Research article

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A new generation of dual-mode optical thermometry based on $\text{ZrO}_2\text{:Eu}^{3+}$ nanocrystals

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Abstract: For achieving well-performing optical thermometry, a new type of dual-mode optical thermometer is explored based on the valley-to-peak ratio (VPR) and fluorescence lifetime of Eu^{3+} emissions in the $\text{ZrO}_2\text{:Eu}^{3+}$ nanocrystals with sizes down to 10 nm. In the VPR strategy, the intensity ratio between the valley (600 nm) generated by the emission band overlap and the 606 nm peak ($^5\text{D}_0 \rightarrow ^7\text{F}_2$), which is highly temperature sensitive, is employed, giving the maximum relative sensing sensitivity (S_r) of $1.8\% \text{ K}^{-1}$ at 293 K and good anti-interference performance. Meanwhile, the 606 nm emission exhibits a temperature-dependent decay lifetime with the highest S_r of $0.33\% \text{ K}^{-1}$ at 573 K, which is due to the promoted nonradiative relaxation with temperature. These results provide useful information for constructing high-performance dual-mode optical thermometers, which may further stimulate the development of photosensitive nanomaterials for frontier applications.

Keywords: temperature sensing; valley-to-peak ratio; decay lifetime; nanocrystals; rare earth ion.

1 Introduction

Accurate temperature determination is required in many scientific and engineering areas. The traditional contact thermometers have limitations in several situations, such as the nano- or submicrometer regimes,

fast-moving objects, inside cells and corrosive environments, etc. [1–3]. In contrast, optical thermometers based on luminescent nanocrystals doped with rare earth (RE) ions have the unique advantages of contactless operation, rapid response, and high spatial resolution, which are useful wherever contact measurement is not feasible [4–8]. There are various optical parameters adopted as thermometric indices, including fluorescence intensity, emission bandwidth, fluorescence lifetime, spectral shift, and fluorescence intensity ratio (FIR). Currently, the FIR- and lifetime-based techniques have attracted most attention.

Generally, the FIR technique is based on the intensity ratio of two emission bands from thermally coupled levels (TCLs) of an RE ion [9, 10]. For instance, Brites's group has realized the temperature readout of a nanofluid based on the TCLs of $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ in an upconversion (UC) $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ nanothermometer [10]. However, the restricted energy spacing between TCLs ($200 < \Delta E < 2000 \text{ cm}^{-1}$) is a limitation for further improvement of the sensitivity of the thermometer [11]. Therefore, several new strategies based on two different luminescent centers have been proposed to overcome the disadvantages of the TCL route, such as the nonthermally coupled levels of two different RE³⁺ ions ($\text{Tb}^{3+}\text{:}^5\text{D}_4/\text{Pr}^{3+}\text{:}^3\text{D}_2$ [12], $\text{Eu}^{2+}\text{:}5\text{d-4f}/\text{Eu}^{3+}\text{:}^5\text{D}_0$ [13], etc.), the combination of RE³⁺ and transition-metal (TM) ions ($\text{Bi}^{3+}/\text{RE}^{3+}$ [14], $\text{Eu}^{3+}/\text{Mn}^{2+}$ [15], $\text{Mn}^{4+}/\text{Ho}^{3+}$ [16], etc.), the RE³⁺/defective dual emission system ($\text{Pr}^{3+}\text{:CaTiO}_3$ [17], $\text{Eu}^{3+}\text{:TiO}_2$ [18], etc.), the RE-MOF/dye combination (Eu-MOF/perylen [19]), etc. For example, Gao and coworkers have reported that a luminescent thermometer based on the FIRs of Pr^{3+} to Tb^{3+} in $\text{Tb}^{3+}/\text{Pr}^{3+}\text{:NaGd}(\text{MoO}_4)_2$ could give outstanding temperature sensitivity due to different thermal dependences of $\text{Tb}^{3+}\text{-Mo}^{6+}$ and $\text{Pr}^{3+}\text{-Mo}^{6+}$ inter-valence charge transfer states [4, 11, 12]. However, all these strategies are based on the intensity ratio that originates from different emission centers, whose response to several environmental disturbances might be slightly different, leading to possible measurement errors. On the contrary, a better anti-interference performance could be realized if ratiometric thermometry is based on the signals from the same upper energy level of an RE ion.

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However, relevant investigations are quite scarce. Therefore, how to design a ratiometric thermometric material with high sensitivity and anti-interference property has a great value for practical applications.

Alternatively, fluorescence-lifetime-based thermometry is also a very attractive and important detection scheme, which can achieve calibration-free measurement and is immune to inhomogeneous light fields, external electromagnetic interference, and so on [20, 21]. In the past studies, phosphors doped with TM ions (such as Cr^{3+} , Mn^{4+} , etc.) were mostly favored for lifetime-based temperature sensing [16, 20]. For example, Chen et al. reported a transparent bulk glass ceramic containing $\text{Cr}^{3+}\text{:LiGa}_2\text{O}_5$ nanoparticles to achieve considerable sensitivity based on the Cr^{3+} emission lifetime [20]. This is because the TM ions with $3d^n$ electron configurations have strong electron-phonon coupling, leading to significant variation in their lifetimes with temperature. However, the temperature-dependent decay lifetime of Eu^{3+} -doped luminescent nanocrystals has been seldom studied as a temperature probe.

Moreover, to improve the thermometric performance, some scholars have constructed novel dual-mode optical thermometers based on the FIRs of RE^{3+} ions and the lifetimes of TM^{3+} ions. For example, Wang et al. have realized a dual-mode optical thermometry platform $\text{LiTaO}_3\text{:Ti}^{4+}$, $\text{Eu}^{3+}\text{@PDMS}$, in which the FIRs of the Eu^{3+} emission to the Ti^{4+} emission and the luminescence lifetime of Ti^{4+} ions were used as the detecting parameters simultaneously [22]. Similarly, it has been reported that $\text{Yb}^{3+}/\text{Er}^{3+}/\text{Cr}^{3+}$ -doped transparent bulk glass ceramic could reach the highest sensing sensitivity of $0.25\% \text{ K}^{-1}$ based on the FIR between TCLs of $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ in Er^{3+} ion and $0.59\% \text{ K}^{-1}$ based on the decay lifetime of $\text{Cr}^{3+}:^2\text{E} \rightarrow ^4\text{A}_2$ [21]. To date, most of the dual-mode optical thermometers are based on the RE/TM dual activators, which may suffer from the drawback of detrimental energy interaction between RE and TM ions [23]. However, high-performance dual-mode thermometers based on RE^{3+} single-doped nanomaterials have been rarely reported.

Among the various RE^{3+} ions, Eu^{3+} ion is quite popular for thermometric phosphors because of its TCLs of $^5\text{D}_1$ and $^5\text{D}_0$ and high red emission efficiency [24]. Further, the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j=1, 2, 3$, and 4) transitions in Eu^{3+} ion originate from the identical upper energy level of $^5\text{D}_0$ without Stark components, and the lower energy levels of $^7\text{F}_j$ are adjacent with small energy gaps. Hence, the emissions from Eu^{3+} ions have the potential to accomplish ratiometric temperature sensing with the signals from the same upper energy level. Meanwhile, ZrO_2 is a suitable host matrix for UC luminescent materials because of its advantages such as relatively low phonon energy

($\sim 470 \text{ cm}^{-1}$), good physical and chemical stability, excellent biocompatibility, high refractive index, and wide bandgap ($\sim 5 \text{ eV}$) [25–27].

In this work, a new approach to designing the dual-mode optical thermometer based on the highly temperature-dependent valley-to-peak ratio (VPR) and the fluorescence lifetime of Eu^{3+} emission in ZrO_2 is proposed for the first time. $\text{ZrO}_2\text{:Eu}^{3+}$ nanocrystals with different Eu^{3+} concentrations were prepared by a facile gel combustion method. The phase composition and microstructure of the samples were investigated in detail. At 361 nm, the temperature sensing behaviors based on the intensity ratio between the valley formed by the overlap of the emission bands and the fluorescent peak of Eu^{3+} ions ($\text{VPR} = I_{600}/I_{606}$) were investigated. Meanwhile, the influence of temperature on fluorescence decay behaviors of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition in Eu^{3+} ions was systematically analyzed under 460 nm excitation to explore its possible application in optical thermometry. The effects of the doping concentration on both VPR- and lifetime-based thermometric properties were also studied. The results demonstrate that the current probe based on $\text{Eu}^{3+}\text{:ZrO}_2$ nanocrystals is versatile, highly sensitive, repeatable, and anti-interference, with the unique combination of VPR and lifetime techniques.

2 Experimental

2.1 Materials and synthesis

The $\text{ZrO}_2\text{:xEu}^{3+}$ nanocrystals ($x=0, 0.5, 2.5, 5, 7.5, 10 \text{ mol}\%$) were synthesized using a gel combustion method. Zirconium oxynitrate hydrate ($\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$; 99.99% purity), europium nitrate hexahydrate ($\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; 99.99% purity), and citric acid ($\text{C}_6\text{H}_8\text{O}_7$; 99.8% purity) were used as raw materials. First, appropriate amounts of nitrates were dissolved in deionized water separately. According to the stoichiometric ratio, the solutions were mixed together, and then citric acid was added with the citric acid/metal ion molar ratio of 3.5. After thoroughly mixing for 30 min, ammonia was dropped into the mixture to adjust the pH to ~ 7 . Subsequently, the homogeneous solution was heated to 90°C for 8 h to form a wet gel, which was further dried at 120°C for 8 h. Then, the xerogel was heated in a muffle furnace at 300°C for 2 h. Finally, the $\text{ZrO}_2\text{:Eu}^{3+}$ nanocrystals were successfully prepared by sintering at 800°C for 2 h. The obtained fluffy white powder was ground for the subsequent measurements of phase structure, microscopic morphology, and optical properties.

2.2 Characterization

The crystal structures of the nanophosphors were characterized by an X-ray diffractometer (Bruker D2 PHASER diffractometer) (Bruker AXS GMBH, Karlsruhe, Germany) with $\text{CuK}_{\alpha 1}$ ($\lambda = 1.5418 \text{ \AA}$) excitation in the 2θ range $10\text{--}80^\circ$. Raman measurements were performed using a Renishaw SPEX-Ramalog laser Raman spectrometer system using 785 nm excitation (Renishaw, Wotton-under-Edge, UK). The electron paramagnetic resonance (EPR) (German Magnetech, Berlin, Germany) spectra were measured by a Bruker A300-10/12 spectrometer at room temperature. The actual valences of the element Eu were characterized by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250 Xi) (Thermo Electron Corporation, Waltham, MA, USA) using AlK_{α} radiation. Transmission electron microscopy (TEM) (FEI, Waltham, MA, USA) and high-resolution TEM (HRTEM) observations were carried out on an FEI Tecnai G2 F20 S-WTINE instrument equipped with an energy-dispersive X-ray spectrum (EDS) analyzer. The diffuse reflectance spectra (DRS) were recorded by a UV-vis spectrophotometer (Shimadzu UV-3600, Shimadzu International Trade Shanghai Co., Ltd., China). Quantum efficiency was estimated using an Edinburgh FS5 spectrophotometer equipped with an integrating sphere. The photoluminescence (PL) spectra and photoluminescence excitation (PLE) spectra were recorded by a spectrometer (Horiba Jobin Yvon Fluorolog-3, HORIBA Jobin Yvon, Palaiseau, France) equipped with a 450 W xenon lamp. Time-resolved emission spectra (TRES) and luminescent decay curves were recorded on the same spectrometer excited by a spectral LED-460. A heating device (TAP-02 temperature control system) was used for adjusting the sample temperature. Temperature-dependent luminescent spectra were recorded by an Everfine EX 1000 phosphor excitation and thermal quenching system.

3 Results and discussion

3.1 Phase identification and morphology observation

Figure 1A shows the X-ray diffraction (XRD) patterns of $\text{ZrO}_2\text{:Eu}^{3+}$ nanocrystals with the doping concentration varying from 0 to 10 mol%. The ZrO_2 phase transition with the Eu^{3+} concentration was discovered. The undoped ZrO_2 and $\text{ZrO}_2\text{:}0.5\%\text{Eu}^{3+}$ nanocrystals exhibit a mixture of monoclinic (PDF#37-1484) and tetragonal phases (PDF#50-1089). The monoclinic (M) phase vanishes with further increase in doping concentration. Eventually, the pure tetragonal (T) phase is observed for the samples with Eu^{3+} concentration $\geq 2.5\%$. In addition, according to the Scherrer formula [28], the average grain sizes of the samples were calculated, and the results are shown in Figure 1B. It can be observed that the grain size of the samples decreases from 16 to 9.1 nm with the increase in Eu^{3+} concentration from 0 to 10%, respectively. There can be two reasons for the reduction in grain size. First, an extra retarding force on the grain boundary of ZrO_2 impedes the grain growth, which is caused by the substituted Eu^{3+} ions [29]. Second, the Zr^{4+} concentration decreases with increasing Eu^{3+} doping ratio, suppressing the diffusivity of ZrO_2 and slowing down the grain growth.

Owing to the relatively low resolution of XRD identification [30], the phases were further distinguished via their Raman spectra. As is known, the vibrational bands at 333 , 380 , 475 , and 616 cm^{-1} are the characteristic peaks of the monoclinic phase, while those at 267 , 316 , 460 , and 640 cm^{-1} correspond to the tetragonal phase [31]. In Figure 2A, the spectra of ZrO_2 and $\text{ZrO}_2\text{:}0.5\%\text{Eu}^{3+}$ feature the monoclinic phase together with the tetragonal phase. With increasing Eu^{3+} , the bands due to the monoclinic phase weaken and disappear gradually. When the Eu^{3+} concentration reaches

Figure 1: Characterization of phase structure.

(A) XRD patterns of $\text{ZrO}_2\text{:Eu}^{3+}$ (x mol%) nanocrystals. (B) Grain size vs. Eu^{3+} doping concentration.

Figure 2: The phase transformation, the evolution of oxygen vacancy and the valence state of Eu ions.

(A) Raman spectra of $\text{ZrO}_2\text{:xEu}^{3+}$: (i) 0%, (ii) 0.5%, (iii) 2.5%, (iv) 5%, (v) 7.5%, and (vi) 10%. (B) Room-temperature EPR spectra of the samples with different doping concentrations. (C) High-resolution XPS spectrum for Eu element in $\text{ZrO}_2\text{:10%Eu}^{3+}$ nanocrystals.

2.5 mol%, only bands of the tetragonal phase are observed, which agrees with the results of XRD.

The phase transition of ZrO_2 is mainly due to the generation of oxygen vacancies caused by the substitution of Zr^{4+} ions by Eu^{3+} ions for charge compensation. To probe the existence of the oxygen vacancies, the EPR spectra of the samples were measured. As shown in Figure 2B, the symmetrical EPR signal at $g = 2.003$ is observed for the samples with different concentrations, which is typical of oxygen vacancies [32]. For the undoped sample, the signal intensity is relatively low, and a small number of oxygen vacancies are generated, probably due to the fierce chemical reaction in the combustion process and the relatively imperfect structure of the nanocrystalline grains [33]. The EPR signal intensifies with the increase of Eu^{3+} concentration, indicating an increase in the oxygen vacancy concentration. Consequently, the oxygen vacancies could lead to ionic rearrangement and phase structure modification from monoclinic to tetragonal. Further, although the oxygen vacancies have been produced in the Eu^{3+} doped samples, the valence state of Eu^{3+} has not been affected, as confirmed by XPS. As shown in Figure 2C, there are only characteristic Eu^{3+} binding peaks at 1134.3 and 1163.6 eV, which are assigned to $\text{Eu}^{3+} 3d_{5/2}$ and $\text{Eu}^{3+} 3d_{3/2}$, respectively. No characteristic peaks from Eu^{2+} ions can be seen, indicating that the impacts of Eu^{2+} on the phase transition and optical properties can be ruled out.

Representative TEM images of $\text{ZrO}_2\text{:10%Eu}^{3+}$ nanocrystals are shown in Figure 3A,B. The crystallites are nearly spherical in shape, and their sizes are in the range 5–15 nm. Besides, the nanocrystals exhibit some tendency to aggregate as a result of the heat treatment process. The selected area electron diffraction (SAED) pattern is shown in Figure 3C. Only the characteristic Debye-Scherrer rings corresponding to the tetragonal structure are observed, revealing the formation of the nanocrystalline tetragonal phase. A close observation of the microstructure shown in HRTEM observation further confirms that the crystallite sizes are ~10 nm (Figure 3D). Meanwhile, Figure 3E shows that the interplanar spacings are 0.18 and 0.15 nm, which match with the d -spacing of the (112) and (013) lattice planes of tetragonal ZrO_2 phase, respectively. Furthermore, the EDS spectrum in Figure 3F shows that the nanocrystals are composed of only the elements Zr, O, and Eu, confirming that Eu^{3+} has been effectively incorporated into ZrO_2 nanocrystals.

3.2 Luminescence properties

3.2.1 UV-visible absorption study

Figure 4A shows the DRS of the tetragonal $\text{ZrO}_2\text{:Eu}^{3+}$ nanocrystals with different concentrations. The spectral

Figure 3: The morphology observation of $\text{ZrO}_2\text{:Eu}^{3+}$ nanocrystals.

(A, B) TEM images of $\text{ZrO}_2\text{:10%Eu}^{3+}$ nanocrystals. (C) SAED pattern. (D) HRTEM image. (E) Fourier-filtered HRTEM image of the region I in (D). The inset is the Fourier-transformed image. (F) EDS spectrum.

Figure 4: The analyses of UV-visible absorption property and optical bandgap.

(A) Diffuse reflection spectra and (B) Tauc plots for $\text{ZrO}_2\text{:Eu}^{3+}$ nanocrystals with different concentrations (inset: the variation of bandgap energy with Eu^{3+} concentration).

bands around 209 and 253 nm are due to the host absorption and $\text{Eu}^{3+}\text{--O}^{2-}$ charge transfer, respectively [30, 34]. The weak absorption bands located at 394 and 465 nm can be attributed to the transitions from the ground state $^7\text{F}_0$ to the excited states $^5\text{L}_6$ and $^5\text{D}_2$ of Eu^{3+} ions, respectively. Additionally, the Tauc plot was used to estimate the optical bandgap energy of the samples. The relation between the incident photon energy ($h\nu$) and optical bandgap energy (E_g) is expressed as [29]

$$(F(R_\alpha)h\nu)^2 = A(h\nu - E_g), \quad (1)$$

where $F(R_\alpha)$ is the absorption coefficient, and A is a constant. The optical bandgap values are obtained via the intercept on the $h\nu$ -axis by extrapolating the curve to $(F(R_\alpha)h\nu)^2 = 0$. As shown in Figure 4B, the optical energy bandgaps of $\text{ZrO}_2\text{:Eu}^{3+}$ nanocrystals decrease from 5.06 to 4.84 eV with increasing Eu^{3+} concentration. The optical bandgap energy is affected by many factors such as the

electronic structure, structural defects, phase transitions, etc. [35, 36]. In the present system, the blue shift of the bandgap energy could be related to the substitution of the smaller Zr^{4+} ion (0.72 Å) by the larger Eu^{3+} ion (0.947 Å), which induces a slight rearrangement in the vicinity of the Zr^{4+} ions and thus the variation of their exchange interaction [37]. Meanwhile, there is the possibility of generation of intermediate energy levels in the bandgap region due to the oxygen vacancies, leading to the reduction of the optical bandgap energy [28].

3.2.2 Photoluminescence study

Figure 5A shows the PL excitation spectra of $\text{ZrO}_2\text{:10%Eu}^{3+}$ nanocrystals by monitoring the emission at 606 nm of Eu^{3+} ions. The excitation bands are observed at 361 nm ($^7\text{F}_0 \rightarrow ^5\text{D}_4$), 385 nm ($^7\text{F}_0 \rightarrow ^5\text{L}_7$), 395 nm ($^7\text{F}_0 \rightarrow ^5\text{L}_6$), 414 nm ($^7\text{F}_0 \rightarrow ^5\text{D}_3$), and 464 nm ($^7\text{F}_0 \rightarrow ^5\text{D}_2$) [38]. Figure 5B shows the emission spectra of $\text{ZrO}_2\text{:Eu}^{3+}$ (x mol%) nanocrystals ($x=2.5, 5, 7.5, 10$) under 361 nm excitation. The peaks at

591 and 654 nm are attributed to the magnetic dipole transitions of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_3$ of Eu^{3+} ions, respectively, which are insensitive to the site symmetry. On the other hand, the peaks at 606 and 715 nm correspond to the electric dipole transitions of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$, respectively, which are only permitted for an Eu^{3+} ion located in a low-symmetry site with no inversion center [39]. Accordingly, the intensity ratio between the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions is defined as the asymmetric ratio to reflect the local crystal field symmetry surrounding the Eu^{3+} ions [40]. The inset of Figure 5B shows that the ratio between the 606 and 591 nm emissions based on intensity maxima (I_{606}/I_{591}) increases gradually with the increase of Eu^{3+} concentration, revealing reduced local symmetry. This is because both the production of oxygen vacancies and the different ionic radii of Eu^{3+} and Zr^{4+} distort the symmetry of the host matrix. Consequently, the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ red emission is more predominant at higher Eu^{3+} concentration. Moreover, Figure 5C shows that the line widths of the 591 and 606 nm emission peaks increase gradually as the Eu^{3+} concentration increases. This phenomenon

Figure 5: Photoluminescence behaviors and the corresponding mechanism.

(A) Excitation (black curve) and emission spectrum (red curve) of $\text{ZrO}_2\text{:10%Eu}^{3+}$. (B) Emission spectra of the tetragonal $\text{ZrO}_2\text{:Eu}^{3+}$ (x mol%) nanocrystals under 361 nm excitation. (C) Emission spectra normalized to the peak at 606 nm. (D) Schematic energy level diagram as well as the PL mechanism of Eu^{3+} in ZrO_2 .

is called inhomogeneous broadening, which is related to the increasing asymmetry of the chemical surrounding of the Eu^{3+} ions. Besides, there is an obvious valley centered at 600 nm formed by the overlap between the emission bands of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions, as the two emissions originate from the same $^5\text{D}_0$ level to the lower TCLs of $^7\text{F}_1$ and $^7\text{F}_2$ with the energy gap of only several hundred wavenumbers (Figure 5D).

Figure 6A shows the 2D color-filled contour of the time-resolved emission spectra from the $\text{ZrO}_2\text{:10%Eu}^{3+}$ nanocrystals under 460 nm excitation. The emission decay traces monitored at the transitions ($^5\text{D}_0 \rightarrow ^7\text{F}_j$, $j = 1, 2, 3, 4$) are clearly observed, indicating the relatively long lifetimes of these emissions (in the order of milliseconds). To further elucidate the impact of the doping concentration, the decay curves of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition (606 nm) under 460 nm excitation were investigated at room temperature, as shown in Figure 6B. The decay curves of the samples can be fitted via a bi-exponential equation as [41]

$$I = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2) + I_0, \quad (2)$$

where I and I_0 stand for the emission intensities at time t and 0, respectively; I_1 and I_2 are two parameters; and τ_1 and τ_2 represent the fast and slow components of luminescence lifetimes, respectively. The average decay time (τ_{eff}) is estimated by the following equation [42]:

$$\tau_{\text{eff}} = \frac{I_1 \tau_1^2 + I_2 \tau_2^2}{I_1 \tau_1 + I_2 \tau_2}. \quad (3)$$

As shown, there is a reduction of the average lifetime from 2.83 to 2.01 ms with the increase in concentration. There can be three reasons for this. First, the reduction of local symmetry caused by Eu^{3+} doping benefits the breaking of the transition selection rules, the enhancement of

radiative transition probability, and thus the reduced radiative decay time of Eu^{3+} ions [43]. Second, the increasing concentration of Eu^{3+} ions shortens the distance between the neighboring activator ions, resulting in a stronger interaction between them, which could accelerate the nonradiative relaxation processes and thus contribute to decrease in lifetime [44]. The third reason is related to the increasing number of oxygen vacancies with Eu^{3+} concentration, which consumes parts of the excitation energy.

3.3 Optical temperature sensing behaviors

Typical temperature-dependent PL spectra of $\text{ZrO}_2\text{:10%Eu}^{3+}$ nanocrystals under 361 nm excitation are shown in Figure 7A. The luminous intensities of the emission peaks are seen to decrease gradually with increasing temperature. Concurrently, the measured quantum efficiency decreases from ~12.05% to ~8.23% when the temperature rises from 293 to 473 K. The above phenomenon is mainly attributed to the accelerated nonradiative de-excitation processes in these small nanocrystals, which dissipate the excitation energy at elevated temperatures [18, 45].

In the meantime, the normalized PL spectra shown in Figure 7B clearly reveals that the full widths at half-maximum (FWHMs) of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emissions increase with increasing temperature. This can be explained by the fact that fluctuations in the local environment will cause the homogeneous broadening of spectral lines due to the enhanced thermal vibration and electron-phonon interaction, when the temperature is increased [46, 47]. To further analyze the relationship between the FWHM and temperature, Figure 7C shows the variation in the line width of the 591 nm emission as a function of temperature. Clearly, the FWHM shows a near-linear dependence on the temperature owing to the

Figure 6: The luminescence decay dynamics of $\text{ZrO}_2\text{:Eu}^{3+}$ nanocrystals.

(A) 2D color-filled contour of TRES for $\text{ZrO}_2\text{:10%Eu}^{3+}$. (B) Emission decay curves of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition for the $\text{ZrO}_2\text{:Eu}^{3+}$ (x mol%) samples.

Figure 7: The study on the optical thermometric behaviors based on VPR technique.

(A) PL spectra of $\text{ZrO}_2:10\%\text{Eu}^{3+}$ nanocrystals at different temperatures excited at 361 nm. The inset shows the corresponding 2D color-filled contour of temperature-dependent PL spectra. (B) Normalized emission spectra recorded at 293, 373, and 473 K, respectively, where the intensity was normalized at 606 nm. (C) FWHM of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition (γ) vs. temperature. The inset shows the change of S_r with temperature. (D) Variation of VPR as a function of temperature. (E) Temperature dependence of S_r for samples with different Eu^{3+} concentrations. (F) Plots of VPR (I_{600}/I_{606}) vs. temperature measured in three heating and cooling cycles for $\text{ZrO}_2:10\%\text{Eu}^{3+}$.

homogeneous spectral line broadening, which is similar to the observation in the Nd:YAG ceramic [48]. The slope of the fitted line is ~ 0.012 , which means that the bandwidth

increases with the temperature at a rate of $\sim 0.012 \text{ nm K}^{-1}$. And the corresponding relative temperature sensing sensitivity (S_r) can be calculated, which is defined as

$S_r = |1/\text{FWHM}| \cdot |d\text{FWHM}/dT|$. As shown in the inset of Figure 7C, the maximum S_r value is $\sim 0.12\% \text{ K}^{-1}$ at 293 K, which is smaller than that of many conventional FIR-based optical thermometric materials.

Moreover, as the emission peaks of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (591 nm) and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (606 nm) transitions are quite close, there is a valley at 600 nm formed as a result of the overlap of the two peaks. When the temperature rises, the intensity of valley gradually increases with respect to that of 606 nm emission, which is a result of the increase in FWHM and decrease in emission intensity, as detailed above. Owing to their different thermal responses, the valley intensity at 600 nm and the peak intensity at 606 nm can be applied for ratiometric temperature sensing. Figure 7D shows the variation of the ratio I_{600}/I_{606} as a function of temperature. Obviously, I_{600}/I_{606} shows an almost linear increase with increasing temperature. Therefore, the relationship between the VPR of I_{600}/I_{606} and temperature can be fitted by a linear function as follows:

$$\text{VPR} = a(T - T_0) + b, \quad (4)$$

where a represents the slope of the linear curve, b is a constant, and T_0 is the initial temperature.

For the comparison with different thermometric techniques, the important parameter S_r is evaluated, which describes the change rate of VPR at a specific temperature. S_r can be written as [49]

$$S_r = \frac{1}{\text{VPR}} \frac{d(\text{VPR})}{dT}. \quad (5)$$

Figure 7E shows the temperature dependence of S_r for samples with different concentrations. It can be seen that the highest S_r increase results with the increase of Eu^{3+} concentration. As illustrated in Figure 5C, the spectral broadening becomes severe with the increase in Eu^{3+} concentration owing to the more asymmetrical site of Eu^{3+} ions and the increased interaction between the luminescent center and the phonon, which may favor the enhancement of thermal sensitivity. For $\text{ZrO}_2\text{:}10\%\text{Eu}^{3+}$, the highest S_r value is $1.8\% \text{ K}^{-1}$ at 293 K, which is higher than that of many conventional optical thermometric materials such as $\text{Eu}^{3+}\text{:Ca}_7\text{V}_4\text{O}_{17}$ ($0.024\% \text{ K}^{-1}$) [50], $\text{Eu}^{3+}\text{:YVO}_4$ ($1\% \text{ K}^{-1}$) [51], $\text{Nd}^{3+}\text{:YAG}$ ($0.15\% \text{ K}^{-1}$) [2], $\text{Ho}^{3+}/\text{Yb}^{3+}\text{:CaWO}_4$ ($0.5\% \text{ K}^{-1}$) [52], and $\text{Er}^{3+}/\text{Yb}^{3+}\text{:BaMoO}_4$ ($1.05\% \text{ K}^{-1}$) [53].

Furthermore, the temperature uncertainty ΔT is generally used to describe the dispersion of the calculated values within which the actual temperature value is expected to lie, which is defined as [12]

$$\Delta T = \frac{1}{S_r} \frac{\delta \text{VPR}}{\text{VPR}}, \quad (6)$$

where $\delta \text{VPR}/\text{VPR}$ denotes the uncertainty in the determination of the thermal parameter, depending on the experimental detection setup. The minimum temperature uncertainties are evaluated to be $\sim 1 \text{ K}$ for $\text{ZrO}_2\text{:}2.5\%\text{Eu}^{3+}$, $\sim 0.44 \text{ K}$ for $\text{ZrO}_2\text{:}5\%\text{Eu}^{3+}$, $\sim 0.40 \text{ K}$ for $\text{ZrO}_2\text{:}7.5\%\text{Eu}^{3+}$, and $\sim 0.27 \text{ K}$ for $\text{ZrO}_2\text{:}10\%\text{Eu}^{3+}$. Apparently, the smallest ΔT in $10\%\text{Eu}^{3+}$ -doped sample benefits from the largest S_r . In addition, measurement stability is the key for practical applications. The temperature-recycle measurement results of the $\text{ZrO}_2\text{:}10\%\text{Eu}^{3+}$ sample, presented in Figure 7F, reveal that the changes of VPR as a function of temperature are repeatable and reversible during the cycling tests. Besides the high sensing sensitivity, reasonable temperature uncertainty, and good thermal stability, VPR-based thermometry guarantees improved anti-interference performance since the $^5\text{D}_0 \rightarrow ^7\text{F}_1/^7\text{F}_2$ transitions derived from the same upper excited level may change with the temperature in the same degree. Further, the wavelength interval from the valley to peak is narrow (6 nm), which is favorable to the consistent absorption and scattering losses for the two wavelengths (600 and 606 nm). Thus, the losses caused by absorption and scattering can be easily eliminated via the ratio process.

VPR-based thermometry may also be valid for other RE^{3+} -doped materials. To verify this, $\text{ZrO}_2\text{:Er}^{3+}$ (1.5 mol%) UC luminescent nanocrystals were synthesized by the same gel combustion method, and the applicability of VPR strategy was investigated. Er^{3+} ion was chosen as an example, which has been widely studied for optical thermometry due to its rich UC energy levels [54]. Under 980 nm excitation, the intensity of the valley at 558 nm of the sample increases with an increase in temperature, while the intensity of the 568 nm emission decreases (see Figure S1 in Supporting Information). Thus, the VPR (I_{558}/I_{568}) shows a linear temperature dependence and displays the maximum S_r of $0.54\% \text{ K}^{-1}$ at 293 K. For comparison, the temperature sensing behaviors were also evaluated based on the FIR between the TCLs of $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$. As shown in Figure S2, the FIR data can be fitted to temperature obeying the Boltzmann distribution [55]. The highest S_r value is $\sim 0.69\% \text{ K}^{-1}$ at 293 K, which is lower than that of $\text{ZrO}_2\text{:}10\%\text{Eu}^{3+}$ based on the VPR technique ($1.8\% \text{ K}^{-1}$).

On the other hand, to design fluorescence-lifetime-based thermometry, the Eu^{3+} PL decay behaviors were studied at different temperatures. Taking $\text{ZrO}_2\text{:}10\%\text{Eu}^{3+}$ as an example, Figure 8A shows that the increase in temperature leads to the continuous reduction of lifetime for the 606 nm emission. This can be attributed to the promoted nonradiative de-excitation processes at higher temperatures [56]. The relationship between the fluorescence lifetime and the absolute temperature can be fitted by the Struck and Fonger model [18] as

Figure 8: The measurement results for the lifetime-based temperature sensing.

(A) Temperature-dependent PL decay curves of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition (606 nm) for $\text{ZrO}_2\text{:10\%Eu}^{3+}$ nanocrystals. (B) Decay lifetime vs. absolute temperature for samples with different concentrations. (C) Temperature dependence of S_r .

$$\tau(T) = \frac{1}{A + B \exp\left(-\frac{\Delta E}{kT}\right)}, \quad (7)$$

where $\tau(T)$ is the fluorescence lifetime at a certain temperature, A is a constant, k is the Boltzmann constant, B is the frequency factor, and ΔE is the thermal-quenching activation energy. The fitted results of the samples are plotted in Figure 8B. The correlation coefficient of up to 0.9995 indicates the achievement of perfect fitting. Accordingly, the thermal quenching process could be related to the crossover process, which is similar to that in some other Eu^{3+} -doped materials [28, 37]. In a crossover process, the electrons at excited levels of the Eu^{3+} ions could be thermally activated to the $\text{Eu}^{3+}\text{--O}^{2-}$ charge transfer (CT) region by overcoming the energy barrier, as the temperature increases. Then, these electrons return to the ground state via the crossing point between CT and the ground state through nonradiative relaxation, leading to thermal quenching and lifetime reduction [57, 58]. Similarly, S_r should be calculated as follows:

$$S_r = \left| \frac{1}{\tau} \frac{d\tau}{dT} \right|. \quad (8)$$

Figure 8C shows the S_r curves as a function of temperature for different samples. Evidently, the maximum S_r value monotonously increases with the increase in concentration. The interaction of the Eu^{3+} ions and the number of oxygen vacancies increase with the increase of Eu^{3+} content, contributing to the higher nonradiative de-excitation probability. Thus, the more concentrated sample exhibits stronger thermally induced luminescence quenching and faster reduction of luminescence lifetime when the temperature rises. For the optimal $\text{ZrO}_2\text{:10\%Eu}^{3+}$, its S_r keeps increasing with increasing temperature, with the maximum S_r of $\sim 0.33\% \text{ K}^{-1}$ achieved at 573 K. The relative sensitivity of the present phosphor is comparable to that of $\text{Cr}^{3+}\text{:YAlO}_3$ ($0.19\% \text{ K}^{-1}$), $\text{Cr}^{3+}\text{:MgAl}_2\text{O}_4$ ($0.37\% \text{ K}^{-1}$) [59], and $\text{Sm}^{3+}\text{:YNbO}_4$ ($0.43\% \text{ K}^{-1}$) [60]. Hence, the present nanocrystals can act as a new generation of optical thermometric media to realize both the VPR- and lifetime-based temperature readout.

4 Conclusion

In conclusion, Eu^{3+} -doped ZrO_2 nanocrystals were synthesized to investigate the temperature-dependent luminescence properties and the possibility for a new type of

dual-mode luminescence thermometer. The ZrO_2 samples doped with Eu^{3+} concentration $\geq 2.5\text{mol}\%$ were confirmed to belong to the tetragonal phase with average crystallite sizes of ~ 10 nm. At 361 nm excitation, the valley intensity centered at 600 nm increases monotonously compared to that of the 606 nm emission ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) with the increase of temperature. Based on the VPR between the valley (600 nm) and the 606 nm peak, a high S_r of $1.8\% \text{ K}^{-1}$ could be achieved in $\text{ZrO}_2\text{:}10\%\text{Eu}^{3+}$. VPR-based thermometry is also applicable in $\text{ZrO}_2\text{:Er}^{3+}$ UC nanocrystals, indicating its promising potential in temperature measurement. Further, the thermal depopulation of the $^5\text{D}_0$ state results in the reduction in lifetime of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition with temperature. Consequently, a highest S_r of $0.33\% \text{ K}^{-1}$ is obtained, with the lifetime of the 606 nm emission as thermometric parameter. Obviously, the dual-mode temperature readout can provide more accurate measurement than readout using only one type. We believe that the present work provides a guidance for the exploration of well-performing temperature sensors.

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