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Enhanced photoluminescence and ultrahigh temperature sensitivity from NaF flux assisted CaTiO₃: Pr³⁺ red emitting phosphor

Xiuying Tian^{1,2}, Shixun Lian^{1,*}, Changyan Ji², Zhi Huang³, Jin Wen², Zhanjun Chen²,

Hongxia Peng², Shumei Wang², Jing Li², Jilin Hu², Yangxi Peng²

1 Key Laboratory of Sustainable Resources Processing and Advanced Materials of Hunan Province, Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha, 410081, China

2 Hunan Provincial Key Laboratory of Fine Ceramics and Powder Materials, School of Materials and Environmental Engineering, Hunan University of Humanities, Science and Technology, Loudi,417000, China

3 National Electronic Ceramic Product Quality Supervision and Inspection Center, Loudi, Hunan, 417000, China

*Corresponding author

Shixun Lian, Tel: 0731-88865345; Fax: 0731-88865345

Email: sxlian@hunnu.edu.cn

ABSTRACT

The Pr^{3+} doped CaTiO₃ red emitting phosphor with enhanced PL and ultrahigh temperature sensing was prepared via NaF flux assisted solid-state reaction. All samples had the orthorhombic perovskite phase and no impurity was found. The typical sample mainly had sphere-like morphology with particle size of ~670 nm. The optical bandgap values were ~3.62-3.63eV. The Pr^{3+} quenching content was 0.6 mol% and the ET mechanism for quenching was the d-d interaction with the critical distance of 26.09 Å. A certain amount of NaF flux could enhance red emission attributed to ${}^{1}D_{2} \rightarrow {}^{3}H_{4}$ transition owing to improving the crystallinity of phosphors and reducing point defects near Pr^{3+} through the substitution of O^{2-} by F⁻ and Ca²⁺ by Na⁺. The energy storage trap (oxygen vacancy) near IVCT state played the key role for trapping electrons, accounting for the LAG emission and the average depth of trap was 0.39 eV. The CIE chromaticity coordinates were very close to that of the ideal red light and the CP was as high as 99.98%. The maximal S_a and S_r was as high as ~0.015 K⁻¹ and~ 5.2% K⁻¹, respectively. The thermal induced relaxation between the ${}^{3}P_{i}$ levels and ${}^{1}D_{2}$ level through the IVCT state was supposed to account for the excellent optical temperature sensing. Our work may provide a useful inspiration for developing ultrahigh sensitive optical temperature sensors.

Keywords:

Calcium titanate; Praseodymium; Optical thermometry; Intervalence charge transfer state

1. Introduction

Rare earth (RE) ions doped perovskite structure materials (ABO₃) have drawn great attention due to their applications in lighting and displays[1-3], temperature sensing[3, 4], photocatalysts[5, 6] and ferroelectrics[4, 7, 8]. In various perovskites, such as CaTiO₃, SrTiO₃, BaTiO₃, PbTiO₃ and so on, CaTiO₃ (CTO) has been preferred as one of the most important and suitable host materials due to its low phonon energy, excellently physical and chemical properties[9]. Among different RE ions, the trivalent praseodymium ion (Pr^{3+}) has been considered as one of the most promising activators owing to the rich emission in the visible region [10, 11]. Recently, Pr^{3+} doped CTO phosphor has been investigated because of the photoluminescence (PL) and long-afterglow (LAG) properties, which make it a promising candidate to substitute currently available red luminescent materials in applications such as flat panel display (FPD), field emission display (FED), electroluminescent (EL) devices, optical amplifiers (OA), lasers, medical imaging, warning signs and soft illumination[12-17]. When Pr^{3+} doped CTO phosphor is excited by UV light, there is only a single red emission peak at ~ 614 nm, very close to ideal red [12, 17]. It is attributed to ${}^{1}D_{2} \rightarrow {}^{3}H_{4}$ transition of Pr^{3+} , because of the nonradiative decay quenching from ${}^{3}P_{0}$ to ${}^{1}D_{2}$. Moreover, it can be also explained by various non-radiative de-excitation channels such as multi-phonon relaxation, cross-relaxation, intersystem crossing through low-lying levels of the 4f5d configuration, the metal-metal intervalence charge transfer (IVCT) state and electron-hole recombination energy transfer[18]. The electron-hole

recombination energy transfer model was proposed by Barandiarán et al. in 2017. It was indicated that the sole presence of the ${}^{1}D_{2} \rightarrow {}^{3}H_{4}$ red emission was attributed to the direct electron-hole recombination energy transfer from the host to the ${}^{1}D_{2}$ level of the Pr^{3+} dopant[18]. However, it is found that the IVCT state model has been widely accepted up to now, especially in the field of temperature sensing. In 2014, Zhang et al. reported a potential optical thermometric NaRETiO₄:Pr³⁺ (RE=Y, Gd) based on the IVCT state[19]. In 2016, Tang et al. discovered an optical thermometric Pr^{3+} doped (K_{0.5}Na_{0.5})NbO₃ based on the IVCT state[20]. In 2017, Gao et al. demonstrated a novel temperature sensing strategy utilizing the IVCT state interfered Pr³⁺ luminescence to perform optical thermometry[21]. Shi et al. discovered a potential optical thermometric material through IVCT state interfered photoluminescence of Pr^{3+} doped La₂MgTiO₆ phosphor[22]. In 2018, Wu et al. reported the self-calibrated optical thermometer LuNbO4:Pr³⁺/Tb³⁺ based on IVCT state[23]. Gao et al. found a double-perovskite Pr³⁺: Gd₂ZnTiO₆ thermometric phosphor based on IVCT state[24]. Cheng et al. summarized the distinctive strategy in luminescent thermometry based on IVCT state[25]. In 2019, Lei et al. reported that IVCT state interfered Pr^{3+} luminescence was a promising pathway to develop ultrahigh optical thermometric materials[26]. Nowadays, great efforts have been made to develop optical thermometry due to its promising applications in severe environments[26]. Especially, fluorescence intensity ratio (FIR) technique has attracted broad interest for the accurate and non-contact measurement, independent of the fluorescence loss and fluctuations of excitation light. Most of the investigations about

FIR temperature sensing utilize two temperature-dependent thermal coupling levels (TCLs). However, the relative temperature sensitivity (S_r) is the most important parameter to evaluate temperature sensing property, depending on the effective energy separation (ΔE) of the two TCLs. To avoid exceedingly low upper-level populations, ΔE is generally less than 2000 cm⁻¹, indicative of the highest S_r value not exceeding $2878/T^{2}[4, 20]$. In 2014, Pr^{3+} doped β -NaYF₄ phosphor with the S_r value of $657.7/T^{2}$ based on the TCLs (${}^{3}P_{0}$ and ${}^{3}P_{1}$ of Pr^{3+}) was reported by Zhou et al.[27]. Tian et al. discovered an optical thermometric β -NaYF₄: Nd³⁺ with S_r value of 2805/T² based on TCLs (${}^{4}F_{7/2}$ and ${}^{4}F_{3/2}$ of Nd³⁺)[28]. In 2018, Liu et al. achieved a S_r value of 2103.7/ T^2 in β -NaYF₄:Tm³⁺/Yb³⁺ based on TCLs (³F_{2,3} and ³H₆ of Tm³⁺)[29] and a S_r value of 1053.82/ T^2 in β-NaYF₄: Yb³⁺/Er³⁺ based on TCLs (²H_{11/2} and ⁴S_{3/2} of Er³⁺)[30]. Tang et al.[4] demonstrated that the S_r value of $Sr_{0.7}Ba_{0.3}TiO_3$: Pr^{3+} based on the TCLs (³P₀ and $^{3}P_{1}$ of Pr³⁺) was only 745.2/ T^{2} . To the best of our knowledge, the highest S_r value based on the FIR technique using TCLs is $2805/T^2$. Indeed, the above S_r value is less than $2878/T^2$. Thus, the limited S_r value hinders the commercial application of temperature sensor based on FIR technique. For Pr^{3+} doped optical thermometric phosphors, *FIR* technique based on TCLs (${}^{3}P_{1}$ and ${}^{3}P_{0}$) is not suitable for modern temperature detection with ultrahigh sensitivity. Yet lately, a distinctive strategy in luminescent thermometry based on IVCT state has been proposed to circumvent the limitation of TCLs[25]. In 2016, Gao et al. reported a novel optical thermometric Tb^{3+}/Pr^{3+} : NaGd(MoO₄)₂ with ultrahigh S_r value of 3735.4/ T^2 based on the diverse thermal responses from two IVCT

states[31]. Tang et al. achieved the ultrahigh S_r value of $7997/T^2$ from Pr^{3+} -doped $(K_{0.5}Na_{0.5})NbO_3$ based on IVCT state[20]. In 2017, Gao et al. reported a novel Pr^{3+} doped Na₂La₂Ti₃O₁₀ thermometric phosphor with ultrahigh S_r value of 4964.8/ T^2 based on IVCT state[21]. In 2018, Wu et al. discovered an optical thermometer LuNbO₄: Pr^{3+}/Tb^{3+} with ultrahigh S_r value of $3724/T^2$ based on two IVCT states[23]. A novel Pr^{3+} doped Ba_{0.7}Sr_{0.3}TiO₃ optical thermometric phosphor with ultrahigh S_r value of $4275.1/T^2$ based on IVCT state have been reported by Tang et al.[4]. In 2019, Lei et al. demonstrated a novel optical thermometric material Pr^{3+} : $Y_2Ti_2O_7$ with ultrahigh S_r value of $4385.9/T^2$ based on diverse thermal response from trap emission (TE) and IVCT state interfered Pr^{3+} red luminescence[26]. Moreover, Sun et al. reported a novel optical thermometric Pr³⁺-doped (K_{0.5}Na_{0.5})NbO₃-CaTiO₃ diphase ceramics based on the temperature-dependent FIR of ${}^{3}P_{1} \rightarrow {}^{3}H_{5}/{}^{1}D_{2} \rightarrow {}^{3}H_{4}[32]$, in spite of the fact that the S_r value of $1617.12/T^2$ was not high, which gave us deep inspiration for temperature sensing of Pr³⁺ doped CTO phosphor based on FIR technique of IVCT state interfered non-thermal coupling levels(NTCLs). However, the low emitting efficiency of Pr^{3+} doped CTO phosphor has confined the potential application to integrated optical and electrical devices, assigned to some undesirable defects such as trivalent titanium ions (Ti_{Ti}) , oxygen vacancies (V_{O}^{*}) and calcium vacancies (V_{Ca}^{*}) near Pr^{3+} , which can contribute to quench the Pr^{3+} emission[12]. However, some traps (like V_{α}) can improve the LAG emission intensity and decay time[17]. As known, the PL property of Pr³⁺ doped CTO phosphor can be enhanced by adding the sensitizers, charge

compensators and fluxes[12, 17, 33-36]. Recently, the flux assisted method has arisen as an effective way to enhance the PL intensity, crystallinity and efficiency[35]. Among these fluxes, such as NH₄Cl, NH₄F, H₃BO₃, LiF, NaF and so on, NaF flux has been gaining much attraction due to the relatively high melting point (993°C) and boiling point (1695°C), appropriate for the growth and ripening of particles[37]. In 2012, Dai et al discovered that the emission intensity of $Y_{1.55}Ti_2O_7$:0.45Eu³⁺ phosphor was enhanced by adding NaF as a flux[37]. In 2013, Manjunatha et al. reported that thermoluminescence(TL) property of Sm³⁺ doped CdSiO₃ phosphor was improved by the NaF flux assisted method[38]. In 2015, Liu et al. demonstrated that adding NaF as a flux could further improve the emission intensity of Lu₃(Al,Si)₅(O,N)₁₂:Ce³⁺ phosphor[39]. In 2017, for structure determination, a single crystal of Na₃Pr(PO₄)₂ has been grown by NaF flux assisted synthesis[40]. However, to the best of our knowledge, the enhanced PL and ultrahigh temperature sensing properties of NaF flux assisted Pr³⁺ doped CTO phosphor have been not investigated.

In this work, Pr^{3+} doped CTO phosphor with enhanced PL and ultrahigh temperature sensing was synthesized via NaF flux assisted solid-state reaction. The doping amounts of Pr^{3+} ion and NaF flux were optimized in order to enhance the PL emission intensity. Energy transfer (ET) mechanism between Pr^{3+} ions for quenching was investigated. The LAG property of the typical sample was investigated and the distribution of energy storage trap was discussed. The emission intensities of ${}^{3}P_{1} \rightarrow {}^{3}H_{6}$ and ${}^{1}D_{2} \rightarrow {}^{3}H_{4}$ were used to measure the FIR values in order to obtain the temperature sensing behavior. The S_a and S_r values of NaF flux assisted Pr^{3+} doped CTO phosphor were calculated. Moreover, the sole presence of ${}^1D_2 \rightarrow {}^3H_4$ red emission was explained by energy level diagram and thermal induced nonradiative relaxation process based on IVCT state was also discussed by the configurational coordinate diagram.

2. Experimental

2.1 Materials

Titanium dioxide (TiO₂) from Hunan Xiangzhong Fine Chemical Plant and calcium carbonate (CaCO₃) from Sinopharm Chemical Reagent Co., Ltd. were used as raw materials in this work. Sodium fluoride (NaF) from Shanghai Chemical Reagent Co., Ltd. was used as a flux and charge compensator. Absolute ethyl alcohol (C₂H₅OH) as a grinding agent was purchased from Hunan Huihong Chemical Reagent Co., Ltd. Praseodymium oxalate [Pr₂(C₂O₄)₃·10H₂O, 99.99%] as an activator was purchased from Yiyang Hongyuan Rear Earth Co., Ltd.

2.2 Preparation of samples

CaTiO₃: xPr^{3+} powder (CTO: xPr^{3+} , where the molar ratio of $Pr^{3+}/CaTiO_3 x = 0\%$, 0.45%, 0.6%, 0.75% and 0.9%) and CaTiO₃: 0.6% Pr^{3+} with different amounts of NaF flux (CTO: 0.6% $Pr^{3+}+yNaF$, where the molar ratio of NaF/CaTiO₃ y is 0%, 1.0%, 1.5%, 2.0%, 2.5%, 3.0% and 3.5%) were prepared by the conventional solid-state reaction method. For preparing CTO: xPr^{3+} , TiO₂ and CaCO₃ as raw materials,

 $Pr_2(C_2O_4)_3 \cdot 10H_2O$ as an activator were mixed thoroughly in the presence of absolute ethyl alcohol and grinded for 45min. And then the mixture was dried in the oven for 1h. After drying, the mixture was transferred to the resistance furnace. The temperature initially went up to 800 °C at 8 °C/min, and then rose to 1300 °C at 4 °C/min for 2h in air. For the preparation of CTO: 0.6% $Pr^{3+}+yNaF$, the total process was the same as the above.

2.3 Characterization

The X-ray diffraction (XRD) patterns were obtained from a PANalytical X'Pert PRO X-ray diffractometer with Cu K_a radiation (λ =0.15406 nm). The surface morphologies were characterized by a Hitachi-SU8010 field-emission scanning electron microscope (FE-SEM) operating at 10 kV. Ultraviolet–visible diffuse reflectance (UV–vis DR) spectra were recorded on a Shimadzu UV-2700 UV–vis Spectrophotometer. The photoluminescence excitation (PLE) and PL spectra were obtained from Hitachi F-7000 Fluorescence Spectrophotometer at room temperature. The 365 nm UV excitation light was switched off after 5min irradiation to the typical samples. The LAG emission spectrum was recorded by a Luminescence Meter System (Beijing Nuclear Instrument Factory). TL spectrum was also measured using the above Luminescence Meter System equipped with a temperature-controlled oven and a PC data acquisition system (FJ427A1). The temperature-dependent PL spectra were recorded on Hitachi F-4500 Fluorescence Spectrophotometer with a standard TAP-02 to control the temperature.

3. Results and discussion

3.1 XRD analysis



Fig. 1 (a) XRD patterns of CTO: xPr^{3+} (where x = 0%, 0.45%, 0.6%, 0.75% and 0.9%); (b) XRD patterns of CTO and CTO: 0.6% $Pr^{3+}+yNaF$ (where y = 0%, 2% and 3%); (c) Rietveld XRD refinement of CTO: 0.6% $Pr^{3+}+2\%NaF$ from the GSAS software; (d) Crystal structure of Pr^{3+} doped CTO.

The phase composition is identified from the XRD pattern. The curves of CTO: xPr^{3+} samples (where x = 0%, 0.45%, 0.6%, 0.75% and 0.9%) are arranged gradually from the bottom to the top, as shown in Fig. 1a. The detected diffraction peaks of all samples were consistent well with the orthorhombic perovskite in the *Pnma* (62) space group

(JCPDS#22-0153) without observing any impurity peak from the secondary phase. It indicated that all samples had pure single orthorhombic phase and the Pr^{3+} ions were successfully incorporated into the CTO host lattice. However, owing to the similar ionic radii in the twelve-coordinated state between the Pr^{3+} (1.30 Å) and Ca^{2+} ions(1.34 Å)[41], Pr^{3+} ions substituted for Ca^{2+} ions in CTO host lattice. As shown in Fig. 1a, the little position changes of the strongest peak (121) within the margin of error were attributed to the negligible effect of a small quantity of Pr^{3+} ions on the host crystal structure[42].

The XRD patterns of CTO and CTO: 0.6% $Pr^{3+}+yNaF$ (y=0 %, 2% and 3%) are shown in Fig.1b. The detected diffraction peaks of all samples were also consistent well with the orthorhombic perovskite in the *Pnma* (62) space group (JCPDS#22-0153) without observing any impurity peak from the secondary phase. It was worth noting that the position changes of the strongest peak (121) were also within the margin of error. Herein, Pr^{3+} ions (1.30 Å) preferentially occupied the sites of the Ca²⁺ ions (1.34 Å) in the CTO host crystals, due to the similar ionic radii. As the F⁻ ion (1.33 Å) was very similar with that of the O²⁻ ion (1.40 Å), the substitution of O²⁻ in the host lattice by F⁻ took place. Moreover, as the radii in the twelve-coordinated state of Na⁺ ion (1.39 Å) was also similar with that of Ca²⁺ ion (1.34Å)[32], Na⁺ ions occupied the sites of the Ca²⁺ ions. Although a small quantity of Na⁺ and F⁻ ions had negligible effect on the host structure[42], NaF flux improved the crystallinity due to the narrowing of the XRD line width, as shown in Fig.1b.

Table 1 reveals the mean crystallite sizes for the crystal plane (040) estimated by Scherrer Formula[43] as follows:

$$D_{hkl} = \frac{k\lambda}{\beta_{hkl}\cos\theta}$$
(1)

where D_{hkl} is the mean crystallite size, λ is the wavelength of X-ray radiation (Cu K_{α} radiation, $\lambda = 0.15406$ nm), k is the shape factor and usually taken as 0.896, β_{hkl} is the full width at half maximum (FWHM), after subtraction of equipment broadening, and θ is the Bragg angle. From Table 1, it was seen that the mean crystallite sizes were in the range of 47.6-73.1 nm. Moreover, for CTO:0.6%Pr³⁺+yNaF (y=0, 2%, 3%) the crystallinity of Pr³⁺ doped CTO was improved with the addition of NaF flux, as it promoted the growth and ripening of particles[37].

Samples	$2 heta_{(040)}/^{\circ}$	$\beta_{(040)}/^{\circ}$	D ₍₀₄₀₎ /nm
СТО	47.556	0.189	54.1
CTO:0.45%Pr ³⁺	47.567	0.171	62.4
CTO:0.6%Pr ³⁺	47.614	0.208	47.6
CTO:0.75%Pr ³⁺	47.564	0.184	56.4
CTO:0.9%Pr ³⁺	47.593	0.181	57.7
CTO:0.6%Pr ³⁺ +2.0%NaF	47.567	0.193	52.6
CTO:0.6%Pr ³⁺ +3.0%NaF	47.413	0.155	73.1

Table 1 Crystallite size of different samples for crystal plane (040)

With the help of the GSAS software, Rietveld XRD refinement is performed to verify the crystal structure and space group. Rietveld XRD refinement of $CTO:0.6\% Pr^{3+}+2\%$ NaF is shown in Fig. 1c. Herein, the observed and calculated diffraction patterns were

in accordance well with each other, which indicated that the typical sample had pure orthorhombic perovskite phase with the space group of *Pnma* (62). The R_{wp} , R_p and χ^2 was 8.62 %, 6.55% and 2.82, respectively (Table 2). Moreover, the pure CTO crystals had orthorhombic perovskite structure with unit-cell parameters of a = 5.3938 Å, b = 7.6326 Å, c =5.4227 Å, V= 223.25 Å³, Z =4, $\alpha = \beta = \gamma = 90^{\circ}$ and the CTO: 0.6% Pr³⁺+2% NaF had lattice parameters of a = 5.2950 Å, b = 7.6463 Å, c = 5.4642Å, V= 221.23 Å³, Z =4, $\alpha = \beta = \gamma = 90^{\circ}$, which were close to the data of standard card (JCPSD#22-0153) and the typical orthorhombic perovskite crystal structure of Pr³⁺ doped CTO is shown in Fig.1d. It was clearly seen that the orthorhombic perovskite structure made up of the tilted Ti-O octahedra with conterminal oxygen atoms, resulting in the lower symmetry around Pr³⁺, which could mix opposite-parity into 4f configurational levels, subsequently improving the red ¹D₂→³H₄ emission probabilities of Pr³⁺[12].

Parameters CTO:0.6%Pr ³⁺ +2%NaF		perovskite (JCPSD#22-0153)				
Phase structure	orthorhombic	orthorhombic				
Space group	<i>Pnma</i> (62)	<i>Pnma</i> (62)				
a (Å)	<mark>5.2950</mark>	<mark>5.3812</mark>				
b (Å)	<mark>7.6463</mark>	<mark>7.6436</mark>				
c (Å)	<mark>5.4642</mark>	<mark>5.4405</mark>				
V (Å ³)	221.23	223.78				
Z	4	4				
R_{wp}	8.62%	_				
R_p	6.55%	_				
χ^2	2.82	_				

Table 2 Refined lattice parameters of the typical sample

3.2 FE-SEM



Fig. 2 (a) and (b) FE-SEM images under different magnifications and (c) particle size distribution of the pure CTO; (d) and (e) FE-SEM images under different magnifications and (f) particle size distribution of the CTO: $0.6\% Pr^{3+} + 2\%$ NaF.

FE-SEM images under different magnifications and particle size distribution of the pure CTO are shown in Figs.2a-c. It was revealed that the pure CTO sample possessed spherical morphology with smooth surface. There existed a certain degree of aggregation and the mean particle size was about 802 nm based on Gauss fitting, as shown in Figs. 2a-c. Figs.2d-f indicate FE-SEM images under different magnifications and the particle size distribution of CTO: $0.6\% Pr^{3+}+2\% NaF$. It was worth noting that the CTO: $0.6\% Pr^{3+}+2\% NaF$ had mostly sphere-like morphology, but it also exhibited the quasi-cubic morphology and the mean particle size was about 670 nm based on Gauss 54.1 nm, while the crystallite size of the CTO: $0.6\% Pr^{3+}+2\% NaF$ was 52.6 nm. It was obviously noticeable that addition of NaF flux enhanced the crystallinity of Pr^{3+} doped

CTO phosphor particles, consistent with the result of XRD.

3.3 UV-vis DR spectra



Fig. 3 (a) UV-vis DR spectra and (b) plots of $[F(R_{\infty})hv]^2$ versus photon energy (hv) of the CTO: 0.6%Pr³⁺ and CTO: 0.6%Pr³⁺ +2%NaF

UV-vis DR spectra are used for investigating the optical properties of samples. Figs. 3a and b show UV-vis DR spectra and the plots of $[F(R_{\infty})hv]^2$ versus photon energy (hv) of the CTO: 0.6%Pr³⁺ and CTO: 0.6%Pr³⁺ + 2%NaF. As shown in Fig.3a, it was obviously noticeable that the two typical samples had the strong absorption band (marked as A) centered at ~277 nm and absorption band (marked as B) centered at ~330 nm, assigned to absorption bands of CTO host material. By comparing the spectra of the sample CTO and CTO: xPr^{3+} from Fig. S1, it was found that there existed the strong and broad absorptions at ~277nm and ~330 nm, indicating that bands A and B belonged to absorption bands of CTO host material. It was generally considered that the absorption band (marked as C) at ~365 nm originated from IVCT state between Pr^{3+} and Ti^{4+}

 $(Pr^{3+}-O-Ti^{4+}\rightarrow Pr^{4+}-O-Ti^{3+})$. Moreover, it was also observed that the band (marked as D) in the range of 450-500 nm was attributed to 4f-4f transitions of the Pr^{3+} ion. The peak at ~495 nm originated from ${}^{3}H_{4}\rightarrow {}^{3}P_{0}$ transition, the peak at ~476 nm was ascribed to ${}^{3}H_{4}\rightarrow {}^{3}P_{1}$ transition and the peak at ~455 nm was assigned to ${}^{3}H_{4}\rightarrow {}^{3}P_{2}$ transition. As shown in Fig.3b, plots of $[F(R_{\infty})hv]^{2}$ versus photon energy (hv) of the two typical samples are used to determine the direct optical bandgap values (E_{g}) by using Kubelka–Munk (K–M) and Tauc's functions[44] as follows:

$$R_{\infty} = \frac{R_{sample}}{R_{BaSO_4}}$$
(2a)

$$F(R_{\infty}) = \frac{\left(1 - R_{\infty}\right)^2}{2R_{\infty}} = \frac{K}{S}$$
(2b)

$$\left[F(R_{\infty})hv\right]^2 = A(hv - E_g)$$
(2c)

where R_{∞} is the ratio of the light scattered from the sample and an ideal non-absorbing reference sample (BaSO₄); $F(R_{\infty})$ is the K–M function; S is the scattering coefficient; K is the absorption coefficient; hv is the photon energy and E_g is the bandgap energy. The values of E_g for the CTO: 0.6% Pr³⁺ and CTO: 0.6% Pr³⁺+2% NaF were ~3.63 and 3.62 eV, respectively. To obtain the bandgap values of other samples, UV-vis DR spectra and plots of $[F(R_{\infty})hv]^2$ versus hv are shown in Fig.S1, S2 and S3. It was worth noting that the estimated bandgap values of all samples were ~3.63 or 3.62 eV and there was almost no considerable change in the optical bandgap values of

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all samples. Considering that the bandgap energies were related with crystallite and particle sizes, morphologies and crystallinities of samples, it could be concluded that neither morphologies nor crystallinities nor crystallite and particle sizes alone could account for the approximate invariance of bandgap energies, while it could be attributed to a combination of several effects.

3.4 PLE and PL analysis

PLE spectra detected at 614 nm of CTO: xPr^{3+} (where x = 0.45%, 0.6%, 0.75% and 0.9%) are shown in Fig.4a. It could be observed that there were several typical peaks in the range of 200–530 nm. It was worth noting that the intensities of PLE increased firstly and then decreased with the increasement of Pr^{3+} concentration. The broad absorption bands in the range of 200-350 nm would be related to the absorption of CTO host material, combined with the results of UV-vis DR spectra. The band (marked as A) centered at ~277 nm and the band (marked as B) centered at ~332 nm could be attributed to $O(2p) \rightarrow Ti(3d)$ charge transfer. As mentioned above, the environment of Ti^{4+} was octahedral and the 3d orbital was split into two different energy levels (eg and t_{2g}) in the TiO_6 octahedral crystal field. Thus, the band A was assigned to $O(2p) \rightarrow Ti(3d)_{eg}$ and the band B was attributed to $O(2p) \rightarrow Ti(3d)_{t2g}$ [45]. The higher the intensities of bands A and B, the higher ET efficiency from the CTO host material to Pr^{3+} . The band (marked as C) centered at ~365 nm was ascribed to IVCT state between



Fig.4 (a) PLE spectra detected at 614 nm; (b) PL spectra excited by band B; (c) PL intensity comparison of the CTO: xPr^{3+} (where x = 0.45%, 0.6%, 0.75% and 0.9%) excited by band B; (d) Linear fitting of log(I/x) vs log(x) in the CTO: xPr^{3+} beyond the concentration quenching (x > 0.6%)

 Pr^{3+} and Ti^{4+} (Pr^{3+} -O- Ti^{4+} → Pr^{4+} -O- Ti^{3+})[17]. Moreover, a low-energy weak tail in range of ~380-420 nm might be related to low-lying 4f5d of Pr^{3+} [45]. The weak peaks in the range of 450-500 nm (marked as D) were attributed to 4f-4f transitions of Pr^{3+} ions. When emission intensity of band D was enlarged by 50 times (inset of Fig.4a), it was observed that the peak at ~495 nm was attributed to ${}^{3}H_{4}$ → ${}^{3}P_{0}$ transition, the peak at ~476 nm was ascribed to ${}^{3}H_{4}\rightarrow {}^{3}P_{1}$ transition and the peak at ~455 nm was assigned to ${}^{3}H_{4}\rightarrow {}^{3}P_{2}$ transition. PL spectra of CTO: xPr^{3+} (where x = 0.45%, 0.6%, 0.75% and 0.9%) excited by band B are shown in Fig.4b. There existed a single sharp peak centered at ~614 nm, which was contributed to ${}^{1}D_{2}\rightarrow {}^{3}H_{4}$ transition. However, the emission from ${}^{3}P_{j}$ (j=0, 1, 2) to ${}^{3}H_{4}$ transitions was hardly observed, which would be well discussed later. It was noted that the emission intensity at ~614 nm increased initially and then decreased with the increase of the Pr^{3+} concentration. From Fig.4c, it was observed that when the Pr^{3+} concentration was 0.6%, the emission intensity was strongest. The concentration quenching effect occurred due to the decrease of $Pr^{3+}-Pr^{3+}$ distance in the CTO host when the Pr^{3+} concentration was more than 0.6%. Hence, the critical distance (R_{c}) between Pr^{3+} ions for concentration quenching can be calculated by using the following Eq.(3)[46]:

$$R_{\rm c} \approx 2 \left[\frac{3V}{4\pi x_c Z} \right]^{\frac{1}{3}}$$
(3)

where V is the volume of the unit cell, x_c is the critical concentration of Pr^{3+} ions, and Z is the number of formula units per unit cell. As mentioned above, for pure CTO host, V = 223.25 Å³, Z = 4, and for Pr^{3+} doped CTO phosphors, the x_c is 0.6%. The calculated R_c of $Pr^{3+}-Pr^{3+}$ in CTO host is ~26.09Å.

As known, the nonradiated ET includes radiation reabsorption, exchange interaction, and electric multipolar interactions. Only when the excitation and emission spectra widely overlap, can the radiation reabsorption occur[47]. In our work, it was obviously noticeable that the radiation reabsorption could be ruled out. Moreover, the R_c for exchange interaction was less than 5 Å, while the calculated R_c (~26.09Å) mentioned above exceeded far the value. Thus, the exchange interaction was also almost impossible, whereas the electric multipolar interaction was most possible for the ET mechanism between Pr^{3+} ions in the CTO host.

To obtain the concrete electric multipolar interaction type among Pr^{3+} ions for concentration quenching, linear fitting of log(I/x) versus log(x) in the CTO: xPr^{3+} beyond the concentration quenching (x > 0.6%) is shown in Fig. 4d . The electric multipolar types among Pr^{3+} ions can be evaluated by the following Eq. (4)[48, 49]:

$$\frac{I}{x} = \left[1 + \beta(x)^{\theta/3}\right]^{-1} \tag{4}$$

where *I* is the emission intensity, *x* is the Pr^{3+} ion concentration (x > 0.6%), β is a constant and θ is the electric multipolar character. The θ value can be 6, 8 and 10, attributed to electric dipole–dipole (d-d), dipole–quadrupole (d-q), or quadrupole– quadrupole (q-q) interactions[48], respectively. A slope equal to $-1.6185 = -\theta/3$ by linear fitting of log(I/x) versus log(x) in the CTO: xPr^{3+} beyond the concentration quenching (x > 0.6%) could be obtained and the θ value was 4.8555, approximately close to 6. Therefore, it was mostly suitable that the d-d interaction accounts for concentration quenching.

As known, NaF flux assisted method has been considered as an effective way to enhance the PL property[37]. Fig.5a shows PLE spectra of CTO: 0.6%Pr³⁺+yNaF (where y is 0%, 1.0%, 1.5%, 2.0%, 2.5%, 3.0% and 3.5%) detected at 614 nm. The band A in the range of 270-280 nm was attributed to $O(2p) \rightarrow Ti(3d)_{eg}$. The band B in the range of 315-335 nm was identified as $O(2p) \rightarrow Ti(3d)_{t2g}$ and the band C was at ~365 nm, ascribed to IVCT state. The low-energy weak tail at ~390 nm might be related to low-lying 4f5d of Pr³⁺. According to the PLE spectra, we can construct the energy level scheme of Pr³⁺ doped CTO material, as shown in Fig. 5b. As mentioned above, the CTO: 0.6% Pr³⁺+2% NaF had the strongest intensity in PLE spectra, which could be explained by the energy level diagram. It was observed that there were three important excitation processes. The first (1st) was that the electron was directly excited up to Ti(3d)_{eg} state by ~275 nm UV light, and could relax to IVCT state, and then to ${}^{1}D_{2}$ level, finally generated red ${}^{1}D_{2} \rightarrow {}^{3}H_{4}$ emission. The second (2nd) was that the electron was excited to $Ti(3d)_{t2g}$ state by ~330 nm UV light and relaxed to IVCT state as $Pr^{3+}-O-Ti^{4+}\rightarrow Pr^{4+}-O-Ti^{3+}$, then to ${}^{1}D_{2}$ level directly and finally gave up red ${}^{1}D_{2}\rightarrow {}^{3}H_{4}$ emission. The third (3rd) was that the electron was excited from ${}^{3}H_{4}$ ground state of Pr^{3+} to the bottom of CB as $Pr^{3+}-O-Ti^{4+}\rightarrow Pr^{4+}-O-Ti^{3+}$ (IVCT state) by ~365 nm UV light, and then relaxed to ${}^{1}D_{2}$ level directly and finally generated red ${}^{1}D_{2} \rightarrow {}^{3}H_{4}$ emission. It was worth noting that in the three cases, the ${}^{3}P_{1} \rightarrow {}^{3}H_{4}$ or ${}^{3}P_{1} \rightarrow {}^{3}H_{6}$ emission could rarely be observed owing to the depressed relaxation to ${}^{3}P_{1}$ based on the IVCT state, which could account for the observation of a single red ${}^{1}D_{2} \rightarrow {}^{3}H_{4}$ emission. It could be clearly



Fig.5 (a) PLE spectra detected at 614 nm; (b) energy level diagram of Pr^{3+} doped CTO material; (c) Main excitation wavelength changes; (d) $I_{band B}/I_{band A}$ ratio; (e) PL spectra and intensity comparison(inset) excited by band A; (f) PL spectra and the intensity comparison (inset) of CTO: 0.6% Pr^{3+} +yNaF (where y is 0%, 1.0%, 1.5%, 2.0%, 2.5%, 3.0% and 3.5%) excited by band B

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seen that the excitation intensity increased many-fold by adding a certain amount of NaF flux. The improved intensity was understood to be associated with the enhanced ET efficiency from the CTO host material to Pr^{3+} ions. Thus, it could be concluded that NaF flux plays an important role in controlling favorable recombination kinetics of charge carriers accounting for the emission process. The main excitation wavelength changes from bands A and B are observed from Fig.5c. It was worth noting that the excitation peaks from band B had a slight blue-shift (332-319 nm) with increasement of NaF concentration. The corresponding excitation energy was about 3.73-3.89ev, slightly larger than optical bandgap values (3.62 or 3.63 eV) from UV-vis DR spectra, which was almost within the experimental error. The excitation peaks (273-279 nm) from band A did not change significantly with increasement of NaF concentration, attributed to the negligible effect of a small quantity of Na⁺ and F⁻ ions on the host structure[42].

Fig. 5d exhibits the ratio of PLE intensity from band B and that from band A ($I_{band B}$ / $I_{band A}$) of the CTO: 0.6%Pr³⁺+yNaF. As for CTO: 0.6%Pr³⁺, the contribution to PL intensity excited by band B was predominate, but for CTO: 0.6%Pr³⁺+yNaF, the contribution to PL intensity was almost completely dominated by band A. However, when the NaF concentration is 2%, the $I_{band B}/I_{band A}$ ratio was 1.01, which revealed that the contribution to PL intensity from band B was almost on a par with that from band A. Fig.5e reveals the PL spectra and intensity comparison(inset) of CTO: 0.6%Pr³⁺+yNaF excited by band A. When NaF concentration was 2%, the PL intensity reached the maximum value (~3.14 times that of CTO: 0.6%Pr³⁺). Fig. 5f shows the PL spectra and

the intensity comparison (inset) of CTO: $0.6\% Pr^{3+}+yNaF$ excited by band B. When NaF concentration was 2%, the PL intensity has the maximum value (~2.14 time that of CTO: $0.6\% Pr^{3+}$). As mentioned above, the enhanced PL property was attributed to the improved crystallinity of Pr^{3+} doped CTO with the addition of NaF flux. However, it was observed that when the NaF concentration was more than 2%, the PL intensity decreased. It indicated that excess NaF flux could quench PL intensity. As known, Pr ions could have two valences (+3 and +4) in host materials. Generally, Pr^{3+} occupied site of Ca^{2+} , forming the Pr_{Ca}^{-*} as Eq. (5a), while Pr^{4+} substituted for Ti⁴⁺ to form the Pr_{Ti}^{\times} as Eq. (5b). When the CTO host material was at 1300 °C, it was common that the concentrations of Schottky defects ($V_{Ca}^{-''}$ and V_{O}^{-*}) were relatively higher[17]. The intrinsic Schottky defects were formed as Eq. (5c). Simultaneously, Pr^{4+} immigrated to calcium site from titanium site as Eq. (5d) and changed into Pr^{3+} . This process could be taken for a decomposition of PrO_2 to Pr_2O_3 and the $V_{Ti}^{-'''}$ and V_{O}^{-*} could annihilate as Eq. (5e).

$$Pr_2O_3 \rightarrow 2Pr_{Ca} + V_{Ca}'' + 3O_0^{\times}$$
(5a)

$$PrO_2 \to Pr_{Ti}^{\times} + 2O_0^{\times}$$
(5b)

$$null \to V_{Ca}'' + V_O'' \tag{5c}$$

$$2Pr_{\mathrm{Ti}}^{\times} + 2V_{Ca}^{"} + O_{\mathrm{O}}^{\times} \rightarrow 2Pr_{Ca}^{\times} + 2V_{Ti}^{""} + V_{O}^{\times} + 1/2O_{2}(g) \uparrow$$
(5d)

$$V_{Ti}^{m} + 2V_{o}^{\bullet} \rightarrow null \tag{5e}$$

$$NaF \to Na_{Ca}' + F_O' \tag{5f}$$

 $F^- \to F_o \cdot + V_{Ca}^{\ "} \tag{5g}$

However, some undesirable defects such as V_{Ca}'' , V_{O} and Ti_{Ti} were close to Pr^{3+} , contributing to the quenching of Pr³⁺ emission. Generally, the suitable Pr³⁺ doping concentration was quite lower, so the possibility of undesirable defects meeting Pr³⁺ was not favorable[12]. On the one hand, NaF flux could improve the crystallinity of phosphors, resulting in higher oscillating strengths for optical transitions and enhanced PL emission. On the other hand, as the radii were similar to each other, Na⁺ ion substituted for Ca^{2+} and F⁻ ion replaced O²⁻ as Eq. (5f). Thus, the elimination of the concentrations of V_{Ca} and V_o near Pr^{3+} contribute to improvement of PL intensity. There was, of course, another explanation for enhanced PL intensity. When Na_{Ca}' compensated Pr_{Ca} , the additional F⁻ could occupy site of O²⁻, forming F_o and V_{Ca} as Eq. (5g). This kind of V_{Ca} was in favor of reducing Pr^{4+} into Pr^{3+} as Eq. (5d), beneficial for improving the PL intensity[50]. Moreover, this kind of V_{Ca} could cause the disorder host structure, originating the lower symmetry at Pr^{3+} sites, which could mix opposite-parity into 4f configurational levels, subsequently improving the red emission $({}^{1}D_{2} \rightarrow {}^{3}H_{4})$ probabilities of $Pr^{3+}[12]$. However, the defects formed by excess NaF flux also acted as non-radiative recombination centers and quenched PL intensity. In conclusion, a certain amount of NaF could improve the ET efficiency from the CTO host material to Pr³⁺. Thus, the NaF flux assisted CTO: Pr³⁺ red emitting phosphor could be suggested as a promising material in red region for FED application as the next-generation FPD.



3.5 Afterglow decay and TL spectra

Fig.6 (a)The afterglow decay and fitting curves; (b) TL glow and fitting curves of

CTO:0.6%Pr³⁺+2%NaF after irradiation of 365 nm UV light for 5 min at room temperature

The afterglow decay curve of CTO: $0.6\% Pr^{3+}+2\% NaF$ was recorded after irradiation of 365 nm UV light for 5 min at room temperature, as shown in Fig.6a. The afterglow decay curve is fitted well by the bi-exponential Eq. (6a) as follows:

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(\frac{t}{\tau_2}\right)$$
(6a)

$$\tau_{avg} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$
(6b)

where t is the time, I(t) is the afterglow emission intensity at time t, A_1 and A_2 are constants, τ_1 and τ_2 are the decay time for the exponential components, respectively. The average afterglow decay time (τ_{avg}) for the bi-exponential function can be expressed as in Eq. (6b). The τ_1 , τ_2 and τ_{avg} were 8.6 s, 55.7s and 44.8 s for CTO: 0.6%Pr³⁺+2%NaF, respectively. It was well known that the LAG in Pr³⁺ doped CTO is associated with V_o " as the electron capture center. As shown in Fig. 5b, the energy level of the V_o " was usually below the IVCT state. After some time, the captured electron could be excited to IVCT state and relax to ¹D₂. Thus, afterglow intensity and time could be determined by the concentration and depth of the energy storage trap V_o ". The τ_{avg} for CTO: 0.6%Pr³⁺+2%NaF was 44.8s, which was significantly better than the result of similar perovskite material reported by Ryu[42].

To investigate the distribution of energy storage traps in CTO: $0.6\% Pr^{3+}+2\% NaF$, TL curve was measured from room temperature to 200 °C, after irradiation of 365 nm UV light for 5 min at room temperature, as shown in Fig. 6b. It was revealed that there was a wide TL peak, which was fitted well by Gaussian function. It could be attributed to the energy storage trap V_o . The depth of energy trap is estimated using the Eq. (7) as follows:

$$E = 3.5 \left(\frac{kT_m^2}{\omega}\right) - 2kT_m \tag{7}$$

where *E* is the average depth of traps, T_m is the peak temperature, ω is the FWHM of the peak, and *k* is the Boltzmann constant (8.61733×10⁻⁵ eV·K⁻¹). By Gaussian fitting curve, T_m was 334.15K (61 °C), ω was 76 K. Thus, the average depth of trap

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E was 0.39 eV, which was close to the result (0.41eV) reported in the literature[51]. Only could the traps with appropriate depths be expected to promote the LAG emission. It was indicated that the irradiation in the IVCT state (~365nm) could promote the electron transfer from Pr^{3+} to Ti⁴⁺ forming IVCT state and the V_o " near IVCT state played the key role for trapping electrons, accounting for the LAG emission. Therefore, this red LAG phosphor could be considered as a promising material for potential applications in medical imaging, warning signs and soft illumination.





Fig.7(a) The CIE chromaticity diagram and magnified CIE coordinates (inset) of CTO: $0.6\% Pr^{3+}$ excited by band A (upper)and band B (lower); (b) The CIE chromaticity diagram and magnified CIE coordinates (inset) of CTO: $0.6\% Pr^{3+}+2\%$ NaF excited by band A (upper)and band B (lower)

The Commission Internationale De I'eclairage (CIE) and magnified CIE chromaticity

coordinates (inset) of CTO: $0.6\% Pr^{3+}$ and CTO: $0.6\% Pr^{3+}+2\%$ NaF excited by bands A (upper) and B (lower) are illustrated in Figs. 7a and b. The coordinate (x, y) of CTO: $0.6\% Pr^{3+}$ based on band A was calculated to be (0.658, 0.3414) and the coordinate (x, y) of CTO: $0.6\% Pr^{3+}$ based on band B was (0.6659, 0.3338). The coordinate (x, y) of CTO: $0.6\% Pr^{3+}+2\%$ NaF based on band A was (0.6599, 0.3396) and the coordinate (x, y) of CTO: $0.6\% Pr^{3+}+2\%$ NaF based on band B was (0.6657, 0.334). The coordinate (x, y) of CTO: $0.6\% Pr^{3+}+2\%$ NaF based on band B was (0.6657, 0.334). The coordinate (x, y) of CTO: $0.6\% Pr^{3+}+2\%$ NaF based on band B was (0.6657, 0.334). The coordinate (x, y) of CTO: $0.6\% Pr^{3+}+2\%$ NaF based on band B was (0.6657, 0.334). The coordinate (0.6659, 0.3338) and (0.6657, 0.334) were very close to that of the ideal red light (0.67, 0.33)[52].

To obtain the quality of the red emission, the color purity (CP) of the typical samples can be calculated as Eq.(8)[53].

$$CP = \frac{\sqrt{(x - x_i)^2 + (y - y_i)^2}}{\sqrt{(x_d - x_i)^2 + (y_d - y_i)^2}} \times 100\%$$
(8)

where (x, y) is the color coordinate of the typical sample, (x_i, y_i) is the CIE coordinate of the white illumination and (x_d, y_d) is the CIE coordinate of the dominant wavelength. The CP of CTO: 0.6%Pr³⁺+2%NaF based on band B reached up to 99.98%. The CTO: 0.6%Pr³⁺+2%NaF had a strong PL emission with good color coordinate and high CP, which was a promising candidate for application in FED area.

3.7 Temperature sensitivity analysis



Fig.8(a) The temperature-dependent PL spectra excited by band B in the range of 298–523 K of CTO:0.6%Pr³⁺+2%NaF in 25-K increments; (b) the relative intensity measured at different temperatures; (c) the linear fitting of $\ln(I_0/I-1)$ vs 1/kT; (d) *FIR* values based on non-thermal coupling levels of ${}^{3}P_{1} \rightarrow {}^{3}H_{6} / {}^{1}D_{2} \rightarrow {}^{3}H_{4}$ as a function of temperature; (e) absolute sensitivity (*S_a*) as a function of temperature; (f) relatively sensitivity (*S_r*) as a function of temperature in the range of 298–523 K

The temperature-dependent PL spectra excited by band B in the range of 298–523 K of CTO: 0.6% Pr³⁺+2% NaF in 25-K increments were measured, as shown in Fig.8a. It was observed that a dominant red peak centered at ~614 nm was attributed to ${}^{1}D_{2} \rightarrow {}^{3}H_{4}$. With the increase of temperature, the relative intensity ratio of PL intensity at different temperatures to PL intensity at 298 K decreased gradually, ascribed to the thermal quenching effect, as shown in Fig. 8b. However, a weak peak at 560 nm attributed to ${}^{3}P_{1} \rightarrow {}^{3}H_{6}$ and another weak and broad peak in the range of 700-730 nm originating from ${}^{3}P_{1} \rightarrow {}^{3}F_{4}$ and ${}^{3}P_{0} \rightarrow {}^{3}F_{4}$ were hardly observed. The mechanism of the red emission was explained by the configurational coordinate diagram, as shown in Fig. 9a. When electron was excited to CB by UV light initially, and then populated at the IVCT state via the nonradiative process, and relaxed to the ${}^{3}P_{i}(j=0, 1, 2)$ or to ${}^{1}D^{2}$ levels. Due to the strong coupling of the IVCT state with ${}^{1}D_{2}$ level, the relaxation to ${}^{3}P_{i}$ (j=0, 1, 2) was depressed and the relaxation to ${}^{1}D_{2}$ level was dominated. Therefore, the ${}^{3}P_{1} \rightarrow {}^{3}H_{6}$, ${}^{3}P_{1} \rightarrow {}^{3}F_{4}$ or ${}^{3}P_{0} \rightarrow {}^{3}F_{4}$ transitions were hardly monitored and only a single red emission attributed to ${}^{1}D_{2} \rightarrow {}^{3}H_{4}$ transition was observed. It could be concluded that the IVCT state played an important role on the nonradiative relaxation processes. Moreover, to understand thermal quenching of CTO: 0.6%Pr³⁺+2%NaF, the value of activation energy (E_a) was an important parameter. The value of E_a can be evaluated by the linear fitting of $\ln(I_0/I-1)$ versus 1/kT for CTO: 0.6% Pr³⁺+2% NaF according to Eq.(9)[49], as shown in Fig.8c.

$$\ln\left(\frac{I_0}{I}\right) = \ln A - \frac{E_a}{kT} \tag{9}$$

Herein, I_0 is the initial PL intensity at 298 K, I represents the PL intensity at different temperatures. A is a constant, E_a is the activation energy from the bottom of ${}^{1}D_{2}$ level to the cross-over of the IVCT state with ground state ${}^{3}H_{4}$ level and the Boltzmann constant k is $8.61733 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1}$. According to the linear fitting of $\ln(I_0/I-1)$ versus 1/kT, the slope was equal to $-(0.575\pm0.011) = -E_a$. Thus, E_a was approximately determined to be 0.575±0.011eV (4637-4726 cm⁻¹), which was slightly less than the value (~0.7 eV, 5400-5500 cm⁻¹) of Pr³⁺ doped CTO powder reported by Inaguma et al.[54], and slightly larger than that of CTO: Pr^{3+} (~0.5 eV, 4000 cm⁻¹) reported by Boutinaud et al.[55]. Moreover, the multi-phonon relaxation also contributed to the rate (W_{NR}) of ${}^{3}P_{j} \rightarrow {}^{1}D_{2}$ non-radiative de-excitation. The maximum phonon energy $h\omega_{max}$ in CTO was at about 639 cm⁻¹[56]. Then, six phonons were required to bridge the energy gap $\Delta E' \approx 3700 \text{ cm}^{-1} \text{ of } {}^{3}\text{P}_{j} \text{ and } {}^{1}\text{D}_{2} \text{ levels. The rate } W_{NR}$ of ${}^{3}P_{i} \rightarrow {}^{1}D_{2}$ multi-phonon relaxation can be estimated by the modified exponential energy-gap Eq. (10) under 300 K[55]:

$$W_{NR} = \beta_{\rm e1} \exp\left[-\alpha \left(\Delta E' - 2h\,\omega_{\rm max}\right)\right] \tag{10}$$

with $\beta_{e_1} = 10^7 \text{ s}^{-1}$ and $\alpha = 4.5(\pm 1) \times 10^{-3} \text{ cm}$. So, the rate W_{NR} of ${}^{3}P_0 \rightarrow {}^{1}D_2$ non-radiative de-excitation could be estimated to be ~185 s⁻¹ below 300 K. The rate W_{NR} of ${}^{3}P_{j} \rightarrow {}^{1}D_2$ multi-phonon relaxation over 300 K can be estimated according to Eq. (11)[55] as follows:

$$W_{NR}(T) = W_{NR}(0) \left[1 + \left(\exp\left(\frac{h \omega_{max}}{kT}\right) \right)^{-1} \right]^{p}$$
(11)

where *p* is phonon number. The rate W_{NR} of ${}^{3}P_{j} \rightarrow {}^{1}D_{2}$ multi-phonon relaxation at 523 K could be calculated to be 480 s⁻¹. The rate W_{NR} was too small to account for the thermal quenching. *FIR* values of ${}^{3}P_{1} \rightarrow {}^{3}H_{6} / {}^{1}D_{2} \rightarrow {}^{3}H_{4}$ were mainly dependent on the temperature due to the thermal-induced relaxation and quenching through the IVCT state. The *FIR* values of I_{560}/I_{614} can be expressed by the following Eq. (12) as follows:

$$FIR = \frac{I_{560}}{I_{614}} = C \exp\left(\frac{-\Delta E}{kT}\right)$$
(12)

where *C* is a constant, ΔE is the effective energy gap from ${}^{3}P_{j}$ to ${}^{1}D_{2}$ level $(\Delta E = E_{2} - E_{1}, E_{1})$ is the energy barrier from the bottom of ${}^{3}P_{j}$ level to the cross-over of ${}^{3}P_{j}$ level with IVCT state and E_{2} is the energy barrier from the bottom of ${}^{1}D_{2}$ level to the cross-over of ${}^{1}D_{2}$ level with IVCT state), and the Boltzmann constant *k* is $8.61733 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1}$. From Fig.8d, through a nonlinear fitting of the experimental data, $\Delta E / k$ could be obtained and was equal to ~4624.4, with a deviation of ± 228.7 . Therefore, ΔE is ~0.398 eV (~3214 cm⁻¹). However, the important parameters for temperature measurement are the absolute and relative sensitivity (*S_a* and *S_r*), which can be expressed by the Eqs. (13a) and (13b).

$$S_a = \frac{d(FIR)}{dT} = C \exp\left(\frac{-\Delta E}{kT}\right) \frac{\Delta E}{kT^2} = FIR \frac{\Delta E}{kT^2}$$
(13a)

$$S_r = \frac{1}{FIR} \frac{d(FIR)}{dT} = \frac{\Delta E}{kT^2} \times 100\%$$
(13b)

The S_a as a function of temperature is illustrated in Fig.8e. The maximum value of S_a at 523 K could be obtained and was equal to ~0.015 K⁻¹. Moreover, we could obtain the ultrahigh S_r of 4624.4/ T^2 , which was 6 times higher than that of the sensors based on the TCLs (³P₀ and ³P₁) of Pr³⁺ doped materials and the maximum value of S_r at 298 K is ~5.2% K⁻¹, as shown in Fig. 8f. The reported optical sensors based on *FIR* of Pr³⁺ doped materials are listed in Table 3. The ultrahigh S_r of 4624.4/ T^2 had been very remarkable, in spite of less than the value of 7997/ T^2 reported by Tang et al.[20] and the value of 4964.8/ T^2 reported by Gao et al.[21]. Moreover, it was worth noting that the S_r value was mainly dependent on the effective energy gap ΔE or energy barrier E_2 , i.e., the energetic position of the IVCT state.

To better understand thermal induced relaxation process between ${}^{3}P_{j}$ level and ${}^{1}D_{2}$ level through the IVCT state of CTO: 0.6% Pr³⁺+2% NaF, the configurational coordinate diagram is applied, as shown in Fig. 9b. As discussed above, the S_{r} value was mainly dependent on the effective energy gap ΔE or energy barrier E_{2} . If the energy barrier E_{2} was too small, the thermal quenching became serious due to facilitation of electron transition from the ${}^{1}D_{2}$ level to the IVCT state. If the energy barrier E_{2} was overlarge,

Host materials	FIR	$S_r(\mathbf{K}^{-1})$	Temperature (K)	References
СТО	${}^{3}P_{1} \rightarrow {}^{3}H_{6} / {}^{1}D_{2} \rightarrow {}^{3}H_{4}$	$4624.4/T^2$	298-523	This work
(K _{0.5} Na _{0.5})NbO ₃	$^{1}\text{D}_{2} \rightarrow {}^{3}\text{H}_{4} / {}^{3}\text{P}_{0} \rightarrow {}^{3}\text{H}_{4}$	7997/ <i>T</i> ²	293-456	[20]
β -NaYF ₄	${}^{3}P_{1} \rightarrow {}^{3}H_{5} / {}^{3}P_{0} \rightarrow {}^{3}H_{5}$	$657.7/T^2$	120-300	[27]
BaSrTiO ₃	$^{1}\text{D}_{2} \rightarrow {}^{3}\text{H}_{4} / {}^{3}\text{P}_{0} \rightarrow {}^{3}\text{H}_{4}$	$4275.1/T^2$	290-513	[4]
BaSrTiO ₃	${}^{3}P_{1} \rightarrow {}^{3}H_{5} / {}^{3}P_{0} \rightarrow {}^{3}H_{5}$	$745.2/T^2$	290-403	[4]
NaGd(MoO ₄) ₂	$^{1}\text{D}_{2} \rightarrow ^{3}\text{H}_{4} / ^{5}\text{D}_{4} \rightarrow ^{7}\text{F}_{5}$	3735.4/T ²	303-483	[31]
LuNbO ₄	$^{1}\text{D}_{2} \rightarrow ^{3}\text{H}_{4} / ^{5}\text{D}_{4} \rightarrow ^{7}\text{F}_{5}$	3724/T ²	283-493	[23]
Y ₂ Ti ₂ O ₇	$TE/^{1}D_{2} \rightarrow {}^{3}H_{4}$	4385.9/T ²	289-573	[26]
$Na_{2}La_{1.96}Pr_{0.04}Ti_{3}O_{10}$	$^{1}\text{D}_{2} \rightarrow {}^{3}\text{H}_{4} / {}^{3}\text{P}_{0} \rightarrow {}^{3}\text{H}_{4}$	$4964.8/T^2$	303-543	[21]
(K _{0.5} Na _{0.5})NbO ₃ +CTO	${}^{3}P_{1} \rightarrow {}^{3}H_{5} / {}^{1}D_{2} \rightarrow {}^{3}H_{4}$	$1617.1/T^2$	300-473	[32]

Table 3 Summarized temperature sensing properties of Pr³⁺ doped phosphors



Fig. 9 The configurational coordinate diagram showing luminescence mechanism of ${}^{1}D_{2} \rightarrow {}^{3}H_{4}$ red emission (a) and thermal induced nonradiative relaxation processes (b)

the electron transition from the ${}^{1}D_{2}$ level to the IVCT state was about to be confined, which made temperature-dependent characteristic poor. In the two cases above, they were negative to the temperature sensing. Therefore, energy barrier E_{2} was supposed to a suitable value for application to thermometry properties. Moreover, the *FIR* technique based on ${}^{3}P_{1} \rightarrow {}^{3}H_{6}/{}^{1}D_{2} \rightarrow {}^{3}H_{4}$ in our case may have provided a fresh and favorable route for optical thermometry.

4. Conclusions

The Pr^{3+} doped CTO red emitting phosphor with enhanced PL and ultrahigh temperature sensing was prepared via NaF flux assisted solid-state reaction. All samples had the orthorhombic perovskite phase in the *Pnma* (62) space group and no impurity was found. The typical sample (CTO: $0.6\%Pr^{3+}+2\%NaF$) mainly possessed sphere-like morphology with particle size of ~670 nm. The optical bandgap values of all samples were ~3.62-3.63 eV. When the Pr^{3+} concentration was 0.6 mol%, the quenching occurred. The critical distance was ~26.09Å and the ET mechanism for concentration quenching was the d-d interaction. A certain amount of NaF flux could enhance the PL intensity due to improving the crystallinity of phosphors and reducing point defects through substitutions of O²⁻ by F and Ca²⁺ by Na⁺. The energy storage trap V_o ^{**} near IVCT state played the key role for trapping electrons, accounting for the LAG emission. The average depth of trap *E* was 0.39 eV. The CIE chromaticity coordinates were very close to that of the ideal red light and the CP was as high as 99.98%. From the temperature-dependent PL spectra, the E_a was ~0.575 eV (~4637 cm⁻¹) and ΔE was ~0.398 eV (~3214 cm⁻¹). The typical sample with the maximal S_a and S_r being as high as ~0.015 K⁻¹ and~ 5.2% K⁻¹ would to be a promising inorganic optical temperature sensing material. The configurational coordinate diagram revealed that the thermal induced relaxation between the ${}^{3}P_{j}$ levels and ${}^{1}D_{2}$ level through the IVCT state was supposed to account for the excellent optical temperature sensing.

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