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## Dual-emissive $\text{Ln}^{3+}/\text{Mn}^{4+}$ Co-doped double perovskite phosphor *via* site-beneficial occupation†

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The non-contact temperature detectors based on fluorescence intensity ratio (FIR) technology have been widely studied. In the past few decades, researchers have been working on optical temperature measurement *via* FIR technology based on the two thermally-coupled energy levels (TCLs) of rare-earth ions. However, the FIR method based on TCLs has inherent limitations, which hinder further improvement of relative sensitivity ( $S_r$ ). In order to further improve the temperature measurement performance, we have designed a dual-activator luminescence system of  $\text{La}_2\text{LiSbO}_6$  (LLSO) perovskite co-doped with rare-earth ( $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$ ) ions and transition metal ( $\text{Mn}^{4+}$ ) ions according to the site-beneficial occupation principle. LLSO provides suitable occupation sites for  $\text{Tb}^{3+}/\text{Dy}^{3+}$  ions and  $\text{Mn}^{4+}$  ions. The experimental results show that these doped ions can enter the matrix successfully and emit luminescence simultaneously. The emission peaks of  $\text{Tb}^{3+}/\text{Dy}^{3+}$  ions and  $\text{Mn}^{4+}$  ions are well separated, which provides a good signal identification ability for temperature detection. In addition,  $\text{Tb}^{3+}/\text{Dy}^{3+}$  ions and  $\text{Mn}^{4+}$  ions have different sensitivities to the environment due to their different external electronic configurations, which leads to different thermal quenching responses of their fluorescence emission intensity. The decline rate of  $\text{Mn}^{4+}$  ions is much faster than that of  $\text{Tb}^{3+}/\text{Dy}^{3+}$  ions, which is very useful for temperature measurement based on FIR technology. Therefore,  $\text{Tb}^{3+}/\text{Dy}^{3+}$  ions can be used as reference signals, whereas  $\text{Mn}^{4+}$  ions are suitable detection signals. We have investigated the temperature detection performance at different luminescent positions of luminescent ions. The results show that the fluorescence intensity ratio between  $\text{Tb}^{3+}/\text{Dy}^{3+}$  ions and  $\text{Mn}^{4+}$  ions in the materials exhibits excellent temperature sensing performance in the temperature range of 303–523 K. The maximum relative sensitivity and absolute sensitivity of  $\text{Tb}^{3+}$  and  $\text{Mn}^{4+}$  co-doped LLSO phosphors are 0.946%  $\text{K}^{-1}$  and 0.00193  $\text{K}^{-1}$ , respectively; the maximum relative sensitivity and absolute sensitivity of  $\text{Dy}^{3+}$  and  $\text{Mn}^{4+}$  co-doped LLSO phosphors are 0.796%  $\text{K}^{-1}$  and 0.00832  $\text{K}^{-1}$ , respectively, which are much higher than those of some optical thermometric materials reported previously. The self-reference optical temperature measurement method based on double luminescent centers proposed in this paper can provide a new viewpoint for the development of high-performance thermometers.

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## 1. Introduction

So far, luminescent materials constituting of luminescent ions and a host have been widely applied in white light-emitting diodes (W-LEDs), three-dimensional displays, medical equipment, temperature sensing and other fields.<sup>1–9</sup> In recent years, the use of fluorescent materials as optical thermometers has

attracted considerable attention of researchers because of their advantages of non-contact, real-time measurement, high spatial resolution and high accuracy.<sup>10–15</sup> The contactless fluorescent temperature indicators overcome the shortcomings of traditional thermometers and are implemented far and wide in substances with small size or in harsh environment.<sup>16,17</sup>

Generally speaking, the matrix materials for optical temperature measurement include nanorods, nanoparticles, core-shell particles, glass ceramics containing fluorine nanocrystals and oxide blocks.<sup>18–22</sup> This means that the phosphor can be resistant to oxidation and high temperature, and not react in harsh environment and remain stable. Trivalent lanthanide ions and some transition group ions are used as luminescent centers or activators in optical thermometry. Fluorescence temperature

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measurement is realized by monitoring the luminescent signal related to temperature, such as fluorescence intensity, peak position, bandwidth, fluorescence lifetime, and fluorescence intensity ratio (FIR).<sup>23–30</sup> The temperature detection method based on FIR has the advantages of self-reference and is not affected by external factors except temperature; it has superiorities over other temperature measurement methods and has been widely applied. Generally speaking, most optical thermometers using FIR technology are based on two thermally-coupled energy levels (TCLs) of rare-earth ions, such as  $\text{Er}^{3+}$  ( $^2\text{H}_{11/2}$  and  $^4\text{S}_{3/2}$ );  $\text{Nd}^{3+}$  ( $^4\text{F}_{5/2}$  and  $^4\text{F}_{3/2}$ );  $\text{Dy}^{3+}$  ( $^4\text{I}_{5/2}$  and  $^4\text{F}_{9/2}$ ); and  $\text{Eu}^{3+}$  ( $^5\text{D}_1$  and  $^5\text{D}_0$ ).<sup>10,14,31–35</sup> For temperature sensors based on TCLs, FIR obeys the Boltzmann distribution law, so relative sensitivity (Sr) is proportional to the corresponding TCL energy gap. However, the range of TCLs is generally 200–2000  $\text{cm}^{-1}$ , which makes it difficult to further improve Sr. In order to find an efficient FIR method to improve the performance of temperature measurement, the emission of different activation centers must overcome the inherent limitations of the FIR method based on TCLs, and provide a possibility for efficient temperature measurement. One of the emitting centers is used as the temperature probe and the other as the reference center. The emission intensity of activators usually decreases with the increase of temperature, but the quenching degree of different activators varies with temperature, one of which is faster and the other is slower, resulting in a large difference in FIR values between the two activators at different temperatures, so as to improve the temperature measurement performance. Rare-earth (RE) ions are a kind of special optical probes because their 4f active electrons are shielded by external electron sublayers, which makes them less sensitive to the environment, but enough to observe changes.<sup>36</sup> Transition metal (TM) ions have a 3d<sup>n</sup> electronic configuration and are very sensitive to the surrounding environment. Therefore, the emission of TM ions is more affected by temperature than that of RE ions. Therefore, the dependence of TM ions and trivalent RE ions on temperature is different. It is expected that FIR based on TM ions and trivalent RE ions will change greatly with temperature, which should have high temperature sensitivity. In recent years, as a transition metal

activator,  $\text{Mn}^{4+}$  has attracted much attention due to its low cost, deep red emission and wide excitation band.<sup>37–40</sup>

As is known, it is also very important to choose a suitable matrix as the carrier of activators. Not all matrix-doped ions can emit light, but if the matrix provides suitable sites for the doped ions to replace, then they can emit fluorescence. For example, the luminescence and thermometric properties of  $\text{NaLaMgWO}_6:\text{Eu}^{3+},\text{Mn}^{4+}$  phosphors were studied by Zhou *et al.*<sup>41</sup> In the  $\text{NaLaMgWO}_6$  matrix,  $\text{Eu}^{3+}$  ions often replace  $\text{La}^{3+}$  sites. Similarly,  $\text{Mn}^{4+}$  ions are more likely to replace  $\text{W}^{6+}$  ion sites. Double perovskite compounds have attracted much attention due to their high stability and low price.  $\text{La}_2\text{LiSbO}_6$  is a typical perovskite structure, which is composed of  $[\text{LiO}_6]$ ,  $[\text{SbO}_6]$  octahedron and  $[\text{LaO}_8]$  dodecahedron. The crystal structure of the  $\text{La}_2\text{LiSbO}_6$  compound was first reported by López *et al.* in 1990.<sup>42</sup> Its structure is monoclinic  $\text{GdFeO}_3$  type perovskite. A large number of octahedral sites in  $\text{La}_2\text{LiSbO}_6$  (LLSO) are favorable for  $\text{Mn}^{4+}$  ions to enter the structure and promote luminescence. In this work, novel  $\text{LLSO}:\text{Tb}^{3+},\text{Mn}^{4+}$  and  $\text{LLSO}:\text{Dy}^{3+},\text{Mn}^{4+}$  phosphors with strong efficient dual-activator luminescence are devised and synthesized by a high-temperature solid-state method. LLSO host provides favorable site occupation for  $\text{Mn}^{4+}$  and  $\text{Tb}^{3+}/\text{Dy}^{3+}$ , specifically  $\text{Mn}^{4+}$  occupies the Sb site and  $\text{Tb}^{3+}/\text{Dy}^{3+}$  occupies the La site, and makes them emit fluorescence. The luminescence properties and temperature dependence of these phosphors were tested and analyzed in detail, which showed their application prospects in optical temperature sensors.

## 2. Experimental section

### 2.1 Synthesis of samples

$\text{LLSO}:0.005\text{Mn}^{4+}$ ,  $\text{LLSO}:0.09\text{Tb}^{3+}, 0.005\text{Mn}^{4+}$  and  $\text{LLSO}:0.09\text{Dy}^{3+}, 0.005\text{Mn}^{4+}$  (the unit is mol%) phosphors and LLSO host were successfully synthesized *via* a high-temperature solid-state method.  $\text{La}_2\text{O}_3$  (A.R.),  $\text{Li}_2\text{CO}_3$  (A.R.),  $\text{Sb}_2\text{O}_3$  (A.R.),  $\text{MnCO}_3$  (A.R.),  $\text{Dy}_2\text{O}_3$  ( $\geq 99.9\%$ ),  $\text{Tb}_4\text{O}_7$  (99.99%) as raw materials were weighed according to the stoichiometric ratio, in which  $\text{Li}_2\text{CO}_3$  was over



**Fig. 1** (A) XRD patterns of  $\text{LLSO}: 0.005\text{Mn}^{4+}$ ;  $\text{LLSO}: 0.09\text{Tb}^{3+}, 0.005\text{Mn}^{4+}$ ;  $\text{LLSO}: 0.09\text{Dy}^{3+}, 0.005\text{Mn}^{4+}$  and  $\text{LLSO}$  host. (B) Crystal structure schematic diagram of  $\text{La}_2\text{LiSbO}_6$ .



3%. The raw materials were mixed and ground thoroughly in an agate mortar for 30 min. After full grinding, the mixed powder was transferred into an alumina crucible and calcined in air at 1200 °C for 2 h. After cooling to room temperature, the intermediate was taken out and ground into powder, and then returned to the crucible for repeated calcination. After cooling again, the product was ground into powder and put into a sample tube for testing.

## 2.2 Measurement and characterization

X-ray powder diffraction (XRD) of the samples was performed using an X-ray diffractometer (Bruker D8) containing Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) with the operating conditions of 40 kV and 15 mA, and the XRD patterns were collected in the range of  $10^\circ$ – $80^\circ$  with the scanning steps of 0.02. The photoluminescence excitation (PLE) and emission (PL) spectra of samples were measured using a Hitachi F-7000 fluorescence spectrometer at room temperature with a 150 W xenon lamp as the excitation source. The quantum yields and decay curves of the samples were measured by an Edinburgh FS5 spectrophotometer; temperature-dependent photoluminescence (PL) characteristics were monitored *via* this spectrophotometer combined with a heating device (TAP 02).

## 3. Results and discussion

### 3.1 Crystal structure

The crystal structures of Mn<sup>4+</sup> doped LLSO phosphors, Tb<sup>3+</sup>/Mn<sup>4+</sup> and Dy<sup>3+</sup>/Mn<sup>4+</sup> co-doped LLSO phosphors as well as undoped samples were identified from the XRD patterns, as shown in Fig. 1(A). The diffraction peaks of the LLSO host match well with the standard card of LLSO (PDF#81-0839), indicating that the host has been successfully prepared. The XRD diffraction peaks of single doped and co-doped samples are consistent with those of LLSO, which proves that the introduction of Mn<sup>4+</sup>, Tb<sup>3+</sup>/Mn<sup>4+</sup> or Dy<sup>3+</sup>/Mn<sup>4+</sup> do not produce any impurity phase and cannot change the crystal structure. This indicates that these dopants are successfully incorporated into the LLSO host. Fig. 1(B) presents the crystal structure of the LLSO matrix. It is clearly seen that [LiO<sub>6</sub>] and [SbO<sub>6</sub>] connect with each other alternately through a common site to form octahedral chains, which is conducive to the entry of Mn<sup>4+</sup> ions into its structure and promotes the luminescence of Mn<sup>4+</sup> ions. La<sup>3+</sup> ions occupy the eight-coordination sites. Considering the probable mechanism of effective ionic radii and coordination number (CN) of Mn<sup>4+</sup> ion (0.53 Å, CN = 6) and Sb<sup>5+</sup> (0.60 Å, CN = 6), it is easier for the Mn<sup>4+</sup> activator to enter the Sb<sup>5+</sup> locus. Similarly, Tb<sup>3+</sup>/Dy<sup>3+</sup> ions prefer to replace the La<sup>3+</sup> locus, which can be proved by calculating the value of the radius difference percentage ( $D_r$ ), which is reported by Davolos<sup>43</sup> and needs to be within 30%. The  $D_r$  values can be calculated using the equation:

$$D_r = \frac{R_m(\text{CN}) - R_d(\text{CN})}{R_m(\text{CN})} \times 100\% \quad (1)$$

where  $R_m$  and  $R_d$  are the radii of matrix cations and doped cations, respectively. CN is the coordination number. The  $D_r$  values between matrix cations and doped cations are listed in

Table 1 The  $D_r$  values between matrix cations and doped cations

| Matrix cations (CN)  | Doped cations (CN)   | $R_m/\text{\AA}$ | $R_d/\text{\AA}$ | $D_r/\%$ |
|----------------------|----------------------|------------------|------------------|----------|
| Li <sup>+</sup> (6)  | Mn <sup>4+</sup> (6) | 0.76             | 0.530            | 30.26    |
| Sb <sup>5+</sup> (6) | Mn <sup>4+</sup> (6) | 0.60             | 0.530            | 11.67    |
| Li <sup>+</sup> (6)  | Tb <sup>3+</sup> (6) | 0.76             | 0.923            | -21.45   |
| La <sup>3+</sup> (8) | Tb <sup>3+</sup> (8) | 1.160            | 1.040            | 10.34    |
| Sb <sup>5+</sup> (6) | Tb <sup>3+</sup> (6) | 0.60             | 0.923            | -53.83   |
| Li <sup>+</sup> (6)  | Dy <sup>3+</sup> (6) | 0.76             | 0.912            | -20      |
| La <sup>3+</sup> (8) | Dy <sup>3+</sup> (8) | 1.160            | 1.027            | 11.47    |
| Sb <sup>5+</sup> (6) | Dy <sup>3+</sup> (6) | 0.60             | 0.912            | -52      |

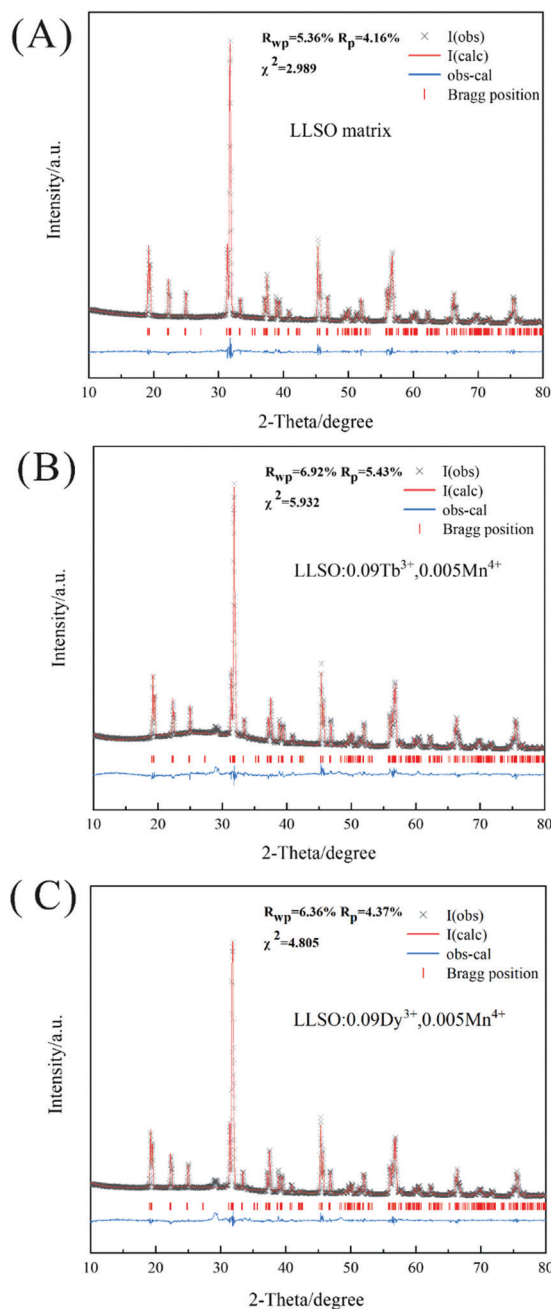


Fig. 2 Rietveld refinement patterns for X-ray diffraction patterns of (A) LLSO matrix; (B) LLSO: 0.09Tb<sup>3+</sup>, 0.005Mn<sup>4+</sup> and (C) LLSO: 0.09Dy<sup>3+</sup>, 0.005Mn<sup>4+</sup>.



**Table 2** The relevant Rietveld refinement parameters and crystallographic data

| Parameter                  | LLSO matrix                  | LLSO:0.09Tb <sup>3+</sup> , 0.005Mn <sup>4+</sup> | LLSO:0.09Dy <sup>3+</sup> , 0.005Mn <sup>4+</sup> |
|----------------------------|------------------------------|---|---|
| space group                | <i>P2<sub>1</sub>/n</i> (14) | <i>P2<sub>1</sub>/n</i> (14)                      | <i>P2<sub>1</sub>/n</i> (14)                      |
| <i>a</i> (Å)               | 5.6195                       | 5.6134  | 5.6137  |
| <i>b</i> (Å)               | 5.7236                       | 5.7278  | 5.7259  |
| <i>c</i> (Å)               | 7.9670                       | 7.9607  | 7.9605  |
| $\alpha = \gamma$ (deg)    | 90.000                       | 90.000  | 90.000  |
| $\beta$ (deg)              | 89.776                       | 89.742  | 89.745  |
| <i>V</i> (Å <sup>3</sup> ) | 256.247                      | 255.953   | 255.876   |
| Units, <i>Z</i>            | 2                            | 2   | 2   |
| <i>R<sub>p</sub></i> (%)   | 4.16                         | 5.43  | 4.37  |
| <i>R<sub>wp</sub></i> (%)  | 5.36                         | 6.92  | 6.36  |
| $\chi^2$                   | 2.989                        | 5.932   | 4.805   |

Table 1. It can be clearly seen that Mn<sup>4+</sup> ions will replace Sb<sup>5+</sup> sites in the matrix, and Tb<sup>3+</sup>/Dy<sup>3+</sup> ions can be doped into La<sup>3+</sup> sites.

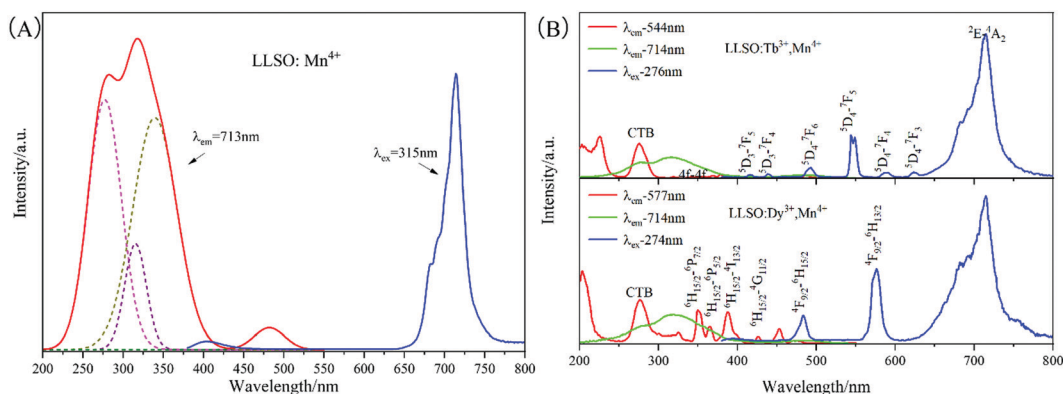
Fig. S1 (ESI<sup>†</sup>) shows the SEM images of each sample. It is not difficult to see that the samples exhibit irregular particle sizes in the range of 1–3 μm. In order to further confirm the structure of the synthesized samples, the standard data of LLSO were used as a reference, and Rietveld refinement of the existing samples was performed using GASA software. The final refinement mode is shown in Fig. 2, and the relevant refining parameters and crystallographic data are summarized in Table 2. The obtained final refinement parameters (*R<sub>wp</sub>*, *R<sub>p</sub>* and  $\chi$ ) show that the actual structure is in good agreement with the initial structure. The *V* values of the co-doped samples decreased because Tb<sup>3+</sup> (1.040 Å, CN = 8)/Dy<sup>3+</sup> (1.027 Å, CN = 8) and Mn<sup>4+</sup> (0.530 Å, CN = 6) replaced La<sup>3+</sup> (1.160 Å, CN = 8) and Sb<sup>5+</sup> (0.60 Å, CN = 6) sites, respectively, in the crystal lattice.

### 3.2 Fluorescence properties and optical thermometry

Fig. 3 shows the PL and PLE spectra of Mn<sup>4+</sup> single-doped LLSO and Dy<sup>3+</sup>/Tb<sup>3+</sup>, Mn<sup>4+</sup> co-doped LLSO phosphors at room temperature. The excitation peaks in the range of 260–280 nm are due to the charge transfer of electrons from the oxygen ligands to the central metal atom. As shown in Fig. 3(A), the PL spectrum with 315 nm excitation wavelength presents an

emission band centered at 713 nm, which originates from the spin-forbidden <sup>2</sup>E → <sup>4</sup>A<sub>2</sub> transition of the Mn<sup>4+</sup> ion. The PLE spectrum of Mn<sup>4+</sup> monitored at 713 nm shows a wide hump in the range of 250–400 nm, three peaks centered at 276 nm, 319 nm and 354 nm were fitted by Gaussian peak splitting, and are due to the charge transfer (CT) from O<sup>2-</sup> to Mn<sup>4+</sup>, <sup>4</sup>A<sub>2</sub> → <sup>4</sup>T<sub>1</sub> and <sup>4</sup>A<sub>2</sub> → <sup>2</sup>T<sub>2</sub> spin-allowed transitions of Mn<sup>4+</sup>, respectively. The excitation peak at 480 nm corresponds to the Mn<sup>4+</sup>: <sup>4</sup>A<sub>2</sub> → <sup>4</sup>T<sub>2</sub> spin-forbidden transitions. Fig. 3[(B)a] illustrates the PLE spectrum of Tb<sup>3+</sup> and Mn<sup>4+</sup> ions co-doped LLSO phosphor, which was monitored at 544 nm. It consists of a broad band centered at 276 nm that is attributed to the charge transfer (CT) from O<sup>2-</sup> to Tb<sup>3+</sup> and the peaks between 300–385 nm are attributed to 4f → 4f transitions of Tb<sup>3+</sup>. Under 276 nm excitation, the emission spectrum of LLSO:Tb<sup>3+</sup>,Mn<sup>4+</sup> phosphor shows a series of sharp peaks at 492 nm, 544 nm, 591 nm and 624 nm as emission centers, which are <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>*J*</sub> (*J* = 6, 5, 4, and 3) transitions. In addition, two weak emission peaks at 416 nm and 439 nm are due to <sup>5</sup>D<sub>3</sub> → <sup>7</sup>F<sub>5</sub> and <sup>5</sup>D<sub>3</sub> → <sup>7</sup>F<sub>4</sub> transitions, respectively. As depicted in Fig. 3[(B)b], the PLE spectrum of LLSO:Dy<sup>3+</sup>,Mn<sup>4+</sup> phosphor, monitored at 577 nm emission wavelength displays several excitation bands centered at 350 nm, 365 nm, 388 nm and 427 nm attributed to <sup>6</sup>H<sub>15/2</sub> → <sup>6</sup>P<sub>7/2</sub>, <sup>6</sup>H<sub>15/2</sub> → <sup>6</sup>P<sub>5/2</sub>, <sup>6</sup>H<sub>15/2</sub> → <sup>4</sup>I<sub>13/2</sub>, and <sup>6</sup>H<sub>15/2</sub> → <sup>4</sup>G<sub>11/2</sub> transitions, respectively. The PL spectrum under 274 nm excitation exhibits two characteristic emission peaks at 484 nm and 576 nm that are attributed to <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2</sub> and <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub> transitions, respectively. In the PL and PLE spectra of the co-doped phosphors, the characteristic peaks of Mn<sup>4+</sup> ions are clearly presented. We measured the quantum yields of the double-doped samples. The quantum yield of LLSO:0.09Tb<sup>3+</sup>,0.005Mn<sup>4+</sup> phosphor was up to 45.95%, while the quantum yield of LLSO:0.09Dy<sup>3+</sup>,0.005Mn<sup>4+</sup> phosphor was 23.42%.

In order to further study whether there is energy transfer between Ln<sup>3+</sup> and Mn<sup>4+</sup>, we analyzed the decay curves of samples with different concentrations, as shown in Fig. S2 (ESI<sup>†</sup>). It can be seen that with the increase of Tb<sup>3+</sup> concentration, the lifetime of Mn<sup>4+</sup> does not increase obviously, so there is no energy transfer from Tb<sup>3+</sup> to Mn<sup>4+</sup>. However, with the increase of Dy<sup>3+</sup> concentration, the lifetime of Mn<sup>4+</sup> decreases, so there is no energy transfer from Dy<sup>3+</sup> to Mn<sup>4+</sup> as



**Fig. 3** The PL and PLE spectra of (A) LLSO: 0.005Mn<sup>4+</sup>; (B) LLSO: 0.09Tb<sup>3+</sup>, 0.005Mn<sup>4+</sup> and LLSO: 0.09Dy<sup>3+</sup>, 0.005Mn<sup>4+</sup>.





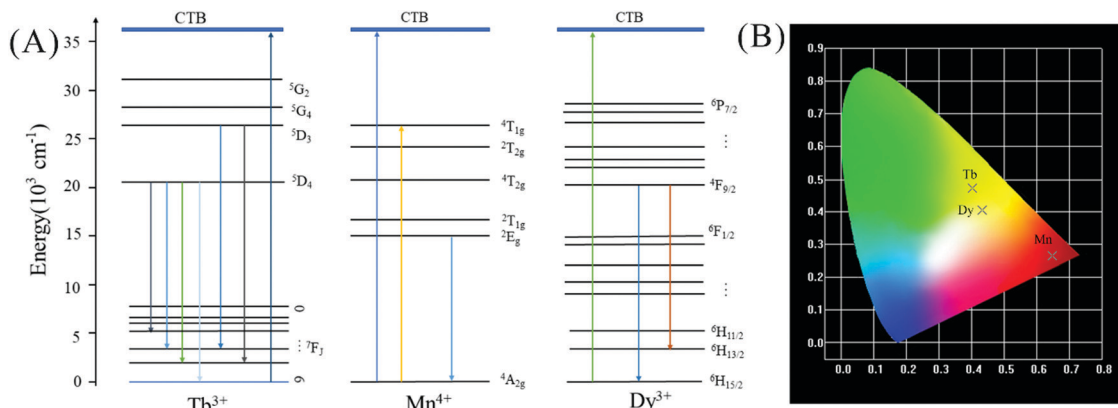


Fig. 4 (A) The light-emitting mechanism of  $La_2LiSbO_6: Tb^{3+}/Dy^{3+}, Mn^{4+}$ . (B) CIE(x, y) coordinate diagram of  $LLSO: 0.005Mn^{4+}$ ;  $LLSO: 0.09Tb^{3+}, 0.005Mn^{4+}$  and  $LLSO: 0.09Dy^{3+}, 0.005Mn^{4+}$ .

well. On the basis of the excitation and emission spectra received, we conjecture that the possible luminescence mechanism for  $Tb^{3+}/Dy^{3+}$  ions and  $Mn^{4+}$  ions co-doped LLSO phosphors is shown in Fig. 4(A). Under the excitation of 276 nm or 274 nm, the electrons of  $Mn^{4+}$  immediately absorb energy, which is pumped from the ground state to the excited state, and then they relax to the low phonon energy  $^2E_g$  state through non-radiative relaxation. Ultimately, they return to the ground state and emit red light through radiative transitions. In the meantime,  $Tb^{3+}$  and  $Dy^{3+}$  ions are excited from the ground state to a higher excited state. Then, they are relaxed to the lower

excited state through a nonradiative transition. Finally, they return to the ground state by releasing the observed photon radiation. CIE coordinates of these phosphors are shown in Fig. 4(B); the CIE coordinates of  $LLSO:0.005Mn^{4+}$  phosphor are (0.6481, 0.2653) in the dark red region, and the CIE coordinates of  $LLSO:0.09Tb^{3+}/0.09Dy^{3+}, 0.005Mn^{4+}$  phosphors are (0.4018, 0.4721) and (0.4319, 0.4052) in the yellow-green region and light yellow region, respectively.

According to the PLE spectra of  $Tb^{3+}/Dy^{3+}, Mn^{4+}$  co-doped LLSO phosphors, we probed the emission spectra at different excitation wavelengths, as shown in Fig. 5(A) and (B). As can be

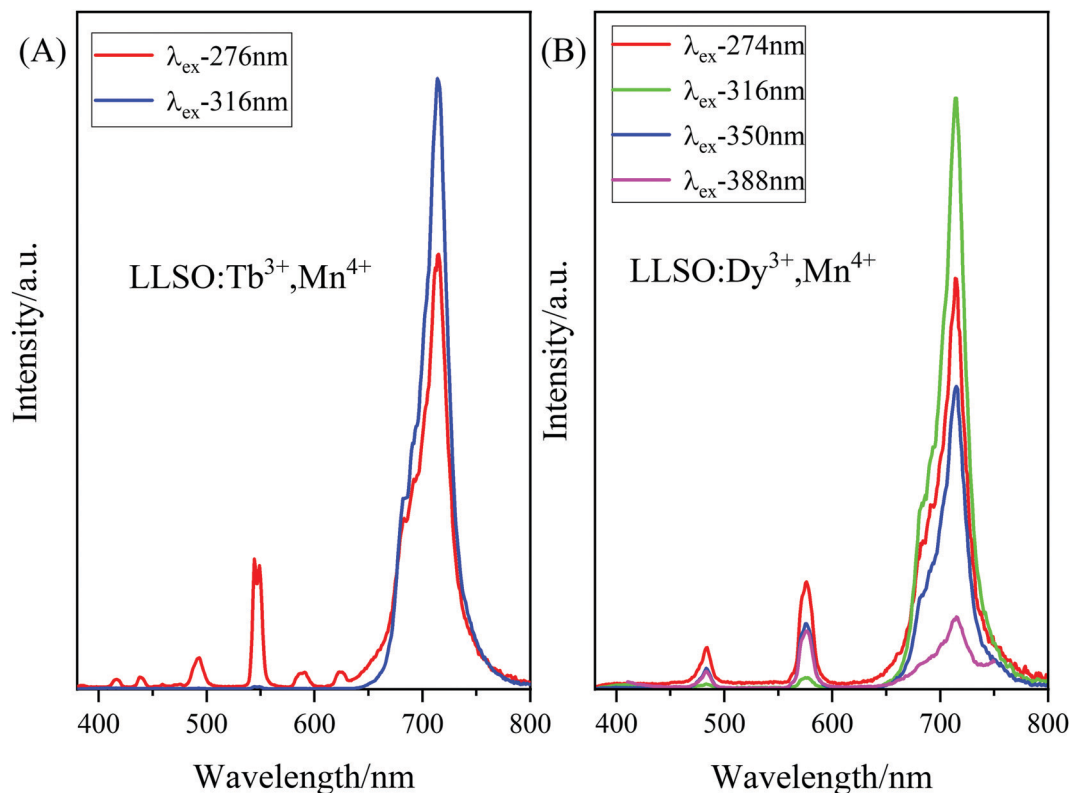


Fig. 5 The PL spectra of (A)  $La_2LiSbO_6: 0.09Tb^{3+}, 0.005Mn^{4+}$  and (B)  $LLSO: 0.09Dy^{3+}, 0.005Mn^{4+}$  excited at different wavelength.



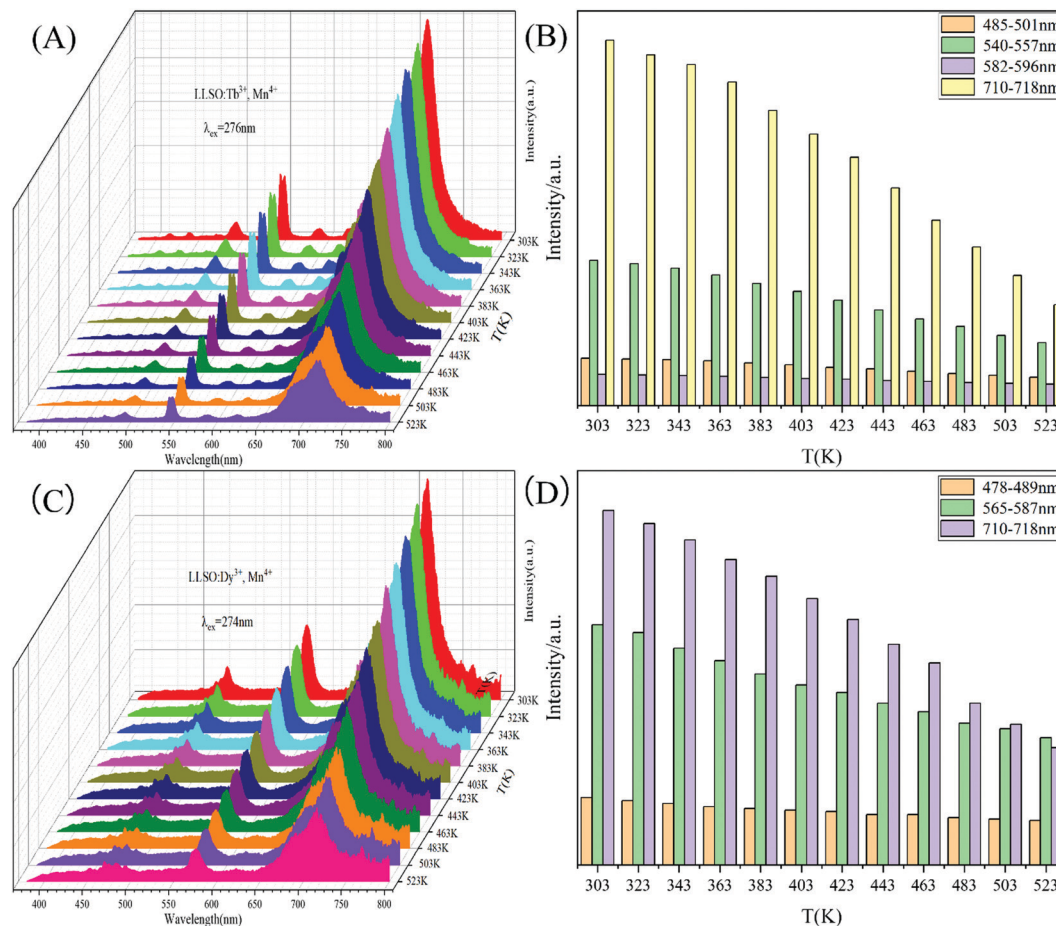


Fig. 6 The temperature-dependent PL spectra of (A)  $\text{La}_2\text{LiSbO}_6: 0.09\text{Tb}^{3+}, 0.005\text{Mn}^{4+}$  and (C)  $\text{LLSO}: 0.09\text{Dy}^{3+}, 0.005\text{Mn}^{4+}$ . (B), (D) The PL emission intensity of different band at various temperature.

seen from Fig. 5(A), the emission spectra of the  $\text{LLSO}:\text{Tb}^{3+}, \text{Mn}^{4+}$  phosphor excited at 276 nm show the appearance of characteristic peaks of  $\text{Tb}^{3+}$  and  $\text{Mn}^{4+}$  ions, and the luminescence intensity was high. Similarly, as shown in Fig. 5(B), the emission spectra of the  $\text{LLSO}:\text{Dy}^{3+}, \text{Mn}^{4+}$  phosphor excited at 274 nm show the

characteristic peaks of  $\text{Dy}^{3+}$  and  $\text{Mn}^{4+}$  ions, and the luminescence intensity was high. Therefore, we chose 276 nm and 274 nm as the excitation wavelengths for the  $\text{Tb}^{3+}/\text{Dy}^{3+}, \text{Mn}^{4+}$  co-doped phosphors to test the emission spectra at different temperatures.

In order to further explore the temperature-dependent properties of phosphors, PL spectra of  $\text{LLSO}:0.09\text{Tb}^{3+}/0.09\text{Dy}^{3+}, 0.005\text{Mn}^{4+}$  phosphors were monitored in the temperature range of 303–523 K, as shown in Fig. 6(A) and (C), respectively. With the increase of temperature, the luminescence intensity of  $\text{Tb}^{3+}/\text{Dy}^{3+}$  and  $\text{Mn}^{4+}$  decreases, which is caused by heat quenching. The corresponding CIE colorimetric diagrams based on PL spectra at different temperatures are shown in Fig. S3 in the ESI.† As the temperature was increased from 303 to 523 K, a significant change in FIR ( $I_{\text{Tb}}/I_{\text{Mn}}$ ) caused the transition of the chromaticity coordinates (0.3754, 0.4272) to (0.3494, 0.3898). Similarly, a significant change in FIR ( $I_{\text{Dy}}/I_{\text{Mn}}$ ) caused the transition of the chromaticity coordinates (0.3826, 0.3715) to (0.3479, 0.3514). We integrated the intensities of the characteristic peaks of each ion by area integral, and their column graphs are shown in Fig. 6(B) and (D). Obviously, the luminescence intensity of  $\text{Mn}^{4+}$  ions decreases much faster, which is due to the unique  $3d^3$  electron configuration of  $\text{Mn}^{4+}$  ions and is very sensitive to the external environment, resulting in stronger

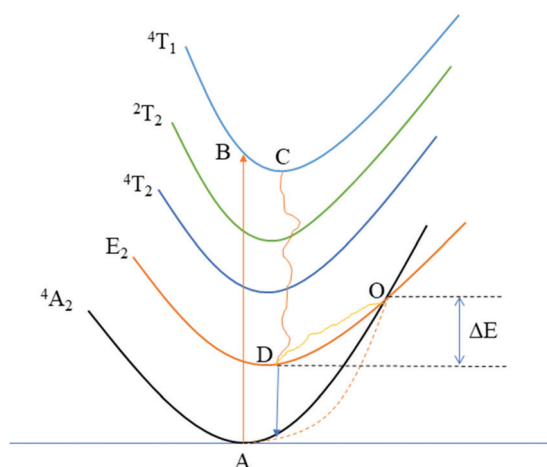


Fig. 7 Configurational coordinate diagrams of  $\text{Mn}^{4+}$  ions.



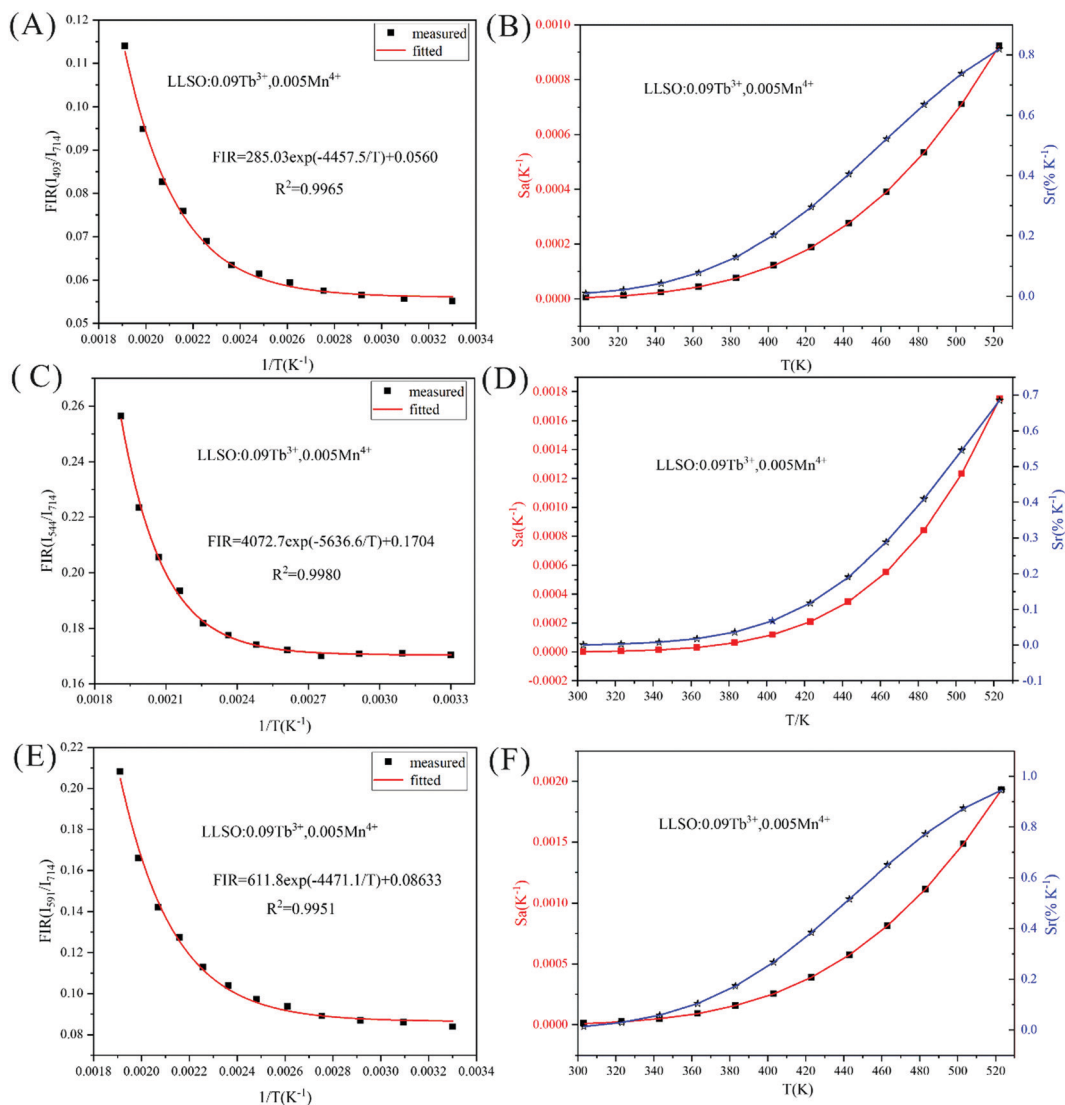


Fig. 8 FIR values,  $S_r$  and  $S_a$  values of  $\text{La}_2\text{LiSbO}_6:0.09\text{Tb}^{3+},0.005\text{Mn}^{4+}$  at different temperatures.

electron-phonon coupling and more intense heat quenching. Fig. 7 is the configuration coordinate diagram of  $\text{Mn}^{4+}$  in the LLSO host, which shows the possible thermal quenching mechanism of  $\text{Mn}^{4+}$ . As shown in Fig. 7,  $\text{Mn}^{4+}$  ions are first excited from the  ${}^4\text{A}_2$  state to the B point of the  ${}^4\text{T}_{1g}$  state, and relaxed to the bottom C point of the excited state after losing partial energy, which is due to the instability of  $\text{Mn}^{4+}$  ions at point B. Then it is relaxed to the E state through a nonradiative process, and then, by emitting red light (releasing photons) back to the ground state. However, with the increase in temperature, an increasing number of electrons in the  ${}^2\text{E}$  state gain energy and get thermally excited, which makes them more willing to reach the intersection point of  ${}^4\text{A}_2$  and  ${}^2\text{E}$  and then return to the ground state by radiation. The energy absorbed in this process is usually referred to as the activation energy of thermal quenching ( $\Delta E$ ). According to eqn (2), the  $\Delta E$  values of  $\text{Tb}^{3+}$  ion and  $\text{Mn}^{4+}$  ion are 0.364 eV and 0.255 eV,

respectively; the  $\Delta E$  values of  $\text{Dy}^{3+}$  ion and  $\text{Mn}^{4+}$  ion are 0.330 eV and 0.256 eV, respectively. This is the reason why the thermal quenching of  $\text{Mn}^{4+}$  ion emission is faster than that of  $\text{Tb}^{3+}/\text{Dy}^{3+}$  ions. This is very useful for temperature measurement based on FIR technology.

In order to explore the sensitivity of the co-doped phosphors, eqn (2) can be used to express the temperature dependence of the emission intensity according to Boltzmann distribution and thermal quenching mechanism.<sup>44,45</sup>

$$I(T) = \frac{I_0}{1 + A \exp(-\Delta E/k_B T)} \quad (2)$$

where  $I_0$  is the emission intensity at the initial temperature (303 K in this work),  $I(T)$  refers to the emission intensity at temperature  $T$  (unit is K),  $A$  is a constant,  $\Delta E$  is the activation energy of heat quenching, and  $k_B$  corresponds to the Boltzmann constant ( $k_B = 8.629 \times 10^{-5}$  eV  $\text{K}^{-1}$ ). Considering a



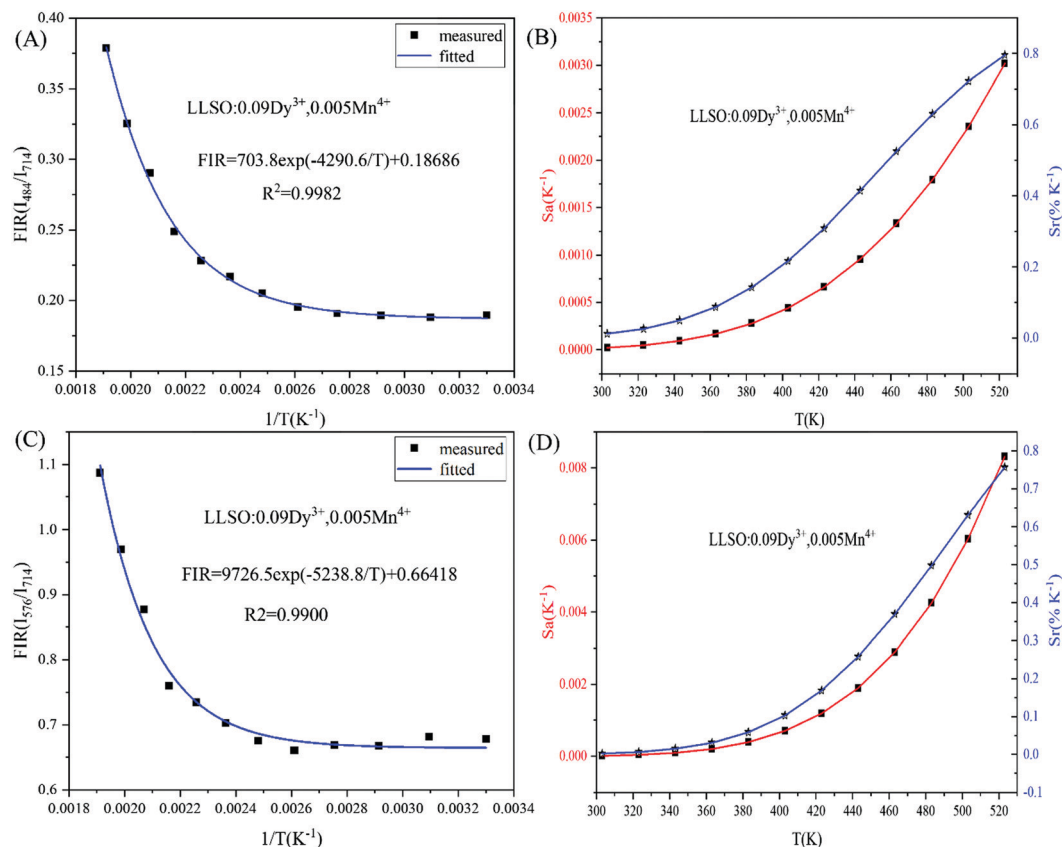


Fig. 9 FIR values,  $S_r$  and  $S_a$  values of  $\text{La}_2\text{LiSbO}_6:0.09\text{Dy}^{3+},0.005\text{Mn}^{4+}$  at different temperatures.

reasonable approximation, the temperature-dependent FIR of  $\text{Tb}^{3+}/\text{Dy}^{3+}$  and  $\text{Mn}^{4+}$  can be expressed as:

$$\text{FIR} = \frac{I_{\text{RE}}}{I_{\text{Mn}}} = \frac{I_{0,\text{RE}}}{I_{0,\text{Mn}}} \frac{1 + A_{\text{Mn}} \times \exp(-\Delta E_{\text{Mn}}/k_{\text{B}}T)}{1 + A_{\text{RE}} \times \exp(-\Delta E_{\text{RE}}/k_{\text{B}}T)} \approx B + C \times \exp(-E/k_{\text{B}}T) \quad (3)$$

where  $B$  and  $C$  are constants,  $E$  refers to the modified thermal quenching activation energy for the  $\text{RE}^{3+}/\text{Mn}^{4+}$  dual-emitting system. The FIR values between  $\text{Tb}^{3+}$  and  $\text{Mn}^{4+}$  with different luminescence centers at different temperatures are shown in Fig. 8, and the FIR values between  $\text{Dy}^{3+}$  and  $\text{Mn}^{4+}$  with different luminescence centers at different temperatures are shown in Fig. 9. We use exponential fitting for these values, and the fitting relationship and fitting degree are presented in the figure. It can be seen from the figure that the exponential relationship between FIR and  $1/T$  fits very well. For temperature

sensing, sensitivity is a very important parameter to evaluate the performance of the temperature sensor. Absolute sensitivity  $S_a$  and relative sensitivity  $S_r$  can be defined as:

$$S_a = \left| \frac{d(\text{FIR})}{d(T)} \right| = C \exp(-E/k_{\text{B}}T) \times \frac{E}{k_{\text{B}}T^2} \quad (4)$$

$$S_r = \left| \frac{1}{\text{FIR}} \times \frac{d(\text{FIR})}{d(T)} \right| \times 100\% = \frac{C \exp(-E/k_{\text{B}}T)}{B + C \exp(-E/k_{\text{B}}T)} \times \frac{E}{k_{\text{B}}T^2} \times 100\% \quad (5)$$

Table 3 The maximum  $S_a$  and  $S_r$  values of  $\text{La}_2\text{LiSbO}_6:0.09\text{Tb}^{3+}/\text{Dy}^{3+},0.005\text{Mn}^{4+}$  at different luminous centers

| Doped ions                      | Luminous centers (nm) | Maximum $S_a$ ( $\text{K}^{-1}$ ) | Maximum $S_r$ (% $\text{K}^{-1}$ ) |
|---------------------------------|-----------------------|-----------------------------------|------------------------------------|
| $\text{Tb}^{3+}/\text{Mn}^{4+}$ | 493/714               | 0.000924                          | 0.820                              |
| $\text{Tb}^{3+}/\text{Mn}^{4+}$ | 544/714               | 0.00175                           | 0.686                              |
| $\text{Tb}^{3+}/\text{Mn}^{4+}$ | 591/714               | 0.00193                           | 0.946                              |
| $\text{Dy}^{3+}/\text{Mn}^{4+}$ | 484/714               | 0.00302                           | 0.796                              |
| $\text{Dy}^{3+}/\text{Mn}^{4+}$ | 576/714               | 0.00832                           | 0.757                              |

The values of  $S_a$  and  $S_r$  are calculated and shown in Fig. 8. The maximum values of  $S_a$  and  $S_r$  of different luminescent centers are shown in Table 3. Similarly, FIR values between  $\text{Dy}^{3+}$  and  $\text{Mn}^{4+}$  ions and corresponding  $S_a$  and  $S_r$  values of different luminous centers at different temperatures are shown in Fig. 9, and their maximum  $S_a$  and  $S_r$  values are shown in Table 3. Obviously, with the increase of temperature, the relative temperature sensitivity and absolute temperature sensitivity are gradually improved, reaching the maximum at 523 K. The maximum  $S_a$  and  $S_r$  of  $\text{Tb}^{3+}, \text{Mn}^{4+}$  co-doped LLSO phosphor appeared in the 591 nm/714 nm luminescence centers, which were  $0.00193 \text{ K}^{-1}$  and  $0.946\% \text{ K}^{-1}$ , respectively. The maximum  $S_a$  and  $S_r$  of  $\text{Dy}^{3+}, \text{Mn}^{4+}$  co-doped LLSO phosphor appeared in the 576 nm/714 nm luminescence centers, which were  $0.00302 \text{ K}^{-1}$





Table 4 Temperature sensing performances of several typical temperature sensors

| Hosts  | Doped ions                          | Temperature range (K) | Excitation wavelength (nm) | $S_r$ (%K <sup>-1</sup> ) | $S_a$ (K <sup>-1</sup> ) | Ref.      |
|--|-------------------------------------|-----------------------|----------------------------|---------------------------|--------------------------|-----------|
| LaOBr  | Ce <sup>3+</sup> , Tb <sup>3+</sup> | 293–433               | 350                        | 0.42                      | —                        | 46        |
| LiNbO <sub>3</sub>   | Yb <sup>3+</sup> , Tm <sup>3+</sup> | 323–773               | 980                        | 0.7                       | 0.0088                   | 47        |
| Sr <sub>3</sub> GdNa(PO <sub>4</sub> ) <sub>3</sub> F            | Tb <sup>3+</sup> , Eu <sup>3+</sup> | 303–483               | 275                        | 0.16                      | 0.00234                  | 48        |
| K <sub>3</sub> LuF <sub>6</sub>                                  | Yb <sup>3+</sup> , Er <sup>3+</sup> | 300–773               | 980                        | 0.376                     | —                        | 49        |
| Na <sub>3</sub> Sc <sub>2</sub> P <sub>3</sub> O <sub>12</sub>   | Eu <sup>2+</sup> , Mn <sup>2+</sup> | 293–473               | 340                        | 1.556                     | —                        | 50        |
| SrY <sub>2</sub> O <sub>4</sub>                                  | Bi <sup>3+</sup> , Eu <sup>3+</sup> | 313–563               | 330                        | 0.86                      | 0.0433                   | 51        |
| Ca <sub>2</sub> YZr <sub>2</sub> Al <sub>3</sub> O <sub>12</sub> | Bi <sup>3+</sup> , Eu <sup>3+</sup> | 297–573               | 278                        | 0.66                      | 0.00826                  | 52        |
| BaLaMgNbO <sub>6</sub>   | Dy <sup>3+</sup> , Mn <sup>4+</sup> | 230–470               | 355                        | 1.82                      | —                        | 53        |
| Lu <sub>3</sub> Al <sub>5</sub> O <sub>12</sub>                  | Tb <sup>3+</sup> , Mn <sup>4+</sup> | 270–420               | 355                        | 2.8                       | 0.043                    | 54        |
| Ca <sub>2</sub> LaNbO <sub>6</sub>                               | Eu <sup>3+</sup> , Mn <sup>4+</sup> | 298–498               | 396                        | 1.51                      | 0.0399                   | 55        |
| NaLaMgWO <sub>6</sub>  | Eu <sup>3+</sup> , Mn <sup>4+</sup> | 303–523               | 320                        | 0.86                      | 0.0302                   | 41        |
| La <sub>2</sub> LiSbO <sub>6</sub>                               | Tb <sup>3+</sup> , Mn <sup>4+</sup> | 303–523               | 276                        | 0.946                     | 0.00193                  | This work |
| La <sub>2</sub> LiSbO <sub>6</sub>                               | Dy <sup>3+</sup> , Mn <sup>4+</sup> | 303–523               | 274                        | 0.796                     | 0.00302                  | This work |

and 0.796% K<sup>-1</sup>, respectively. The energy difference between Tb<sup>3+</sup> (591 nm)/Dy<sup>3+</sup> (576 nm) ions and Mn<sup>4+</sup> (714 nm) ions is about 2900 cm<sup>-1</sup> and 3400 cm<sup>-1</sup>, which is much larger than the traditional TCLs of rare-earth ions. This indicates that the  $S_r$  of the phosphors with double luminescent centers is higher than that of the phosphors based on TCLs, which is traceable. These  $S_r$  and  $S_a$  are comparable to many other typical co-doped systems listed in Table 4. In addition, temperature resolution ( $\delta T$ ) is also an important index to reflect the temperature measurement performance of thermometers, which can be defined as:

$$\delta T = \frac{1}{S_r} \times \frac{\partial \Delta}{\Delta} \quad (6)$$

where  $\partial \Delta / \Delta$  represents the relative error and its value is about 0.5% in temperature measurement by FIR technology. Because of their excellent relative sensitivity, the minimum resolutions of LLSO:0.09Tb<sup>3+</sup>,0.005Mn<sup>4+</sup> phosphors and LLSO:0.09Dy<sup>3+</sup>,0.005Mn<sup>4+</sup> phosphors are 0.529 K and 0.628 K, respectively. The peak positions of Mn<sup>4+</sup> and Tb<sup>3+</sup>/Dy<sup>3+</sup> are separated, which can provide a good signal discrimination performance. The results show that LLSO:0.09Tb<sup>3+</sup>/Dy<sup>3+</sup>, 0.005Mn<sup>4+</sup> samples are suitable for optical thermometers.

## 4. Conclusion

In all, we have successfully constructed a dual-luminescent system of Tb<sup>3+</sup>/Dy<sup>3+</sup>, Mn<sup>4+</sup> co-doped antimonate by using a green synthesis method, which is based on the site-beneficial occupation principle. When Tb<sup>3+</sup>/Dy<sup>3+</sup> ions and Mn<sup>4+</sup> ions enter the matrix, they will occupy different cation sites, in which Mn<sup>4+</sup> ions will replace Sb<sup>5+</sup> sites in the matrix, and Tb<sup>3+</sup>/Dy<sup>3+</sup> ions can be doped into La<sup>3+</sup> sites. By analyzing their luminescence spectra, the emission of Tb<sup>3+</sup>/Dy<sup>3+</sup> ions and Mn<sup>4+</sup> ions can be simultaneously observed under excitation at 276 nm or 274 nm and the intensity is very ideal. On this basis, their possible luminescence mechanism is speculated.

Because of the different thermal quenching behavior between RE ions and TM ions, the emission intensity of Mn<sup>4+</sup> is much faster than that of Tb<sup>3+</sup> and Dy<sup>3+</sup> ions with the increase in temperature. Therefore, Tb<sup>3+</sup>/Dy<sup>3+</sup> ions can be used as reference signals, whereas Mn<sup>4+</sup> ions are suitable detection

signals. The fluorescence intensity ratio (FIR) of Tb<sup>3+</sup>/Dy<sup>3+</sup> ions and Mn<sup>4+</sup> ions are significantly affected by temperature. Therefore, the material exhibits excellent temperature measurement performance in the temperature range of 303–523 K. Based on FIR technology, the maximum relative sensitivity and absolute sensitivity of Tb<sup>3+</sup> and Mn<sup>4+</sup> co-doped LLSO phosphors are 0.946% K<sup>-1</sup> (523 K) and 0.00193 K<sup>-1</sup>, respectively; the maximum relative sensitivity and absolute sensitivity of Dy<sup>3+</sup> and Mn<sup>4+</sup> co-doped LLSO phosphors are 0.796% K<sup>-1</sup> and 0.00832 K<sup>-1</sup>, respectively, which are much higher than those of some optical thermometric materials reported previously. In addition, the emission peaks of Tb<sup>3+</sup>/Dy<sup>3+</sup> ions and Mn<sup>4+</sup> ions are well separated, which provides a good signal identification ability for temperature detection. This work hews out a new strategy to develop high-performance optical temperature sensing materials that have extensive application potentiality in non-contact temperature detection.

## Conflicts of interest

There are no conflicts of interest to declare.

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