Temperature-Induced Phase Transition and Temperature Sensing Behavior in Yb³⁺ Sensitized Er³⁺ Doped YPO₄ Phosphors

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Abstract

$\text{YPO}_4:\text{Er}^{3+}$, Yb^{3+} microcrystals have been manufactured using hydrothermal synthesis and annealed at different temperature for 3 h. With the increases of calcination temperature, the phase transformation of yttrium phosphate from hexagonal to tetragonal phase is reported base on the representation of X-ray diffraction (XRD). Besides, the size and morphology of yttrium phosphate have been clearly observed by employing field-emission scanning electron microscopy (FE-SEM). By selective annealing temperature and doped concentration procedure, $\text{YPO}_4:1\%\text{Er}^{3+}$, 15% Yb^{3+} phosphors that annealed at 1000°C for 3 h after hydrothermal synthesis show the strongest luminescence intensity under a 980 nm laser diode excitation. The temperature sensing behavior of $\text{YPO}_4:1\%\text{Er}^{3+}$, 15% Yb^{3+} phosphors has also been investigated in detail. The result indicated that $\text{YPO}_4:1\%\text{Er}^{3+}$, 15% Yb^{3+} phosphors could be considered as potential materials for optical temperature sensors.

Keywords: Rare earth-doped phosphate; Phase transition; UC luminescence; Optical temperature sensing

1. Introduction

Temperature plays an important role in practically every physical, chemical and biological procedure, creation clear temperature principle critical for their control and application. [1-2] Traditional measurement of temperature relies on the principle of heat-expansion and cold-contraction. [3] While in many industry the conventional temperature sensors are no longer applicable, such as coal mines, oil refineries, intracellular temperature, and corrosive environments. [4-6] Unlike the conventional temperature sensors, lanthanide-doped thermometers have characteristic luminescence behaviors, for instance, bandwidth of emission, luminous intensities of different bands, decay time, etc. which are variable with temperature. So, lanthanide-doped phosphors can be used as a non-invasive thermometer by supervise its luminescence properties. [7, 8]

Rare earth (RE) doping materials have highly promising and attract more and more attention from researchers. RE elements have fully filled outer (5s and 5p) electronic shells shielding the unfilled inner (4f) orbital, which making RE luminous materials possess characteristic electronic, chemical and optical properties, and are broadly applied to high-performance magnets, luminescence devices, displays, bio-labeling, optical imaging or phototherapy, etc. [9,10] Among all potential hosts, RE phosphates (REPO_4) has been extensively applied in many territories such as laser hosts, moisture sensors, phosphors, heat-resistant materials, biological labels, photon up-conversion materials and nuclear waste disposal because it has high index of refraction, high thermal and chemical stability. [11-13] In addition, REPO_4 consists of several crystal structures, such as hexagonal, tetragonal, and monoclinic phases. In low temperature environment, REPO_4 exists in hexagonal structure. It can translate monoclinic structure when temperature increases. While the tetragonal phase always intends to be

acquired after calcination at 900°C or higher temperature. [14] In recent years, YPO₄ has many applications because of its excellent luminous efficiency, good chemical stability and especially low biological toxicity. It is well known that RE or transition metals doped YPO₄ nano-/micro-materials are significant phosphors and extensively applied in high-pressure mercury lamp, displays and cathode ray tube etc. [15]

So far, for all we know, very little research about phase transition and temperature sensing behavior of YPO₄ doped with Er³⁺ and Yb³⁺ ions have been addressed. In this work, we explore its phase transition temperature, optimal annealing temperature, optimal doping concentrations, luminescent spectrum and temperature sensing behavior. The experimental results demonstrate that tetragonal YPO₄:Er³⁺, Yb³⁺ material has more stronger luminescent ability and can be as a very promising candidate for non-invasive accurate optical temperature sensors.

2. Experimental Details

2.1 Experimental

2.1.1 Materials

Yttrium oxide, erbium oxide and ytterbium oxide (99.99%) were completely dissolved in concentrated HNO₃ at elevated temperature and formed solutions of 0.08 M, 0.05 M and 0.05 M, respectively. All the other chemicals were analytical grade and used without any further purification. (NH₄)₂HPO₄ solid was used as the source of phosphate. And tri-sodium citrate was chelating agent. Deionized water was applied in the whole process.

2.1.2 Synthesis

In an exemplary procedure, 33.6 ml of Y(NO₃)₃ solution, 0.4 ml of Er(NO₃)₃ solution and 6ml of Yb(NO₃)₃ solution were mixed with 2 mmol of trisodium citrate (Cit³⁻) to form the RE³⁺-Cit³⁻ complex (1:1molar ratio for Cit³⁻/RE³⁺).

After magnetic stirring for 20 min, 20 ml of an aqueous solution containing 2.8 mmol (1.4:1 molar ratio for $(\text{NH}_4)_2\text{HPO}_4/\text{RE}^{3+}$) of $(\text{NH}_4)_2\text{HPO}_4$ was added into the above mentioned solution drop by drop under stirring. Meanwhile, a transparent solution became more and more murky. Before the hydrothermal step, we adjusted the pH value of the mixture to 6 and stirred for 1 h. At the last step, the mixture was transferred in a 60 ml Teflon bottle held in a stainless steel autoclave sealed and kept at 180°C for 24 h. After solution was cooled down to room temperature naturally and removed the supernatant, the sediment was centrifuged and washed with deionized water and ethanol three times. The uniformly distributed hexagonal $\text{YPO}_4 \cdot 0.8\text{H}_2\text{O}:1\%\text{Er}^{3+}$, 15% Yb^{3+} was acquired by dried in air at 60°C for 12 h. In addition, tetragonal phase $\text{YPO}_4:1\%\text{Er}^{3+}$, 15% Yb^{3+} can be acquired by annealed at 1000°C for 3 h. The other Er^{3+} and Yb^{3+} doped YPO_4 samples were manufactured by the same method, except for different doping concentration.

2.2 Characterization

The crystal structures and phase purities of the powder X-ray diffraction (XRD) measurements were performed on a Rigaku-Dmax 2500 diffractometer at a scanning rate of 15°/min in the 2θ range from 10° to 65°, with graphite monochromatized Cu K α radiation ($\lambda=0.15405$ nm). The morphology and size of the lanthanide-doped materials were characterized by a field-emission scanning electron microscope (FE-SEM, XL30, Philips). The up-conversion luminescence spectrum was measured by exciting the sample with 980 nm laser diode (LD) using a Zolix Omni- λ 500 spectrograph. A CCD detector combined with a monochromator was used for signal collection from 450 to 750 nm. The $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped YPO_4 samples were filled in an iron sample cell and the temperature of the sample was increased from 313 to 573 K heated by resistive wire elements. A copper-constant thermocouple buried in the

sample was used to monitor the sample's temperature with a measurement error of ± 1.5 K. All the measurements were performed at room temperature.

3. Results and Discussion

3.1 Structure and Morphology of Yttrium Phosphate

3.1.1 XRD

Figure 1 shows the representational XRD patterns of $\text{YPO}_4 \cdot 0.8\text{H}_2\text{O} / \text{YPO}_4: 1\% \text{Er}^{3+}, 5\% \text{Yb}^{3+}$ powders prepared at room temperature and annealed from 600°C to 1200°C for 3 h after hydrothermal method at 180°C for 24 h. Before annealing, the diffraction peaks are accurately matched with the JCPDS file of hexagonal phase of $\text{YPO}_4 \cdot 0.8\text{H}_2\text{O}$ (JCPDS 42-0082). After annealing at 600°C , the hexagonal phase still exists. When annealed temperature reaches to 700°C , the tetragonal phase completely appears and no diffraction peaks of the hexagonal phase can be detected. Hence we confirm that the phase transformation completely occurs. In addition, the XRD patterns of $\text{YPO}_4: 1\% \text{Er}^{3+}, 5\% \text{Yb}^{3+}$ powders prepared by annealed at 700°C , 800°C , 900°C , 1000°C , 1100°C and 1200°C for 3 h after hydrothermal routine are precisely in accord with the standard tetragonal phase of YPO_4 (JCPDS 11-0254). The results above reveal that the $\text{Yb}^{3+}/\text{Er}^{3+}$ ions perfectly entry the lattice of host and the host structure has no change. Because the ion radius of $\text{Yb}^{3+}/\text{Er}^{3+}$ are much bigger than Y^{3+} , the Bragg reflections of $\text{YPO}_4 \cdot 0.8\text{H}_2\text{O}$ and YPO_4 shift some smaller angles that still can be regard as acceptable error. Besides, the XRD patterns of $\text{YPO}_4: x\text{Er}^{3+}, y\text{Yb}^{3+}$ [(1) $y=5\%$; $x=0.5\%, 0.8\%, 1\%, 2\%, 3\%$, and (2) $x=1\%$; $y=10\%, 15\%, 20\%$] powders prepared by annealed at 1000°C for 3 h after hydrothermal method at 180°C for 24 h are displayed in Figure S1 and S2 (Supplemental information), respectively. All diffraction peaks are also precisely in consistent with the standard tetragonal phase of YPO_4 (JCPDS 11-0254), but some smaller shift can still be detected.

3.1.2 FE-SEM

The representative morphologies of the as-synthesized lanthanide-doped yttrium phosphate before and after annealing are shown in Fig. 2. The Fig. 2A shows that the as-prepared $\text{YPO}_4 \cdot 0.8\text{H}_2\text{O}:1\%\text{Er}^{3+}, 5\%\text{Yb}^{3+}$ morphology before calcination is the hexagonal prism and its superficial width of about 1 μm . When calcination temperature reaches to 700°C , the morphology of $\text{YPO}_4:1\%\text{Er}^{3+}, 5\%\text{Yb}^{3+}$ wrinkles, which may attribute to the tetragonal phase transformed along with the process of dehydration (Fig. 2B). **Like most fluorescent materials, in high calcination temperature, tetragonal $\text{YPO}_4:1\%\text{Er}^{3+}, 5\%\text{Yb}^{3+}$, $\text{YPO}_4:2\%\text{Er}^{3+}, 5\%\text{Yb}^{3+}$ and $\text{YPO}_4:1\%\text{Er}^{3+}, 15\%\text{Yb}^{3+}$ become highly aggregate, which were exhibited in the Fig. 2C, Fig. 2E and Fig. 2G, respectively. The particles aggregate and form irregular shape. But, the particles are still loose and it seems that there remains some irregularity in the form of gap among them. This porous construction may be due to release of multiple gases during the calcination process. [16] The morphology of material changes with phase transition when the calcination temperature increases, which is shown in the Fig. 2A, 2B and 2C. Under the conditions of different doped concentration, before calcination, the morphologies of $\text{YPO}_4 \cdot 0.8\text{H}_2\text{O}:2\%\text{Er}^{3+}, 5\%\text{Yb}^{3+}$ and $\text{YPO}_4 \cdot 0.8\text{H}_2\text{O}:1\%\text{Er}^{3+}, 15\%\text{Yb}^{3+}$ don't have obviously changed, which can be clearly observed in Fig. 2D and Fig. 2F, respectively.**

3.2 UC Luminescence

As we all know, $\text{YPO}_4 \cdot 0.8\text{H}_2\text{O}$ and YPO_4 lattice have different crystal structure. And the mechanism of luminescence is related to crystal structure. Thus, we compared the luminescence intensity of both phases in the same condition. Under 980 nm irradiation (Fig. 3(a)), obviously, the $\text{YPO}_4:1\%\text{Er}^{3+}, 5\%\text{Yb}^{3+}$ (tetragonal phase,

sinter temperature 1000°C) produce stronger emission than $\text{YPO}_4 \cdot 0.8\text{H}_2\text{O} : 1\% \text{Er}^{3+}$, 5% Yb^{3+} (hexagonal phase, sinter temperature 600°C). This phenomenon may due to the presence of water molecules in the $\text{YPO}_4 \cdot 0.8\text{H}_2\text{O}$ crystal, hence the radiationless process has advantages over the radiative process. [17] After annealed at 1000°C for 3 h, yttrium phosphate phase transforms from hexagonal to tetragonal along with the process of dehydration and the distance of luminescence centers becomes closer, which enhances the energy transfer (ET) between the luminescence centers. From the Fig. 3(a), $\text{YPO}_4 : 1\% \text{Er}^{3+}$, 5% Yb^{3+} have **three emission bands**, which are $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ (525 nm), $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (550 nm) and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (660 nm), respectively. Besides, $\text{YPO}_4 : 1\% \text{Er}^{3+}$, 5% Yb^{3+} have stronger red emission and the reasons of this phenomenon are as follows. In $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped materials, due to the large absorption cross-section of $\text{Er}^{3+}/\text{Yb}^{3+}$ elements, the excited state absorption (ESA) of $^4\text{I}_{13/2} \rightarrow ^4\text{F}_{9/2}$ and $^4\text{I}_{11/2} \rightarrow ^4\text{F}_{7/2}$ and cooperation energy transfer (CET) of Yb^{3+} ($^2\text{F}_{5/2}$) to Er^{3+} ($^4\text{F}_{7/2}$) are diminished whereas energy transfer upconversion (ETU) of $^4\text{I}_{11/2} \rightarrow ^4\text{F}_{9/2}$ that exists in between adjacent Er^{3+} becomes a dominant mechanism. The co-doping of Yb^{3+} made great energy gather at Er^{3+} ($^4\text{I}_{15/2}/^4\text{I}_{11/2}/^4\text{I}_{13/2}$). Consequently, the $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ jump of Er^{3+} is considerably increased, which makes red luminescence intensity stronger than green luminescence intensity in microcrystalline powders. [18]

Green emission bands play an important role in our study. Thus, we only select 500-575 nm as our research contents. With the increase of calcination temperature, luminescence intensity increases and reaches to the top at 1000°C, which is presented in Fig. 3(b). Because of the defects existed in YPO_4 lattices, the probability of quenching and nonradiative multiphonon relaxation increases at low calcination temperatures. And the defects decrease with the increase of the crystallinity and the crystallite size when the calcination temperature increases, at the same time, the

quenching effect and nonradiative relaxation are also decreased. Both red and green emissions have been greatly enhanced under 1000°C. When the temperature is over 1000°C, the lattices may be destroyed. So luminescence intensity decreases. [19]

After the optimal calcination temperature was confirmed, we also found out the optimum doped concentration of $\text{Er}^{3+}/\text{Yb}^{3+}$ ions under room temperature and a 980 nm laser diode excitation. With the doped concentration of Er^{3+} ions varied from 0.5% to 3% making Yb^{3+} ions doped concentration fixed at 5%, the luminescence intensity increased after an initial decrease (Fig. 3(c)). And the Fig. 3(d) show the same form of changing curve of luminescence intensity accompanied Yb^{3+} ions doped concentration varied from 5% to 20% fixing Er^{3+} ions doped concentration at 1%. **Obviously, $\text{YPO}_4:1\%\text{Er}^{3+}, 15\%\text{Yb}^{3+}$ demonstrates strongest emission under a 980 nm laser diode excitation. This is attributed to the more populated green and red emitting levels of Er^{3+} , which due to the cross relaxation (CR) process among Er^{3+} ions, an efficient ET from the sensitizer Yb^{3+} to Er^{3+} for the larger absorption cross-section of Yb^{3+} around 980 nm and larger energy overlap between Yb^{3+} and Er^{3+} . [27, 30, 47] The luminescence intensity decreased visibly with the content of Er^{3+} more than 1% due to the concentration quenching effect. This effect can also demonstrate the presence of the energy transfer between nearest Er^{3+} and $\text{Yb}^{3+}/\text{Er}^{3+}$ ions. As the concentration of Er^{3+} increases, all of Er^{3+} and $\text{Er}^{3+}/\text{Yb}^{3+}$ ions become closer, which improves non-radiative relaxation and causes the decrease of UC luminescence intensity. [35] Similarly, the UC emission intensities also decreases remarkably with the Yb^{3+} concentration increased beyond 15% at constant Er^{3+} concentration, which may be attribute to the energy back transfer (EBT). [44, 45] With the increase of Yb^{3+} concentration, the ratio between EBT from Er^{3+} to Yb^{3+} and energy transfer from Yb^{3+} to Er^{3+}**

become higher and higher. [46] And the distances of Er^{3+} ions become wider, which weakens the CR process and causes the drop of the red to green emission intensity ratio as the Fig. 4 presents.

Aim to confirm the total number of photons which are involved in the green luminous mechanisms of $\text{YPO}_4:1\%\text{Er}^{3+}$, 15% Yb^{3+} microcrystals, the mutative curve of the green ($^2\text{H}_{11/2}/^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) luminous intensity with different pumping power of 980 nm diode laser have been functional represented in Fig. 5. The relation between the green intensity I_{green} and the pumping laser intensity obeys the following equation:

$$I_{\text{green}} \propto (P_{\text{pump}})^n$$

where n represents the quantity of photons of pump the UC excited state. [20, 21] By the analysis and calculation on the experimental data, the slopes of the two fitted lines matching with 525 nm and 550 nm emissions are 2.3 and 2.0, respectively. In conclusion, green UC emission is two-photon process and one green UC emission photon need two near-infrared (NIR) excitation photons in all the systems of $\text{YPO}_4:1\%\text{Er}^{3+}$, 15% Yb^{3+} .

As we all know, Er^{3+} ions have two emission bands marched with green emission and red emission in visible luminescence field, respectively. Almost all Er^{3+} -doped materials have similar UC luminous mechanism, which already has been widely researched. [22-25] In addition to the above mentioned mechanism of red emission, Fig. 6 shows a possible UC mechanism of green emission. The infrared excitation power at 980 nm is mainly absorbed by Yb^{3+} ions' ground state and then transmitted to adjacent Er^{3+} ions. The following sections explain this procedure in more detail. The energy gap between $^2\text{F}_{5/2}$ and $^2\text{F}_{7/2}$ state of Yb^{3+} ions associated with the energy of a 980 nm photon. Then the Yb^{3+} ions at $^2\text{F}_{7/2}$ ground state can jump to $^2\text{F}_{5/2}$ by a GSA process. In a second step, ET occurs between the energy levels $^4\text{I}_{11/2}$ of Er^{3+} ions and

$^2F_{5/2}$ of Yb^{3+} ions and Er^{3+} ions be first populated. While the metastable state $^4I_{11/2}$ of Er^{3+} ions can obtain second photon energy from another Yb^{3+} ions previously excited or the ESA process. Finally, Er^{3+} ions are excited to $^4F_{7/2}$ level by two-photon process. However, the $^4F_{7/2}$ level of Er^{3+} ions is not steady and always transfers to lower energy levels by Non-Radiative (NR), which populates to the lower thermally coupled levels $^2H_{11/2}/^4S_{3/2}$ and $^4F_{9/2}$. Last, red range emission (660 nm) and green range emission (525 nm, 550 nm) are revealed in the emission spectra, respectively.

3.3 Temperature Sensing Ability

The temperature sensing UC luminescent performance of $YPO_4:1\%Er^{3+}, 15\%Yb^{3+}$ microcrystalline is investigated in terms of intensity of two green emissions to explore its properties as optical temperature sensors. As the $^2H_{11/2}$ and $^4S_{3/2}$ thermally states of Er^{3+} have a low energy gap (about 770 cm^{-1}), the state of $^2H_{11/2}$ can also be populated effectually from $^4S_{3/2}$ by environmental temperature elevated, which will lead to the accelerate of $^2H_{11/2} \rightarrow ^4I_{15/2}$ (525 nm) transition. This temperature controlled population is following Boltzmann distribution. [26] With the temperature controlled population at the $^2H_{11/2}$ and $^4S_{3/2}$ two levels and neglecting the influence of self-absorption, the fluorescence intensity ratio (FIR) of green UC luminescence originated from $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions can be expressed as [27]

$$FIR = \frac{I_H}{I_S} = B \times \exp\left(-\frac{\Delta E}{k_B T}\right) \quad (1)$$

$$\ln(FIR) = \ln(B) + \left(-\frac{\Delta E}{k_B T}\right) = \ln(B) + \left(-\frac{C}{T}\right) \quad (2)$$

where I_H and I_S are the luminescence intensity corresponding to $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions, respectively. ΔE is the energy gap between the $^2H_{11/2}$ and $^4S_{3/2}$ levels. k_B is Boltzmann's constant. T is the absolute temperature. B is a constant that can be acquired by linear fitting of $\ln(FIR)$ and T^{-1} and determines by the experiment

instrument and the inner spectroscopic properties of the optical material, which is shown in Fig. 7. By linear fitting, we can obtain the slope and intercept of fitting straight-line whose value is $C=1101.5\pm5.4$ and $\ln(B)=1.71\pm0.01$, respectively. These give the energy gap between $^2H_{11/2}$ and $^4S_{3/2}$ levels as $765.6\pm3.8\text{ cm}^{-1}$, which match well with the real energy gap (770 cm^{-1}) of $^2H_{11/2}$ and $^4S_{3/2}$ thermal coupling levels of Er^{3+} .

Through the nonlinear fitting method, we can obtain the relationship between FIR and absolute temperature. **Figure 8 shows that there is a good linear relation between FIR and absolute temperature within the range of 313-573 K.** Thus, we can use this linear relationship to measuring temperature. While in a real world application, the accuracy of thermometer is an important parameter. And this parameter of optical thermometer can be calculated by the following formula [28, 29]

$$\Delta T = \frac{\Delta R k_B T^2}{R \Delta E} = \frac{\Delta R T}{R C} \quad (3)$$

Where ΔT be defined as the error of measuring temperature and ΔR is standard deviation of FIR. The average value of measured temperature which can be obtain from multi-group data of R and T is found to be only $\pm 0.24\text{ K}$, which demonstrate this $\text{YPO}_4:1\%\text{Er}^{3+}$, $15\%\text{Yb}^{3+}$ microcrystalline can get great accuracy of measuring temperature.

According to the acquired Boltzmann's schemes, the sensitivity of luminescent thermometer can be defined by [30]

$$S = \frac{\partial(FIR)}{\partial T} = B \exp\left(-\frac{\Delta E}{k_B T}\right) \frac{\Delta E}{k_B T^2} = FIR \times \frac{\Delta E}{k_B T^2} \quad (4)$$

where S is the sensitivity and other factors have already been explained. Figure 9 expresses the dependence of sensitivity of the presented $\text{YPO}_4:1\%\text{Er}^{3+}$, $15\%\text{Yb}^{3+}$ microcrystalline with growth of absolute temperature. Black line is the theory data

and red point is the actual data. Obviously, their compatibility is high. The highest value of sensitivity is found to be $2.71 \times 10^{-3} \text{ K}^{-1}$ at 548 K. Table 1 shows other host materials doped with Er^{3+} and $\text{Er}^{3+}/\text{Yb}^{3+}$ as excellent temperature sensing parameters. Compare with the other materials doped with Er^{3+} and $\text{Er}^{3+}/\text{Yb}^{3+}$, this $\text{YPO}_4:1\%\text{Er}^{3+}$, $15\%\text{Yb}^{3+}$ phosphor can become a promising material to be used in making the accurate optical temperature sensor.

4. Conclusions

In summary, tetragonal YPO_4 microcrystals doped with Yb^{3+} and Er^{3+} ions have been synthesized by using hydrothermal routine and extra annealing at different temperature for 3 h. In the step of annealing, the dehydration of $\text{YPO}_4 \cdot 0.8\text{H}_2\text{O}$ occurs when calcination temperature up to approximate 700°C , which causes phase transition. Then, through the selective annealing temperature and doped concentration procedure, we confirm that $\text{YPO}_4:1\%\text{Er}^{3+}$, $15\%\text{Yb}^{3+}$ phosphors synthesized by annealing at 1000°C for 3 h after hydrothermal method show the strongest luminescence intensity under a 980 nm laser diode excitation. And the ratio of fluorescent intensity of $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ (525 nm) and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (550 nm) has been measured between room 313 and 573 K for the optical thermometry performance based on emission spectrum under excitation of 980 nm laser. The maximum calculated sensor sensitivity is 0.0027 K^{-1} at 548 K. All these results suggest that $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped YPO_4 phosphor materials can be used in UC luminescence imaging and accurate temperature measurement and so on.

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Figure and Table Captions

Table 1 Summarized performance Er^{3+} and $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped materials as temperature sensing parameters. Values of the maximum sensitivity, the temperature range as well as the excitation wavelength are also included.

Fig. 1 XRD powder patterns of $\text{YPO}_4 \cdot 0.8\text{H}_2\text{O} : 1\% \text{Er}^{3+}, 5\% \text{Yb}^{3+}$ prepared by unroasted and annealed at 600°C for 3 h after hydrothermal method at 180°C for 24 h. And the XRD patterns of $\text{YPO}_4 : 1\% \text{Er}^{3+}, 5\% \text{Yb}^{3+}$ powders prepared by annealed at 700°C , 800°C , 900°C , 1000°C , 1100°C and 1200°C for 3 h after hydrothermal method at 180°C for 24 h.

Fig. 2 The FE-SEM images of hexagonal phase and tetragonal phase. Hexagonal $\text{YPO}_4 \cdot 0.8\text{H}_2\text{O} : 1\% \text{Er}^{3+}, 5\% \text{Yb}^{3+}$ (A), $\text{YPO}_4 \cdot 0.8\text{H}_2\text{O} : 2\% \text{Er}^{3+}, 5\% \text{Yb}^{3+}$ (D) and $\text{YPO}_4 \cdot 0.8\text{H}_2\text{O} : 1\% \text{Er}^{3+}, 15\% \text{Yb}^{3+}$ (F) synthesized by hydrothermal method; Tetragonal $\text{YPO}_4 : 1\% \text{Er}^{3+}, 5\% \text{Yb}^{3+}$ (B) synthesized by annealed at 700°C for 3 h after hydrothermal method; Tetragonal $\text{YPO}_4 : 1\% \text{Er}^{3+}, 5\% \text{Yb}^{3+}$ (C), $\text{YPO}_4 : 2\% \text{Er}^{3+}, 5\% \text{Yb}^{3+}$ (E) and $\text{YPO}_4 : 1\% \text{Er}^{3+}, 15\% \text{Yb}^{3+}$ (G) synthesized by annealed at 1000°C for 3 h after hydrothermal method;

Fig. 3 (a) UC luminescence spectra of $\text{YPO}_4 : 1\% \text{Er}^{3+}, 5\% \text{Yb}^{3+}$ (tetragonal phase, sinter temperature 1000°C) and $\text{YPO}_4 \cdot 0.8\text{H}_2\text{O} : 1\% \text{Er}^{3+}, 5\% \text{Yb}^{3+}$ (hexagonal phase, sinter temperature 600°C); (b) UC luminescence spectra of $\text{YPO}_4 : 1\% \text{Er}^{3+}, 5\% \text{Yb}^{3+}$ (tetragonal phase) prepared by annealed at 700°C , 800°C , 900°C , 1000°C , 1100°C and 1200°C for 3 h; (c) UC luminescence spectra of $\text{YPO}_4 : x\% \text{Er}^{3+}, 5\% \text{Yb}^{3+}$ ($x = 0.5, 0.8, 1, 2, 3$) prepared by annealed at 1000°C for 3 h; (d) UC luminescence spectra of $\text{YPO}_4 : 1\% \text{Er}^{3+}, y\% \text{Yb}^{3+}$ ($y = 5, 10, 15, 20$) prepared by annealed at 1000°C for 3 h.

Fig. 4 The dependence of the red to green emission intensity ratio with different Yb^{3+} concentration.

Fig. 5 The log–log plots of UC emission intensity of $\text{YPO}_4:1\%\text{Er}^{3+}$, $15\%\text{Yb}^{3+}$ as a function of a 980 nm laser pumping power.

Fig. 6 The energy level diagram of Er^{3+} and Yb^{3+} doped materials under a 980 nm laser diode excitation.

Fig. 7 Logarithmic figure of FIR ($I_{525}/I_{550\text{nm}}$) as a function of the inverse absolute temperature under a 980 nm laser diode excitation.

Fig. 8 FIR ($I_{525}/I_{550\text{nm}}$) as a function of the absolute temperature in the range of 313-573 K.

Fig. 9 Variation of sensitivity with increasing temperature in $\text{YPO}_4:1\%\text{Er}^{3+}$, $15\%\text{Yb}^{3+}$.

Table 1 Summarized performance Er^{3+} and $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped materials as temperature sensing parameters. Values of the maximum sensitivity, the temperature range as well as the excitation wavelength are also included.

Host	Temperature Range [K]	Excitation Wavelength (nm)	Maximum Sensitivity [K^{-1}]	Ref.
fluorotellurite glass	300–550	800	0.0054	[31]
Oxy-fluoride ceramics glass	303–823	980	0.0047	[32]
$\text{La}_2\text{O}_2\text{S}$ phosphor	290–573	971	0.0080	[24]
LiNbO_3 particles	285–453	980	0.0075	[26]
$\text{CaLa}_2\text{ZnO}_5$ phosphor	298–513	980	0.0059	[43]
$\text{Ga}_2\text{S}_3:\text{La}_2\text{O}_3$ glass	293–498	1060	0.0052	[33]
Al_2O_3 nanoparticles	295–973	978	0.0051	[34]
Er–Mo: $\text{Yb}_2\text{Ti}_2\text{O}_7$ nanophosphor	290–610	976	0.0074	[30]
Er–Mo: $\text{Yb}_3\text{Al}_5\text{O}_{12}$ nanocrystals	295–973	980	0.0048	[35]
GaWO_4 phosphor	303–873	980	0.0073	[36]
yttrium silicate powders	300–600	975(pulse)	0.0070	[37]
yttrium silicate powders	300–600	975	0.0056	[32]
silicate glass	296–723	978	0.0033	[38]
silicate glass	296–673	978	0.0023	[39]
phosphate glass ceramics	298–450	975	0.0016	[40]
La_2O_3 phosphor	303–600	980	0.0091	[41]
Y_2O_3	298–573	980	0.0050	[42]
YAG	298–573	980	0.0017	[42]
LaAlO_3	298–573	980	0.0032	[42]
YPO_4	313–573	980	0.0027	This work

Graphical Abstract

With the increases of calcination temperature, the phase of yttrium phosphate transforms from hexagonal to tetragonal phase at 700°C and the fluorescence intensity ratio (FIR) of green UC luminescence originated from $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions of Er^{3+} also rectilinearly increases.