Coprecipitation synthesis of α-(La,Yb,Er)₂W₂O₉ tungstate as a novel upconversion phosphor for optical thermometry

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ABSTRACT

Phase-pure α-(La,Yb,Er)₂W₂O₉ upconversion (UC) phosphors were synthesized via room temperature coprecipitation and subsequent calcination at 1073–1273 K. The pH of the coprecipitation system and the RE³⁺ to WO₄²⁻ ratio were found crucial for the formation of the target α phase. Phase transformation from cubic β-(La,Yb,Er)₂W₂O₉ to triclinic α-(La,Yb,Er)₂W₂O₉ occurred when calcination temperature was above 873 K. The UC luminescence including power/temperature dependent emission, decay kinetics of the main emission, emission color, and underlying UC mechanism were systematically investigated. The phosphor exhibited bright green luminescence under 978 nm laser excitation. The main emission [5S 2/2→7I 15/2] was analyzed to decay in a single exponential manner and have a decay time of 153.86 μs at room temperature. A three-photon mechanism was suggested responsible for the observed UC luminescence through analyzing the UC intensity against excitation power via logarithmic data transformation. The performance of optical temperature sensing was evaluated and compared with other typical UC phosphors. It was shown that the phosphor has relatively high maximum Sx and Sy values of 0.02694 K⁻¹ (548 K) and 0.01699 K⁻¹ (298 K) for the thermally coupled [H 11/2, S 3/2] and [5S 2/2] energy levels in the 298–548 K temperature range.

1. Introduction

Sensing temperature based on luminescence materials attracts many attentions [1–9]. Such thermometry monitors temperature based on the change of peak shape/intensity/shift, fluorescence lifetimes, and luminescence intensity ratio (FIR) of certain phosphors against temperature, and has the advantages of high sensitivity, remote observation, and good spatial resolution [10]. Luminescence materials play crucial role in high-performance thermometry including the selection of matrix hosts and the activator pairs [1]. Among various activators for temperature sensing, the Yb-Er sensitizer-activator pair attracts many attentions due to the thermally coupled levels (TCL) of ²H 11/2, ⁴S 3/2 [5–7,9–13]. As for the host matrix, good thermal properties are desirable. Since Yb-Er pairs are typically used in upconversion phosphors, thus fluoride matrices were the most widely studied due to their low phonon energy [14,15]. Nevertheless, fluorides also have limitations of deliquesce, high toxicity, and reserved resistance to heat [16]. Thus it is still highly desired to develop various other hosts for Yb-Er pairs and investigate the temperature sensing properties.

Rare earth tungstate is a big family including various compounds of RE₂(WO₄)₃, NaRE(WO₄)₂, RE₂O₃·WO₃, RE₂W₃ O₁₂, RE₁₋₄W₆O₁₄, RE₃WO₃O₁₄, etc. The composition and structure diversity of tungstate provide numerous physical and chemical properties for various applications and have attracted great interest. Among the tungstates, RE₃W₂O₉ compounds attracted special attention due to dielectric properties [17], photocatalytic properties [18], and their potential application in the fields of capacitor, fast oxide-ion conductors [19,20], and solid oxide fuel cells (SOFCs) [21,22]. Recently, researchers found that α-(La,Eu)₃W₂O₉ shows promising downconversion photoluminescence and has quantum yield as high as 77% [23]. The upconversion performance of Yb/Er/Tm and Yb/Ho/Er/Tm tri-doped and quadr-doped Gd₁₋₃W₂O₉ were also investigated and it was found that phosphors utilizing tungstate hosts are beneficial to achieve upconversion and downshifting luminescence of rare-earth ions because of their high thermal and chemical stability to powerful irradiation [24]. The good reputation for thermal stability of reported tungstates indicates that RE₃W₂O₉ may be potential good candidate for temperature sensing. It is promising that Yb-Er pair shows good upconversion luminescence and temperature sensing properties in RE₃W₂O₉. In RE₃W₂O₉ family, La₃W₂O₉ is polymorphism and crystallized in...
triclinic α phase and cubic β phase [25], while for RE = Ce-Gd members, the compounds were all in monoclinic system in the P2_1/c space group [17]. As we know, the 4 f shell of La³⁺ is vacant with unavailable f–f transitions, which are necessary for luminescent host materials. Compared with other rare earth, lanthanum is cheaper in price and more abundant in storage [26].

In this work, the α-(La,Yb,Er)₂W₂O₉ was synthesized via simple precipitation followed by calcination route and well dispersed powders were obtained without the addition of any organic reagents. The upconversion properties of Yb-Er in the α-La₂W₂O₉ were firstly reported, and the temperature sensing properties were evaluated and compared with other typical UC phosphors. Relatively high Sₜ and Sₚ values and good temperature resolution (δₜ) were achieved.

2. Experimental procedure

2.1. Reagents and sample synthesis

The rare earth sources for particle synthesis are RE₂O₃ oxide (RE = La, Er, Yb; 99.99% pure) from Huizhou Ruier Rare Chemical Hi-Tech Co. Ltd. (Huizhou, China). The other reagents of Na₂WO₄·2H₂O, NH₃·H₂O, and HNO₃ were analytical grade and were purchased from Shenyang Chemical Reagent Factory (Shenyang, China). All the chemicals were used as received without further purification. Milli-Q water (resistivity >18 MΩ·cm) was used throughout the experiment. The rare earth nitrate solutions (0.1 M) were obtained by dissolving the corresponding rare earth oxides in concentrated nitric acid, followed by evaporation to dryness at 373 K to remove superfluous HNO₃ and a final dilution with Milli-Q filtered water.

In a typical synthetic procedure, Na₂WO₄ solution (0.1 M) was added into rare earth nitrate RE(NO₃)₃] solution (RE:W = 1:1 in mole; RE = La, Yb, Er; La:Yb: Er = 88:10:2 in mole) and stirring for 30 min, the pH of the suspension was 6, and then NH₃·H₂O was added to adjust the pH of the system to designated value of 9 and 10. The suspension was collected via centrifugation right after the designed pH was reached. The product was washed with distilled water three times to remove by-products, and rinsed with ethanol once. After 24 h drying at 343 K in air oven, precursor powder was obtained for further processing and characterizations. The precursor was calcined in muffle furnace under the air atmosphere at different temperatures ranging from 673 to 1273 K for 1 h, with a heating rate of 278 K/min.

2.2. Characterization

Phase identification was performed via X-ray diffractometry (XRD; Model dx-2700b, Haoyuan, Dandong, China) under 40 kV/40 mA using nickel-filtered Cu-Kα radiation (λ = 0.15406 nm) and a scanning speed of 1°/min for 2θ = 5–70°. Micromorphologies of samples were observed via field emission scanning electron microscopy (FE-SEM; Model 5–5000, Hitachi, Tokyo, Japan) under an acceleration voltage of 5 kV. Fourier transform infrared spectroscopy (FT-IR) was conducted on a Scimitar 2000 Near FT-IR Spectrometer (Shimadzu, Japan) by the standard KBr pellet method. Optical properties of the activator free α-La₂W₂O₉ host and a Yb-Er codoped α-La₂W₂O₉ were studied via UV-vis absorption spectroscopy (Model PE-750, PerkinElmer, American) using BaSO₄ for calibration. The room temperature upconversion (UC) luminescence spectra were measured with an FLS 1000 fluorospectrophotometer (Edinburgh Instruments Ltd., Herrsching am Ammersee, Germany). The excitation source was a 978 nm continuous wavelength (CW) laser (2 W, Model MDL-III-980–2W-18050833). Fluorescence decay kinetics of the main UC emissions were measured with the lifetime testing unit of the FLS 1000 equipment. Temperature dependent UC spectra were measured using the same fluorospectrophotometer equipped with a TAP-02 high temperature controller in the range of 298–548 K.

3. Results and discussion

3.1. Select synthesis of (La₀.₈₈Yb₀.₁Er₀.₀₂)₂W₂O₉ nanopowder

Figure 1 is the XRD patterns of the precursor precipitated at pH = 9 and the products calcined from the precursor at different temperatures in the air for 1 h. It is seen that the room temperature precipitated precursor is amorphous phase. After 673 K calcination, the phase keeps its amorphous nature, and pure β-(La,Yb,Er)₂W₂O₉ phase was obtained at 873 K. All the diffractions of the 1073 and 1273 K products can be well indexed to the ICDD card 34–0704 indicating that pure α-(La,Yb,Er)₂W₂O₉ was obtained. It is also note that the diffraction peaks of Yb-Er doped samples shift to larger 2-theta angle for both α-phase and β-phase. This is because the radii of Yb³⁺ and Er³⁺ are smaller than that of La³⁺ [27] and contracted cell dimension would result when the position of La³⁺ is replaced by Yb³⁺-Er³⁺. However, different shift degree was observed, i.e. a moderate shift was observed in the α-phase compared with the β phase. The phenomenon was assumed to be caused by the difference in the amount of Yb³⁺-Er³⁺ and ionic radii in the solid solution of α and β phase. The La³⁺ form the 9- and 10-fold coordination polyhedra in triclinic α-La₂W₂O₉ [25]; however, it is suggested that the Yb³⁺ and Er³⁺ would prone to occupy 9-fold site in α-La₂W₂O₉ since 10-fold coordination polyhedra are hard to form for smaller Yb³⁺ and Er³⁺ [27]. The crystal structure of β-La₂W₂O₉ was not reported previously, but it was reported that it has a similar structure with β-La₂Mo₂O₉ where La³⁺
form octahedron (sixfold site) [28]. Thus the Yb$^{3+}$-Er$^{3+}$ was easier to enter the β phase, and caused more cell contraction. What’s more, the radii difference (Δr) of host ion La$^{3+}$ and activator/sensitizer ion Yb$^{3+}$-Er$^{3+}$ at CN = 6 are bigger than those at CN = 9 as shown in Table 1, which would also cause more cell contraction when Yb$^{3+}$-Er$^{3+}$ solutes into β phase.

Phase evolution of the precursors precipitated at pH = 10 and pH = 6 were shown in Figure S1 and Figure S2. The pH = 10 precursor shows similar thermal decomposition behaviors with the pH = 9 precursor, and α-(La,Yb,Er)$_2$W$_2$O$_9$ phase with trace impurities was obtained at 1073–1273 K. The pH = 6 precursor (direct precipitation without the addition of NH$_3$-H$_2$O) showed different thermal decomposition behavior: amorphous phase was obtained by 673 K calcination, and 873–1273 K calcination produced (La,Yb,Er)$_2$ (WO$_4$)$_3$ rather than α-(La,Yb,Er)$_2$W$_2$O$_9$. The W:RE ratio in (La,Yb,Er)$_2$(WO$_4$)$_3$ is 1.5 which is higher than the value of 1.0 in the starting materials. The formation of W-rich phase (La,Yb,Er)$_2$(WO$_4$)$_3$ was believed to be caused by the insufficient precipitation of RE$^{3+}$ in the acidic environment of pH = 6. It thus proved that the pH monitor of the precipitation process is crucial for the formation of the target La$_2$W$_2$O$_9$. In addition, the RE:W ratio in the starting materials is also proved to be important for the formation of the target phase, as can be seen in Figure S3, main phase of La$_2$(WO$_4$)$_3$ and NaLa(WO$_4$)$_2$ rather than α-La$_2$W$_2$O$_9$ were obtained from 1273 K calcination when the RE:W ratios in starting materials are 1.5 and 2. Since Na-containing NaLa(WO$_4$)$_2$ was obtainable during the synthesis, possible presence of Na in La$_2$W$_2$O$_9$ from pH = 9 and pH = 10 products were checked via EDS considering that trace amount of Na may affect the crystallization behavior, powder morphology, and luminescence intensities of resulting samples. The results are shown in Table 1-2 and it was found that there is no Na in the two products.

Figure 2 shows the micro-morphologies of the precursor precipitated at pH = 9 and the products calcined from it at different temperatures. The amorphous precursor contains irregularly shaped agglomerates, which were formed from ultrasmall nanoparticles. The 673 K product shows similar morphology with slightly better dispersibility and partial grown particles. Most precursor aggregations disappear by 873 K calcination, and much bigger separated particles (~250 nm) were obtained. Particles (~500 nm) with relatively uniform size and well dispersibility were obtained at 1073 K. The particles increase to 900 nm by 1273 K calcination. It is seen from the above analysis that the original ultra thin nanoparticles undergo considerable growth, and the adjacent original particles form elongated and branched shapes with relatively good dispersion via calcination above 873 K and the formed elongated shapes grow bigger with increasing temperatures. The good particle dispersion can persist till 1273 K calcination. The morphology evolution of pH = 10 precursor at different temperatures was shown in Figure S4, it is seen that similar final

Table 1. Summary of ion radii of La$^{3+}$, Yb$^{3+}$ and Er$^{3+}$ [27] at different coordination numbers (CN) and the radii difference (Δr) between La$^{3+}$ and Yb$^{3+}$/Er$^{3+}$.

| CN | r$_{La^{3+}}$ (Å) | r$_{Er^{3+}}$ (Å) | r$_{Yb^{3+}}$ (Å) | Δr(La$^{3+}$ and Yb$^{3+}$/Er$^{3+}$) | Δr(La$^{3+}$ and Er$^{3+}$) |
|----|------------------|------------------|------------------|---------------------------------|------------------|
| 10 | 1.270 Å          | 1.062 Å          | 1.042 Å          | 14.3%                           | 12.7%            |
| 9  | 1.216 Å          | 1.082 Å          | 1.042 Å          |                                 |                  |
| 6  | 1.042 Å          | 0.89 Å           | 0.868 Å          | 15.9%                           | 13.8%            |

Figure 1. XRD patterns of the precursor precipitated at pH = 9 (a) and the products calcined from the precursor at 673 K (b), 873 K (c), 1073 K (d), and 1273 K (e).
micromorphology of particles were obtained compared with that from the pH = 9 precursor after 1273 K calcination in the air.

The functional groups in the amorphous precursor and the products calcined from it at different temperatures were further investigated via FT-IR analysis as shown in Figure 3. The broad vibration at ~3390 cm\(^{-1}\) in RT precursor/673 K calcination products are due to the hydration and surface-adsorbed water in the products [29]. The peaks at 1087 and 1051 cm\(^{-1}\) are arising from vibrations of hydroxyl groups (\(\text{OH}\)). It is seen that the three vibrations basically gradually become weak with increasing temperature and disappear at 873 K, which corresponding well with the fact that the hydration/absorption water was removed with increasing temperature. In the precursor and 673 K products (Figure 3(a-b)) the broad absorptions below 1000 cm\(^{-1}\) which centered at ~815 cm\(^{-1}\) are attributable to the vibration of W-O, no split was found due to the amorphous nature and the low crystallinity of the products. The 873 K product (Figure 3(c)) shows split tungstate vibrations at 934, 808, and 660 cm\(^{-1}\) as the crystalline \(\beta-(\text{La,Yb,Er})_2W_2O_9\) phase was formed and the crystallinity were improved compared with the precursor and 673 K product (Figure 1). In 1073–1273 K products (\(\alpha-(\text{La,Yb,Er})_2W_2O_9\), Figure 3(d-e)) a group of absorption peaks were found at ~910, 844, 788, 680, and 580 cm\(^{-1}\), which are attributable to the W-O symmetric/anti-symmetric stretching and O-W-O symmetric/anti-symmetric deformation vibrations [29,30]. The vibrations of 873 K product were less well-resolved and split compared with these in 1073 K product which is on one hand due to the lower crystalline, and on the other hand due to the lower site symmetry of triclinic \(\alpha\) phase (1073 K product) than cubic \(\beta\) phase (873 K product), as the low symmetry allows the tungstate vibrations to significantly split. Compared with the 1073 K product the IR absorption in 1273 K product appear at basically the same position but are more split as higher calcination temperature leads to better crystallinity.

UV-Vis absorption of pristine \(\alpha-\text{La}_2W_2O_9\) and Yb-Er codoped \(\alpha-\text{La}_2W_2O_9\) tungstate were further investigated and shown in Figure 4. It is seen that the pure \(\alpha-\text{La}_2W_2O_9\)
La$_2$W$_2$O$_9$ shows strong absorption in range of 200–340 nm. The Yb-Er codoped α-La$_2$W$_2$O$_9$ tungstate shows broader absorption in 200–400 nm range, and the absorption of Er$^{3+}$ activator appears at 523 nm and 655 nm. The slightly lower absorption of Yb-Er codoped α-La$_2$W$_2$O$_9$ may due to the light pink color due to the Er doping. Estimations of bandgap energies can be made from the absorption spectra. The relation between absorption coefficient ($\alpha$) and incident photon energy ($h\nu$) can be written as $\alpha = B_d(h\nu-E_g)^{1/2}$ for directly allowed transition [31,32]. The $\alpha$ in the equation represents the absorption coefficient, $B_d$ is the absorption constant, $h\nu$ is the energy of incident photons, and $E_g$ is the band gap energy [31,32]. From the spectral data of absorption in (Figure 4(a)) (A: the absorbance), the ($Ah\nu$)$^2$-$h\nu$ plots can be drawn and were shown in (Figure 4(b)). Extrapolating the linear parts of ($Ah\nu$)$^2$-$h\nu$ plots yields band gap values of ~3.83 and 3.65 eV for α-La$_2$W$_2$O$_9$ and α-(La,Yb,Er)$_2$W$_2$O$_9$, respectively. The Yb-Er doping slightly narrow the band gap of the compound. The band gap of α-La$_2$W$_2$O$_9$ has not been experimentally determined previously, and thus no data were available for comparison. The band gap obtained herein coincides with the value (~3.42) from first principle calculation (Figure S5).

3.2. Photoluminescence properties of α-(La$_{0.88}$Yb$_{0.1}$Er$_{0.02}$)$_2$W$_2$O$_9$ phosphors

(Figure 5(a)) compares the upconversion spectra of α-(La$_{0.88}$Yb$_{0.1}$Er$_{0.02}$)$_2$W$_2$O$_9$ phosphor calcined from pH = 9 and pH = 10 precursor at 1273 K under 978 nm laser excitation. It is seen that the two phosphors shows similar UC spectral features with three groups of sharp emissions observed. The two sharp and splitting green emission groups at 523 nm and 540/548/553 nm were originated from $4^2H_{11/2} \rightarrow 4^4I_{15/2}$ and $4^4S_{3/2} \rightarrow 4^4I_{15/2}$ transitions of Er$^{3+}$ with $4^4S_{3/2} \rightarrow 4^2I_{15/2}$ transitions stronger. The relatively weak red emissions at 655/671 nm were from $4^4F_{9/2} \rightarrow 4^4I_{15/2}$ transitions. What is more, the α-(La$_{0.88}$Yb$_{0.1}$Er$_{0.02}$)$_2$W$_2$O$_9$ phosphor from the pH = 9 precursor shows ~6 times stronger intensity compared with that from the pH = 10 precursor for the strongest UC emission. The conventional
downconversion luminescence of the two phosphors was also studied and the results are shown in Figure 5 (b-c). It is seen that the excitation spectra consist of a broad band centered at ~320 nm and a series of sharp peaks in the 350–500 nm region. The broad band can be assigned to the excitation of La2W2O8 host since the bandgap energy of La2W2O8 was determined to be ~3.83 eV (Figure 4), which corresponds to a wavelength of 323 nm according to the equation \( \lambda = \frac{1240}{E} \) (E = 3.83 eV). The sharp peaks located in the range of 350–500 nm were caused by 4f transitions of Er3+ with the details of transition labeled in the figure. The emission spectra excited by 378 nm UV light show profiles similar to the spectra excited by 980 nm near infrared light. Again, the phosphor from the pH = 9 precursor shows stronger intensity (~15% stronger). The stronger luminescence of \( \alpha-(\text{La}_{0.38}Yb_{0.1} \text{Er}_{0.02})_2 \text{W}_2 \text{O}_8 \) phosphor from the pH = 9 precursor is believed to be caused by the morphology evolution of the two phosphors. Although the two phosphors have similar final micro-morphology, the intermediate products show different behaviors. The enlarged view of the 873 K product from the pH = 10 precursor (Figure S6) obviously shows more nanoparticles of precursor (yellow circles), while the product from pH = 9 precursor (Figure S7) shows uniform morphology of enlarged shapes particles. This leads to different extents of crystallization for the two final products and may have led to the observed superior luminescence of the pH = 9 product. Additionally, the impurity in \( \alpha-(\text{La}_{0.38} \text{Yb}_{0.1} \text{Er}_{0.02})_2 \text{W}_2 \text{O}_8 \) phosphor from the pH = 10 precursor (Figure S1) may also be responsible for the inferior luminescence.

The UC spectra of the two phosphors with varying excitation power (0.3–1.0 W) were shown in Figure S8 and Figure S9. It is seen that for both phosphors, increasing excitation power did not change peak shape and position but monotonically raised the emission intensity. From the equation of \( I_{\text{em}} = P^n \), the number of photons \( (n) \) needed to excite ground state electrons to emitting state can be estimated [5]. The log-log plots of \( I_{\text{em}} \) and \( P \) for different emissions of the phosphor calcined from pH = 9 precursor were shown in Figure 6. The slopes of the plots are the number of photons \( (n) \) needed. The slopes of the plots \( (n \text{ values}) \) are about 3 in Figure 6 which suggest that a three-photon mechanism is basically responsible for the observed UC luminescence.

Figure 5. Upconversion luminescence spectra under 978 nm laser excitation (0.3 W) (a) and conventional downconversion luminescence excitation (b) and emission spectra (c) taken for the \( \alpha-(\text{La}_{0.38} \text{Yb}_{0.1} \text{Er}_{0.02})_2 \text{W}_2 \text{O}_8 \) phosphor calcined from the pH = 9 and pH = 10 precursors at 1273 K.

Figure 6. Logarithmic fitting of the UC intensity against excitation power.
3.3. Temperature sensing properties of (La$_{0.88}$Yb$_{0.1}$Er$_{0.02}$)$_2$W$_2$O$_8$ nanoparticle

To sensing temperature it is important to evaluate the temperature dependent luminescence properties of the phosphor. The temperature dependent UC spectra of (La$_{0.88}$Yb$_{0.1}$Er$_{0.02}$)$_2$W$_2$O$_8$ particles under 978 excitation were shown in (Figure 7(a)). It is seen that similar spectra profiles were observed at different temperatures as analyzed in Figure 5 and the peak shape and position were not obviously influenced by temperatures. The International de L’Eclairage (CIE) chromaticity coordinates at different temperatures can be calculated from the emission spectra and the coordinates shift from (0.23, 0.74) (RT) to (0.18, 0.78) (548 K) (Figure S10). Figure 7(b)) shows the relationship of the relative intensities of different emissions with temperatures. It is found that the intensity of green emissions at 523/531 nm ($^3$H$_{11/2}$$\rightarrow$$^4$I$_{15/2}$) increase with increasing temperature and reach maxima at ~400 K, and the intensity drops to 47.4%/45.4% of their initial value at the highest temperature of 548 K. While intensity lose was observed right after the temperature increased for the green emissions at 540/543/548/554 nm ($^5$S$_{3/2}$$\rightarrow$$^4$I$_{15/2}$). It is also noted that the thermally coupled $^3$H$_{11/2}$$\rightarrow$$^4$I$_{15/2}$ and $^4$S$_{3/2}$$\rightarrow$$^4$I$_{15/2}$ transitions show quite different intensity loss rates with increasing temperatures. This indicates that the studied phosphors may sense temperature via fluorescence intensity ratio (FIR) mode of the thermally coupled $^3$H$_{11/2}$$\rightarrow$$^4$I$_{15/2}$ and $^4$S$_{3/2}$$\rightarrow$$^4$I$_{15/2}$ transitions and be employed as a potential probe. The $^4$F$_{9/2}$$\rightarrow$$^4$I$_{15/2}$ (655/671 nm) red emission slightly lose intensity with initial increased temperature and the intensities fluctuate before 400 K and then monotonously decrease with increasing temperature. At the highest measurement temperature of 548 K, the intensity of 655 and 671 nm emissions drops to 45.4%, and 35.9% of the initial value, respectively. It is seen that the red emissions at 655/671 nm also show obvious different intensity loss ratios compared with the green emission at 540/543/548/554 nm ($^5$S$_{3/2}$$\rightarrow$$^4$I$_{15/2}$), which indicates that the non thermally coupled transitions of $^4$F$_{9/2}$$\rightarrow$$^4$I$_{15/2}$ and $^4$S$_{3/2}$$\rightarrow$$^4$I$_{15/2}$ may also sense temperature via FIR mode and will be checked in the following section.

The temperature sensing performance of the thermally coupled $^3$H$_{11/2}$$\rightarrow$$^4$I$_{15/2}$ and $^4$S$_{3/2}$$\rightarrow$$^4$I$_{15/2}$ transitions were firstly checked and the trend of $^3$H$_{11/2}$$\rightarrow$$^4$I$_{15/2}$ and $^4$S$_{3/2}$$\rightarrow$$^4$I$_{15/2}$ FIR with temperature was shown in (Figure 8(a)). It is seen that with increasing temperature the $I_{523}/I_{554}$ FIR monotonous increase and can be fitted in single-exponential equation of FIR ($I_{523}/I_{554}$) = 77.19exp((−1510.73/T) + 0.41) (T = 298–548 K).

The above equation corresponding well with Boltzmann distribution FIR = Nexp(−ΔE/kT)+ C, where ΔE is the energy gap between the thermally coupled $^3$H$_{11/2}$ and $^4$S$_{3/2}$ levels, k the Boltzmann constant (0.695 K$^{-1}$cm$^{-1}$), N and C the constant, and T the temperature in Kelvin. This proved that the α-(La$_{0.88}$Yb$_{0.1}$ Er$_{0.02}$)$_2$W$_2$O$_8$ phosphors can be used for temperature sensing via FIR mode.

The $S_A$ (absolute sensitivity) and $S_R$ (relative sensitivity) are two important factors to quantify the quality of the temperature sensing phosphors which can be derived from the following equations [4,5,7]:

$$S_A = \frac{\left| \frac{d(FIR)}{d(T)} \right|}{(FIR - C) + \frac{\Delta E}{kT^2}}$$

$$S_R = \frac{\left| \frac{d(FIR)}{d(T)} \right|}{FIR} = \frac{FIR - C}{FIR} \times \frac{\Delta E}{kT^2}$$

The $S_A$ and $S_R$ values derived from the above equation for thermally coupled $^3$H$_{11/2}$ and $^4$S$_{3/2}$ levels of α-(La$_{0.88}$Yb$_{0.1}$ Er$_{0.02}$)$_2$W$_2$O$_8$ phosphors were shown in (Figure 8(b)) as the function of measurement temperature. The results show that the $S_A$ and $S_R$ reach maximum value of 269 × 10$^{-4}$ and 170 × 10$^{-4}$ K$^{-1}$ at 298 and 550 K respectively across the measurement temperature range.

Table 2 summary the $S_A$ and $S_R$ values for some typical temperature sensing phosphors and it was found that the maximum $S_A$ obtained in this work is much higher than list systems which indicated the promising

![Figure 7](image-url)
The temperature sensing properties of the studied system. The \( S_R \) is higher than most systems, but inferior than systems such as Yb-Er codoped Li₄ZrF₁₂ [33].

Except \( S_R \) and \( S_F \), temperature resolution (\( \delta_T \)) is another important factor which reflect the minimum detectable temperature for an temperature sensing system and can be obtained via the following equation:

\[
\delta T = \frac{1}{\delta F/R} \delta F/IR
\]

where \( S_R \) is the relative sensitivity described above, \( \delta F/IR \) is the relative uncertainty of FIR. The \( \delta F/IR \) value mainly depends on experimental setup and can reach 0.03% for the spectrophotometer (FLS 1000) used in this work. The \( S_R \) value has been calculated from the equation (2) above, thus the \( \delta_T \) of \( L_{229}/L_{554} \) FIR was calculated and the results were shown in Figure S11. The minimum \( \delta_T \) was found to be \(-0.017 \) K at 298 K, which is significantly better than report systems such as GdVO₄:Sm³⁺ (0.14 K) [34] and NaGd(WO₄):Yb,Er (0.037 K) [7].

The temperature sensing performance of the non thermally coupled \( \delta F_{9/2-4I_{15/2}} \) and \( \delta S_{3/2-4I_{15/2}} \) transitions were also checked and the trend of \( L_{229}/L_{555} \) FIR and \( L_{229}/L_{671} \) FIR with temperature were shown in Figure S12. However, it was found that although the two non thermally coupled transitions show obvious different intensity loss rate with increasing temperature, the FIR of the two transitions show irregular trend and cannot employed as temperature sensor.

(Figure 9(a)) shows the decay kinetics for the 540 nm emission of \( \alpha-(La_{0.88}Yb_{0.1}Er_{0.02})_{2}W_{2}O_{9} \) phosphor from \( \text{pH} = 9 \) precursor and the decay curves measured at other temperatures were shown in Figure S13. After fitting it was found that the main emission decay in single exponential mode by equation \( l(t) = A \exp(\frac{-t}{\tau})+B \). The single exponential fitting mode further proved that the Yb³⁺ and Er³⁺ prone to occupy 9-fold site in \( \alpha-La_{2}W_{2}O_{9} \) as analyzed in Figure 1. Microsecond lifetime of 118.22 µs at 548 K temperatures was obtained after fitting. The main emission at other temperatures show similar decay behavior and the derived \( \tau, A/B \) values and the chi-square factor (\( \chi^2 \)) of fittings for different temperatures are summarized in Table S3. The \( \chi^2 \) values for all the fittings are around 1 indicating high quality of the fitting. The derived lifetime of \( \alpha-(La_{0.88}Yb_{0.1}Er_{0.02})_{2}W_{2}O_{9} \) phosphors in the temperature range of \( RT \) to 548 K was shown in Figure S14 from where it is seen that the lifetime of the main emission monotonously decrease from RT

| Ion pair | Host            | Range (K) | \( S_R (K^{-1}) \times 10^{-4} \) | \( S_F (K^{-1}) \times 10^{-4} \) | Ref |
|---------|-----------------|-----------|-----------------------------------|-----------------------------------|-----|
| Yb⁺⁺/Er³⁺  | Sr₆(YPO₄)₄       | 298–573   | 50.7 (253 K)                      | 1026.5 (72)                      | [5] |
| Yb⁺⁺/Er³⁺  | La₂(WO₄)₃       | 300–550   | 97 (510 K)                        | -                                 | [6] |
| Yb⁺⁺/Er³⁺  | NaGd(WO₄)₂      | 300–550   | 174 (548 K)                       | 80 (373 K)                       | [7] |
| Ce⁺⁺/Mn⁺⁺  | Ca₆Al₂PO₄(SiO₄) | 298–523   | 48 (258 K)                        | 210 (96)                         | [8] |
| Yb⁺⁺/Er³⁺  | NaYF₄:Ga        | -         | 46 (498 K)                        | -                                 | [9] |
| Yb⁺⁺/Er³⁺  | KBaY(MoO₄)₂     | 250–460   | 130.6 (420 K)                     | 180 (250 K)                      | [10]|
| Yb⁺⁺/Er³⁺  | NaBiF₄          | 303–523   | -                                 | 107 (303 K)                      | [11]|
| Yb⁺⁺/Er³⁺  | NaScF₄(EDTA)    | 298–573   | 32.8 (548 K)                      | 41.3 (548 K)                     | [12]|
| Yb⁺⁺/Er³⁺  | Li₂ZrF₆         | 123–800   | 26 (550 K)                        | 395 (123 K)                      | [13]|
| Yb⁺⁺/Er³⁺  | LiZrF₆          | 123–900   | 52 (550 K)                        | 565 (123 K)                      | [14]|
| Eu⁺⁺       | T-LaVO₄         | 298–525   | 27 (123 K)                        | 190 (123 K)                      | [15]|
| Tb⁺⁺/Mn²⁺  | SCP             | -         | 162 (573 K)                       | 61.2 (298 K)                     | [16]|
| Eu⁺⁺/Eu⁺⁺  | Ca₆Al₂Si₁₋ₓO₇   | 303–443   | 240 (303 K)                       | 246 (443 K)                      | [17]|
| Eu⁺⁺/Yb⁺⁺  | YF₃:Ge         | 303–563   | 13 (250 K)                        | -                                 | [18]|
| Yb⁺⁺/Er⁺⁺  | La₂W₂O₉        | 298–550   | 269 (298 K)                       | 170 (550 K)                      | This work
4. Conclusions

A novel tungstate upconversion (UC) phosphors \( \alpha-(\text{La}, \text{Yb}, \text{Er})_2 \text{WO}_9 \) were obtained through selected coprecipitation. The UC properties of the as-made \( \alpha-(\text{La}, \text{Yb}, \text{Er})_2 \text{WO}_9 \) phosphors were systematically investigated under varying excitation power and temperatures, and the temperature sensing performances of the phosphors were comprehensively evaluated. The main conclusions are summarized as follows:

1. Phase-pure \( \alpha-(\text{La}, \text{Yb}, \text{Er})_2 \text{WO}_9 \) phosphors can be obtained by coprecipitation of \( \text{RE(NO}_3)_3 \) and \( \text{Na}_2\text{WO}_4 \) with the addition of \( \text{NH}_3\cdot\text{H}_2\text{O} \) in pH range of 9–10 followed by 1073–1273 K calcination under a \( \text{WO}_4^{2-}/\text{RE}^{3+} \) molar ratio of 1:1. The phosphors show morphologies of favorable dispersion and size uniformity without organic additive.

2. The \( \alpha-(\text{La}, \text{Yb}, \text{Er})_2 \text{WO}_9 \) phosphors showed two groups of sharp and splitting strong green UC emission at 523/529 nm \( (^{2}I_{11/2} \rightarrow ^{4}I_{15/2}) \) and 540/548/553 nm \( (^{4}S_{3/2} \rightarrow ^{4}I_{15/2}) \) and a group of weak red emission at 655/671 nm \( (^{4}F_{9/2} \rightarrow ^{4}I_{15/2}) \) with 540 nm the strongest under 978 nm excitation (0.3–1.0 W). The UC intensity of \( \alpha-(\text{La}, \text{Yb}, \text{Er})_2 \text{WO}_9 \) from pH = 9 precursor was 6.11 times stronger than that from the pH = 10 precursor mainly due to morphology evolution of the two phosphors.

3. The \( \alpha-(\text{La}, \text{Yb}, \text{Er})_2 \text{WO}_9 \) UC phosphors were found to be well capable of sensing temperature via FIR mode by thermally coupled \( ^{2}I_{11/2} \rightarrow ^{4}I_{15/2} \) levels. The \( \alpha-(\text{La}, \text{Yb}, \text{Er})_2 \text{WO}_9 \) has maximum absolute sensitivity \( (S_a) \) and relative sensitivity \( (S_b) \) of 269 \( \times \) \( 10^{-4} \) and 170 \( \times \) \( 10^{-4} \) \text{K}^{-1} at 298 and 550 K and the minimum temperature resolution \( (\delta_T) \) was found to be \( \sim0.017 \text{ K} \) at 298 K.

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Disclosure statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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