Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Realizing a novel dazzling far-red-emitting phosphor $NaLaCaTeO_6:Mn^{4+}$ with high quantum yield and luminescence thermal stability via the ionic couple substitution of $Na^{+}+La^{3+}$ for $2Ca^{2+}$ in $Ca_3TeO_6:Mn^{4+}$ for indoor plant cultivation LEDs

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Experimental information

Materials synthesis

A series of materials with the chemical formula $NaLaCaTe_{1-x}O_6:xMn^{4+}$ (NLCTO:xMn^{4+}, x = 0-0.04) and $Na_yLa_yCa_{3-2y}TeO_6:0.01Mn^{4+}$ ($N_yL_yC_{3-2y}TO:0.01Mn^{4+}$, y = 0-1.5) were synthesized using a high-temperature solid-state reaction method. Stuff Na_2CO_3 (A.R.), La_2O_3 (99.99%), TeO_2 (99.99%) and MnO_2 (A.R.) were weighted according to the given chemical formula and ground in an agate mortar with a pestle after the addition of necessary ethanol to obtain the homogeneous mixture. Then, the mixture was ground again for 1 min followed by dried an oven with 60 ^{0}C, and they were transferred into a ceramic crucible for pre-calcination in a furnace under air condition at 500 ^{0}C for 2 h and subsequent calcination at 1100 ^{0}C for 6 h, keeping a heating rate of 5 °C/min. Finally, the products were cooled within the furnace and ground for another 1 min for subsequent characterization.

Characterization

An X-ray diffraction (XRD) measurement was conducted on the setup of Thermo Scientific ARLX'TRA diffractometer equipped with a Cu Kα source (λ = 1.5405 Å), maintaining the scanning rate at 5°/min in the scattering angle range (2θ) of 15°-65°. Rietveld refinement for a powder X-ray diffraction (PXRD) pattern required the different scanning range of 5-90° with a processing rate of 0.5°/min. Energy Dispersive X-Ray Fluorescence (XRF) measurement was done on the Rigaku NEX CG setup. Photoluminescence (PL), quantum yield (QY) and lifetimes were recorded on an Edinburgh Instruments FLSP 920 UV-vis-NIR spectrofluorimeter, equipped with a 450 W continuous xenon lamp and a 60 W pulsed xenon lamp. Additionally, the measurement of temperature-dependent PL spectrum was implemented with the assistance of a temperature controller Model 336 from Lakeshore Company.

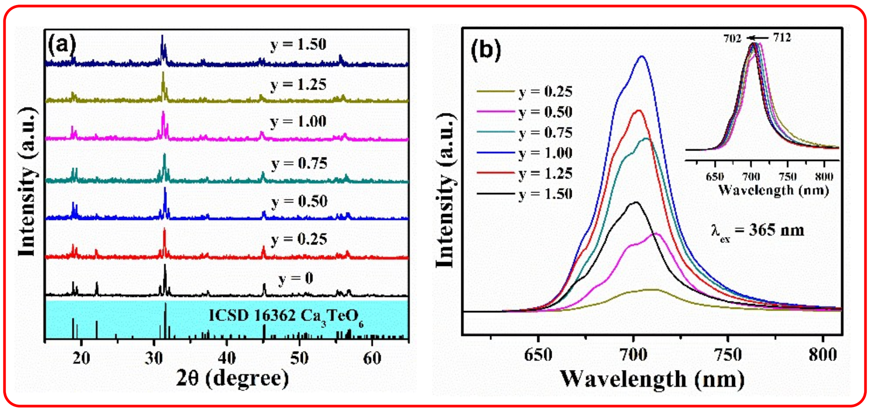

Fig. S1 (a) XRD patterns for $N_yL_yC_{3-2y}TO:0.01Mn^{4+}$ (y = 0-1.5) with the different Na^+ and La^{3+} substituted concentration. (b) PL emission spectra (λ_{ex} = 365 nm) for $N_yL_yC_{3-2y}TO:0.01Mn^{4+}$ (y = 0.25-1.5), inset is the corresponding normalized PL emission spectra.

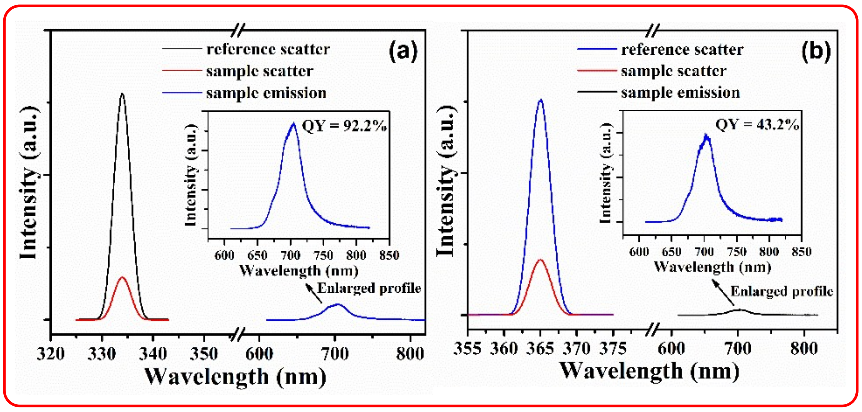

Fig. S2 The reference, sample absorption and sample emission for calculating quantum yield (QY) for NLCTO:0.01Mn^{4+} samples under 334 (a) and 365 nm (b) excitations.

The quantum yield can be obtained using the integrated sphere method as follows:[1]

$$\eta = \frac{\int L_{emission}}{\int E_{blank} - \int E_{sample}} \tag{S1}$$

where $L_{emission}$ is the integrated value of the emission spectrum, E_{blank} and E_{sample} are the integrated values of the “excitation” band of the blank and the excitation band of the sample (since the sample absorbs part of the light, this value will be smaller than E_{blank}), respectively.

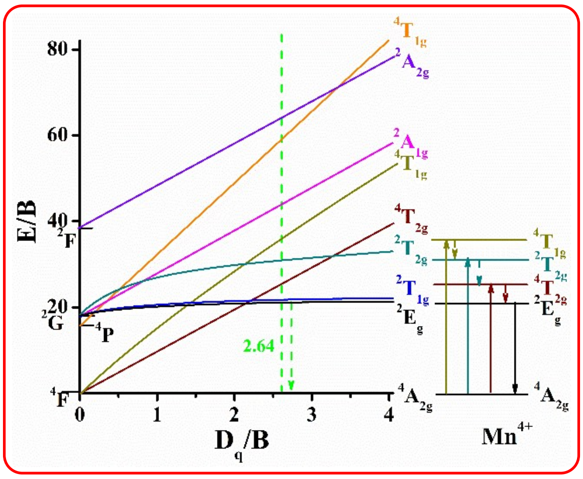

Fig. S3 Simplified Tanabe-Sugano energy level diagram of the Mn^{4+} (d^3) electron configuration in the octahedral crystal field of the NLCTO host.

The local crystal-field strength (D_q) around the Mn^{4+} ions by the next equation:[2]

$$D_q = E\left({}^4T_{2g} \leftarrow {}^4A_{2g}\right)/10 \tag{S2}$$

According to the PL emission and excitation spectra, the peak energy of the $^4T_{2g} \leftarrow {}^4A_{2g}$ transition is 21008 cm^{-1} (476 nm), therefore, the D_q is estimated to be 2101 cm^{-1}. By using the energy difference between the $^4T_{2g} \leftarrow {}^4A_{2g}$ (21008 cm^{-1}) and $^4T_{1g} \leftarrow {}^4A_{2g}$ (29070 cm^{-1}) transitions (which turns out to be 8062 cm^{-1}), the Racah parameter B can be calculated according to the equation:[3]

$$\frac{D_q}{B} = \frac{15(x-8)}{x^2-10x} \tag{S3}$$

where x is:

$$x = \frac{E\left({}^4T_{1g} \leftarrow {}^4A_{2g}\right) - E\left({}^4T_{2g} \leftarrow {}^4A_{2g}\right)}{D_q} \tag{S4}$$

Therefore, the parameter B can be estimated to be 796 cm^{-1} After that, the second Racah parameter C can be estimated from the following equation:

$$\frac{E\left({}^2E_g \rightarrow {}^4A_{2g}\right)}{B} = \frac{3.05C}{B} - \frac{1.8B}{D_q} + 7.9 \tag{S5}$$

According to the emission spectrum, the peak energy of $^2E_g \rightarrow {}^4A_{2g}$ transition is about 14164 cm^{-1}, after combining the parameter B and D_q above, consequently, the parameter C is 2760 cm^{-1}.

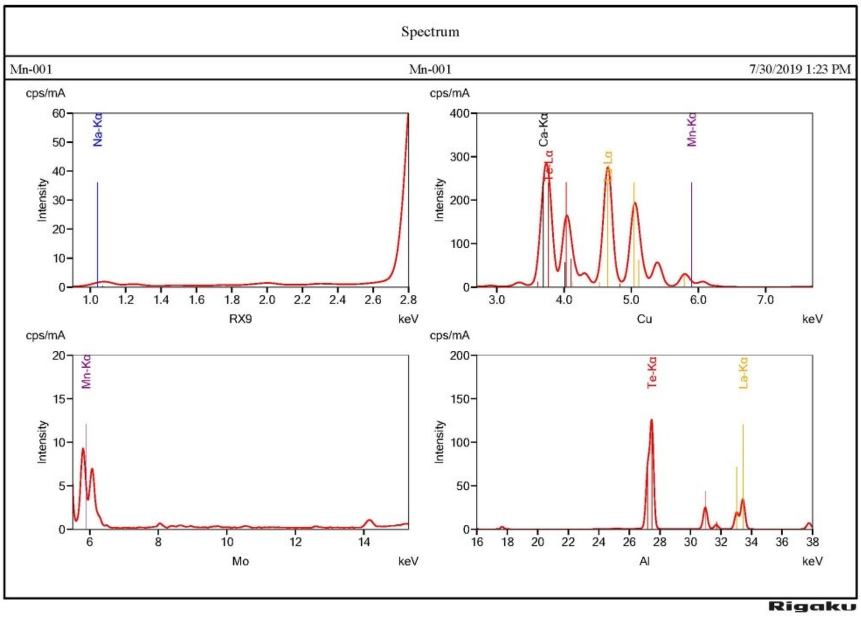

Fig. S4 XRF spectra for the representative NLCTO:0.01Mn^{4+} sample.

Result of elemental analysis:

No.	Component	Result	Unit	Statistical error	Detection limit	Quantitation limit
1	O	0.00	mass%			
2	Na	7.04	mass%	0.264	0.560	1.68
3	La	41.82	mass%	0.177	0.0499	0.150
4	Ca	12.16	mass%	0.0398	0.0884	0.265
5	Te	38.8	mass%	0.142	0.0360	0.108
6	Mn	0.17	mass%	0.0134	0.0069	0.0208

Calculated elemental molar ratio

Na:La:Ca:Te:Mn = 0.306:0.303:0.304:0.305:0.00309

Since O is a light element, it can not be detected by the XRF measurement in current case and it can be ignorable for calculation.

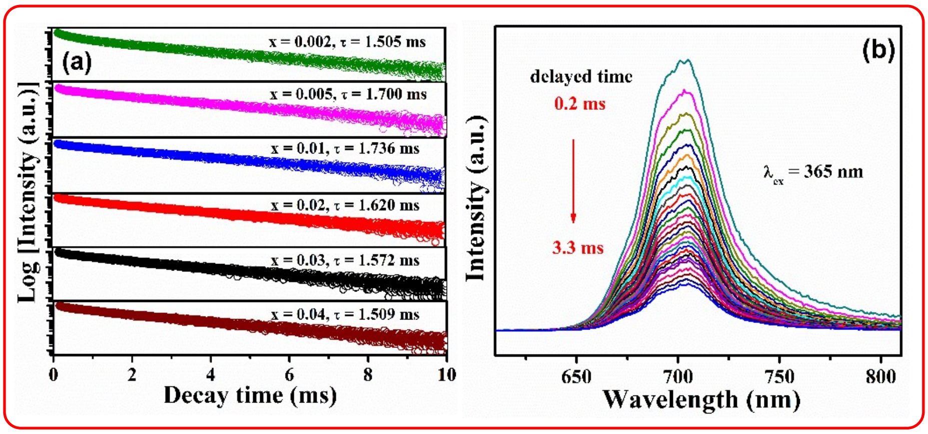

Fig. S5 (a) Decay curves (λ_{ex} = 365 nm, λ_{em} = 706 nm) and calculated decay times of series NLCTO:xMn^{4+} samples as a function of x. (b) Time-resolved emission spectra (λ_{ex} = 365 nm) for NLCTO:0.01Mn^{4+} with the delayed time from 0.2 ms to 3.3 ms.

The double-exponential function is used for decay curves fitting, which can be expressed as follows:[4]

$$I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$

(6)Where $I(t)$ and I_0 are the intensity at the time of t and 0, respectively, A_1 and A_2 are the constants, τ_1 and τ_2 stand for the fluorescence lifetimes for the fast and slow decay, respectively. The average lifetimes (τ) can be estimated by the following formula:

$$\tau = \left(A_1\tau_1^2 + A_2\tau_2^2\right) / \left(A_1\tau_1 + A_2\tau_2\right) \quad (7)$$

Table S1 Detailed crystallographic data of refinement parameters for the NLCTO and NLCTO:0.01Mn^{4+} samples.

Sample	**NLCTO**	**NLCTO:0.01Mn^{4+}**
Space group	*P121/c1*	*P121/c1*
Symmetry	monoclinic	monoclinic
a, Å	5.6200(4)	5.6307(3)
b, Å	5.8302(4)	5.8355(3)
c, Å	8.0511(4)	8.0699(4)
V, $Å^3$	263.80(3)	265.16(2)
Z	2	2
A = γ,°	90	90
β	90.188	90.342
2θ-interval,°	5-90	5-90
R_{wp}/%	13.72%	13.60
R_p/%	11.20%	10.80
χ^2	1.116	1.203

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