

**Tunable photoluminescence properties of Pr<sup>3+</sup>/Er<sup>3+</sup>-doped  
0.93Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>-0.07BaTiO<sub>3</sub> low-temperature sintered  
multifunctional ceramics**

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## Abstract

Pr<sup>3+</sup>/Er<sup>3+</sup>-doped 0.93Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>-0.07BaTiO<sub>3</sub> ceramics have been fabricated at a low sintering temperature of 960°C using a sintering aid of Li<sub>2</sub>CO<sub>3</sub>. The effects of energy transfer between Pr<sup>3+</sup> and Er<sup>3+</sup> on their photoluminescence properties have been investigated. Our results reveal that the down-conversion emissions of Pr<sup>3+</sup> are weakened and the lifetimes are shortened by the co-doping of Er<sup>3+</sup>. As a result, when both Pr<sup>3+</sup> and Er<sup>3+</sup> are excited simultaneously, with increasing the concentration of Er<sup>3+</sup>, the green emissions from Er<sup>3+</sup> increase but the red emissions from Pr<sup>3+</sup> decrease. Moreover, the emission color of the ceramics can be reversibly changed between red, yellow and yellowish green by using excitation sources of different wavelengths. Strong up-conversion green emissions with short lifetimes arisen from Er<sup>3+</sup> have also been observed for the ceramics under the excitation of 980 nm. Owing to the Li<sub>2</sub>CO<sub>3</sub> sintering aid, the low-temperature sintered ceramics also exhibit reasonably good ferroelectric and piezoelectric properties, and hence should be promising for multifunctional applications such as electro-optical coupling devices.

*Keywords:* doped BNTBT; photoluminescence; energy transfer; ferroelectrics; multifunction

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## 1. Introduction

Recently, lanthanide ions ( $\text{Ln}^{3+}$ )-activated inorganic luminescent materials have attracted great attention owing to their potential applications in flat-panel displays, luminescent lamps, solid-state lasers and other photonic devices [1-3]. The unique electronic structure of  $\text{Ln}^{3+}$  enables them to serve as luminescent centers in the photoluminescence (PL) process. Among  $\text{Ln}^{3+}$ ,  $\text{Pr}^{3+}$  are well-known for their strong down-conversion (DC) visible (e.g. red) and near-infrared emissions under the excitation of ultraviolet (UV) light. The  $\text{Pr}^{3+}$ -doped luminescent materials have then been widely studied for the applications in multi-wavelength laser systems [4] as well as the use as a spectroscopic probe in investigating crystal structures and phase transitions of the host materials [5]. On the other hand,  $\text{Er}^{3+}$  exhibit not only strong DC visible emissions but also efficient up-conversion (UC) green and red emissions under infrared irradiation [1,6]. The UC PL has widespread applications in various fields, such as biological assays, color displays and medical imaging [7-9]. Co-doping of  $\text{Pr}^{3+}$  and  $\text{Er}^{3+}$  is an effective approach to realize energy transfer and to quench the excited levels due to their similar energy levels [10,11], making it possible to tailor PL intensities, tune emission colors and change luminescent efficiencies [12].

$\text{Ln}^{3+}$ -doped ferroelectrics with multifunctional performances have been extensively studied for the miniaturization and multi-functionalization of devices [13].  $(1-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{BaTiO}_3$  (BNT-xBT,  $x = 0.06-0.07$ ) is one of the promising lead-free candidates possessing a high piezoelectric coefficient ( $d_{33} = 420$  pC/N for single crystals and 155 pC/N for ceramics) and a large electromechanical coupling

coefficient ( $k_t = 70\%$  for single crystals and  $k_p = 36.7\%$  for ceramics) [14]. An electric field-induced giant strain response (a reversible strain of  $\sim 0.43\%$ ) and outstanding PL enhancement (increased by  $\sim 40\%$ ) have been observed in  $\text{Pr}^{3+}$ -modified BNT-0.07BT ceramics [15]. The effects of vacancies on PL of  $\text{Er}^{3+}$ -doped BNT-0.07BT ceramics have also been investigated [6]. It has been shown that, via the doping of  $\text{Er}^{3+}$  at various sites of the host lattices, oxygen or cation vacancies are produced and the PL emissions can then be adjusted from the visible to mid-infrared regions. However, there is little work studying the co-doping effect of various  $\text{Ln}^{3+}$  on BNT-xBT ceramics. In general, a high sintering temperature (e.g.,  $1200^\circ\text{C}$  for  $\text{Er}^{3+}$ -doped BNT-0.07BT) [6] is required for preparing well-densified BNT-xBT-based ceramics. This, however, may cause certain volatilization losses of Bi and Na and induce adverse effects of the ferroelectric and piezoelectric properties. Liquid-phase sintering using sintering aids such as  $\text{CuO}$ ,  $\text{V}_2\text{O}_5$  and  $\text{Li}_2\text{CO}_3$  is a common technique to reduce the sintering temperatures of most ferroelectric ceramics [16-18].

In the present work, 1-mol%  $\text{Li}_2\text{CO}_3$  sintering aid has been used to prepare  $\text{Pr}^{3+}/\text{Er}^{3+}$ -doped BNT-0.07BT ceramics at a low sintering temperature of  $960^\circ\text{C}$ . The DC PL properties of  $\text{Pr}^{3+}$  and  $\text{Er}^{3+}$  as well as the UC PL properties of  $\text{Er}^{3+}$  have been studied systematically. The effects of the co-doping on the emission intensities, colors and lifetimes have been studied. The piezoelectric, dielectric and ferroelectric properties of the ceramics have also been investigated for exploring multifunctional applications.

## 2. Experimental

0.93Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>-0.07BaTiO<sub>3</sub> ceramics co-doped with 0.25 mol% Pr<sup>3+</sup> and x mol% Er<sup>3+</sup> were prepared by a conventional solid-state method using high-purity metal oxides or carbonate powders: Na<sub>2</sub>CO<sub>3</sub> (99.5%), Bi<sub>2</sub>O<sub>3</sub> (99.9%), TiO<sub>2</sub> (99.9%), BaCO<sub>3</sub> (99.5%), Pr<sub>6</sub>O<sub>11</sub> (99.9%) and Er<sub>2</sub>O<sub>3</sub> (99.99%). 1 mol% Li<sub>2</sub>CO<sub>3</sub> (99%) was added as a sintering aid in preparing the ceramics for reducing the sintering temperature. The ceramics are abbreviated as Li-Pr-BNTBT-Er-x. The stoichiometric ratio of the composition were first mixed thoroughly in ethanol using zirconia balls for 8 h, and then dried and calcined at 850°C for 2 h. After the calcination, Li<sub>2</sub>CO<sub>3</sub> powders were added. The resulting mixture was ball-milled again for 8 h and mixed thoroughly with a 5-wt% polyvinyl alcohol binder solution, and then pressed into disk samples. The samples were finally sintered at 960°C for 8 h in air. All the sintered ceramics were thinned down to a thickness of 0.6 mm. Silver electrodes were fired on both surfaces of the samples at 750°C for 30 min for the measurements of dielectric, ferroelectric and piezoelectric properties. The samples were poled under a dc field of 5 kV/mm at 60°C in a silicone oil bath for 20 min.

The crystalline structure of the sintered samples was examined using X-ray diffraction (XRD) analysis with CuK<sub>α</sub> radiation (SmartLab, Rigaku Co., Japan). The PL excitation and emission spectra were measured using a spectrophotometer (FLSP920, Edinburgh Instruments, UK). A 450-W Xenon lamp was used as the excitation source for the measurements of DC PL, while a 980-nm diode laser with a maximum power of 2 W (MDL-III, CNI Optoelectronics Tech. Co., China) was used for the measurements of UC PL. For the decay curve measurements, 980-nm pulsed

signals of the diode laser were generated by a function generator (AFG3251, Tektronix, USA), which could provide a transistor-transistor logic (TTL) signal with a repetition rate of 100 Hz and duty circle of 10%. All the PL measurements were carried out at room temperature. A conventional Sawyer-Tower circuit was used to measure the polarization hysteresis ( $P$ - $E$ ) loops at 10 Hz. The dielectric constant and dielectric loss were measured (at 1 kHz) using an impedance analyzer (HP 4294A, Agilent Technologies Inc., Palo Alto, CA). The piezoelectric coefficient ( $d_{33}$ ) was measured using a piezo- $d_{33}$  meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, China).

### 3. Results and discussion

The XRD patterns of the Li-Pr-BNTBT-Er- $x$  ( $x = 0, 0.25, 0.5$ ) ceramics are shown in Fig. 1. All the ceramics possess a perovskite structure (indexed by JCPDS card no. 46-0001,  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ) and no secondary phase is observed. This suggests that  $\text{Pr}^{3+}$ ,  $\text{Er}^{3+}$  as well as  $\text{Li}^+$  have diffused into the BNTBT lattices. Owing to the similar radii,  $\text{Pr}^{3+}$  (1.29 Å, CN = 12) and  $\text{Er}^{3+}$  (1.22 Å, CN = 12) may replace  $\text{Bi}^{3+}$  (1.32 Å, CN = 12) at the A sites, while  $\text{Li}^+$  (0.76 Å, CN = 6) replace  $\text{Ti}^{4+}$  (0.605 Å, CN = 6) at the B sites. Probably due to the fact that  $\text{Pr}^{3+}$  and  $\text{Er}^{3+}$  are smaller than  $\text{Bi}^{3+}$  while  $\text{Li}^+$  is larger than  $\text{Ti}^{4+}$ , no obvious shifting of the diffraction peaks is observed.

Fig. 2 shows the photoluminescence excitation (PLE) spectra of the Li-Pr-BNTBT-Er-0.5 ceramic monitoring at 610 nm (emitting wavelength of  $\text{Pr}^{3+}$ ) and 548 nm (emitting wavelength of  $\text{Er}^{3+}$ ). As shown in Fig. 2a, the spectrum consists of

three groups of excitation peaks (ranging from 445-460 nm, 460-480 nm and 485-500 nm), which are resulted from the excitation of  $\text{Pr}^{3+}$  from the  $^3\text{H}_4$  ground level to the  $^3\text{P}_2$ ,  $^3\text{P}_1$  and  $^3\text{P}_0$  levels, respectively. On the other hand, five main PLE peaks arising from the excitations of  $\text{Er}^{3+}$  from the  $^4\text{I}_{15/2}$  ground level to the  $^4\text{G}_{11/2}$ ,  $^2\text{H}_{9/2}$ ,  $^4\text{F}_{3/2}$ ,  $^4\text{F}_{5/2}$ , and  $^4\text{F}_{7/2}$  levels, respectively, are observed at 381, 408, 443, 450 and 487 nm (Fig. 2b). The weak PLE peak observed at 468 nm is attributed to the transition  $^3\text{H}_4 \rightarrow ^3\text{P}_1$  of  $\text{Pr}^{3+}$ . These results suggest that the efficient excitation sources for the ceramics should be of 468 nm, 487 nm as well as 450 nm. Accordingly, the DC PL spectra of the Li-Pr-BNTBT-Er-x ceramics have been measured. The results are shown in Fig. 3. Under the excitation of 468 nm (for  $\text{Pr}^{3+}$ ), a wide red emission band attributed to the transition  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  of  $\text{Pr}^{3+}$  is observed centered at 610 nm (Fig. 3a) [15]. Very weak green emission bands resulting from the transitions  $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$  and  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$  of  $\text{Er}^{3+}$  are also observed in the range of 525-570 nm for the ceramics with  $x = 0.25$  and 0.5. On the other hand, as shown in Fig. 3b, two green emission bands (centered at 528 and 549 nm) as well as a red emission band (centered at 610 nm) are observed when the ceramics are excited at 487 nm (for both  $\text{Pr}^{3+}$  and  $\text{Er}^{3+}$ ). The red emission band is attributed to the same transition of  $\text{Pr}^{3+}$ , while the green emissions are resulted from the transitions  $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$  and  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$  of  $\text{Er}^{3+}$ . Similar emissions are observed for the ceramics excited at 450 nm (Fig. 3c). As both  $\text{Er}^{3+}$  and  $\text{Pr}^{3+}$  are excited, the strengths of the green and red emission bands become similar. For all the three excitation cases, the red emission band becomes weaker while the green emission bands become stronger as  $x$  increases. Obviously, as the Li-Pr-BNTBT-Er-0

ceramic does not contain  $\text{Er}^{3+}$ , no green emission bands are observed in its PL spectra under the excitation of 468, 487 and 450 nm.

Fig. 4 shows the energy level diagrams of  $\text{Er}^{3+}$  and  $\text{Pr}^{3+}$  together with the relevant energy transfer mechanisms. Under the excitation of 468 nm,  $\text{Pr}^{3+}$  in the  $^3\text{H}_4$  ground level are excited to the  $^3\text{P}_1$  level. After that, they may relax non-radiatively to the  $^3\text{P}_0$  and  $^1\text{D}_2$  levels through the multi-phonon relaxation (MPR) process, and then relax radiatively to the  $^3\text{H}_4$ , giving the red emissions ( $^1\text{D}_2 \rightarrow ^3\text{H}_4$ ) as shown in Fig. 3a. However, for the ceramics with  $x > 0$ , i.e., co-doping with  $\text{Er}^{3+}$ , energy transfer (ET) processes from  $\text{Pr}^{3+}$  to  $\text{Er}^{3+}$  (ET1:  $^3\text{P}_1(\text{Pr}^{3+}) + ^4\text{I}_{15/2}(\text{Er}^{3+}) \rightarrow ^3\text{H}_4(\text{Pr}^{3+}) + ^4\text{F}_{7/2}(\text{Er}^{3+})$ ) may take place, leading to a decrease in the populations of the  $^3\text{P}_0$  and then  $^1\text{D}_2$  levels. As a result, the red emission becomes weaker as  $x$  increases (Fig. 3a). On the other hand, the excited  $\text{Er}^{3+}$  in the  $^4\text{F}_{7/2}$  level may relax non-radiatively through MPR to the  $^2\text{H}_{11/2}$  and  $^4\text{S}_{3/2}$  levels, and then relax radiatively to the  $^4\text{I}_{15/2}$  ground level, giving the weak green emissions as observed for the ceramics with  $x = 0.25$  and  $0.5$  (Fig. 3a).

As both  $\text{Pr}^{3+}$  and  $\text{Er}^{3+}$  can be excited directly by the 487-nm or 450-nm lights, the corresponding PL processes for the ceramics with  $x > 0$  become different. Under the excitation of 487 nm,  $\text{Pr}^{3+}$  in the  $^3\text{H}_4$  ground level are excited to the  $^3\text{P}_0$  level, while  $\text{Er}^{3+}$  in the  $^4\text{I}_{15/2}$  ground level are excited to the  $^4\text{F}_{7/2}$  level. The excited  $\text{Pr}^{3+}$  may relax non-radiatively to the  $^1\text{D}_2$  level and then radiatively to the  $^3\text{H}_4$  level, generating a red emission at 610 nm [15]. Meanwhile, the excited  $\text{Er}^{3+}$  may relax non-radiatively to the  $^2\text{H}_{11/2}$  or  $^4\text{S}_{3/2}$  levels, and then relax radiatively to the  $^4\text{I}_{15/2}$  ground level, producing the green emissions at 528 and 549 nm, respectively (Fig. 3b). The PL



processes upon the excitation of 450 nm are very similar, except that both  $\text{Pr}^{3+}$  and  $\text{Er}^{3+}$  are first excited to a higher energy level ( $^3\text{P}_2$  and  $^4\text{F}_{5/2}$ , respectively), and then relax non-radiatively to the energy level  $^1\text{D}_2$  and  $^4\text{F}_{7/2}$ , respectively. The subsequent PL processes for producing the red and green emissions then become the same as those upon the excitation of 487 nm. Unlike the indirect excitation of  $\text{Er}^{3+}$  via ET1 (Fig. 4),  $\text{Er}^{3+}$  of the ceramics (with  $x > 0$ ) are excited directly by the efficient 487-nm and 450-nm sources (Fig. 2b). As a result, the resulting green emissions are strong and become dominant (Figs. 3b and 3c). As the concentration of  $\text{Er}^{3+}$  (i.e.,  $x$ ) is low and does not exceed the quenching concentration reported for various Er-doped luminescent materials (i.e., at least 2 mol%) [19], the observed intensity of the green emissions increases with increasing  $x$ . As also shown in Figs. 3b and 3c, the intensity ratio of the green to red emissions upon the 487-nm excitation is larger than that upon the 450-nm excitation, suggesting that the 487-nm light is the most efficient excitation source for  $\text{Er}^{3+}$ . This is consistent with the results of PLE shown in Fig. 2b.

The CIE (Commission Internationale de L'Eclairage, France) color coordinates of the Li-Pr-BNTBT-Er- $x$  ceramics calculated from the DC PL spectra (Fig. 3) are shown in Fig. 5. Under the excitation of 468 nm, the emission color is red and remains almost unchanged with increasing  $x$ . However, it changes significantly under other excitations. For the 450-nm irradiation, it changes from red (at  $x = 0$ ) to yellow (at  $x = 0.25$  and  $0.5$ ), whereas it changes from orange (at  $x = 0$ ) to yellowish green (at  $x = 0.25$  and  $0.5$ ) under the excitation of 487 nm. The results suggest that the emission color can be effectively and reversibly tuned by the excitation sources. For example,

the emission color for the Li-Pr-BNTBT-Er-0.25 ceramic can be reversibly changed between red, yellow and yellowish green by irradiating with 468-nm, 450-nm and 487-nm lights, respectively.

The decay curves of emission at 610 nm, corresponding to the transition  $^1D_2 \rightarrow ^3H_4$  of  $Pr^{3+}$ , for the ceramics under the excitation of 468 nm are shown in Fig. 6. As there is no energy transfer process, the decay curve for the ceramic with  $x = 0$  (i.e., singly doped with  $Pr^{3+}$ ) has been fitted to a single exponential function:

$$I = I_0 \exp\left(-\frac{t}{\tau}\right) \quad (1)$$

where  $\tau$  is the emission lifetime and  $I_0$  is the initial emission intensity at  $t = 0$ . The calculated  $\tau$  for the Li-Pr-BNTBT-Er-0 ceramic is 99  $\mu$ s. On the other hand, because of the energy transfer process between  $Pr^{3+}$  and  $Er^{3+}$  (i.e., ET1, Fig. 4), the decay curve for the ceramics with  $x > 0$  becomes non-exponential and then has been fitted to the following equation:

$$\bar{\tau} = \frac{\int_0^{\infty} I(t)tdt}{\int_0^{\infty} I(t)dt} \quad (2)$$

where  $\bar{\tau}$  is the average lifetime and  $I(t)$  is the emission intensity at a time  $t$  after the cutoff of excitation light. The calculated  $\bar{\tau}$  for the Li-Pr-BNTBT-Er-0.25 and Li-Pr-BNTBT-Er-0.5 ceramics are 81  $\mu$ s and 71  $\mu$ s, respectively. The efficiency of an energy transfer process  $\eta$  can be estimated from the luminescence lifetime using the following equation [20]:

$$\eta = 1 - \frac{\tau_1}{\tau_2} \quad (3)$$

where  $\tau_1$  and  $\tau_2$  are the luminescence lifetimes with and without the effect of energy transfer process, respectively. Accordingly, by using the calculated  $\tau$  value for  $\tau_1$  and the calculated  $\bar{\tau}$  values for  $\tau_2$ , the  $\eta$  values of ET1 (Fig. 4) in the Li-Pr-BNTBT-Er-0.25 and Li-Pr-BNTBT-Er-0.5 ceramics have been determined to be about 18% and 28%, respectively. Owing to the increase of the efficiency, the dwell times of  $\text{Pr}^{3+}$  in the  $^3\text{P}_1$ ,  $^3\text{P}_0$  and  $^1\text{D}_2$  excited levels decrease with increasing  $x$ , and thus leading to the decrease in the observed lifetimes (Fig. 6). On the other hand, as the efficiency is not very high, the red emission (at 610 nm) is not suppressed significantly by ET1, and thus only leading to a small decrease in the intensity as shown in Fig. 3a. Similarly, owing to the low efficiency, the green emissions arisen from ET1 are weak.

The decay curves of emissions at 528, 549 and 610 nm under the excitations of 487 and 450 nm are shown in Figs. 7 and 8, respectively. As the Li-Pr-BNTBT-Er-0 ceramic contains no  $\text{Er}^{3+}$ , the observed decay curves of the green emissions at 528 and 549 nm (corresponding to the  $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$  and  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$  transitions of  $\text{Er}^{3+}$ ) should be due to the background of the measurement (Figs. 7a-b and 8a-b) [21]. The calculated  $\tau$  (using Eq. 1) for the red emission at 610 nm (corresponding to the transition  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  of  $\text{Pr}^{3+}$ ) under the excitation of 487 and 450 nm (Figs. 7c and 8c) are 97 and 94  $\mu\text{s}$ , respectively, which are similar to that observed upon the 468-nm irradiation. For the ceramics with  $x > 0$ , as both  $\text{Er}^{3+}$  and  $\text{Pr}^{3+}$  are excited, energy transfer processes ET2 ( $^3\text{P}_0(\text{Pr}^{3+}) + ^4\text{I}_{15/2}(\text{Er}^{3+}) \leftrightarrow ^3\text{H}_4(\text{Pr}^{3+}) + ^4\text{F}_{7/2}(\text{Er}^{3+})$ , Fig. 4) and ET3 ( $^3\text{P}_2(\text{Pr}^{3+}) + ^4\text{I}_{15/2}(\text{Er}^{3+}) \leftrightarrow ^3\text{H}_4(\text{Pr}^{3+}) + ^4\text{F}_{5/2}(\text{Er}^{3+})$ , Fig. 4) may take place under

the excitation of 487 and 450 nm, respectively. As a result, the corresponding decay curves become non-exponential. As shown in Figs. 7 and 8, the calculated  $\bar{\tau}$  (using Eq. 2) for the green emissions changes only slightly about 95  $\mu\text{s}$  upon various irradiations, while those for the red emission decrease with increasing  $x$ . These suggest that both ET2 and ET3 for transferring energy from  $\text{Pr}^{3+}$  to  $\text{Er}^{3+}$  are more efficient than for those transferring energy from  $\text{Er}^{3+}$  to  $\text{Pr}^{3+}$ .

Apart from the DC emissions, the UC PL properties of the Li-Pr-BNTBT-Er- $x$  ceramics with  $x > 0$  have been investigated. Fig. 9 shows the UC emission spectra under the excitation of 980 nm with different powers (0.19-0.67 W). In general, three emission bands attributed to the transitions  $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$  (528 nm, green),  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$  (549 nm, green) and  $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$  (670 nm, red) are observed. Among them, the green emission at 549 nm is the strongest, while the red emission is the weakest. As the irradiation power increases, the emission intensity increases while the spectra remain almost unchanged in shape. As illustrated in Fig. 4, the UC process involves the excitation of  $\text{Er}^{3+}$  in the  $^4\text{I}_{15/2}$  ground level to the  $^4\text{F}_{7/2}$  level, via the ground state absorption (GSA) following by excited state absorption (ESA) or energy transfer up-conversion (ETU) processes. After that, the excited  $\text{Er}^{3+}$  may relax non-radiatively to the  $^2\text{H}_{11/2}$ ,  $^4\text{S}_{3/2}$  and  $^4\text{F}_{9/2}$  levels through MPR, and then relax radiatively to the  $^4\text{I}_{15/2}$  ground level, producing two green emissions at 528 and 549 nm and a red emission at 670 nm, respectively. The (integrated) PL intensities  $I$  of the green emissions have been evaluated and plotted as a function of irradiation power  $P$  in the insets of Fig. 9. A linear relationship (in log-log plot) between  $I$  and  $P$  is observed for both green

emissions of the ceramics. Based on the theoretical consideration of the multi-photon absorption process, the relationship between I and P can be represented by a power law [22]:

$$I \propto P^n \quad (4)$$

where  $n$  is the number of photons required for the UC process. The calculated  $n$  for the green emissions at 528 and 549 nm are 1.98 and 1.93, respectively, for the Li-Pr-BNTBT-Er-0.25 ceramic, while those for the Li-Pr-BNTBT-Er-0.5 ceramic are 1.97 and 1.81, respectively. These suggest that two-photon processes are involved in populating the  $^2H_{11/2}$  and  $^4S_{3/2}$  levels for producing the UC green emissions [23].

Fig. 10 shows the decay curves of UC emissions at 528 nm ( $^2H_{11/2} \rightarrow ^4I_{15/2}$ ) and 549 nm ( $^4S_{3/2} \rightarrow ^4I_{15/2}$ ) under the excitation of 980 nm. Owing to ETU (Fig. 4) of the UC process, the decay curves are non-exponential, and the corresponding  $\bar{\tau}$  calculated using Eq. 2 are 105 and 121  $\mu\text{s}$ , respectively, for the ceramic with  $x = 0.25$ , while those for the ceramic with  $x = 0.5$  are 119 and 144  $\mu\text{s}$ , respectively. Probably due to the shorter ionic distance between  $\text{Er}^{3+}$ , the probability of non-radiative transition decreases and thus the lifetimes for the Li-Pr-BNTBT-Er-0.5 ceramic are longer than those for the Li-Pr-BNTBT-Er-0.25 ceramic. On the other hand, the lifetimes for the transition  $^4S_{3/2} \rightarrow ^4I_{15/2}$  are longer than those of the transition  $^2H_{11/2} \rightarrow ^4I_{15/2}$ . These should be due to the small energy difference between the  $^4S_{3/2}$  and  $^2H_{11/2}$  levels (Fig. 4), which facilitates MPR and thus increases the dwell time of  $\text{Er}^{3+}$  in the  $^4S_{3/2}$  level. Nevertheless, the lifetimes are still short enough for green-light display applications.

Fig. 11 shows the  $P$ - $E$  loops of the Li-Pr-BNTBT-Er- $x$  ceramics. The Li-Pr-BNTBT-Er-0 ceramic exhibits a fairly saturated  $P$ - $E$  loop with a large remanant polarization ( $P_r = 23 \mu\text{C}/\text{cm}^2$ ) and a low coercive field ( $E_c = 0.98 \text{ kV}/\text{mm}$ ). After the doping of  $\text{Er}^{3+}$ , the loop becomes flattened, showing a decrease in  $P_r$  and a slightly increase in  $E_c$ . The observed  $P_r$  and  $E_c$ , together with the piezoelectric coefficient ( $d_{33}$ ), dielectric constant ( $\epsilon_r$ ) and dielectric loss ( $\tan \delta$ ), of the ceramics are listed in Table 1. For  $x = 0$ , the ceramic exhibits a large  $d_{33}$  (163 pC/N), a high  $\epsilon_r$  (1646) and a low  $\tan \delta$  (0.056). Although the observed  $d_{33}$  and  $\epsilon_r$  of the low-temperature sintered ceramic are slightly lower than those of a un-doped BNT-0.07BT ceramic (194 pC/N and 1813, respectively) [24], the decrease should be partly arisen from the doping of  $\text{Pr}^{3+}$  [15]. These suggest that  $\text{Li}_2\text{CO}_3$  is an effective sintering aid not only for lowering the sintering temperature (from  $1200^\circ\text{C}$  to  $960^\circ\text{C}$ ) but also for retaining the good piezoelectric and dielectric properties. In general, the piezoelectric and dielectric properties of low-temperature sintered ferroelectric ceramics will be deteriorated because of the secondary phase arisen from liquid-phase sintering. As evidenced by the XRD patterns (Fig. 1), the ceramics should contain no secondary phase or the secondary phase should be very little. This suggests that after facilitating densification, part of the liquid may vaporize and part of the constituent  $\text{Li}^+$  may diffuse into the ceramics (for replacing  $\text{Ti}^{4+}$ ). Indeed, part of it may also residue at the grain boundaries and cannot be detected owing to the small amount. Similar to other Er-doped ferroelectric ceramics [24,25], the observed  $d_{33}$  and  $\epsilon_r$  decrease with increasing  $x$ . Nevertheless, the observed  $d_{33}$  and  $P_r$ , e.g., 69 pC/N and  $14 \mu\text{C}/\text{cm}^2$ ,

respectively, for the Li-Pr-BNTBT-Er-0.25 ceramic, are still reasonably high and meet the practical application.

#### **4. Conclusions**

Li-Pr-BNTBT-Er-x ceramics have been prepared at a low sintering temperature of 960°C. Due to the energy transfer process, the DC emissions of Pr<sup>3+</sup> are weakened and the lifetimes are shortened by the doping of Er<sup>3+</sup>. As a result, when both Pr<sup>3+</sup> and Er<sup>3+</sup> are excited simultaneously, the green emissions produced mainly by Er<sup>3+</sup> increases while the red emissions produced mainly by Pr<sup>3+</sup> decreases with increasing the concentration of Er<sup>3+</sup>. Moreover, the emission color of the ceramics (with a fixed Er<sup>3+</sup> concentration) can be reversibly changed between red, yellow and yellowish green by using excitation sources of different wavelengths. Strong UC green emissions arisen from Er<sup>3+</sup> are also observed for the ceramics under the excitation of 980 nm. In addition to the short lifetimes, the ceramics should be promising for green-light display applications. Our results also reveal that Li<sub>2</sub>CO<sub>3</sub> is not only an effective sintering aid for lowering the sintering temperature but also for retaining the good piezoelectric and dielectric properties of the ceramics. Owing to the reasonably good ferroelectric and piezoelectric properties, the ceramics should also be promising for multifunctional applications such as electro-optical coupling devices.

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**Table 1** The ferroelectric ( $P_r$  and  $E_c$ ), piezoelectric ( $d_{33}$ ) and dielectric ( $\epsilon_r$  and  $\tan \delta$ ) properties of the Li-Pr-BNTBT-Er-x ceramics.

Samples	$P_r$ ( $\mu\text{C}/\text{cm}^2$ )	$E_c$ (kV/mm)	$d_{33}$ (pC/N)	$\epsilon_r$ @ 1 kHz	$\tan \delta$ @1 kHz
x = 0	23	0.98	163	1646	0.056
x = 0.25	14	0.96	69	1306	0.048
x = 0.5	9	1.09	41	1395	0.048

## Figure Captions

**Fig. 1** XRD patterns of the Li-Pr-BNTBT-Er-x ( $x = 0, 0.25, 0.5$ ) ceramics.

**Fig. 2** Photoluminescence excitation spectra of the Li-Pr-BNTBT-Er-x ( $x = 0, 0.25, 0.5$ ) ceramic monitoring at (a) 610 nm and (b) 548 nm.

**Fig. 3** Photoluminescence emission spectra of the Li-Pr-BNTBT-Er-x ( $x = 0, 0.25, 0.5$ ) ceramics under the excitation of (a) 468 nm, (b) 487 nm and (c) 450 nm.

**Fig. 4** Energy level diagrams of  $\text{Er}^{3+}$  and  $\text{Pr}^{3+}$ .

**Fig. 5** The CIE color coordinates of the Li-Pr-BNTBT-Er-x ceramics under the excitation of 468, 487 and 450 nm.

**Fig. 6** Decay curves of 610 nm emission under the excitation of 468 nm for the Li-Pr-BNTBT-Er-x ( $x = 0, 0.25, 0.5$ ) ceramics.

**Fig. 7** Decay curves of (a) 528 nm, (b) 549 nm and (c) 610 nm emission under the excitation of 487 nm for the Li-Pr-BNTBT-Er-x ( $x = 0, 0.25, 0.5$ ) ceramics.

**Fig. 8** Decay curves of (a) 528 nm, (b) 549 nm and (c) 610 nm emission under the excitation of 450 nm for the Li-Pr-BNTBT-Er-x ( $x = 0, 0.25, 0.5$ ) ceramics.

**Fig. 9** The UC emission spectra under the excitation of 980-nm laser at powers in the range of 0.19 to 0.67 W for the Li-Pr-BNTBT-Er-x ((a)  $x = 0.25$ , (b)  $x = 0.5$ ) ceramics. The insets are emission intensities log-log plotted as a function of laser powers.

**Fig. 10** Decay curves of the UC emission from the energy levels of  $\text{Er}^{3+}$ : (a)  ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$  and (b)  ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$  for the Li-Pr-BNTBT-Er-x ( $x = 0.25, 0.5$ ) ceramics.

**Fig. 11**  $P$ - $E$  loops of the Li-Pr-BNTBT-Er-x ( $x = 0, 0.25, 0.5$ ) ceramics.