Sm³⁺-Mn⁴⁺ activated Sr₂GdTaO₆ red phosphor for plant growth lighting and optical temperature sensing

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Abstract: Optical temperature sensing and plant growth lighting multifunctional applications can be realized by red luminescent materials. In this paper, novel Sm³⁺ and Sm³⁺-Mn⁴⁺ activated Sr₂GdTaO₆ (SGTO) red phosphors for plant growth and optical temperature sensing were comprehensively analyzed. The phase, luminescence property and thermal stability of the material were tested. For PL performance, SGTO:0.075Sm³⁺ exhibits the maximum emission intensity in the range (560-670 nm). The emission range of SGTO:0.075Sm³⁺ after introducing Mn⁴⁺ is mainly dark red light emission in the range from 630 to 750 nm, and the optimum doping concentration of Mn⁴⁺ is determined to be 0.3%. The emission band of SGTO:0.075Sm³⁺ and SGTO:0.075Sm³⁺, 0.003Mn⁴⁺ matches the absorption band of the plants. For optical temperature sensing properties, the relative sensitivity (*S_r*) and absolute sensitivity (*S_a*) of SGTO:0.075Sm³⁺, 0.003Mn⁴⁺ are 2.94 K⁻¹ (298 K) and 0.635 K⁻¹ (573 K), respectively. The results indicate that Sm³⁺-Mn⁴⁺ activated SGTO red phosphor is a luminescent material with potential application in plant growth and optical temperature sensing field.

Key words: Phosphors; Double perovskite; Optical temperature sensing; Plant growth.

1 Introduction

Temperature detection has important applications in medical diagnostic, aerospace field, daily life, industrial production and agricultural science [1-8]. Therefore, the accuracy and ease of temperature assessment are the focus of current research in the scientific community. Non contact, low interference, real-time response, high resolution and non-invasive are the advantages of optical temperature sensing technology [9-14]. Fluorescence intensity ratio (FIR) technology avoids the influence of external conditions on temperature detection due to its excellent accuracy, remote detection and reversible luminescence [15-17]. Importantly, the influence of fluorescence loss and excited state fluctuation on FIR technology is weak. Compared with fluorescence lifetime temperature environments [18-20]. However, the appropriate energy difference between the activated ions (200-2000 cm⁻¹) is the key factor to realize FIR technology. Therefore, developing efficient luminescent materials based on FIR technology is a challenging task.

Researchers focus on the development of double activated ions doped luminescent materials based on FIR technology. For example, Huang et al. obtained $La_2MoO_6:Yb^{3+}/Er^{3+}$ phosphor with excellent performance in temperature measurement by adjusting the cross relaxation characteristics between activated ions [21]. Zhou et al. synthesized NaLaMgWO₆:Mn⁴⁺, Eu³⁺ phosphor. The temperature detection range is 303-523 K, and the maximum FIR is 0.86% K⁻¹ [22]. Li et al. synthesized CaMoO₄:Tb³⁺,

Eu³⁺ phosphor with high sensitive temperature detection performance by precipitation method [23]. Luminescent materials based on FIR technology show excellent performance in optical temperature detection. However, double red activator Sm³⁺/Mn⁴⁺ co-doped red phosphor is poorly studied and rarely reported. Furthermore, it is reasonable to study inorganic luminescent materials with double red emission centers applied in the field of plant growth lighting.

Due to the complex energy level of 4f electron layer, Sm³⁺ ions present narrowband emission $({}^{4}G_{5/2} \rightarrow {}^{4}H_{7/2}, {}^{4}G_{5/2} \rightarrow {}^{4}H_{5/2}, {}^{4}G_{5/2} \rightarrow {}^{4}H_{9/2}, {}^{4}G_{5/2} \rightarrow {}^{4}H_{11/2})$ in orange-red region [24, 25]. By comparison, the $3d^3$ energy level of Mn⁴⁺ at the center of octahedron is split into triple degenerate state (t_{2g}) and double degenerate state (e_g) . Therefore, Mn⁴⁺ has broadband emission in the red light region. Hopefully, the valence charge transfer state between metal ions provides a novel quenching path for the crossing of excited state and ground state energy levels, which plays an important role in novel temperature monitoring. Importantly, both rare earth ions Sm³⁺ and transition metal ions Mn⁴⁺ with different temperature dependence can be excited by near ultraviolet (UV) and partial blue light. Therefore, Sm³⁺ and Mn⁴⁺ co-doped temperature sensing materials are expected to realize FIR technology. In addition, the emission areas of Sm³⁺ and Mn⁴⁺ ions cover the orange-red, dark-red and far-red light, which match the absorption of phytochromes P_R (660 nm) and P_{FR} (730 nm) [26-28]. Our previous work has proved that stable double perovskites Sr₂GdTaO₆ (SGTO) is a suitable host for Mn⁴⁺-doped [30]. Therefore, we firmly believe that Sm³⁺-Mn⁴⁺ co-doped SGTO

phosphor is expected to achieve optical temperature sensing and plant growth lighting multifunctional applications.

In this work, a series of novel SGTO:Sm³⁺and SGTO:Sm³⁺, Mn⁴⁺ phosphors were synthesized by high-temperature solid-state method. SGTO as a host provides suitable substitution sites for Sm³⁺ and Mn⁴⁺ ions, where Sm³⁺ and Mn⁴⁺ ions replace Gd³⁺ sites and Ta⁵⁺ sites, respectively. The elemental composition, morphology, luminescence mechanism and thermal stability of the materials were studied. As a result, SGTO:Sm³⁺and SGTO:Sm³⁺, Mn⁴⁺ phosphors are expected to play an important role in the field of plant growth lighting and optical temperature sensing.

2. Experimental Section

2.1. Sample preparation

The experimental drugs, SrCO₃ (99.99%), Gd₂O₃ (99.99%), Sm₂O₃ (99.99%), MnO₂ (99.99%) and Ta₂O₅ (99.99%) were purchased from Aladdin Reagents Co., Ltd. A series Sm³⁺ doped and Sm³⁺/Mn⁴⁺ co-doped SGTO red phosphors were synthesized by high-temperature solid-state reaction. The above experimental drugs were weighed accurately according to the ratio of the target compounds. All raw materials were poured into the ball mill tanks, with anhydrous ethanol and ZrO₂ ball as the medium. The ball mill tanks were fixed in the ball mill, and the powders were dried in the oven after 12 h of high-speed operation. The powders were first calcined at 750 °C for 6 h to decompose carbonate. Then the powders were calcined at 1350 °C for 8 h. The caked samples were broken into powder for subsequent testing.

2.2. Measurement and characterization

The phase of sample was collected by DX-2700B model X-ray diffractometer (XRD, Cu, K α , λ =0.154178 nm). The morphology, microstructure and composition were observed by high resolution scanning electron microscope (SEM, Hitachi SU-5000), energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectrometer (XPS, ESCALAB). The light absorption property was tested by UV-Vis spectrometer (UV-2450PC, Shimadzu), BaSO₄ powder as the reference material. Photoluminescence property was tested by fluorescence spectrometer (Hitachi F-7000, 450W Xi). The thermal stability was tested by the same fluorescence spectrometer with a temperature control system.

3 Results and discussion

Fig.1 (a) shows the crystal structure of SGTO. The spatial configuration of SGTO double perovskites material belongs to monoclinic crystal system with the space group P2₁/n [29]. Cell parameters are as follows, *a*: 5.8380(2) Å, *b*: 5.9165(4) Å, *c*: 8.2989(2) Å, β : 90.125(1)°[30]. Many studies have shown that atomic substitution is related to the ionic radius and coordination number (CN). Ions substitution occurs easily when ionic radius difference is less than 30%. Table.1 shows the radius deviation between the radius of Sm³⁺ ions and Ta⁵⁺, Sr²⁺, and Gd³⁺ ions in the host (SGTO). The CN of Ta⁵⁺, Sr²⁺ and Gd³⁺ in the host are all 6. All ions have the possibility of being substituted. *R_r* is the percentage difference of radius, which is used to evaluate the radius difference

between Sm³⁺ ion and cations. Formula (1) is as follows [33]:

where, R_h (CN) and R_d (CN) represent the radius of the ions in the host and the radius of the Sm³⁺ ion, respectively. It is found that the radius of Sm³⁺ (0.96 Å, CN=6) and Gd³⁺ (0.94 Å, CN=6) are very similar under the same conditions. Besides, the possibility of ions substitution can also be determined by C/IR. C/IR represents the ratio of charge to radius. The data show that the ionic radius of Sm³⁺ ion and C/IR are similar to Gd³⁺ ions, because they belong to lanthanide elements. Therefore, it can be inferred that Sm³⁺ preferentially replaces Gd³⁺. Fig.1 (b) shows the XRD patterns of SGTO:xSm³⁺ phosphors (*x*=0, 0.03, 0.05, 0.075, 0.1, 0.125, 0.15). Compared with the standard card (PDF#47-0527, Sr₂EuTaO₆), the diffraction peaks of all samples match the characteristic diffraction peaks. No impurity phase is observed even if the doping amount reaches 15%. The results show that Gd³⁺ is successfully replaced by Sm³⁺ in SGTO host.

ions	CN	Ions radius (Å)	Rr (%)	C/IR
Sm^{3+}	6	0.96	-	3.13
Ta ⁵⁺	6	0.64	17.19	7.81
Sr^{2^+}	6	1.18	55.09	1.70
Gd^{3+}	6	0.94	43.62	3.19

Table 1. R_r between Sm³⁺ ion and metal cations in SGTO host.



Fig. 1 (a) Crystal structure of SGTO. (b) XRD patterns of SGTO:*x*Sm³⁺.

Fig. 2 (a) shows the SEM images of SGTO:0.075Sm³⁺. The particles show an irregular shape and the diameter is about 1-3 µm. The EDS spectra and mapping of SGTO:0.075Sm³⁺ (Fig. 2 (b-f)) show the distribution of Sr, Gd, Ta, O, and Sm elements. Fig. 2 (g-j) describe the XPS spectra of SGTO:0.075Sm³⁺ phosphor. The characteristic combination of Sr²⁺ and Gd³⁺ can be detected, the peaks 147.7 and 141.6 eV can be attributed to Gd4d_{3/2} and Gd4d_{5/2}, respectively, the peaks 134.4 and 132.9 eV are attributed to Sr3d_{3/2} and Sr3d_{5/2}, respectively. Beside, Ta4f_{5/2} and Ta4f_{7/2} with low binding energy are found at 27.2 eV and 25.3 eV, respectively. Importantly, Sm³⁺ ions were detected, Sm3d_{3/2} (1109.6 eV) and Sm3d_{5/2} (1083.1 eV), which strongly proves that Sm³⁺ ions are successfully doped into SGTO host.



Fig. 2 (a) SEM image of SGTO:0.075Sm³⁺. Element distributions: (b) Sr, (c) Gd, (d) Ta, (e) O, (f) Sm. XPS spectra of (g) SGTO:0.075Sm³⁺, (h) Sr3d and Gd4d, (i) Ta4f, (j) Sm3d.

Fig. 3 (a) shows the PLE spectrum of SGTO:0.075Sm³⁺ phosphor (λ_{em} =606 nm). The PLE spectrum is mainly contributed by the ${}^{6}H_{5/2} \rightarrow {}^{4}F_{7/2}$ (408 nm) energy level leap. Several other absorption peaks: ${}^{6}H_{5/2} \rightarrow {}^{4}I_{11/2}$ (468 nm), ${}^{6}H_{5/2} \rightarrow {}^{6}P_{7/2}$, ${}^{4}P_{7/2}$ (419 nm), ${}^{6}H_{5/2} \rightarrow {}^{4}I_{9/2}$ (483 nm), ${}^{6}H_{5/2} \rightarrow {}^{4}L_{15/2}$ (383 nm), ${}^{6}H_{5/2} \rightarrow {}^{6}P_{5/2}$ (437 nm), ${}^{6}H_{5/2} \rightarrow {}^{4}I_{13/2}$ (450 nm), ${}^{6}H_{5/2} \rightarrow {}^{4}D_{3/2}$ (358 nm). Fig. 3 (b) shows the PL spectrum of SGTO:0.075Sm³⁺ (λ_{em} =408 nm). The PL spectrum is mainly composed of four parts (sort by intensity): ${}^{4}G_{5/2} \rightarrow {}^{4}H_{7/2}$, ${}^{4}G_{5/2} \rightarrow {}^{4}H_{5/2}$, ${}^{4}G_{5/2} \rightarrow {}^{4}H_{9/2}$, ${}^{4}G_{5/2} \rightarrow {}^{4}H_{11/2}$. Among them, peak splitting occurs in ${}^{4}G_{5/2} \rightarrow {}^{4}H_{7/2}$ and ${}^{4}G_{5/2} \rightarrow {}^{4}H_{5/2}$, this indicates that the crystal field splits the partially excited state energy levels of Sm³⁺[34-36]. Fig. 3 (c) and (d) show the PL spectra of samples with different Sm³⁺ concentration and the PL intensity change trend, respectively. Beyond all doubt, SGTO:0.075Sm³⁺ exhibits the strongest PL intensity, and the concentration quenching occurs when the doping amount is greater than 7.5%. A large number of activated ions shorten the distance between each other, R_c is defined as the critical distance leading to concentration quenching and can be calculated by formula (2) [37]:

$$R_{c} = 2\left(\frac{3V}{4\pi x_{c}N}\right)^{\frac{1}{3}}....(2)$$

where, V is the volume of a cell, x_c is the doping concentration at quenching, N is coordination number. Here, V = 286.65 Å³, $x_c = 0.075$, N = 4, we calculate $R_c=6.1$ Å. Obviously, R_c is greater than 5 Å, which inferred that the quenching mechanism of SGTO: Sm³⁺ is multipolar interaction, as shown in formula (3) [37]:

$$I/x = K [1 + \beta(x)^{\theta/3}]^{-1} \dots (3)$$

where, I is PL intensity at optimal doping concentration, x is optimal doping concentration, K and β are constants. The tangent obtained in Fig. 3 (e) is the value of

 θ /3, therefore, θ = 3.651 approach 6, which correspond to dipole-dipole (*d-d*) interaction. Fig. 3 (f) depicts the UV-Vis DR spectra of SGTO:xSm³⁺ phosphors. The absorption part is mainly composed of two parts. The valley in the far UV region is attributed to the energy absorbed by the SGTO host, and the NUV absorption attribution and electronic transition of Sm³⁺. Fig. 4 draws the calculated Commission Internationale de l' Eclairage (CIE) diagram of SGTO:xSm³⁺. The chromaticity coordinates is calculated to be (0.491, 0.499), (0.492, 0.498), (0.505, 0.472), (0.503, 0.478), (0.503, 0.479) and (0.499, 0.482), corresponding to SGTO:xSm³⁺ (*x*=0.03, 0.05, 0.075, 0.01, 0.125 and 0.15).





Fig. 3 (a) PLE spectrum and (b) PL spectrum of SGTO:0.075Sm³⁺ phosphor. (c) PL spectra of SGTO:xSm³⁺ phosphors. (d) PL intensity of SGTO:xSm³⁺ phosphors. (e) Log(x) dependent Log(I/x) and fitting curve. (f) UV-Vis DRS of SGTO:xSm³⁺ phosphors.



Fig. 4 CIE of SGTO:xSm³⁺, inset: photos of SGTO:xSm³⁺ under 365 nm illumination.

Fig. 5 (a) shows the PL intensity dependent temperature curves, temperature detection range from 298 to 573 K. The emission peak is mainly composed of three parts, which is consistent with the previous emission spectra analysis. The PL intensity decreases as temperature rises indicates that thermal quenching phenomenon occurs. In order to better understand the thermodynamic properties of the sample, the Arrhenius

equation is used to calculate the thermal activation energy (E_a) [38]:

$$I(T) = \frac{I_0}{1 + c \exp(-E_a / KT)} \dots (4)$$

where, I_0 and I(T) are the PL intensity at room temperature and temperature (*T*), respectively. K is Boltzmann constant and **c** is constant. After logarithmic deformation of the formula, 10000/T dependent Ln(I₀/I-1) and fitting curve are shown in Fig. 5 (b), the slope =-0.251 means E_a =0.217 eV. This result shows that the excited electrons in the thermal quenching process must at least cross 0.217 eV energy gap, and then return to the ground state in the form of non radiative transition.



Fig. 5 (a) PL spectra of SGTO:0.075Sm³⁺ depend on temperature. (b) 10000/T dependent Ln(I₀/I-1) and fitting curve.

Our previous work has proved that Mn^{4+} ions enter SGTO host after replacing Ta⁵⁺ [30]. Based on the successful synthesis of SGTO:Sm³⁺, therefor, Sm³⁺ and Mn⁴⁺ double red activators co-activated SGTO were further studied. Fig. 6 (a) shows the XRD patterns of SGTO:0.075Sm³⁺, xMn^{4+} (x=0.001, 0.002, 0.003, 0.005, 0.007, 0.009). The strongest emission peak of SGTO:Mn⁴⁺ is 652 nm. Therefore, 606 nm and 652 nm are selected to monitor excitation spectra, respectively, as shown in Fig. 6 (b). The

excitation spectrum shows the characteristic excitation peaks of Sm³⁺ under 606 nm monitoring, while the spectrum is mainly the excitation peak of Mn⁴⁺ under 652 nm monitoring, supplemented by Sm^{3+} peaks. The photoluminescence excitation (PLE) spectra of the samples exhibited broadband absorption (300-550 nm), which is attributed to Mn^{4+} : ${}^{4}A_{2} \rightarrow {}^{4}T_{1}$, ${}^{4}A_{2} \rightarrow {}^{2}T_{2}$ and ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ transitions (Deconvolution can be referred to [30]). In order to balance the emission of Sm³⁺ and Mn⁴⁺, 408 nm is selected as the excitation wavelength. Fig. 6 (c) shows the PL spectra of $SGTO:0.075Sm^{3+}$, xMn^{4+} phosphors. All emission peaks have the same shape but different intensity. Obviously, the emission peaks of Sm³⁺ and Mn⁴⁺ coexist in the PL spectra. The PL intensity of SGTO:0.075Sm³⁺, xMn⁴⁺ is counted by integral. It is found that when the Mn⁴⁺ doping concentration is 0.3 mol%, the PL intensity of the phosphor reaches the extreme value, as shown in Fig. 6 (d). Therefore, SGTO:0.075Sm³⁺, 0.003Mn⁴⁺ phosphor is used for related research of plant growth lighting and optical temperature sensing.



Fig. 6 (a) XRD patterns of SGTO:0.075Sm³⁺, xMn⁴⁺. (b) PLE spectra of SGTO:0.075Sm³⁺, 0.003Mn⁴⁺ (λ_{em} =606 nm and 652 nm). (c) PL spectra of SGTO:0.075Sm³⁺, xMn⁴⁺. (d) PL intensity of SGTO:0.075Sm³⁺, xMn⁴⁺.

Related literature reports that phytochromes P_R and P_{FR} in plant are sensitive to red light[27-29]. The emission spectra of SGTO:0.075Sm³⁺ and SGTO:0.075Sm³⁺, 0.003Mn⁴⁺ and the absorption spectra of P_R and P_{FR} are compared, as shown in Fig. 7 (a) and (b). The PL spectrum of SGTO:0.075Sm³⁺ (${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$, ${}^{4}G_{5/2} \rightarrow {}^{4}H_{7/2}$, ${}^{4}G_{5/2} \rightarrow {}^{4}H_{5/2}$, ${}^{4}G_{5/2} \rightarrow {}^{4}H_{11/2}$) covers the part of the P_R absorption spectra. By comparison, the emission peaks of Sm³⁺ and Mn⁴⁺ co-doped phosphors match well with phytochromes P_R and P_{FR} . Benefit from the emission of Sm³⁺ ions, the problem of insufficient P_R irradiation is effectively compensated. Therefore, SGTO:0.075Sm³⁺, 0.003Mn⁴⁺ with broad emission is more suitable for plant lighting.



Fig. 7 Absorption spectra of phytochromes P_R and P_{FR} and PL spectrum of (a) SGTO:0.075Sm³⁺, (b) SGTO:0.075Sm³⁺, 0.003Mn⁴⁺.

Many studies have shown that transition ions and trivalent rare earth ions usually have different temperature dependence Therefore, the application of Sm^{3+} and Mn^{4+} in the field of temperature sensing is explored by FIR technique. As shown in Fig. 8 (a), the variable temperature spectra of SGTO:0.075Sm³⁺, 0.003Mn⁴⁺ show that the increase of temperature leads to the thermal quenching of the material. However, the quenching of Sm³⁺ and Mn⁴⁺ are different at the same temperature. When the temperature is close to room temperature, the emission of Mn⁴⁺ is absolutely dominant, and the PL intensity of Mn⁴⁺ ions decreases after the temperature increases, as shown in Fig. 8 (b). In order to further study the temperature detection ability of the material, FIR can be fitted exponentially by the following formula [15]:

$$FIR = \frac{I_{Sm}(T)}{I_{Mn}(T)} = \frac{I_{0,}Mn^{4+}}{I_{0,}Sm^{3+}} \frac{1 + A_{Sm^{3+}} \exp(-\frac{E_{Sm^{3+}}}{K_{B}T})}{1 + A_{Mn^{4+}} \exp(-\frac{E_{Mn^{4+}}}{K_{B}T})} \approx B + C \cdot \exp(-\frac{-\Delta E}{K_{B}T}) \dots \dots \dots \dots (5)$$

where, B and C are constants, T is temperature, K_B is Boltzmann constant. As show in

Fig. 8 (c), FIR=24005.46 exp(-5882.35/T) +0.01 is obtained from the data points after exponential fitting, R²=0.995 proves high fitting accuracy. Two important indicators relative sensitivity (S_r) and absolute sensitivity (S_a) are used to judge the application prospect of materials, S_r and S_a can be calculated by the following formula [39]:

The calculated results are plotted in Fig. 8 (d). Obviously, the value of S_r decreases monotonically, but the value of S_a increases monotonically. The maximum values of S_r and S_a are 2.94 K⁻¹ at 298 K and 0.635 K⁻¹ at 573 K, respectively. This result shows that SGTO:0.075Sm³⁺, 0.003Mn⁴⁺ red phosphor has application value in the field of optical temperature sensing [47-48].





Fig. 8 (a) PL spectra of SGTO:0.075Sm³⁺, 0.003Mn⁴⁺ depend on temperature. (b) The normalized PL intensities (Sm³⁺: 4 G^{5/2} \rightarrow 4 H_{5,7/2} and Mn⁴⁺: 2 E_g \rightarrow 4 A_{2g}) at distinct temperatures. (c) Experimental measured and fitting curve of FIR temperature depend on 1/T of SGTO:0.075Sm³⁺, 0.003Mn⁴⁺. (d) S_{g} and S_{r} depend on temperatures (293-573 K).

4. Conclusions

In summary, a series of Sm³⁺ doped and Sm³⁺-Mn⁴⁺ co-doped SGTO red phosphors were synthesized by high-temperature solid-phase reaction method. SGTO:0.075Sm³⁺ exhibits the maximum red emission intensity in the range (560-670 nm). The concentration quenching mechanism of Sm³⁺ in SGTO is *d-d* interaction and E_a =0.217 eV. The emission range of SGTO:0.075Sm³⁺ after introducing Mn⁴⁺ is mainly dark red light emission in the range from 630 to 750 nm, and the optimum doping concentration of Mn⁴⁺ is 0.3%. The PL spectra of SGTO:0.075Sm³⁺, 0.003Mn⁴⁺ match the red light required for plant growth. The maximum value of *S_r* and *S_a* are 2.94 K⁻¹ (298 K) and 0.635 K⁻¹ (573 K), respectively. This work not only illustrates that SGTO:0.075Sm³⁺, 0.003Mn⁴⁺ phosphors have the potential in plant growth lighting and optical temperature sensing, but also provides a model for double red activated ions doped phosphor.

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References

[1] S.A. Wade, S.F. Collins, G.W. Baxter, Fluorescence intensity ratio technique for optical fiber point temperature sensing, J. Appl. Phys. 94 (2003) 4743-4756.

[2] Y. Song, N. Guo, J. Li, R. Ouyang, Y. Miao, B. Shao, Photoluminescence and temperature sensing of lanthanide Eu^{3+} and transition metal Mn^{4+} dual-doped antimoniate phosphor through site-beneficial occupation, Ceram. Int. 46 (2020) 22164-22170.

[3] X.D. Wang, O.S. Wolfbeis, R.J. Meier, Luminescent probes and sensors for temperature, Chem. Soc. Rev. 42 (2013) 7834-7869.

[4] H. Zhang, Z.Y. Gao, G.G. Li, Y.L. Zhu, S.Q. Liu, K. Li, Y.J. Liang, A ratiometric optical thermometer with multi-color emission and high sensitivity based on double

perovskite $LaMg_{0.402}Nb_{0.598}O_3$: Pr^{3+} thermochromic phosphors, Chem. Eng. J. 380 (2020) 122491.

[5] K. Li, M. Shang, H. Lian, J. Lin, Recent development in phosphors with different emitting colors via energy transfer, J. Mater. Chem. C. 4 (2016) 5507-5530.

[6] C.C. Lin, A. Meijerink, R.S. Liu, Critical red components for next-generation white LEDs, J. Phys. Chem. Lett. 7 (2016) 495-503.

[7] D. Chen, S. Liu, Y. Zhou, Z. Wan, P. Huang, Z. Ji, Dual-activator luminescence of RE/TM: $Y_3Al_5O_{12}$ (RE = Eu³⁺, Tb³, Dy³⁺; TM = Mn⁴⁺, Cr³⁺) phosphors for self-referencing optical thermometry, J. Mater. Chem. C. 4 (2016) 9044-9051.

[8] W. Xu, Q. Song, L. Zheng, Z. Zhang, W. Cao, Optical temperature sensing based on the near-infrared emissions from Nd³⁺ /Yb³⁺ codoped CaWO₄, Opt. Lett. 39 (2014) 4635-4638.

[9] S. Pimputkar, J.S. Speck, S.P. Denbaars, S. Nakamura, Prospects for LED lighting, Nat. Photon. 3 (2009) 180-182.

[10] Y.T. Ren, Z.W. Yang, M.J. Li, J.F. Ruan, J.Y. Zhao, J.B. Qiu, Z.G. Song, D.C. Zhou, Reversible upconversion luminescence modification based on photochromism in BaMgSiO₄: Yb³⁺, Tb³⁺ ceramics for anti-counterfeiting applications, Adv. Optical. Mater. 7 (2019) 1900213.

[11] S.L. Shinde, K.K. Nanda, Wide-range temperature sensing using highly sensitive green-luminescent ZnO and PMMA-ZnO film as a non-contact optical probe, Angew. Chem. 125 (2013) 11535-11538. [12] Y. Gao, F. Huang, H. Lin, J.J. Zhou, J. Xu, Y.S. Wang, A novel optical thermometry strategy based on diverse thermal response from two intervalence charge transfer states, Adv. Funct. Mater. 26 (2016) 3139-3145.

[13] X.Y. Yun, J. Zhou, Y.H. Zhu, X. Li, S. Liu, D.H. Xu. A potentially multifunctional double-perovskite Sr₂ScTaO₆: Mn⁴⁺, Eu³⁺ phosphor for optical temperature sensing and indoor plant growth lighting, J. Lumin. 244 (2022) 118724.

[14] C.D.S. Brites, K. Fiaczyk, J.F.C.B. Ramalho, M. Sójka, L.D. Carlos, E. Zych,
 Widening the temperature range of luminescent thermometers through the intra-and interconfigurational transitions of Pr³⁺, Adv. Opt. Mater. 6 (2018) 1701318.

[15] P. Wang, J. Mao, L. Zhao, B. Jiang, C. Xie, Y. Lin, F. Chi, M. Yin, Y. Chen, Double perovskite A₂LaNbO₆: Mn⁴⁺, Eu³⁺(A=Ba, Ca) phosphors: potential applications in optical temperature sensing, Dalton. Trans. 48 (2019) 10062-10069.

[16] Z.L. Ji, Y. Cheng, X.S. Cui, H. Lin, J. Xu, Y.S. Wang, Heating-induced abnormal increase in Yb³⁺ excited state lifetime and its potential application in lifetime luminescence nanothermometry, Inorg. Chem. Front. 6 (2019) 110-116.

[17] A. Pandey, V.K. Rai, Optical thermometry using FIR of two close lying levels of different ions in Y₂O₃:Ho³⁺-Tm³⁺-Yb³⁺phosphor, Appl. Phys. B. 113 (2013) 221-225.

[18] Y.F. Wu, H. Suo, X.Q. Zhao, Z.W. Zhou, C.F. Guo, Self-calibrated optical thermo-meter LuNbO₄:Pr³⁺/Tb³⁺ based on intervalence charge transfer transitions, Inorg. Chem. Front. 5 (2018) 2456-2461.

[19] S.K. Singh, K. Kumar, S.B. Rai, Er³⁺/Yb³⁺ codoped Gd₂O₃ nano-phosphor for

optical thermometry, Sens. Actuator. A. 149 (2009) 16-20.

[20] H. Kusama, O.J. Sovers, T. Yoshioka, Line Shift method for phosphor temperature measurements, Jpn. J. Appl. Phys. 15 (1976) 2349-2358.

[21] F. Huang, T. Yang, S.X. Wang, L. Lin, T. Hu, D.Q. Chen, Temperature sensitive cross relaxation between Er³⁺ ions in laminated hosts: a novel mechanism for thermo-chromic upconversion and high performance thermometry, J. Mater. Chem. C. 6 (2018) 12364-12370.

[22] Z. Long, S. Xiao, X. Yang, Mn⁴⁺, Eu³⁺ Co-doped K_{0.3}La_{1.233}MgWO₆: a potentially multifunctional luminescent material, ACS. Appl. Electron. Mater. 2 (2020) 3889-3897.
[23] S.D. Li, Q.Y. Meng, S.C. Lü, W.J. Sun, Study on optical temperature sensing properties of Tb³⁺, Eu³⁺ co-doped CaMoO₄ phosphor, J. Lumin. 200 (2018) 103-110.

[24] B.J. Han, X.H. Yang, Y.H. Jiang, Z.A. Li, Y. Shen, X.Y. Chang, Jing. R, S. Gao, Highly efficient and thermally stable red emitting CaGdMgNbO₆:Mn⁴⁺ double perovskites for indoor plant growth LEDs, Mater. Today. Commun. 31 (2022) 103809.

[25] L. Mei, H. Liu, L. Liao, Y. Zhang, R.V. Kumar, Structure and photoluminescence properties of red-emitting apatite-type phosphor $NaY_9(SiO_4)_6O_2$: Sm³⁺ with excellent quantum efficiency and thermal stability for solid-state lighting, Sci. Rep. 7 (2017) 15171.

[26] L. Shi, Y.J. Han, Z.G. Zhang, Z.X. Ji, D.C. Shi, X.Y. Geng, H. Zhang, M. Li, Z.W. Zhang, Synthesis and photoluminescence properties of novel Ca₂LaSbO₆:Mn⁴⁺ double perovskite phosphor for plant growth LEDs, Ceram. Int. 45 (2019) 4739-4746.

[27] K.Y. Deng, Y.H. Jin, L.F. Yuan, B. Wang, H.Y. Wu, Y.H. Hu, A thermal-stable Mn⁴⁺-doped far-red-emitting phosphor-converted LED for indoor plant cultivation, Mater. Today. Chem. 26 (2022) 101010.

[28] X. Geng, Y. Xie, X. Hu, X. Ouyang, S. Chen, X. Yao, J. Kong, J. Chen, J Guo, H. Wang, W. Zhou, Greatly enhanced deep-red luminescence performance of Ca₂InSbO₆:Mn⁴⁺ phosphor via multiple optimization strategies, Mater. Today. Chem. 26 (2022) 101006.

[29] Z.J. Wu, L. Li, H. Li, L.S. Mei, W.D. Xia, Y.S. Yi, Y.B. Hua, Designing bifunctional platforms for LED devices and luminescence lifetime thermometers: a case of non-rare-earth Mn⁴⁺ doped tantalate phosphors, Dalton. Trans. 51 (2022) 9062.

[30] B.J. Han, X. Yang, J. Ren, L. Liu, E. Zhao, X. Zhu, J. Zhu, H. Ma, A. Li, P. Teng, Thermally stable deep-red emitting Sr₂GdTaO₆:Mn⁴⁺ double perovskites for indoor plant growth LEDs, Mater. Today. Chem. 23 (2022) 100737.

[31] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865-3868.

[32] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B. 54 (1996) 11169-11186.

[33]X. Geng, Y. Xie, S. Chen, J. Luo, S. Li, T. Wang, S. Zhao, H, Wang, B. Deng, R.
Yu, W. Zhou, Enhanced local symmetry achieved zero-thermal-quenching luminescence characteristic in the Ca₂InSbO₆:Sm³⁺ phosphors for w-LEDs, Chem. Eng.
J. 410 (2021) 128396.

[34] Y.B. Hua, Z.H. Li, Synthesis and photoluminescence properties of novel orange-emitting Sr₂YSbO₆: Sm³⁺ phosphors for potential solid-state lighting, Inorg. Chem. Commun. 128 (2021) 108576.

[35] B.J. Han, J. Ren, P. P Teng, J. B. Zhu, Y. Shen, Z. A. Li, X. L. Zhu, X. H. Yang,
Synthesis and photoluminescence properties of a novel double perovskite Ca₂LaSbO₆:
Sm³⁺ phosphor for w-LEDs, Ceram. Int. 48 (2022) 971-980.

[36] R.P. Cao, W.H. Wang, Y. Ren, Synthesise, energy transfer and tunable emission properties of Ba₂La₂ZnW₂O₁₂: Sm³⁺ phosphors, J. Lumin. 235 (2021) 118054.

[37] G. Blasse, Energy transfer in oxidic phosphors, Phys. Lett. 28 (1968) 444-445.

[38] Q. Wu, Y. Li, Y. Wang, H. Liu, S. Ye, L. Zhao, J. Ding, J. Zhou, A novel narrow-band blue-emitting phosphor of Bi³⁺-activated Sr₃Lu₂Ge₃O₁₂ based on a highly symmetrical crystal structure used for WLEDs and FEDs, J. Adv. Ceram. 401 (2020) 126130.

[39] Y.F. Wu, H. Suo, X.Q. Zhao, Z.W. Zhou, C.F. Guo, Self-calibrated optical thermometer LuNbO₄: Pr³⁺/Tb³⁺ based on intervalence charge transfer transitions, Inorg. Chem. Front. 5 (2018) 2456-2461.