Intensive up-conversion photoluminescence of Er^{3+} -doped $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ ferroelectric ceramics and its temperature sensing

Hua Zou^{*,†}, Jun Li^{*}, Qiufeng Cao^{*}, Xusheng Wang^{*,‡},
Xinwei Hui^{*}, Yanxia Li^{*}, Yao Yu^{*} and Xi Yao^{*}

^{*}Functional Materials Research Laboratory
School of Materials Science and Engineering
Tongji University, Shanghai 201804, P. R. China

and
[†]School of Mathematics and Physics
Jiangsu University of Technology
Changzhou 213001, P. R. China

[‡]xs-wang@tongji.edu.cn

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The intensive up-conversion (UC) photoluminescence and temperature sensing behavior of Er^{3+} -doped $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ (BTN) ferroelectric ceramics prepared by a conventional solid-state reaction technique have been investigated. The X-ray diffraction and field emission scanning electron microscope analyses demonstrated that the Er^{3+} -doped BTN ceramics are single phase and uniform flake-like structure. With the Er^{3+} ions doping, the intensive UC emission was observed without obviously changing the properties of ferroelectric. The optimal emission intensity was obtained when Er doping level was 15 mol.%. The temperature sensing behavior was studied by fluorescence intensity ratio (FIR) technique of two green UC emission bands, and the experimental data fitted very well with the function of temperature in a range of 133–573 K. It suggested that the Er^{3+} -doped BTN ferroelectric ceramics are very good candidates for applications such as optical thermometry, electro-optical devices and bio-imaging ceramics.

Keywords: Ferroelectric; temperature sensor; $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$; photoluminescence.

1. Introduction

Over the past several decades, the visible up-conversion (UC) luminescence of rare earth (RE) ions have received considerable attention in the fields of physics, chemistry, material science and life science because of broad potential application including UC laser and optical amplifier, solar cells, high-density memories, three-dimensional displays, biotechniques and other photonic devices.^{1–3} Many RE ions, such as Er^{3+} , Ho^{3+} and Tm^{3+} , have been studied to observe their UC luminescence, corresponding mechanism and applications.^{4,5} Among these RE ions, the Er^{3+} doping systems remain the key constituents for a majority of UC materials due to the abundant energy level for UC luminescence and high luminescent quenching concentration of Er^{3+} ions.^{6,7} However, Er^{3+} single-doped UC systems have relatively low UC emission efficiency because of their very low absorption cross section of the $^4\text{I}_{11/2}$ level.⁸ Thus, it is a great challenge to obtain Er^{3+} -doped systems with high efficiency.

Up to now, there are some conventional approaches to solve the above problems. The major one is to develop the appropriate host materials because the different crystal fields caused by structural symmetry of the host materials can contribute to inner shell transitions.⁹ Recently, RE-doped

ferroelectric oxides with optical, electrical and mechanical multifunction obtain great attentions for their great potential applications in future optoelectronic devices.¹⁰ By RE doping, our group has developed some multifunctional UC emission ferroelectric oxides, such as $\text{SrBi}_4\text{Ti}_4\text{O}_{15}:\text{Er}^{11}$ and $\text{CaBi}_2\text{Ta}_2\text{O}_9:\text{Er}^{12}$ monophasic oxides with optical-electrical integrations. Among the ferroelectric host materials, ferroelectric $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ (BTN) oxide has high chemical and thermal stability as well as low photo threshold energy which thought to be one of the potential host matrix.¹³ In this work, we focus on the intensive UC luminescence, corresponding mechanism and the application of Er^{3+} -doped BTN ferroelectric multifunctional ceramics.

Because temperature is the most fundamental parameter, the optical temperature sensor has gained tremendous importance.¹⁴ In contrast to other temperature sensors, the optical sensors by UC luminescence, which based on the fluorescence intensity ratio (FIR) technique, possesses the unique advantages such as high sensitivity, high accuracy, contactless and large-scale imaging.^{14–16} Till now, most previous works focused the optical temperature sensor behavior by FIR technique.^{17–20} However, these reports mostly aimed at the glass and oxides matrixes.^{7,19–25} Thus, it is also a

great challenge to obtain Er^{3+} -doped ferroelectric materials with high efficiency for optical temperature sensors.

In this paper, Er^{3+} -doped BTN ceramics were prepared by a conventional solid-state reaction technique. The UC luminescence of the samples and its application for temperature sensing were reported. To the best of our knowledge, this is the first time the Er^{3+} -doped BTN complex ferroelectric oxides have been reported with temperature sensing behavior. With the Er^{3+} ions doping, the intensive UC emission was observed without obviously changing the properties of ferroelectric and the optimum Er^{3+} concentration was 15 mol.%. The temperature sensing behavior was studied by FIR technique of two green UC emission bands, and the experimental data fitted well with the function of temperature in a range of 133–573 K. It suggested that the Er^{3+} -doped BTN ferroelectric ceramics are good candidates for applications such as optical thermometry, electro-optical devices and bio-imaging ceramics.

2. Experimental Methods

The Er^{3+} -doped BTN ceramics were designed according to the formula of $\text{Bi}_{7-x}\text{Er}_x\text{Ti}_4\text{NbO}_{21}$ ($0 < x \leq 0.40$) and the samples were synthesized by a conventional solid-state reaction technique. The raw materials were Bi_2O_3 (99.999%, Sinopharm Chemical Reagent Co. Ltd.), TiO_2 (99.9% Kojundo Chemical Lab), Nb_2O_5 (99.99% Sinopharm Chemical Reagent Co. Ltd.) and Er_2O_3 (99.99%, Sinopharm Chemical Reagent Co. Ltd.). In a typical process, the raw materials were mixed homogeneously with the addition of alcohol, dried and heated at 900°C for 7 h. After calcinations, the ground powders, added with 10 wt.% polyvinyl alcohol (PVA) binder, were pressed into disk-shaped pellets of 10 mm in diameter and about 1.5 mm in thickness. Finally, they were sintered at 1200°C for 2 h in air. The sintered pellets were polished to approximately 0.8 mm in thickness and examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence (PL) at room temperature. Then these pellets were polished to 0.4 mm in thickness to be used for measuring the thermal dependence of PL intensity. After the PL measurement, electrodes were fabricated with fired-on platinum paste and the ferroelectric properties of the samples were measured.

The sample crystallization behavior was examined by XRD (XRD, Bruker D8 Advanced, Germany) and field emission scanning electron microscopy (FESEM, S-4700, Japan). The PL, photoluminescence excitation (PLE) spectra were recorded by using a fluorescence spectrofluorometer (F-7000, Hitachi, Japan). The sample temperature was measured by a Pt-100 thermocouple located at a heating stage controlled by a TP 94 temperature controller (Linkam Scientific Instruments Ltd, Surrey, UK). The polarization–electric field (P–E) hysteresis loops were measured with a precision ferroelectric analyzer (Premier II, Radiant Technologies Inc., Albuquerque, NM).

3. Results and Discussion

Figure 1 shows the XRD patterns of Er -doped BTN ceramics with various Er^{3+} ions concentrations calcined at 1200°C for 2 h. All the diffraction peaks can be indexed to the orthorhombic phase of BTN structure²⁶ with space group symmetry of 12cm, indicating that the obtained samples are single phase and there is no impurity phase associated with the Er^{3+} doping. The scanned refinement XRD patterns near the strongest tetragonal peak (1121) are shown in the inset of Fig. 1. The strongest (1121) shift to the higher angle side with increasing Er^{3+} ion content, is attributed to the lattice shrink because of the smaller Er^{3+} ion substitution for Bi^{3+} ($r_{\text{Er}^{3+}} = 0.096 \text{ nm}$, $r_{\text{Bi}^{3+}} = 0.103 \text{ nm}$, for a coordination number of 12).²⁷

The FESEM cross-sectional morphologies of the Er -doped BTN ceramics is shown in Fig. 2. As can be seen, the

Fig. 1. XRD patterns of the Er^{3+} -doped BTN ceramics for $x = 0, 0.05, 0.10, 0.15, 0.20, 0.30$. The inset shows the refined peaks near the peak (112) for $x = 0, 0.10, 0.20$ and 0.30 .

Fig. 2. FESEM image of Er^{3+} -doped BTN ceramics for $x = 0.15$. The inset shows the ferroelectric hysteresis loops of BTN ceramics for $x = 0, 0.15$, measured at 100°C , 1000 Hz.

Fig. 3. The UC emission spectra of the Er-doped BTN ceramics for $x = 0.15$ excitation with 20 mW. The inset show shows the color images of strong UC luminescence of Er-doped BTN excitation with 20 mW.

ceramics are dense with uniform flake-like grains, which is a typical morphology of bismuth layer-structure ferroelectrics (BLSFs).²⁸ The corresponding inset of ferroelectric hysteresis loops shows the dopants of Er^{3+} ions, which yield UC emission, were not obviously changing the intrinsic properties of ferroelectric. The result is consistent with that reported for Pr^{3+} -doped BTN ceramics.¹³ This means that Er-doped BTN ceramic may be potentially useful in integrated electro-optical devices.

Under 980 nm excitation, the intensive green fluorescence can be observed in the Er^{3+} -doped BTN ceramics. The UC luminescence spectra of the samples under 980 nm excitation with 20 mW are shown in Fig. 3. As can be observed, the spectra exhibit three main emission bands centered at 533, 550 and 670 nm, which can be ascribed to $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$, and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$.^{18,29} Such intense green UC luminescence, which was shown in the inset of Fig. 3, can be easily observed by naked eyes, even at a pump power of 20 mW with 980 nm laser. Furthermore, it is worth to note that only the Er^{3+} doping is the result obtained. The effect could be even better if the photo-sensitizer, such as Yb^{3+} , was codoped with the Er^{3+} ions. Further research will be done in our other works.

Figure 4 shows the UC spectrum of Er^{3+} -doped BTN ceramics with different concentrations of Er^{3+} ion under 980 nm excitation. As seen in Fig. 4, the emission intensity of green UC increased with increasing the Er^{3+} concentrations from 5 to 15 mol.% and then decreased beyond 15 mol.% due to the concentration quenching effect. The concentration quenching here means that, with increasing Er^{3+} ions concentrations, the distance between Er^{3+} ions will decrease, which can promote nonradiative energy transfer.³⁰ Such a result is also observed in other host matrices.³ Based on our results, we concluded that the optimum Er^{3+} doping concentration was 0.15 mol.% (summarized in the inset of Fig. 4).

Fig. 4. UC spectra of Er^{3+} -doped BTN ceramics for $x = 0.05, 0.10, 0.15, 0.20, 0.30, 0.40$ excitation with 20 mW. The inset represents the variation in UC emission intensity with increasing Er^{3+} concentrations.

In the UC process, the intensity of emission is proportional to the n th value of the irradiation pump power³¹:

$$I \propto P^n, \quad (1)$$

where n is the number of pumping photons required to excite the emitting state, I is the emission intensity and P is the laser pumping power. Figure 5 shows the green and red UC emission intensities of Er^{3+} -doped BTN ceramics with $x = 0.15$ plotted on the logarithmic scale as a function of pump power. As shown in Fig. 5, the calculated n values are 1.55 and 1.63 for green and red emission. This result implied that the UC mechanism corresponding to the green and red emission could be explained by a two-photon process. The UC mechanisms were illustrated in the inset of Fig. 5 which

Fig. 5. UC emission intensity versus the pump power. The inset represents the schematic diagram of Er^{3+} energy levels for the UC mechanisms in BTN ceramics.

were typically excited state absorption (ESA) processes.² Under a 980 nm laser excitation, the $^4I_{15/2}$ and $^4I_{11/2}$ are populated by ESA process. Then after the nonradiative relaxation, the emission at 533, 550 and 670 nm was produced by the $^2H_{11/2} \rightarrow ^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition.

Generally, the green UC emission of Er^{3+} ions is especially appropriate for optical thermometry, which attributed to the energy gap of about 840 cm^{-1} between $^2H_{11/2}$ and $^4S_{3/2}$.³² With the thermalization of population, the FIR of green UC emission at 533 and 549 nm can be given by Eq. (2).³³

$$R \equiv \frac{I_{533}}{I_{550}} = \frac{N(^2H_{11/2})}{N(^4S_{3/2})} = \frac{g_F \sigma_F \omega_F}{g_S \sigma_S \omega_S} \exp\left[\frac{-\Delta E}{kT}\right] = C \exp\left[\frac{-\Delta E}{kT}\right], \quad (2)$$

where I_{533} and I_{550} are the integrated intensity of $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$, respectively; N , g , σ , ω are the number of ions, the degeneracy, the emission cross-section, the angular frequency of fluorescence transitions from the $^2H_{11/2}$ and $^4S_{3/2}$ level to $^4I_{15/2}$ level. ΔE is the energy gap between the $^2H_{11/2}$ and $^4S_{3/2}$ level. The pre-exponential constant is given by $C = g_F \sigma_F \omega_F / g_S \sigma_S \omega_S$. Figure 6 shows the FIR of green UC emissions at 533 and 550 nm relative to the temperature range of 150–575 K. As shown in Fig. 6, the experimental data are well fitted to the curve by Eq. (2). The results proved that the Er^{3+} -doped BTN ceramics has a good potential for the development of temperature sensors. According to the fitting curve of the temperature, the coefficient C value is 8.14.

For temperature sensing, the sensitivity is a significant parameter for judging the sensor. The sensor sensitivity can be defined as in Eq. (3).^{14,33}

$$\frac{dR}{dT} = R \left(-\frac{\Delta E}{KT^2} \right). \quad (3)$$

Fig. 6. FIR for green UC emission of Er^{3+} -doped BTN ($x = 0.15$) versus the temperature.

Fig. 7. Sensor sensitivity as a function of the temperature for $x = 0.15$.

Figure 7 shows the corresponding resultant curve of the sensor. With the increase of temperature, the value of sensitivity also increased as shown in Fig. 7. The results indicated that the optimal value of sensitivity was $0.0032\text{--}0.0041\text{ K}^{-1}$ from 333–545 K. Furthermore, several temperature cycles were performed and a good repeatability was obtained.

4. Conclusions

In conclusion, Er -doped BTN ferroelectric ceramics were synthesized and the UC emission was investigated. It was demonstrated that the ceramics can yield intensive UC emission, which was not changing the intrinsic properties of ferroelectric. Moreover, by using the FIR technique, the temperature sensing behavior was investigated in the range of 153–573 K. It revealed that the experimental data was well fitted to function. These results suggest that the Er -doped BTN ceramics are very good candidates for applications such as optical thermometry, electro-optical devices and bio-imaging ceramics.

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