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## 1. Introduction

Fluorescence intensity ratio (FIR) based temperature sensing technology has recently attracted broad interest, due to its unique merits of non-contact, rapid response, as well as high spatial and temperature resolutions, which are in favor of thermometry in harsh environments, micro-systems or fast moving objects.<sup>1–8</sup> In this technique, the FIR temperature probe (*i.e.* phosphors with temperature-dependent luminescence properties) is the critical part that determines the performance of a temperature sensing device. For an ideal FIR thermometric material, both high absolute and relative temperature sensitivities (*S*<sub>a</sub> and *S*<sub>r</sub>) are required, in the desired temperature detecting range.<sup>9–12</sup>

Currently, urgent demands for temperature probing or mapping at a cellular level, microelectronic systems or nanomedicines, have

## Synthesis of Mn<sup>2+</sup>:Zn<sub>2</sub>SiO<sub>4</sub>–Eu<sup>3+</sup>:Gd<sub>2</sub>O<sub>3</sub> nanocomposites for highly sensitive optical thermometry through the synergistic luminescence from lanthanide-transition metal ions<sup>†</sup>

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In this work,  $Mn^{2+}:Zn_2SiO_4-Eu^{3+}:Gd_2O_3$  nanocomposites were fabricated following a multi-step solution route. The fluorescence intensity ratio of  $Mn^{2+}$  to  $Eu^{3+}$  in these composites exhibits remarkable temperature dependence, owing to the diverse thermal quenching behaviors of  $Mn^{2+}$  and  $Eu^{3+}$  ions. Using these nanomaterials to perform thermometry, excellent temperature sensitivity is achieved in the room temperature range. Specifically, the values of relative temperature sensitivity are all beyond 2.5% K<sup>-1</sup> in the whole range of 303–323 K (*i.e.* 30–50 °C), and reach as high as 3.05% K<sup>-1</sup> at 303 K, remarkably higher than those of other inorganic optical thermometric materials at a similar temperature. And the absolute sensitivities are all beyond 0.0089 K<sup>-1</sup> in this temperature range, which is also a relatively high value. These results indicate the  $Mn^{2+}:Zn_2SiO_4-Eu^{3+}:Gd_2O_3$  nanocomposites to be very promising nano-thermometric materials.

brought more stringent requirements for the thermometric material. To fulfill these applications, the candidate phosphors should possess sub-micro grain size,<sup>13,14</sup> as well as both high absolute and relative temperature sensitivities in the room temperature range (typically,  $S_a \ge 0.008 \text{ K}^{-1}$  and  $S_r \ge 2\% \text{ K}^{-1}$  at 303–323 K).<sup>13,14</sup>

The most conventional FIR materials are the lanthanide doped phosphors, in which the emission from thermally coupled level pairs (TCL) of the lanthanide ions (for example,  ${}^{2}\text{H}_{11/2}$  and  ${}^{4}\text{S}_{3/2}$  levels for Er<sup>3+</sup>) is utilized as the temperature label.<sup>15–17</sup> However, for these kinds of thermometric materials, the  $S_a$  values always reach their maximum at a temperature higher than 450 K (177 °C),<sup>11</sup> while at room temperature, few of them could be higher than 0.008  $K^{-1}$ . More seriously,  $S_r$  of these FIR materials is highly related to the energy space ( $\Delta E$ ) between TCL pairs (typically,  $S_r = \Delta E/kT^2$ ).<sup>9</sup> For the most used TCL pairs, *i.e.*  ${}^{2}H_{11/2}$  and  ${}^{4}S_{3/2}$  levels for Er<sup>3+</sup> ions, the S<sub>r</sub> is only about 1.1% K<sup>-1</sup> at 303 K (30 °C). Although the value of  $S_r$  can be increased by using the other TCL pairs with large  $\Delta E$ , such as  ${}^{4}\text{G}_{11/2}$  and  ${}^{2}\text{H}_{9/2}$  levels of  $\text{Er}^{3+}$  ions, which can increase the  $S_{r}$  to about 2.2%  $K^{-1}$  (at 303 K),<sup>18</sup> but concomitantly the  $S_a$  would be reduced to a very low value, owing to the weakening of thermal coupling between the TCL pair.

To achieve higher  $S_a$  and  $S_r$ , other thermometric strategies have been tried. For example the phonon assisted energy transfer between pairs of lanthanide ions (such as, the Tb<sup>3+</sup>/Eu<sup>3+</sup> pair, the Nd<sup>3+</sup>/Yb<sup>3+</sup> pair, as well as the Eu<sup>3+</sup>/Nd<sup>3+</sup> pair). Qiu's group

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designed a doped NaGdF<sub>4</sub> core–shell nanostructure, and utilized the phonon assisted energy transfer from Tb<sup>3+</sup> to Eu<sup>3+</sup> to obtain a constant  $S_a$  of 0.012 K<sup>-1</sup> in a temperature range of 125–300 K, however the highest  $S_r$  in this temperature range was still not very high (only 0.5% K<sup>-1</sup>).<sup>6</sup> Qian's group constructed a Nd<sub>0.577</sub>Yb<sub>0.423</sub>BDC–F<sub>4</sub> metal–organic framework, to achieve the phonon assisted energy transfer from Nd<sup>3+</sup> and Yb<sup>3+</sup>, which exhibits a maximum  $S_r$  of 0.816% K<sup>-1</sup> at 313 K.<sup>19</sup> Yin's group used the energy transfer between Eu<sup>3+</sup> and Nd<sup>3+</sup> to achieve a maximum  $S_r$  of 2.58% K<sup>-1</sup> at 380 K; while at 303 K, the  $S_r$  was about 1.65% K<sup>-1</sup>.<sup>20</sup>

Intervalence charge transfer (IVCT) states inferred that lanthanide luminescence was another proposed strategy for developing thermometric materials with high temperature sensitivity. For example, Cao' group fabricated the Pr:KNa(NbO<sub>3</sub>)<sub>2</sub> phosphor to achieve ultra-high  $S_r$  (8.7% K<sup>-1</sup> at 303 K), but concomitantly the  $S_a$  dropped down to a very low value at 303 K (according to the parameters from Cao's paper, the  $S_a$  can be estimated to be less than 0.0002 K<sup>-1</sup> at 303 K).<sup>21</sup> In our previous works, we also made use of the IVCT participant's lanthanide luminescence, to construct several thermometric materials, such as Tb/Pr:NaGd(MoO<sub>4</sub>)<sub>2</sub><sup>22</sup> and Pr:Na<sub>2</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> micro-crystals.<sup>23</sup> For the former, the maximum  $S_a$  and  $S_r$  reach 0.097 K<sup>-1</sup> (at 483 K) and 2.05% K<sup>-1</sup> (at 403 K), respectively; while for the later the maximum  $S_a$  and  $S_r$  reach 0.40 K<sup>-1</sup> (at 543 K) and 1.96% K<sup>-1</sup> (at 443 K), respectively.

Obviously, the above-mentioned previous works have made great progress in promoting the maximum value of  $S_a$  or  $S_r$ , but simultaneously realizing both high  $S_a$  and  $S_r$  in the room temperature range (303–323 K) is still a great challenge. In addition, most of the thermometric materials developed so far still exhibit large grain sizes. Developing a highly sensitive thermometric material with sub-micro grain size is also a big challenge.

Herein, to achieve higher  $S_a$  and  $S_r$  at room temperature within a nano-sized thermometric material, we constructed Mn<sup>2+</sup>:Zn<sub>2</sub>SiO<sub>4</sub>-Eu<sup>3+</sup>:Gd<sub>2</sub>O<sub>3</sub> nanocomposites. The strategy used in this study is the synergistic luminescence from Mn<sup>2+</sup> and Eu<sup>3+</sup> ions. As is well known, electron-phonon interaction in Mn<sup>2+</sup>:Zn<sub>2</sub>SiO<sub>4</sub> belongs to the so called "strong coupling" system (the Huang–Rhys factor  $S \gg 1$ ),<sup>24,25</sup> in which the luminescence always presents a serious thermal quenching phenomenon. While electron-phonon interaction in Eu<sup>3+</sup>:Gd<sub>2</sub>O<sub>3</sub> belongs to the "weak coupling" system (the Huang-Rhys factor  $S \ll 1$ ),<sup>26,27</sup> in which the luminescence is relatively insensitive against change in the temperature. Therefore, by integrating these two systems within a single nanostructure, it is possible to achieve a FIR with high temperature dependence. In this work, specifically, we synthesized the Mn<sup>2+</sup>:Zn<sub>2</sub>SiO<sub>4</sub> nanorods with a diameter ranging from 50 to 100 nm, and then coated Eu<sup>3+</sup>:Gd<sub>2</sub>O<sub>3</sub> nanoparticles on the surface of these nanorods, forming Mn<sup>2+</sup>:Zn<sub>2</sub>SiO<sub>4</sub>-Eu<sup>3+</sup>:Gd<sub>2</sub>O<sub>3</sub> nanocomposites. As expected, the FIR of Eu<sup>3+</sup> to Mn<sup>2+</sup> in this nanomaterial exhibits remarkable temperature dependence. It is exciting that  $S_a$  and  $S_r$  of this material are calculated to be 0.0089 K<sup>-1</sup> and 3.05% K<sup>-1</sup>, respectively, at room temperature (303 K), which are superior to those of the other inorganic thermometric phosphors at the same temperature. Therefore, the  $Mn^{2+}:Zn_2SiO_4-Eu^{3+}:Gd_2O_3$  nanocomposites can be regarded as very promising nano-thermometric materials. In addition, the strategy proposed in the present work, which integrates "weak/strong coupling" luminescence systems within a nano-composite for high performance thermometry, can also provide inspiration for developing novel optical temperature sensing materials.

### 2. Experimental

#### 2.1. Chemical reagents

The used zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), manganese chloride tetrahydrate (MnCl<sub>2</sub>·4H<sub>2</sub>O), tetraethyl orthosilicate (TEOS), polyethylene glycol (PEG,  $M_{\rm N}$  = 400), gadolinium nitrate hexahydrate (Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O), europium nitrate hexahydrate (Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O), urea (CO(NH<sub>2</sub>)<sub>2</sub>), sodium hydroxide (NaOH) and ammonium hydroxide (NH<sub>3</sub>, 35%) were purchased from Sinopharm Chemical Reagent Company.

#### 2.2. Synthesis of the Mn<sup>2+</sup>:Zn<sub>2</sub>SiO<sub>4</sub> nanorods

A hydrothermal reaction was carried out to synthesize  $Zn_2SiO_4$  nanorods. In a typical synthesis, 10 mmol  $Zn(NO_3)_2 \cdot 6H_2O$ , 1 ml TEOS, 2 g PEG and 1 ml 35% ammonium hydroxide were mixed in 40 ml deionized water. Then, 1 ml NaOH aqueous solution containing 0.8 g NaOH was dropped into the reaction solution. After being stirred for 15 min, this solution was transferred to a 50 ml Teflon-lined stainless autoclave. The autoclave was sealed and maintained at 200 °C for 48 h, and then cooled to room-temperature. A white precipitate was separated by centrifugation, washed with deionized water several times, and then dried at 80 °C for 6 h.

The doping of  $Mn^{2+}$  ions was achieved by including 1 mmol  $MnCl_2 \cdot 4H_2O$  in the reaction solution.

# 2.3. Synthesis of the Mn<sup>2+</sup>:Zn<sub>2</sub>SiO<sub>4</sub>-Eu<sup>3+</sup>:Gd<sub>2</sub>O<sub>3</sub> nanocomposites

In a typical synthesis, 1 g of the per-fabricated  $Mn^{2+}:Zn_2SiO_4$  nanorods was dispersed in 30 ml deionized water, followed by 0.97 mmol Gd( $NO_3$ )<sub>3</sub>·6H<sub>2</sub>O, 0.03 mmol Eu( $NO_3$ )<sub>3</sub>·6H<sub>2</sub>O, and 3 g urea and 2 g PEG. This mixture was kept in a 90 °C water bath for 4 h under stirring. After that, the products were filtered, washed with deionized water, and then calcined at 500 °C for 2 h.

#### 2.4. Characterization

XRD analyses were carried out using a powder diffractometer (DMAX 2500) using Cu K<sub> $\alpha$ </sub> radiation ( $\lambda$  = 0.154 nm). The morphology observation was conducted on a field emission SEM (JSM-6700F) working at 5 kV. Transmission electron microscopy (TEM), high resolution TEM (HRTEM) and selective area electron diffraction (SAED) were performed using a TEM (JEM-2010). PL spectra were measured using a spectrofluorometer (FLS 920) equipped with a xenon lamp (450 W). A temperature controlling stage (THMS 600) was used as the sample holder for

the temperature-dependent luminescence measurement. The actual chemical compositions of the sample were determined by the inductively coupled plasma (ICP) technique using a Perkin Elmer Optima 3300DV spectrometer.

## 3. Results and discussion

# 3.1. Synthesis process and structure of the $Mn^{2+}:Zn_2SiO_4-Eu^{3+}:Gd_2O_3$ nanocomposites

As schematically illustrated in Fig. 1, to fabricate the  $Mn^{2+}:Zn_2SiO_4-Eu^{3+}:Gd_2O_3$  nanocomposites, firstly, we use a hydrothermal reaction to synthesize  $Mn^{2+}:Zn_2SiO_4$  nanorods. The results of structural characterization for the first-step product are presented in Fig. 2 and 3. As demonstrated by XRD shown in Fig. 2, the product is identified to be hexagonal structured  $Zn_2SiO_4$  (PDF 79-2005). No signal of impurities can be detected. Further SEM and TEM observations (Fig. 3) revealed that the products exhibit a rod-like shape with a diameter of 50–100 nm. HRTEM observation and the corresponding fast Fourier transform (FFT) pattern indicate that each nanorod is a single crystal, whose long axis is along the [001] direction, while the side exposures are identified to be  $\{300\}$  lattice planes, as displayed in Fig. 3c and d. The actual molar ratio of  $Mn^{2+}$  to  $Zn^{2+}$  in the  $Mn^{2+}:Zn_2SiO_4$  product is



Fig. 1 Schematic illustration for the fabrication process of  $Mn^{2+}:Zn_2SiO_4-Eu^{3+}:Gd_2O_3$  nanocomposites.



Fig. 2 XRD pattern of the  $Mn^{2+}$ :Zn<sub>2</sub>SiO<sub>4</sub> products; bars on the bottom are the standard data of hexagonal Zn<sub>2</sub>SiO<sub>4</sub> (PDF 79-2005).



Fig. 3 (a) SEM and (b) TEM images of the  $Mn^{2+}:Zn_2SiO_4$  products; (c) HRTEM and (d) corresponding fast Fourier transform (FFT) pattern for an individual  $Mn^{2+}:Zn_2SiO_4$  nanorod.



Fig. 4 XRD pattern of the  $Mn^{2+}:Zn_2SiO_4-Eu^{3+}:Gd_2O_3$  composite product; bars on the bottom are standard data of the hexagonal  $Zn_2SiO_4$  (red bars, PDF 79-2005) and cubic  $Gd_2O_3$  (blue bars, PDF 8802165).

determined to be 5.78:94.22 by inductively coupled plasma (ICP) analysis.

The second step for fabricating  $Mn^{2+}:Zn_2SiO_4-Eu^{3+}:Gd_2O_3$ nanocomposites is a urea assisted precipitation reaction for coating amorphous Eu:Gd(OH)<sub>3</sub> on the surface of the  $Mn^{2+}:Zn_2SiO_4$ nanorods, followed by calcination treatment for transforming the surficial Gd(OH)<sub>3</sub> to Gd<sub>2</sub>O<sub>3</sub> particles, as illustrated in Fig. 1. The results of structural characterization for the final products are presented in Fig. 4 and 5. As demonstrated by XRD shown in Fig. 4, the products are composed of hexagonal structured  $Zn_2SiO_4$  and cubic structured Gd<sub>2</sub>O<sub>3</sub>. No signal of other phases can be detected. SEM and TEM observations (Fig. 5) revealed that the rod-like shape is maintained after calcination, but the surface of these nanorods becomes rough. Further HRTEM observation indicates that the surfaces of the nanorods are



Fig. 5 (a) SEM and (b) TEM images of the  $Mn^{2+}:Zn_2SiO_4-Eu^{3+}:Gd_2O_3$  composite product, (c) HRTEM of an individual  $Mn^{2+}:Zn_2SiO_4-Eu^{3+}:Gd_2O_3$  nanocomposite, (d) and (e) FFT patterns taken from region 1 and region 2 labeled by red frames, respectively.

densely covered by many ~5 nm sized nanoparticles (Fig. 5c). According to FFT patterns taken from surficial and body regions, respectively, it is concluded that the rod-body is hexagonal  $Zn_2SiO_4$ , while the surficial nanoparticles are cubic  $Gd_2O_3$ , as shown in Fig. 5d and e.

#### 3.2. Luminescence properties of the products

Fig. 6 presents the photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the  $Mn^{2+}$ : $Zn_2SiO_4$  nanorods

and  $Mn^{2+}:Zn_2SiO_4-Eu^{3+}:Gd_2O_3$  nanocomposites. As shown in Fig. 6a, for the  $Mn^{2+}:Zn_2SiO_4$  nanorods, a bright green emission that peaked at 520 nm is observed, which is ascribed to the  ${}^{4}T_1 \rightarrow {}^{6}A_1$  transition of the  $Mn^{2+}$  ions. In the PLE spectrum, the band detected at 260 nm is attributed to the Mn-O charge transfer (CT) state.<sup>28</sup> For the  $Mn^{2+}:Zn_2SiO_4-Eu^{3+}:Gd_2O_3$  nanocomposites, except for emission from the  $Mn^{2+}$  ions, typical  $Eu^{3+}$  emissions (peaked at 580 nm, 612 nm and 625 nm) ascribed to the  ${}^{5}D_0 \rightarrow {}^{7}F_1, {}^{7}F_2$  transition can also be observed (Fig. 6b). It is noted in the PLE spectra that the band ascribed to Eu-O CT also located at 260 nm is just similar to that of Mn-O CT. In other words, 260 nm light can excite the emissions of both  $Eu^{3+}$  and  $Mn^{2+}$  ions.

As presented by the temperature-dependent PL spectra shown in Fig. 7a, with an increase of temperature from 303 K to 623 K, the  $Mn^{2+}$  emission weakens rapidly, while the  $Eu^{3+}$  emission exhibits only a relatively slight decrease. The remarkable change in the FIR (*i.e.*  $I_{Eu}/I_{Mn}$ , see Fig. 7b) induces the shift of emission color from green to red, as indexed in the inset of Fig. 7a and the Commission International ed'Eclairage (CIE) diagram presented in Fig. 7c. These results imply the  $Mn^{2+}:Zn_2SiO_4-Eu^{3+}:Gd_2O_3$  nanocomposite to be a promising candidate for luminescence thermometric application. And the small size and uniform shape of this material also benefit the spatial resolution in temperature sensing.

#### 3.3. Origination of the temperature-dependent luminescence

To explain the origination of such diverse temperature dependence for  $Mn^{2+}$  and  $Eu^{3+}$  luminescence, the schematic configurational coordinate diagrams for a "strong coupling" system  $(Mn^{2+})$  and a "weak coupling" system  $(Eu^{3+})$  are presented in Fig. 8. Obviously, the thermal quenching dynamics for these two systems are totally different. For the "strong coupling" system, a parabola for the excitation state is not parallel to that for the ground state in the configurational coordinate,<sup>25</sup> as shown in Fig. 8a. Thermal quenching occurs when the electrons populated at the bottom of the excitation state migrate to the intersection between parabolas of the excitation and ground



Fig. 6 (a) Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the  $Mn^{2+}:Zn_2SiO_4$  nanorods; the inset in (a) shows the photograph of the  $Mn^{2+}:Zn_2SiO_4$  nanorods under ultraviolet (255 nm) excitation. (b) PL and PLE spectra of  $Mn^{2+}:Zn_2SiO_4 - Eu^{3+}:Gd_2O_3$  nanocomposites.

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**Fig. 7** (a) Temperature-dependent PL spectra of the  $Mn^{2+}:Zn_2SiO_4-Eu^{3+}:Gd_2O_3$  nanocomposites under 260 nm excitation; insets show the photos of the sample under UV excitation, taken at 303, 423 and 623 K respectively. (b) Plots of intensity *versus* temperature for both  $Mn^{2+}$  and  $Eu^{3+}$  luminescence. (c) CIE (*x*, *y*) coordinate diagram of the emission color at various temperatures.



Fig. 8 Schematic configurational coordinate diagrams for a (a) "strong coupling" system and (b) "weak coupling" system.



Fig. 9 (a) Experimentally measured and eqn (3) fitted plots of FIR ( $I_{Eu}/I_{Mn}$ ) versus temperature. (b) Absolute sensitivity  $S_a$  and relative sensitivity  $S_r$  versus temperature.

states, and then relax there. The relationship between temperature (T) and PL intensity (I) can be expressed as:

$$\frac{I(T)}{I_0} = \frac{1}{1 + A \exp(-\Delta E/kT)} \tag{1}$$

where  $I_0$  is the PL intensity at 0 K, *A* is a pre-exponential constant, *k* is the Boltzmann constant, *T* is the absolute temperature, and  $\Delta E$  is the quenching activate energy representing the distance from the bottom of the excitation state to the intersection between the excitation and ground states.

While for the "weak coupling" system, parabolas for the excitation and ground states are nearly parallel, as shown in Fig. 8a. The thermal quenching process follows the phonon-participant transition from the excitation state to the ground state, which is a typical high order process, and therefore possesses low probability, especially when the energy gap ( $\Delta E$ ) between the excitation and ground states is much high than the phonon energy of the host.<sup>26,27</sup> The relationship between temperature (*T*) and PL intensity (*I*) from this system can be expressed as:

$$\frac{I(T)}{I_0} = \frac{1}{1 + B \left[\frac{1}{1 - \exp(-\hbar\omega/kT)}\right]^P}$$
(2)

where  $I_0$  is the PL intensity at 0 K, k is the Boltzmann constant, T is the absolute temperature,  $\hbar\omega$  is the available phonon energy of the host, P is the number of phonons needed for relaxation from the excitation to the ground state (typically,  $P = \Delta E/\hbar\omega$ ), and B is a parameter related to the radiative transition rate. For the Gd<sub>2</sub>O<sub>3</sub> host, the highest phonon energy is about 600 cm<sup>-1</sup>,<sup>29</sup> much lower than the energy space between  ${}^{5}D_{0}$  and  ${}^{7}F_{6}$  (about 12 200 cm<sup>-1</sup>).<sup>30</sup> This explains the relative obtuseness of Eu<sup>3+</sup> luminescence against increasing temperature, in Mn<sup>2+</sup>:Zn<sub>2</sub>SiO<sub>4</sub>-Eu<sup>3+</sup>:Gd<sub>2</sub>O<sub>3</sub> nanocomposites.

# 3.3. Temperature sensitivities of the $Mn^{2+}:Zn_2SiO_4-Eu^{3+}:Gd_2O_3$ nanocomposites

To further evaluate the temperature sensing performance of  $Mn^{2+}:Zn_2SiO_4-Eu^{3+}:Gd_2O_3$  nanocomposites, the theoretical relationship between temperature and the FIR of  $Mn^{2+}$  to

 $Eu^{3+}$  is deduced from eqn (1) and (2). With reasonable approximation, the equation of FIR *versus T* can be written as:

$$FIR = \frac{I_{Eu}}{I_{Mn}} = \frac{I_{0,Eu}}{I_{0,Mn}} \frac{1 + A \exp(-\Delta E/kT)}{1 + B[1 - \exp(-\hbar\omega/kT)]^{-P}}$$

$$\approx C + D \exp(-E/kT)$$
(3)

where *C*, *D* and *E* are the parameters related to the constants of  $Mn^{2+}$  and  $Eu^{3+}$  ions in  $Mn^{2+}:Zn_2SiO_4-Eu^{3+}:Gd_2O_3$  nanocomposites. A detailed deducing process is presented in the ESI.† The absolute and relative temperature sensitivities, *S*<sub>a</sub> and *S*<sub>r</sub>, can be further derived and expressed using the following equations:

$$S_{\rm a} = \left| \frac{\partial FIR}{\partial T} \right| = D \exp(-E/kT) \times \frac{E}{kT^2}$$
 (4)

$$S_{\rm r} = 100\% \times \left| \frac{1}{\rm FIR} \frac{\partial \rm FIR}{\partial T} \right| = 100\% \times \frac{D \exp(-E/kT)}{C + D \exp(-E/kT)} \times \frac{E}{kT^2}$$
(5)

As displayed in Fig. 9a, the measured plots of FIR *versus* temperature can be fitted well by eqn (3). Herein, parameter *C* is fitted to be a minus, which may be owing to the approximation made in deducing eqn (3). The  $S_a$  and  $S_r$  values then calculated using eqn (4) and (5) are presented in Fig. 9b. Noteworthily, in the room temperature range (303–323 K, *i.e.* 30–50 °C), Mn<sup>2+</sup>:Zn<sub>2</sub>SiO<sub>4</sub>–Eu<sup>3+</sup>:Gd<sub>2</sub>O<sub>3</sub> nanocomposites exhibit remarkably high temperature sensitivities. The values of  $S_r$  in this temperature range are all beyond 2.5% K<sup>-1</sup>, and reach as high as 3.05% K<sup>-1</sup> at 303 K; while the values of  $S_a$  in this temperature range are all beyond 0.0089 K<sup>-1</sup>. This performance is superior to most of the inorganic optical thermometric materials reported before.

#### 4. Conclusions

In this study, a composite for nano-thermometry  $(Mn^{2+}:Zn_2SiO_4 nanorod coated with Eu^{3+}:Gd_2O_3 nanoparticles)$  is constructed following a multi-step solution route. This optical thermometric nanomaterial integrates "strong coupling" activators

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(*i.e.* Mn<sup>2+</sup> ions) and "weak coupling" ones (*i.e.* Eu<sup>3+</sup> ions) within a single nanostructure, therefore exhibits a FIR with remarkable temperature sensitivity. In particular, in the room temperature range,  $S_a$  and  $S_r$  of this nano-thermometry are extremely high ( $S_a = 3.05\% \text{ K}^{-1}$  and  $S_r = 0.0089 \text{ K}^{-1}$  at 303 K), being superior to most of the other inorganic thermometric materials reported before. Possessing small grain size and high sensitivity at room temperature, this material can be regarded as a very promising nano temperature probe.

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### References

- C. D. S. Brites, P. P. Lima, N. J. O. Silva, A. Millan, V. S. Amaral, F. Palacio and L. D. Carlos, *Adv. Mater.*, 2010, 22, 4499–4504.
- 2 L. H. Fischer, G. S. Harms and O. S. Wolfbeis, *Angew. Chem.*, *Int. Ed.*, 2011, **50**, 4546–4551.
- 3 B. Dong, B. S. Cao, Y. Y. He, Z. Liu, Z. P. Li and Z. Q. Feng, *Adv. Mater.*, 2012, 24, 1987–1993.
- 4 X. T. Rao, T. Song, J. K. Gao, Y. J. Cui, Y. Yang, C. D. Wu,
  B. L. Chen and G. D. Qian, *J. Am. Chem. Soc.*, 2013, 135, 15559–15564.
- 5 X. D. Wang, O. S. Wolfbeis and R. J. Meier, *Chem. Soc. Rev.*, 2013, **42**, 7834–7869.
- 6 S. H. Zheng, W. B. Chen, D. Z. Tan, J. J. Zhou, Q. B. Guo,
  W. Jiang, C. Xu, X. F. Liu and J. R. Qiu, *Nanoscale*, 2014, 6, 5675–5679.
- 7 D. Q. Chen, Z. Y. Wan, Y. Zhou, X. Z. Zhou, Y. L. Yu, J. S. Zhong, M. Y. Ding and Z. G. Ji, ACS Appl. Mater. Interfaces, 2015, 7, 19484–19493.
- 8 J. Lee, H. Yang, C. H. Park, H. H. Cho, H. Yun and B. J. Kim, *Chem. Mater.*, 2016, **28**, 3446–3453.
- 9 W. Xu, H. Zhao, Y. X. Li, L. J. Zheng, Z. G. Zhang and W. W. Cao, Sens. Actuators, B, 2013, 188, 1096–1100.
- 10 A. Benayas, B. del Rosal, A. Perez-Delgado, K. Santacruz-Gomez, D. Jaque, G. Alonso Hirata and F. Vetrone, *Adv. Opt. Mater.*, 2015, 3, 687–694.

- 11 F. Huang, Y. Gao, J. C. Zhou, J. Xu and Y. S. Wang, *J. Alloys Compd.*, 2015, **639**, 325–329.
- 12 D. Q. Chen, Z. Y. Wan and S. Liu, *Anal. Chem.*, 2016, 88, 4099-4106.
- 13 D. Jaque and F. Vetrone, Nanoscale, 2012, 4, 4301-4326.
- 14 C. D. S. Brites, P. P. Lima, N. J. O. Silva, A. Millán, V. S. Amaral, F. Palacio and L. D. Carlos, *Nanoscale*, 2012, 4, 4799–4829.
- 15 M. H. Liu, M. Gu, Y. Tian, P. Huang, L. Wang, Q. F. Shi and C. E. Cui, *J. Mater. Chem. C*, 2017, 5, 4025–4033.
- 16 Y. Y. Tian, Y. Tian, P. Huang, L. Wang, Q. F. Shi and C. E. Cui, *Chem. Eng. J.*, 2016, **297**, 26–34.
- 17 Y. Tian, B. N. Tian, C. E. Cui, P. Huang, L. Wang and B. J. Chen, *RSC Adv.*, 2015, 5, 14123–14128.
- 18 W. Xu, Z. G. Zhang and W. W. Cao, Opt. Lett., 2012, 37, 4865-4867.
- 19 X. S. Lian, D. Zhao, Y. J. Cui, Y. Yang and G. D. Qian, *Chem. Commun.*, 2015, 51, 17676–17679.
- 20 S. S. Zhou, X. T. Wei, X. Y. Li, Y. H. Chen, C. K. Duan and M. Yin, *Sens. Actuators, B*, 2017, 246, 352–357.
- 21 W. Tang, S. C. Wang, Z. L. Li, Y. Sun, L. M. Zheng, R. Zhang,
  B. Yang, W. W. Cao and M. Yu, *Appl. Phys. Lett.*, 2016, 108, 061902.
- 22 Y. Gao, F. Huang, H. Lin, J. C. Zhou, J. Xu and Y. S. Wang, A novel optical thermometry strategy based on diverse thermal response from two intervalence charge transfer states, *Adv. Funct. Mater.*, 2016, 26, 3139–3145.
- 23 Y. Gao, F. Huang, H. Lin, J. Xu and Y. S. Wang, Sens. Actuators, B, 2017, 243, 137-143.
- 24 M. K. Kretov, I. M. Iskandarova, B. V. Potapkin, A. V. Scherbinin, A. M. Srivastava and N. F. Stepanov, *J. Lumin.*, 2012, **132**, 2143–2150.
- 25 G. Blasse, Prog. Solid State Chem., 1988, 18, 79.
- 26 S. Shionoya and W. M. Yen, *Phosphor Handbook*, CRC Press, 1998, p. 423.
- 27 G. Blasse and B. Grabmaier, *Luminescent Materials*, Springer-Verlag, Berlin, 1994.
- 28 J. S. An, J. H. Noh, I. S. Cho, H. S. Roh, J. Y. Kim, H. S. Han and K. S. Hong, *J. Phys. Chem. C*, 2010, **114**, 10330–10335.
- 29 H. Guo, N. Dong, M. Yin, W. P. Zhang, L. R. Lou and S. D. Xia, *J. Phys. Chem. B*, 2004, **108**, 19205–19209.
- 30 P. A. Tanner, Y. Y. Yeung and L. X. Ning, J. Phys. Chem. A, 2013, 117, 2771–2781.