MgGd₄Si₃O₁₃:Ce³⁺, Mn²⁺: A Dual-Excitation Temperature Sensor
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ABSTRACT: A novel apatite-based phosphor MgGd₄Si₃O₁₃[Mg₂Gd₈(SiO₄)₆O₂]:Ce³⁺, Mn²⁺ was designed and successfully synthesized by a solid-state reaction. Based on the different luminescence properties under 298 and 340 nm excitations, its potential application as a dual-excitation luminescent ratiometric thermometer was studied in detail. Under the excitations of 298 and 340 nm, the fluorescent intensity ratio of Ce³⁺ and Mn²⁺ is linearly correlated in the temperature range of 303−473 K. The sensitivity showed an opposite trend with the increase of temperature, and the maximum value was 0.95% K⁻¹. These results indicated that MgGd₄Si₃O₁₃: Ce³⁺, Mn²⁺ can be used as an ideal dual-excitation luminescent ratiometric thermometer.

1. INTRODUCTION

Temperature is one of the important parameters for many physical and chemical reactions. Therefore, it is very significant for many scientific and industrial fields to measure temperature through accurate and effective methods. The fluorescence temperature measurement technology developed based on rare-earth ion-doped inorganic–organic luminescent materials has received wide attention from researchers due to its unique performance, such as realizing noncontact temperature detection, and can work in special environments, such as biological tissues and strong magnetic fields.¹⁻⁵ In the early research, the temperature measurement process is mainly based on the change of emission intensity with temperature. However, because the emission intensity is easily affected by external factors such as PH value and luminescence material aggregation, the accuracy of the fluorescence-based temperature sensors based on this principle will also be adversely affected. For the accuracy of temperature, the fluorescence-intensity-ratio-based thermometers which use the emission intensity ratio of two peaks changing with temperature as parameters are developed.⁶⁻⁷

Recently, the materials that can be used as temperature sensors have been mainly upconversion nanoparticles (UPNPs). There are also some rare-earth ion-doped complexes and MOF ⊂ dye composites. Compared with UPNPs, MOF ⊂ dye composites often require a complex synthesis process.⁸⁻¹⁰ The temperature sensing range of UPNPs is usually excellent; however, the dissatisfactory sensitivity (CaWO₄:Ho³⁺/Yb³⁺: 3.3−923 K, 0.5% K⁻¹) restricted their applications.¹¹,¹² Downconversion luminescent materials containing two or more luminescent centers have been widely used as LED phosphors. Because of the energy transfer between the luminous centers, the emission intensity of these luminous centers may have different trends with temperature. Based on this performance, some multiple-emission-downconversion luminescent materials show good application potential as temperature sensors.¹³⁻¹⁵

In recent years, many compounds with an apatite structure and same chemical formula of A₁₀(XO₄)₆Z₂ have been selected as the host of the luminescent materials because of the superiority of this structure in designing the new materials.¹⁶,¹⁷ In our early work, the luminescence properties of Ce³⁺−Tb³⁺-doped MgGd₄Si₃O₁₃[Mg₂Gd₈(SiO₄)₆O₂] have been studied in detail.¹⁸ Because the different coordination environments of two cation sites in the crystal, MgGd₄Si₃O₁₃:Ce³⁺ exhibits an
obvious difference emission band under different excitation wavelengths (blue emission excited at 298 nm and yellow emission excited at 340 nm). In this work, Ce$^{3+}$–Mn$^{2+}$-doped MgGd$_2$Si$_2$O$_13$ was synthesized to realize the dual-excitation temperature sensors with high sensitivity. The structure and luminescence properties were discussed in detail. Under the excitation of 340 nm, over a wide temperature range (303–473 K), the intensity ratio of Ce$^{3+}$–Mn$^{2+}$ shows satisfactory linear correlation with the temperature and exhibits a good sensitivity of 0.95% K$^{-1}$.

2. RESULTS AND DISCUSSION

2.1. Phase Structure of Mn$^{2+}$ Singly and Ce$^{3+}$, Mn$^{2+}$ Codoped MgGd$_4$Si$_3$O$_{13}$. The X-ray diffraction (XRD) patterns of the synthesized MgGd$_{4-2}$Si$_3$O$_{13}$:xMn$^{2+}$ (0.04 ≤ x ≤ 0.2) and MgGd$_{4-2}$Si$_3$O$_{13}$:0.08Ce$^{3+}$, xMn$^{2+}$ (0 ≤ x ≤ 0.16) samples are provided in Figure 1(a,b). All the patterns match well with the structural refinement result of MgGd$_2$Si$_2$O$_13$, and no obvious impurity peak was detected. For both series of samples, the XRD patterns shifted slightly to the large angle direction with the increase in doping concentration, which is due to the change of lattice parameters caused by the different ion radii of Mn$^{2+}$ (0.67 Å, CN = 6; 0.9 Å, CN = 7) and Mg$^{2+}$ (0.72 Å, CN = 6)/Gd$^{3+}$ (1.07 Å, CN = 7; 1.107 Å, CN = 9). For the purpose of further studying the occupancy of the doped ions Ce$^{3+}$ and Mn$^{2+}$, the structural refinement of MgGd$_{4-2}$Si$_3$O$_{13}$:0.16Mn$^{2+}$ and MgGd$_{4-2}$Si$_3$O$_{13}$:0.08Ce$^{3+}$, 0.16Mn$^{2+}$ is carried out by the Materials Studio program, as shown in Figure 2(a,b). The crystal structure parameters of MgGd$_{4-2}$Si$_3$O$_{13}$:0.16Mn$^{2+}$ and MgGd$_{4-2}$Si$_3$O$_{13}$:0.08Ce$^{3+}$, 0.16Mn$^{2+}$ are given in Table S1, and their atomic coordinates are given in Tables S2 and S3. It can be seen that MgGd$_2$Si$_2$O$_13$: 0.16Mn$^{2+}$ has a slightly smaller cell volume than MgGd$_2$Si$_2$O$_13$: 0.08Ce$^{3+}$, 0.16Mn$^{2+}$. This is because the larger-sized Ce$^{3+}$ (1.07 Å, CN = 7; 1.196 Å, CN = 9) replaces the smaller-sized Gd$^{3+}$ (1.00 Å, CN = 7; 1.107 Å, CN = 9). In addition, the refinement results indicate that Mn$^{2+}$ occupies both Mg/Gd1 and Gd2 sites in the lattice.

2.2. PL Properties. Figure 3(a) shows the photoluminescence excitation (PLE) spectra of MgGd$_{4-2}$Si$_3$O$_{13}$:xMn$^{2+}$ (0.04 ≤ x ≤ 0.2) samples monitored at 602 nm. Several sharp peaks near 312, 273, and 253 nm belong to the $^8S_7/2$ $^6P_J$, $^8S_7/2$ $^6I_J$, and $^8S_7/2$ $^6D_J$ transitions of Gd$^{3+}$. In our previous work, the transitions of Gd$^{3+}$ also appeared in the PLE spectrum of MgGd$_{4-2}$Si$_3$O$_{13}$:Tb$^{3+}$,18 This phenomenon is caused by the obvious energy transfer mechanism from Gd$^{3+}$ to the doped ions. Except for the transition of Gd$^{3+}$, other five distinct peaks located at about 343, 367, 409, 414, and 467 nm existing in the excitation spectra are credited to the absorption transitions of Mn$^{2+}$, respectively. The emission spectra of Mn$^{2+}$-doped MgGd$_2$Si$_2$O$_13$ are displayed in Figure 3(b), which show a broad red emission around 600 nm under 409 nm excitation. When x increases to 0.16, the emission intensity of the sample reaches the maximum. In our previous work, the special luminescence properties of Ce$^{3+}$ were discussed. Because Ce$^{3+}$ occupies different coordination environments in MgGd$_2$Si$_2$O$_13$ (Mg/Gd1 site with nine-coordination and Gd2 site with seven-coordination), under different excitations, Ce$^{3+}$ exhibits distinct emission spectra.18 The PLE spectra of MgGd$_2$Si$_2$O$_13$:0.16Mn$^{2+}$ and MgGd$_2$Si$_2$O$_13$:0.08Ce$^{3+}$, 0.16Mn$^{2+}$ and the PL spectra of...
MgGd₄Si₃O₁₃:0.08Ce³⁺ are displayed in Figure 4, respectively. The emission band peaked at 410 nm is attributed to the emission of Ce³⁺ occupying the Mg/Gd₁ site (Ce₁), and the emission band peaked at 505 nm is attributed to the emission of Ce³⁺ occupying the Gd₂ site (Ce₂). Because the PL spectrum of MgGd₄Si₃O₁₃:0.08Ce³⁺ overlaps significantly with the PLE spectrum of MgGd₄Si₃O₁₃:0.16Mn²⁺, the energy transfer from the Ce³⁺ to Mn²⁺ ions can be expected in the Ce³⁺ and Mn²⁺ codoped host. In addition, the 4f−5d transition of Ce³⁺ is observed in the excitation spectrum of MgGd₄Si₃O₁₃:0.08Ce³⁺, 0.16Mn²⁺ (the green line in Figure 4) monitoring at 602 nm emission (the emission of Mn²⁺), which demonstrates that there is an effective energy transfer effect between Ce³⁺ and Mn²⁺.

In order to study the energy transfer from Ce³⁺ to Mn²⁺, a series of MgGd₄Si₃O₁₃:0.08Ce³⁺, xMn²⁺ (0 ≤ x ≤ 0.16) samples have been prepared. Figure 5a,b displays the PL spectra excited at 298 and 340 nm, respectively. It can be seen that with the increase of Mn²⁺ concentration, the emission intensity of Ce³⁺ decreases monotonically, which can be used as the evidence of energy transfer between Ce³⁺ and Mn²⁺. Therefore, according to the different emission positions of Ce³⁺ and Mn²⁺, the color can be adjusted from blue to red (as shown in Figure S1). Figure S2 displays the decay curves of Ce³⁺, and based on the Dexter’s and Reisfeld’s theories and decay curves, the dominant energy transfer mechanism from Ce³⁺ to Mn²⁺ was identified as a dipole−quadrupole interaction (as shown in Figure S3).¹⁹−²²

2.3. Thermal Stability and Ratiometric Temperature Sensing. The temperature-dependent PL spectra of MgGd₄Si₃O₁₃:0.08Ce³⁺ excited at 298 and 340 nm are shown in Figure 6a,b, respectively. The luminescence intensities of Ce³⁺ decrease obviously with the increase of temperature. Moreover, when the temperature rises to 200 °C, the emission band at 505 nm disappears, while the band at 410 nm occurs. All these changes have been shown in the inset of Figure 6b, which indicates that the thermal stability of Ce₁ and Ce₂ is obviously different. Generally, the Ce³⁺ located at the rigid host lattice is expected to have good thermal stability with a narrow emission band.²³−²⁵ By comparing the emission spectra of Ce₁ and Ce₂, it is found that the half-height width of Ce₁ is

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Figure 3. (a) PLE spectra of MgGd₄Si₃O₁₃:xMn²⁺ (0.04 ≤ x ≤ 0.20) monitored at 602 nm; (b) the PL spectra of MgGd₄Si₃O₁₃: xMn²⁺ (0.04 ≤ x ≤ 0.20) excited at 409 nm.

Figure 4. PLE spectra of MgGd₄Si₃O₁₃:0.16Mn²⁺ (black) and MgGd₄Si₃O₁₃: 0.08Ce³⁺, 0.16Mn²⁺ (green) monitored at 602 nm. The PL spectra of MgGd₄Si₃O₁₃:0.08Ce³⁺ excited at 298 (red) and 340 (blue) nm.

Figure 5. PL spectra of MgGd₄Si₃O₁₃:0.08Ce³⁺, xMn²⁺ (0 ≤ x ≤ 0.16) excited at (a) 298 and (b) 340 nm.

Figure 6. Temperature-dependent PL spectra of MgGd₄Si₃O₁₃:0.08Ce³⁺ monitored at (a) 298; (b) 340 nm.
significantly smaller than that of Ce2, which indicates that the Mg/Gd1 site shows better structural rigidity than the Gd2 site. Therefore, Ce1 has better thermal stability than Ce2. The obvious difference in thermal stability between Ce1 and Ce2 is attributed to the different structural rigidities of Mg/Gd1 and Gd2 sites. Due to the stronger rigidity of the Mg/Gd1 site, Ce1 exhibits a relatively narrower emission band and better thermal stability. The results of normalized spectra (shown in Figure 6c,d) also indicate that with the increase of temperature, the excitation and emission spectra of Ce2 appear more obvious broadening, indicating that Ce2 is more obviously affected by phonons. The spectral broadening results show that after the
electrons of Ce2 are excited to the 5d level, they are more likely to return to the 4f level in a radiation-free way through cross-relaxation, resulting in a more obvious emission intensity reduction.

The temperature-dependent PL spectra of MgGd4Si3O13:0.08Ce3+, 0.16 Mn2+ excited at 298 and 340 nm are shown in Figure 7a,b, respectively. The luminescence intensities of Ce3+ and Mn2+ decrease obviously with the increase of temperature. To further investigate the thermal quenching phenomenon of the MgGd4Si3O13:Ce3+, Mn2+ sample, a configurational coordinate diagram based on the spectra is shown in Figure 8.26−28 When MgGd4Si3O13:Ce3+, Mn2+ was excited under 340 nm excitation, some of the excited electrons jumped to the ground state and produced the yellow light emission, and some of them back to the ground state with nonradiation relaxation by passing through the intersection of the ground state and the excited state, causing the loss of luminescence intensity (① and ②). At the same time, some excited electrons transfer energy to the electrons of Mn2+, making the electrons of Mn2+ transition to the excited state (③). Similarly, some of these transition to the ground state of red light emission, and some of them relax to the ground state without radiation through the intersection of the ground state and the excited state (④). When the material is excited at 298 nm, the excited electrons of Ce1 will not only produce the blue emission and nonradiation relaxation (⑥) and (⑦) but also transfer energy to Ce2 and Mn2+ (⑧ and ⑨). Therefore, under 298 nm excitation, the process ① to ④ and the emission of Ce2 and Mn2+ will also occur.

Based on the above discussion, we can take the luminescence intensity ratio of Ce3+ and Mn2+ (Δ = I_{Ce3+}/I_{Mn2+}) as a temperature measurement parameter. Figure 9a,b shows the changes of the luminescence intensity ratio at different temperatures when MgGd4Si3O13:0.08Ce3+, 0.16 Mn2+ was excited at 298 and 340 nm, respectively.
Mn²⁺ is excited at 298 and 340 nm, respectively. The Δ values are normalized to the Δ_{303K} value (Δ value at room temperature). It can be seen that the normalized Δ values are linearly correlated in the range of 303–473 K. According to the linear fitting results, the relative sensitivity (Sr) can be calculated according to the following formula20

\[ Sr = \left\{ \frac{\partial \Delta}{\partial T} \right\} \]

where Δ is the intensity ratio and T is the temperature. Figure 9c,d exhibits the variation in the Sr values at different temperatures. Under different excitations, the sensitivity shows different trends with the temperature. Under 298 nm excitation, the Sr decreased with the increase of temperature, and the maximum value was 0.21% K⁻¹. Under 340 nm excitation, the Sr increased with the increase of temperature, and the maximum value was 0.95% K⁻¹. Besides, the five-time cyclic heating test of MgGd₄Si₃O₁₃:0.08Ce³⁺, 0.16Mn²⁺ between 303 and 473 K is given in Figure 10. The MgGd₄Si₃O₁₃:0.08Ce³⁺, 0.16Mn²⁺ sample showed that the recycling performance and the change of fluorescence intensity ratio are less than 5% after five cycling steps. The Sr value and temperature range of MgGd₄Si₃O₁₃:0.08Ce³⁺, 0.16Mn²⁺ and some Ce³⁺–Mn²⁺ codoped thermometers are provided in Table 1. Comparing with our previous report [NaBaSc-\((BO_3)_2: Ce^{3+}, Mn^{2+}\)](318051936), the sensitivity of MgGd₄Si₃O₁₃: Ce³⁺, Mn²⁺ is not outstanding, but it still has advantages over other phosphors. These results showed that MgGd₄Si₃O₁₃: Ce³⁺, Mn²⁺ phosphors could be used as a high-sensitivity optical thermometer.

3. CONCLUSIONS

In summary, a novel apatite dual-excitation luminescent ratiometric thermometer MgGd₄Si₃O₁₃: Ce³⁺, Mn²⁺ was successfully synthesized via the solid-state method. The energy transfer between Ce³⁺ and Mn²⁺ was discussed in detail. The luminescent properties of Mn²⁺ and the temperature-dependent luminescent properties of MgGd₄Si₃O₁₃: Ce³⁺, Mn²⁺ have been investigated. Under the excitations of 298 and 340 nm, the fluorescent intensity ratio of Ce³⁺ and Mn²⁺ is linearly related to the temperature in the range of 303–473 K with high sensitivity of 0.95% K⁻¹. The above results indicate that MgGd₄Si₃O₁₃: Ce³⁺, Mn²⁺ can serve as a good candidate material for luminescent ratiometric thermometry.

4. EXPERIMENTAL SECTION

4.1. Preparation of Materials.

All samples in our work were synthesized by the solid-state reaction. The starting materials were Gd₂O₃ (99.99%), MnCO₃ (99.99%), CeO₂ (99.99%), H₂SiO₃ (A.R.), and MgO (A.R.). These materials were used as raw materials without any further purification. After been mixed well in agate mortar, these ingredients were calcinated at 1480 °C in a reducing atmosphere of 20% H₂–80% N₂ for 6 h.

4.2. Characterization.

The phase structures of the obtained samples were tested by a Rigaku D/Max-2400 diffractometer with Ni-filtered Cu Kα radiation. The PL properties (PL, PLE spectra, and PL decay curves) were obtained by a FLS-920T fluorescence spectrophotometer equipped with Xe and nF900 ns Flashlamp source. All the measurements were performed at room temperature. The temperature-dependent emission was tested combined with the heating apparatus (TAP-02).

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04710

**Table 1. Sr Values and Temperature Range of MgGd₄Si₃O₁₃:0.08Ce³⁺, 0.16Mn²⁺ and Some Ce³⁺–Mn²⁺ Codoped Thermometers**

| Material | Sr (% K⁻¹) | Temperature Range (K) | Reference |
|----------|------------|-----------------------|-----------|
| MgGd₄Si₃O₁₃:Ce³⁺, Mn²⁺ | 0.21 | 300–473 | This work |
| (Ca,Sr)₁₀Li(PO₄)₇:Ce³⁺, Mn²⁺ | 0.4 | 293–473 | 30 |
| NaMgBO₃:Ce³⁺, Mn²⁺ | 0.69 | 293–473 | 31 |
| NaBaSc(BO₃)₂:Ce³⁺, Mn²⁺ | 3.16 | 298–473 | 14 |

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

1. Dong, B.; Cao, B.; He, Y.; Liu, Z.; Li, Z.; Feng, Z. Temperature sensing and in vivo imaging by molybdenum sensitized visible
upconversion luminescence of rare-earth oxides. *Adv. Mater.* 2012, 24, 1987–1993.

(2) Chen, D.; Wan, Z.; Zhou, Y.; Zhou, X.; Yu, Y.; Zhong, J.; Ding, M.; Ji, Z. Dual-phase glass ceramic: structure, dual-modal luminescence, and temperature sensing behaviors. *ACS Appl. Mater. Interfaces* 2015, 7, 19484–19493.

(3) Chen, D.; Wan, Z.; Zhou, Y. Optical spectroscopy of Cr3+-doped transparent nano-glass ceramics for lifetime-based temperature sensing. *Opt. Lett.* 2015, 40, 3607–3610.

(4) Gao, Y.; Huang, F.; Lin, H.; Zhou, J.; Xu, J.; Wang, Y. A novel optical thermometry strategy based on diverse thermal response from two intervalence charge transfer states. *Adv. Funct. Mater.* 2016, 26, 3139–3145.

(5) Skripka, A.; Benayas, A.; Marin, R.; Canton, P.; Hemmer, E.; Vetrone, F. Double rare-earth nanothermometer in aqueous media: opening the third optical transparency window to temperature sensing. *Nanoscale* 2017, 9, 3079–3085.

(6) Cui, Y.; Xu, H.; Yue, Y.; Guo, Z.; Yu, J.; Chen, Z.; Gao, J.; Yang, Y.; Qian, G.; Chen, B. A luminescent mixed-lanthanide metal–organic framework thermometer. *J. Am. Chem. Soc.* 2012, 134, 3979–3982.

(7) Rao, X.; Song, T.; Gao, J.; Cui, Y.; Yang, Y.; Wu, C.; Chen, B.; Qian, G. A highly sensitive mixed lanthanide metal–organic framework self-calibrated luminescent thermometer. *J. Am. Chem. Soc.* 2013, 135, 15559–15564.

(8) Jethi, L.; Krause, M. M.; Kambhampati, P. Toward ratiometric nanothermometry via intrinsic dual emission from semiconductor nanocrystals. *J. Phys. Chem. Lett.* 2015, 6, 718–721.

(9) Yang, Y.; Chen, L.; Jiang, F.; Yu, M.; Wan, X.; Zhang, B.; Hong, M. A family of doped lanthanide metal–organic frameworks for wide-range temperature sensing and tunable white light emission. *J. Mater. Chem. C* 2017, 5, 1981–1989.

(10) Cui, Y.; Song, R.; Yu, J.; Liu, M.; Wang, Z.; Wu, C.; Yang, Y.; Wang, Z.; Chen, B.; Qian, G. Dual-emitting MOF-Dye composite for ratiometric temperature sensing. *Adv. Mater.* 2015, 27, 1420–1425.

(11) Xu, W.; Zhao, H.; Li, Y.; Zheng, L.; Zhang, Z.; Cao, W. Optical temperature sensing through the upconversion luminescence from Ho3+/Yb3+ co-doped CaWO4 crystal. *Sens. Actuators, B* 2013, 183, 1096–1100.

(12) Li, D.; Wang, Y.; Zhang, X.; Yang, K.; Liu, L.; Song, Y. Optical temperature sensor through infrared excited blue upconversion emission in Tm3+/Yb3+ co-doped Y2O3. *Opt. Commun.* 2012, 285, 1925–1928.

(13) Zhou, X.; Geng, W.; Ding, J.; Zhao, Z.; Wang, Y. Ca2Na0.5La0.5(SiO4)2(OPO4)2: Eu3+/Eu3+ A novel dual-emitting fluorescent ratiometric temperature sensor. *J. Alloys Compd.* 2019, 784, 5443–5453.

(14) Geng, W.; Zhou, X.; Ding, J.; Wang, Y. Density-functional theory calculations, luminescence properties and fluorescence ratiometric thermo-sensitivity for a novel borate based red phosphor: NaBaSc2(BO3)3:Ce3+, Mn2+. *J. Mater. Chem. C* 2019, 7, 1982–1990.

(15) Yan, B.; Wei, Y.; Wang, W.; Fu, M.; Li, G. Red-tunable LuAl garnet phosphors via Eu3+/Mn2+ energy transfer for optical thermometry sensor application. *Inorg. Chem. Front.* 2021, 8, 746–757.

(16) Tian, Y.; Wei, Y.; Zhao, Y.; Quan, Z.; Li, G.; Lin, J. Photoluminescence tuning of Ca10(P2O7)4Cl2: Ce3+/Eu3+, Tb3+/Mn2+ phosphors: structure refinement, site occupancy, energy transfer and thermal stability. *J. Mater. Chem. C* 2016, 4, 1281–1294.

(17) Zhou, X.; Geng, W.; Ding, J.; Wang, Y.; Yang, Y. Structure, bandgap, photoluminescence evolution and thermal stability improved of Sr replacement apatite phosphors Ca10−xSr2+x(P2O7)4F2:Eu3+ (x= 4, 6, 8). *Dyes Pigm.* 2018, 152, 75–84.

(18) Zhou, X.; Zhang, Z.; Wang, Y. Ce3+ and Tb3+ singly-and co-doped MgGd2Si2O7 for ultraviolet light emitting diodes and field emission displays. *J. Mater. Chem. C* 2015, 3, 3676–3683.

(19) Fan, F.; Zhao, L.; Shang, Y.; Liu, J.; Chen, W.; Li, Y. Thermally stable double-perovskite Ca3TeO6: Eu3+ red-emitting phosphors with high color purity. *J. Lumin.* 2019, 211, 14–19.

(20) Lahoz, F.; Martin, I. R.; Ménendez-Ramos, J.; Nuñez, P. Dopant distribution in a Tm3+/Yb3+ co-doped silica based glass ceramic: an infrared-laser induced upconversion study. *J. Chem. Phys.* 2004, 120, 6180–6190.

(21) Blasse, G. Energy transfer in oxide phosphors. *Phys. Lett. A* 1968, 28, 444–445.

(22) Blasse, G.; Grabmaier, B. C. *Luminescent Materials*; Springer-Verlag: Berlin, Germany, 1994.

(23) Wang, Y.; Ding, J.; Wang, Y.; Zhou, X.; Cao, Y.; Ma, B.; Li, J.; Wang, X.; Seto, T.; Zhao, Z. Structural design of new Ce3+/Eu3+ co-doped or co-doped phosphors with excellent thermal stabilities for WLEDs. *J. Mater. Chem. C* 2019, 7, 1792–1820.

(24) Hu, T.; Molokeev, M. S.; Xia, Z.; Zhang, Q. Aliovalent substitution toward reinforced structural rigidity in Ce3+-doped garnet phosphors featuring improved performance. *J. Mater. Chem. C* 2019, 7, 14594–14600.

(25) Qiao, J.; Zhao, J.; Liu, Q.; Xia, Z. Recent advances in solid-state LED phosphors with thermally stable luminescence. *J. Rare Earths* 2019, 37, 565–572.

(26) Ji, X.; Zhang, J.; Li, Y.; Liao, S.; Zhang, X.; Yang, Z.; Wang, Z.; Qiu, Z.; Zhou, W.; Yu, L.; Lian, S. Improving Quantum Efficiency and Thermal Stability in Blue-Emitting Ba₃Sr₂SiO₆: Ce³⁺ Phosphor via Solid Solution. *Chem. Mater.* 2018, 30, 5137–5147.

(27) Zhang, Q.; Wang, X.; Tang, Z.; Yang, Y.; Wang, Y. A K3Sc3Si2O7: Eu³⁺ based phosphor with broad-band NIR emission and robust thermal stability for NIR pc-LEDs. *Chem. Commun.* 2020, 56, 4644–4647.

(28) Qu, M.; Zhang, X.; Mi, X.; Liu, Q.; Bai, Z. Novel color tunable garnet phosphor of Tb³⁺ and Eu³⁺ co-doped Ca₃Y₂Zr₂Al₂O₁₁ with high thermal stability via energy transfer. *J. Alloys Compd.* 2020, 828, 154398.

(29) McLaurin, E. J.; Bradshaw, L. R.; Gamelin, D. R. Dual-emitting nanoscale temperature sensors. *Chem. Mater.* 2013, 25, 1283–1292.

(30) Zhang, X.; Xu, J.; Guo, Z.; Gong, M. Luminescence and energy transfer of dual-emitting solid solution phosphors (Ca,Sr)₃(PO₄)₅: Ce³⁺, Mn²⁺ for ratiometric temperature sensing. *Ind. Eng. Chem. Res.* 2017, 56, 890–898.

(31) Song, J.; Zhao, W.; Zhang, H.; Liu, Y.; Huang, H.; Yang, H.; Zhang, H.; Zhong, J. Energy transfer and ratiometric Temperature sensing based on the dual-emitting NaMgBO₃: Ce³⁺, Mn²⁺ phosphor. *J. Lumin.* 2021, 232, 117858.