Up-conversion luminescence of Er^{3+} and Yb^{3+} co-doped $\text{CaBi}_2\text{Ta}_2\text{O}_9$ multifunctional ferroelectrics*

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Received 14 May 2014; Revised 22 June 2014; Accepted 23 June 2014; Published 18 July 2014

Er^{3+} and Yb^{3+} co-doped $\text{CaBi}_2\text{Ta}_2\text{O}_9$ (CBT)-based bismuth layered-structure oxides were synthesized by a simple solid-state reaction method. Their up-conversion (UC) luminescence, dielectric and ferroelectric properties were investigated. Two strong green emission bands centered at 526 and 547 nm and a weak red emission band centered at 658 nm were obtained under a 980 nm laser excitation at room temperature. These emission bands originated from the radiative relaxation of Er^{3+} from $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$, and $^4\text{F}_{9/2}$ levels to the ground state $^4\text{I}_{15/2}$, respectively. At the meantime, the fluorescence intensity ratio (FIR) variation of two green UC emissions at 526 and 547 nm has been studied as a function of temperature in the range of 153–603 K. The maximum sensor sensitivity obtained was $39 \times 10^{-4} \text{ K}^{-1}$ at 590 K, which indicated that $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped CBT ceramic is a promising candidate for applications in optical high temperature sensor.

Keywords: Aurivillius-type bismuth layered-structure ferroelectrics; up-conversion luminescence; sensor; fluorescence intensity ratio.

1. Introduction

The Aurivillius-type bismuth layer-structured ferroelectrics (BLSFs) have received great attention in recent years. The general formula of BLSFs is $\text{Bi}_2\text{A}_{m-1}\text{B}_m\text{O}_{3m+3}$, where A is a mono-, di-, or trivalent element (or combination) with cuboctahedral coordination, B is a tetra-, penta-, or hexavalent element (or combination) suited for octahedral coordination, and m is the number of octahedral layers in the perovskite slab.¹ For their high Curie temperature (T_C) and lead-free advantages,² the BLSFs are an attractive alternative to PZT-based materials. Furthermore, the BLSFs have been a hotspot lately for their multifunctional characteristics such as ferroelectric-photo,³ ferroelectric-elastic,⁴ ferroelectric-elastic-magnetic,⁵ ferroelectric-mechanical.^{6,7} The rare earth doped BLSFs possessing both novel photoluminescence and strong ferroelectric functions,^{8–10} which enables the miniaturization and integration of optoelectronic devices possible.

Since its discovery in the 1960s,¹¹ up-conversion (UC) luminescence has been widely studied. UC is defined as an anti-stokes emission that emission energy is higher than excitation photon energy, and green, red and blue emission can be produced via incorporating trivalent rare earth ions such as Er^{3+} ,^{12–14} Tm^{3+} ,^{15,16} and Ho^{3+} ,^{17,18} under near-infrared excitation. Nowadays, researchers pay more attention on the halides, glasses as the host material for their strong UC, while their drawbacks are also apparent that they cannot be resistant to high temperature and have low chemical durability and

undesirable mechanical strength. Thus oxide materials come to our sight as the ideal hosts for the UC applications due to their stable thermal, mechanical and chemical properties.

So far, there have developed lots of techniques based on fluorescence to measure the temperature such as the amplified spontaneous emission, fluorescence lifetime, or the fluorescence intensity ratio (FIR).¹⁹ The basic principle of the FIR technique is to measure the intensity of fluorescence from two closely spaced thermally coupled levels with different temperature dependency, consequently changes in the excitation intensity or in transmission losses in guiding fibers can hardly affect the accuracy of the results. Hence, the FIR-based temperature sensor can be operated in various working environments even in electromagnetically or thermally harsh ones.

$\text{CaBi}_2\text{Ta}_2\text{O}_9$ (CBT) belongs to the family of Aurivillius-type BLSFs, characteristic of its high Curie temperature, low dielectric constant and ferroelectric properties.²⁰ The UC emission properties of Er^{3+} -doped CBT ceramics were investigated as a function of Er^{3+} concentration in our previous work,¹³ and the green emission intensity reached its maximum with Er^{3+} concentration at 0.06 mol. So in the present work, Er^{3+} and Yb^{3+} co-doped CBT ceramics were synthesized by a simple solid-state method. UC luminescence were investigated as a function of Yb^{3+} concentration and incident pump power as well as the structure, dielectric and ferroelectric properties. The optical thermometry in

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*Selected paper from the “2nd International Conference on Mechanoluminescence and Novel Structural Health Diagnosis”, Tongji University, Shanghai, China, 10–13 November 2013.

temperature range of 153–603 K using the FIR technique of green UC emissions at 526 and 547 nm was studied and the sensitivity of the temperature sensor was discussed in this paper.

2. Experimental Procedure

The $\text{Ca}_{1-0.06-x}\text{Er}_{0.06}\text{Yb}_x\text{Bi}_2\text{Ta}_2\text{O}_9$ (denoted as CBT_0.06Er_0.06Yb, $x = 0, 0.02, 0.04, 0.08, 0.16$) ceramics were synthesized by the solid-state reaction method. The starting materials were CaCO_3 (99.99%, Sinopharm Chemical Reagent Co. Ltd.), Er_2O_3 (99.9%, Sinopharm Chemical Reagent Co. Ltd.), Yb_2O_3 (99.99%, Sinopharm Chemical Reagent Co. Ltd.), Bi_2O_3 (99.5%, Sinopharm Chemical Reagent Co. Ltd.) and Ta_2O_5 (99.99%, Sinopharm Chemical Reagent Co. Ltd.). The stoichiometric amounts of starting materials were ground finely in an agate mortar. Then the homogeneous mixture were dried and calcined at 900°C for 2 h in an alumina crucible. After calcination, the ground powder which added with 10 wt.% polyvinyl alcohol (PVA) binder, were pressed into disk-shaped pellets of 10 mm in diameter and about 2 mm in thickness. Finally, the samples were sintered at temperatures of 1280°C for 2 h in a sealed alumina crucible.

The phase structure was identified by an X-ray diffractometer (XRD; D8 Advance; Bruker AXS GmbH) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$), tube voltage 40 kV, tube current 40 mA, and scanning speed 6°/min. The UC emission spectra were measured using a fluorescence spectrofluorometer (F-7000, Hitachi, Japan) and a 980 nm laser diode as the excitation source. 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 temperature dependences of dielectric constant and loss were measured at 10 kHz using an impedance analyzer (Agilent, HP4284A). The ferroelectric properties were characterized using a precision ferroelectric analyzer (Premier II; Radiant Technologies Inc., Albuquerque, NM) with an electric field up to $E = 250 \text{ kV/cm}$ at 100 Hz under gold electrodes.

3. Results and Discussion

Figure 1 shows the XRD patterns of CBT_0.06Er_xYb ceramics with different x ($x = 0, 0.02, 0.04, 0.08$ and 0.16) values sintered at 1280°C for 2 h. The XRD patterns of the samples were well consistent with the standard diffraction pattern data of CBT and were indexed based on an orthorhombic lattice with the A21am space group by using the JCPDS PDF database (PDF#49-0608). The CBT_0.06Er_xYb ceramics showed no secondary phase of the formation of Er oxide, Yb oxide or associated compounds, which indicated that those compounds consisted of a pure phase of bismuth layered structure with $m = 2$. So it can be concluded that Er and Yb were successfully doped into the CBT host to form solid solutions.

Fig. 1. The XRD patterns of CBT_0.06Er_xYb ceramics with different x ($x = 0, 0.02, 0.04, 0.08$ and 0.16) values sintered at 1280°C.

Figure 2 shows the UC emission spectra of CBT_0.06Er_xYb obtained under a 980 nm NIR excitation at room temperature. It can be seen from that, there are three distinct UC emission bands. The two bands centered at 526 and 547 nm corresponding to green light emissions were ascribed to $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transitions of Er^{3+} ions, respectively, and another band centered at 658 nm corresponding to red light emission originated from $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition of Er^{3+} ions. The upper left inset of Fig. 2 shows the variations of the fluorescence intensity of the green and red emission versus the Yb^{3+} doping concentration. With the increase of Yb^{3+} doping concentration, it can be seen that both the green and red emission intensity reached its maximum at $x = 0.08$, and decreased contrarily with Yb^{3+} increasing, owing to the concentration-quenching effect. It is known that when the doping concentration reaches a certain degree, the

Fig. 2. The UC emission spectra of CBT_0.06Er_xYb. The photographs of the upper inset are the variations of the fluorescence intensity of the green and red emission versus the Yb^{3+} doping concentration and the UC emissions of CBT_0.06Er (a), CBT_0.06Er_0.02Yb (b) and CBT_0.06Er_0.08Yb (c) samples respectively from left to right.

Fig. 3. Plot of $\ln I$ versus $\ln P$ for the green and red emissions.

distance between Er^{3+} ions become short and a fraction of energy migrate to the quenchers. Three photographs in the upper inset of Fig. 2 are the UC emissions of CBT_0.06Er (a), CBT_0.06Er_0.02Yb (b) and CBT_0.06Er_0.08Yb (c) samples, respectively. The room-temperature UC emission from Er^{3+} and Yb^{3+} co-doped CBT obtained under a 980 nm excitation was so strong that it was easily observed by the naked eye, and showed color-tunable features. Figure 2(a) shows a type of green color because the intensity of the green emission was more intense than that of red emission. The co-doped of Yb^{3+} can significantly enhance the UC of CBT_Er, especially the red emission, so the color of Fig. 2(b) is kind of yellow compared to Fig. 2(a). Figure 2(c) shows a bright orange color for the intensity of the red emission is as strong as the green one.

To understand the UC luminescence mechanisms, the pump power dependence of UC emissions for the CBT_0.06Er_xYb ceramics was investigated. It is known in an UC process that the UC emission intensity, I , is related to the excitation power, P , according to a power-scaling equation: $I \propto P^n$, where n is the number of pump photons absorbed per UC photon emitted. By plotting emission intensity versus excitation power on a log-log scale, n can be obtained from the slope. The linear fit with the experimental data are shown in Fig. 3 and the slopes n equal to 1.88, 1.70 and 1.60 for the two green and one red emissions, respectively, which indicate that two pump photons were involved in both the green and red UC processes.

Figure 4 shows the possible UC photoluminescence mechanisms of the Er^{3+} and Yb^{3+} co-doped CBT ferroelectric oxide. Under a 980 nm laser excitation, the Er^{3+} ions can be populated to the $^4\text{I}_{11/2}$ excited state via two routes: one involved a ground-state absorption (GSA) of Er^{3+} : $^4\text{I}_{15/2} + h\nu \rightarrow ^4\text{I}_{11/2}$ and the other was energy transfer (ET) from excited Yb^{3+} to Er^{3+} : $^4\text{I}_{15/2}(\text{Er}^{3+}) + ^2\text{F}_{5/2}(\text{Yb}^{3+}) \rightarrow ^4\text{I}_{11/2}(\text{Er}^{3+}) + ^2\text{F}_{7/2}(\text{Yb}^{3+})$. Due to the larger absorption cross section of Yb^{3+} than Er^{3+} and the high transfer probability of Yb^{3+} to Er^{3+} under 980 nm, the second process, as

Fig. 4. Energy level diagram of green and red UC emissions from the Er^{3+} and Yb^{3+} co-doped CBT by a 980 nm LD excitation.

the ET, was the main excitation route of Er^{3+} : $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$. Just as mentioned above, the $^4\text{I}_{11/2}$ level of Er^{3+} populated to the $^4\text{F}_{7/2}$ level also has two routes, the lower efficiency excited state absorption (ESA) of Er^{3+} : $^4\text{I}_{11/2} + h\nu \rightarrow ^4\text{F}_{7/2}$ and the dominant ET as $^4\text{I}_{11/2}(\text{Er}^{3+}) + ^2\text{F}_{5/2}(\text{Yb}^{3+}) \rightarrow ^4\text{F}_{7/2}(\text{Er}^{3+}) + ^2\text{F}_{7/2}(\text{Yb}^{3+})$. Then, owing to the small energy gap with the $^4\text{F}_{7/2}$ level of Er^{3+} and the $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ levels, the $^4\text{F}_{7/2}$ level relaxed nonradiatively to the low-lying levels in a quite short time. Above was how the two $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ green emissions centered at 526 and 547 nm were generated.

In the situation of the red UC emission, there existed two routes involved in the population of the $^4\text{F}_{9/2}$ level. The first was the main process which referred to the ET from Yb^{3+} to Er^{3+} : $^4\text{I}_{13/2}(\text{Er}^{3+}) + ^2\text{F}_{5/2}(\text{Yb}^{3+}) \rightarrow ^4\text{F}_{9/2}(\text{Er}^{3+}) + ^2\text{F}_{7/2}(\text{Yb}^{3+})$, in which the $^4\text{I}_{13/2}$ level was transited from the upper lying $^4\text{I}_{11/2}$ level by a nonradiative relaxation. The $^4\text{I}_{13/2}$ level can also be populated via relaxation from $^4\text{S}_{3/2}$ called the energy back-transfer (EBT). This excitation can be expressed as: $^4\text{S}_{3/2}(\text{Er}^{3+}) + ^2\text{F}_{7/2}(\text{Yb}^{3+}) \rightarrow ^4\text{I}_{13/2}(\text{Er}^{3+}) + ^2\text{F}_{5/2}(\text{Yb}^{3+})$. Then the $^4\text{I}_{13/2}$ level of Er^{3+} emitted red UC fluorescence by radiative relaxation. In addition, the populated $^4\text{I}_{13/2}$ level might be excited to the $^4\text{F}_{9/2}$ red-emitting level in Er^{3+} ions by cross-relaxation process $^4\text{I}_{11/2}(\text{Er}^{3+}) + ^4\text{I}_{13/2}(\text{Er}^{3+}) \rightarrow ^4\text{I}_{15/2}(\text{Er}^{3+}) + ^4\text{F}_{9/2}(\text{Er}^{3+})$, resulting in the increase of red-light emission.

Finally, the Er^{3+} ions in $^4\text{F}_{9/2}$ level relaxed radiatively to the ground state $^4\text{I}_{15/2}$ and thus emitted the red light with wavelength of 658 nm. In the case of CBT_0.06Er, it can be easily found that without the assistance of Yb^{3+} , the intensity of both green and red UC emissions was much weaker than that in the cases of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped ones. The ETs from the host material CBT was not as efficient as Yb^{3+} does.

Figure 5 shows the green UC emission spectra in the wavelength range of 510–580 nm for the Er^{3+} and Yb^{3+} co-doped CBT at the different temperatures in the range of 153–603 K. In this case, we chose CBT_0.06Er_0.08Yb which has

Fig. 5. Green UC emission spectra in the wavelength range 510–580 nm at the temperature range of 153–603 K for the CBT_{0.06}Er_{0.08}Yb sample.

the strongest UC fluorescence as the sample and the pumping power of 980 nm laser as 50 mW. It can be observed in Fig. 5 that the peak positions of 526 and 547 nm emissions were barely moved while the intensities for the two emission bands change dramatically with the temperature. The spectra shows that the 526 nm emission intensity gradually increases with the increase of temperature, while the intensity for 547 nm red emission decreases greatly, indicating that the two different energy levels have different temperature dependence. This property makes it an ideal material for temperature sensing. Hence, FIR which stands for fluorescence intensity ratio, can be defined as¹⁹

$$R = \frac{N(^4H_{11/2})}{N(^4S_{3/2})} = \frac{I_{526}}{I_{547}} = A \exp\left[\frac{-\Delta E}{kT}\right] + B, \quad (1)$$

where N is the number of ions, I is the fluorescence intensity, A is a constant, ΔE is the energy gap between the $^2H_{11/2}$ and $^4S_{3/2}$ levels, k is the Boltzmann constant, T is the absolute temperature, and B is the offset factor. The FIR of green UC emissions at 526 and 547 nm relative to the temperature in the range of 153–603 K is shown in Fig. 6(a). The experimental data are fitted by using Eq. (1). It can be seen that the fitting matches well with the experimental data. The fitted coefficients A and B in Eq. (1) are about 8.5086 and 0.01237, respectively, and ΔE is fitted to be about 1181 cm⁻¹. To understand the rate of change in the FIR in response to the variation of temperature, the sensor sensitivity S can be defined as¹⁹

$$S = \frac{dR}{dT} = R \left(\frac{\Delta E}{kT^2} \right). \quad (2)$$

The corresponding resultant curve is shown in Fig. 6(b). The sensitivity of Er³⁺ and Yb³⁺ co-doped CBT reached its maximal value of about $39 \times 10^{-4} \text{ K}^{-1}$ at the temperature of 590 K.

Figure 7 shows temperature dependence of dielectric constant and dielectric loss at 10 kHz frequency for various

(a)

(b)

Fig. 6. (a) FIR of green UC emissions at 526 and 547 nm relative to the temperature in the range of 153–603 K and (b) Sensor sensitivity dR/dT as a function of the temperature in the temperature range of 153–603 K.

Fig. 7. Dielectric constant and dielectric loss versus temperature of CBT_{0.06}Er_xYb, the inset is the dependence of T_c on Er³⁺ and Yb³⁺ concentrations.

Yb^{3+} and fixed Er^{3+} content. As shown in Fig. 7, the Curie temperature (T_C) increases and the dielectric loss decreases with the increase of Yb^{3+} doping concentration. It can be found in Fig. 7 that the T_C of the CBT_0.06Er_0.08Yb sample shows a maximum at 945°C which is 16°C higher than that of pure CBT and 14°C than the CBT_0.06Er sample.

So it can be concluded that the doping of rare earth ion Er^{3+} can increase the T_C of pure CBT, and the doping of Yb^{3+} can improve the T_C of CBT_0.06Er to a further extent, and with the increase of Yb^{3+} doping concentration, the T_C of CBT_0.06Er $_x$ Yb increases. According to Shimakawa and his colleagues' work,²⁰ the change of Curie temperature is owing to the degree of structural distortion, which can be estimated by the perovskite tolerance factor t . The perovskite tolerance factor t is defined as

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}, \quad (3)$$

where R_A , R_B , and R_O are the effective radii related to oxygen of A-site cation, B-site cation, and oxygen in the general Aurivillius formula unit, respectively. In this case, the doping Er^{3+} and Yb^{3+} substitute the A-site cation Ca^{2+} , and the ionic radius of either Er^{3+} or Yb^{3+} is smaller than that of Ca^{2+} , so R_A decreases as the doping concentration increases, the tolerance factor t of CBT_0.06Er $_x$ Yb decreases. In another work of Suárez *et al.*,²¹ they found that the tolerance factor t is inversely proportional to the Curie temperature T_C . Hence, the Curie temperature increases with the increase of Yb^{3+} concentration.

CBT is known as a member of bismuth-layered pseudo-perovskite compound, but also an important ferroelectric and piezoelectric material, which can be applied in various fields such as ferroelectric, piezoelectric and pyroelectric devices, filters, resonators, and micro-electromechanical systems. The ferroelectric properties of CBT_0.06Er $_x$ Yb were studied in this work, and the results were displayed in Fig. 8. None of the polarization-electric field (P - E) hysteresis loops of the six

Fig. 8. P - E hysteresis loops of CBT_0.06Er $_x$ Yb ($x = 0, 0.02, 0.04, 0.08$ and 0.16) at room temperature.

samples of CBT_0.06Er $_x$ Yb saturated even at an applied electric field 250 kV/cm. But it is enough to prove that the ceramics have ferroelectricity. It can be found that the P - E hysteresis loops of CBT_0.06Er $_x$ Yb are just similar to that of pure CBT, however, the remnant polarization $2P_r$ of the doped samples are smaller than the pure one, and the $2P_r$ decreases as the doping content is increased. It is reported that the replacement of A-site cations by rare earth ions will lead to a reduction in distortion of lattice in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ferroelectric.²² Therefore, in CBT, the increase of Er^{3+} substituting concentration would reduce the distortion of lattice and then weaken domain rotation on the polarization, resulting in the smaller remnant polarization values.

4. Conclusion

The UC luminescence properties of Er^{3+} and Yb^{3+} co-doped oxide materials were investigated as a function of dopant concentration. The CBT_0.06Er $_x$ Yb ceramics with $x = 0.08$ showed the optimum UC emission. The studies of dielectric constant and dielectric loss with temperature showed that introduction of rare earth ion Yb^{3+} increased the Curie temperature of CBT and decreased the dielectric loss. The maximum sensitivity derived from the FIR of the green UC emissions approximates $39 \times 10^{-4} \text{ K}^{-1}$. In summary, our study demonstrates that the multifunctional Er^{3+} and Yb^{3+} co-doped CBT ceramics have the great potential for applications in optical high temperature sensors.

Acknowledgment

This work was supported by the Natural Science Foundation of China (No. 51072136).

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