 nm and a yellow light emission peak at 580 nm, respectively.

The diagrams of Commission Internationale de L’Eclairage (CIE) chromaticity
coordinate of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films were shown in Fig 9. It can be found that CIE chromaticity coordinates of Bi$_{3.75}$Nd$_{0.25}$Ti$_3$O$_{12}$, Bi$_{3.55}$Nd$_{0.45}$Ti$_3$O$_{12}$, Bi$_{3.35}$Nd$_{0.65}$Ti$_3$O$_{12}$ and Bi$_{3.15}$Nd$_{0.85}$Ti$_3$O$_{12}$ are (0.2568, 0.2545), (0.2402, 0.2552), (0.2509, 0.2610), (0.2499, 0.2688), respectively, which are all in the blue region of the CIE diagram.

The ultraviolet (UV) -visible (Vis) -near infrared (NIR) absorption spectra of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films were shown in Fig. 10(a). It can be seen that the films exhibit obvious absorptions from 350 nm to 500 nm. In general, for the indirect transitions, the band gap energy ($E_g$) can be obtained via following formula [42, 43]:

$$a h v^{1/2} = A(h v - E_g)$$  \((1)\)

Where $\alpha$ is the absorption coefficient from the absorption spectrum, $A$ is constant and $h v$ is energy of a photon, respectively. Variations of $(a h v)^{1/2}$ with $h v$ of the films were shown in Fig. 10(b). The values of $E_g$ will be determined from the intersections of the curve tangent and the abscissa [44, 45], as shown in Tab.3. Apparently, the values of $E_g$ decrease gradually with the increase of Nd$^{3+}$ concentration, which is beneficial for enhancing visible light catalytic activity [42, 44]. The value of $E_g$ of Bi$_{3.15}$Nd$_{0.85}$Ti$_3$O$_{12}$ film is 2.67 eV, which is smaller than that reported in Ref. [42] (2.82 eV), which implies the potential application in light catalytic fields as smaller $E_g$ is beneficial for enhancing visible light catalytic activity [42, 44].

4 Conclusions

Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films doped with different concentrations of Nd$^{3+}$ were deposited on the substrate via spin-coating technology. The as-prepared Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films are pure and have very few pores and cracks on the surfaces of the films. The interfaces between Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films and the substrates are clear and flat. Bi$_{3.55}$Nd$_{0.45}$Ti$_3$O$_{12}$ film possess the maximum of $Pr$ (16.86 $\mu$C·cm$^{-2}$) and the minimum of leakage current density (1.02×10$^{-6}$ A·cm$^{-2}$). With the increase of Nd$^{3+}$ concentration, the values of $\varepsilon$ of the films increase and the values of $\tan\delta$ decrease. The films of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ exhibit a blue light emission peak at 437 nm and a yellow light emission peak at 580 nm. With increasing concentration of Nd$^{3+}$, the values of $E_g$ decrease gradually. For the film of Bi$_{3.15}$Nd$_{0.85}$Ti$_3$O$_{12}$, the value of band gap energy is 2.67 eV. The
photoluminescence and ferroelectric properties of Bi$_{3.55}$Nd$_{0.45}$Ti$_3$O$_{12}$ film are, on the whole, good and helpful for the applications in multi-functional devices.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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**Figure Captions**

**Fig. 1**  The preparation process of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films.

**Fig. 2**  a  The XRD patterns of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films;  b  magnified diffraction peaks at about 30.0°.

**Fig. 3**  The FESEM surface morphologies of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films:  a  x=0;  b  x=0.25;  c  x=0.45;  d  x=0.65;  e  x=0.85.

**Fig. 4**  The FESEM cross-section morphologies of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films:  a  x=0;  b  x=0.25;  c  x=0.45;  d  x=0.65;  e  x=0.85.

**Fig. 5**  The P-E hysteresis loops of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films; inset: the values of Pr of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films.

**Fig. 6**  The leakage current densities of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films under different electric field; inset: the leakage current densities of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films at 300 KV·cm$^{-1}$.

**Fig. 7**  a  Variation of dielectric constant with frequency for Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films;  b  variation of dielectric loss with frequency for Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films.

**Fig. 8**  a  The emission spectrum of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films with different doped concentration of Nd$^{3+}$;  b  the excitation spectrum of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films with different doped concentration of Nd$^{3+}$;  c  partial energy level diagram of Nd$^{3+}$.

**Fig. 9**  The diagrams of CIE chromaticity coordinate of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films.

**Fig. 10**  a  UV-Vis-NIR absorption spectra of Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ films;  b  variation of $(ahv)^{1/2}$ with hν.
**Table Captions**

**Tab. 1** The ferroelectric parameters of $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$ films.

**Tab. 2** The leakage current densities of $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$ films.

**Tab. 3** $E_g$ of $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$ films with different concentration of Nd$^{3+}$. 