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# Linear response fluorescent temperature-sensing properties based on Stark sublevels of $\text{Er}^{3+}$ -doped $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3\text{-Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ ceramics

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## ABSTRACT

The  $\text{Er}^{3+}$  doped 0.84(PMN-PT)–0.14PYN ceramics were employed as a temperature-sensing material. The obtained compounds exhibit strong visible upconversion (UC) fluorescence under a 980-nm diode laser excitation. On account of the Stark split effect, the  ${}^2\text{H}_{11/2}$ ,  ${}^4\text{S}_{3/2}$ , and  ${}^4\text{F}_{9/2}$  levels of  $\text{Er}^{3+}$  split into two Stark sublevels, respectively. The fluorescence intensity ratios (FIR) between these sublevels were calculated in a temperature range of 133–573 K, and a linear FIR vs. temperature relation has been found. FIR of A/B shows a wide temperature sensing range with a relatively low sensitivity of  $0.003 \text{ K}^{-1}$ . Meanwhile E/C illustrates the highest sensitivity of  $0.0134 \text{ K}^{-1}$  but in the smallest temperature range 453–573 K. FIR technique provides us a optical thermometric method with constant sensitivity in a wide temperature range.

## 1. Introduction

In recent years, lanthanide (Ln) ion-activated luminescent materials have attracted much attention due to their widely technology applications in photonic devices, next-generation flat-panel display, and temperature sensors [1–4]. Among these applications, optical temperature sensors based on the fluorescence intensity ratio (FIR) technique have been intensively investigated, because this technique can reduce the dependence on measurement conditions and increase measurement accuracy and resolution [5,6]. The previously reported temperature-sensing materials are mainly based on the fluoride and glass host materials. Nevertheless, both fluorides and glasses own relatively poor physical or chemical performance and thermal stability, limiting their applications in practical temperature sensors. Compared with glasses and fluorides, perovskite ferroelectrics possess great thermal and chemical stability [7–9]. In addition, ferroelectrics are known as multi-function materials since they show excellent piezoelectric, ferroelectric and pyroelectric performances. Meanwhile, multi-property coupling has been found in ferroelectrics, such as electro-mechano, electro-optic, and mechano-optic couplings [10–12]. Hence, it is necessary to search for Ln-doped ferroelectrics for the next generation optical temperature sensors.

Among all the optical temperature sensing methods, the FIR technique is an extremely promising one to be considered. It usually determines temperature via calculating the emission intensity ratio

between two thermally coupled energy levels (TCEL) of Ln ions. Such FIR technique can provide accurate measurements with independence on the fluorescence loss and pump power fluctuation [13–16]. Some Ln ions, such as  $\text{Er}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Pr}^{3+}$ , have been utilized as the activators for optical temperature sensors based on the upconversion (UC) luminescence emitting from their TCEL [17–19]. Zou and Du et al. have discussed temperature sensing properties of the UC luminescence of  $\text{Er}^{3+}$  doped ferroelectric ceramics via UC intensity ratio, but exhibiting a rather low sensitivity [20,21]. Basically, a larger energy gap between the TCEL benefits a high sensitivity. However, too large energy gap will lead to the “decoupling” effect at low temperature, which will introduce unavoidable measurement error. Furthermore, the FIR value with the temperature shows an exponential function, resulting in a evident variation of sensitivity with the temperature. Therefore, great efforts are still underway in the development of optical sensing materials with high and temperature-independent sensitivity through FIR technique.

The TCEL can be split into Stark sublevels due to the existence of crystal field with noncentral symmetry, which is generated by the host materials. These Stark sublevels can also be thermally coupled and be used to investigate FIR versus temperature characteristics [22–25]. Baxter et al. have studied FIR properties using the TCEL  ${}^2\text{F}_{5/2(a)}$  and  ${}^2\text{F}_{5/2(b)}$  formed by Stark split from  ${}^2\text{F}_{5/2}$  level of  $\text{Yb}^{3+}$  ions doped in silica fiber [22]. Feng et al. reported that  $\text{Er}^{3+}$ -doped fluoride glass utilizing thermally coupled Stark sublevels  ${}^4\text{S}_{3/2(a)}$  and  ${}^4\text{S}_{3/2(b)}$  of  $\text{Er}^{3+}$  ions has excellent FIR properties [25]. However, the split Stark sublevels was

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not obvious in the glass host due to weak noncentral symmetry of crystal field of the sites occupied by the Ln ions, which leads to strong overlapping emissions from these Stark levels. Meanwhile, the strong overlapping emissions from the sublevels result in a measuring error of the FIR.

In our previous work, we found evident split emissions from  $^4S_{3/2}$ ,  $^2H_{11/2}$  and  $^4F_{9/2}$  levels of the  $Er^{3+}$  ions doped in the ferroelectric  $(0.98-x)(0.6Pb(Mg_{1/3}Nb_{1/3})O_3-0.4PbTiO_3)-xPb(Yb_{1/3}Nb_{1/3})O_3-0.02Pb(Er_{1/2}Nb_{1/2})O_3$  ( $(0.98-x)(PMN-PT)-xPYN:Er^{3+}$ ) ceramics. Among all the prepared specimens according to formula  $(0.98-x)(PMN-PT)-xPYN:Er^{3+}$ , composition  $x = 0.14$  has the strongest UC emission intensity [26]. Three pairs of TCELS of  $Er^{3+}$  ions based on the Stark sublevels were simultaneously observed in  $0.84(PMN-PT)-0.14PYN:Er^{3+}$  ceramics. Under exactly the same circumstances, the temperature sensing characteristics utilizing different Stark sublevels split from  $^2H_{11/2}$ ,  $^4S_{3/2}$  and  $^4F_{9/2}$  of  $Er^{3+}$  were studied. Unlike normal FIR, which is always in line with Boltzmann distribution and fitted in an exponential style, a linear response of FIR versus temperature based on Stark sublevels has been found.

## 2. Experimental

The preparing process for the ceramics can be referred to reference 26. The ceramics were polished for luminescence tests, and UC emission spectra of the resultant ceramics were detected by a spectrofluorimeter (Edinburgh FS5) equipped with a pump power controllable 980 nm laser diode (ADR-1805). The temperature of the ceramics ranging from 133 to 573 K was monitored by the temperature-controlled system (Linkam HFS600E-PB2).

## 3. Results and discussion

### 3.1. UC luminescence performance

To investigate the UC emission behaviors of the synthesized ceramics, the UC emission spectra of the  $0.84(PMN-PT)-0.14PYN:Er^{3+}$  ceramics in the temperature range 133–573 K were recorded for every 10 K during the heating process. As shown in Fig. 1, six typical UC emission spectra of the  $0.84(PMN-PT)-0.14PYN:Er^{3+}$  ceramics at different temperatures were normalized by emission peak F. Upon the irradiation of 980 nm light, it is observed that the sample exhibits the featured emissions of  $Er^{3+}$  ions. The fluorescence emission bands from 515 to 580 nm are ascribed to the transition of  $^2H_{11/2}$ , and  $^4S_{3/2}$  levels to the ground state  $^4I_{15/2}$ , and the emission band between 625 and 725 nm is associated with  $^4F_{9/2} \rightarrow ^4I_{15/2}$  transition of  $Er^{3+}$  ions. Six visible UC emission peaks split through Stark effect are centered at

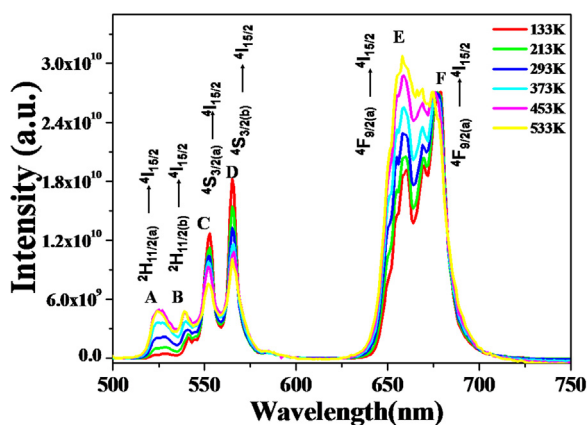


Fig. 1. Temperature-dependent UC emission spectra of the  $Er^{3+}$  doped  $0.84(PMN-PT)-0.14PYN$  ceramics. The emission spectra were normalized to the emission intensities from the  $^4F_{9/2(b)} \rightarrow ^4I_{15/2}$  transition of  $Er^{3+}$  ions.

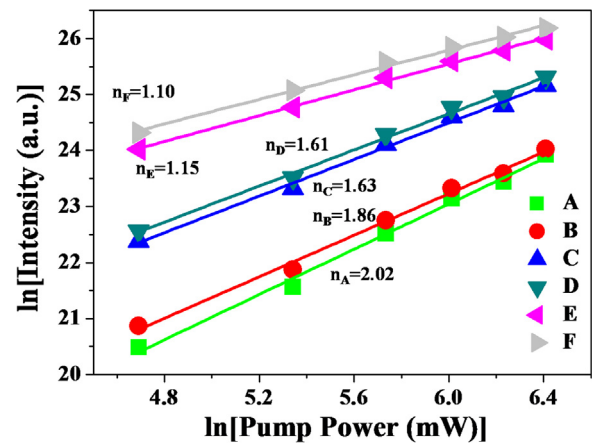


Fig. 2. Ln-ln plot of fluorescence intensity versus excitation power.

around 525, 540, 552, 566, 660 and 679 nm. Evidently, the emissions peaks are distinctly different with the observed results in other hosts such as:  $NaBiF_4$  nano particles [27],  $Na_{0.5}Bi_{0.5}TiO_3$  [28]. For these hosts, only three emissions are obtained in the range of visible light. For convenience, we name these peaks corresponding to the transitions from sublevels ( $^2H_{11/2(a)}$ ,  $^2H_{11/2(b)}$ ) of  $^2H_{11/2}$  to  $^4I_{15/2}$  as A and B, and those from the sublevels ( $^4S_{3/2(a)}$ ,  $^4S_{3/2(b)}$ ) of  $^4S_{3/2}$  to  $^4I_{15/2}$  as C and D, and  $^4F_{9/2(a)}$ ,  $^4F_{9/2(b)} \rightarrow ^4I_{15/2}$  as E and F, as marked in Fig. 1. For the  $0.84(PMN-PT)-0.14PYN:Er^{3+}$  ceramics, doubled peak number is observed here. Such result is due to the split levels  $^2H_{11/2}$ ,  $^4S_{3/2}$ , and  $^4F_{9/2}$ . The Stark split effect accounts for the doubled peaks for a single transition. Since the activators  $Er^{3+}$  are expected to take the B-site in the  $ABO_3$  perovskite, the  $Er^{3+}$  ions significantly deviate from the center position due to that the spontaneous polarization in ferroelectrics is formed by shifted B-site and O ions [32].

To determine the number of the infra-red photons which were required to populate the upper emitting level, the UC emission intensity as a function of pump power was investigated in a ln-ln form as illustrated in Fig. 2. The slope of the curves represents the number of the pump photons involved to populate the upper emission state for unsaturated condition. In the multiphoton UC process, the relation between the UC emission intensity ( $I$ ) and pump power ( $P$ ) can be expressed as [29]:

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

where  $n$  is the number of infra-red photons to obtain the visible emissions. The  $n$  corresponding to A, B, C and D are 2.02, 1.86, 1.63, 1.61. This result indicates that a two-photon process is involved to populate the  $^2H_{11/2}$  and  $^4S_{3/2}$  levels. The  $n$  values for E and F are 1.15, and 1.10, respectively, which are far deviated from 2. This small  $n$  value may be attributed to several processes such as energy back transfer, co-operative energy transfer and cross-relaxation. The slope of 1.6 can be explained by a process involving three absorbed photons which give two emitted photons [26,30,31].

### 3.2. Energy level diagram and UC mechanism

As illustrated in Fig. 3, the simplified energy level diagram of  $Er^{3+}$  and  $Yb^{3+}$  ions along with probable luminescent processes can help us better comprehend the involved UC luminescent mechanism. Superior energy overlaps between the  $Yb^{3+}$  and  $Er^{3+}$  and the energy transfer (ET) from  $Yb^{3+}$  to  $Er^{3+}$  ions takes the domination in the UC luminescent mechanism for the generation of green and red UC emissions. Briefly, the electrons populated at  $^2F_{7/2}$  level are firstly excited to the  $^2F_{5/2}$  level of  $Yb^{3+}$  ions under the excitation of 980 nm light. Afterwards, the captured incident energy will be transferred to the  $Er^{3+}$  ions by the  $Yb^{3+}$  ions and the  $^4I_{11/2}$  level of  $Er^{3+}$  gets populated due to the

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