A novel Mn^{2+} doped $ScTaO_4$ dual-emitting phosphor for high temperature optical thermometry

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Table S1. Crystallographic data, positions of all atoms and the occupancy for the STO:$0.002Mn^{2+}$ phosphor by Rietveld refinement.

Cell parameters	$a = 4.8060$ Å $b = 5.6723$ Å, $c = 5.1152$ Å $\alpha = \gamma = 90°, \beta = 91.6°$ $V = 139.39$ Å^3				
Space group	$P12/c1$, monoclinic				
Reliability factors	$R_{wp} = 5.95$ % $R_p = 4.5$ % $\chi^2 = 4.293$				
Atoms	x	y	z	$B_{iso}/B_{eq}{}^a$	s.o.f^b
Sc1	0.5	0.653	0.25	0.01442	0.998
Sc2	-0.5	-0.653	-0.25	0.01442	0.998
Mn1	0.5	0.653	0.25	0.01442	0.002
Mn2	-0.5	-0.653	-0.25	0.01442	0.002
Ta1	0	0.18192	0.25	0.00554	1
Ta2	0	-0.18192	-0.25	0.00554	1
O1	0.245969	0.173898	-0.08142	0.03694	1

O2	0.428979	-0.30484	0.43935	0.02188	1
O3	-0.24597	-0.1739	0.081417	0.02598	1
O4	-0.22643	0.083607	-0.41481	0.02633	1
O5	0.217765	0.451892	0.402127	0.02133	1

[a]B_{iso}/B_{eq} refers to the general temperature factor. [b]s.o.f refers to the site occupation fraction.
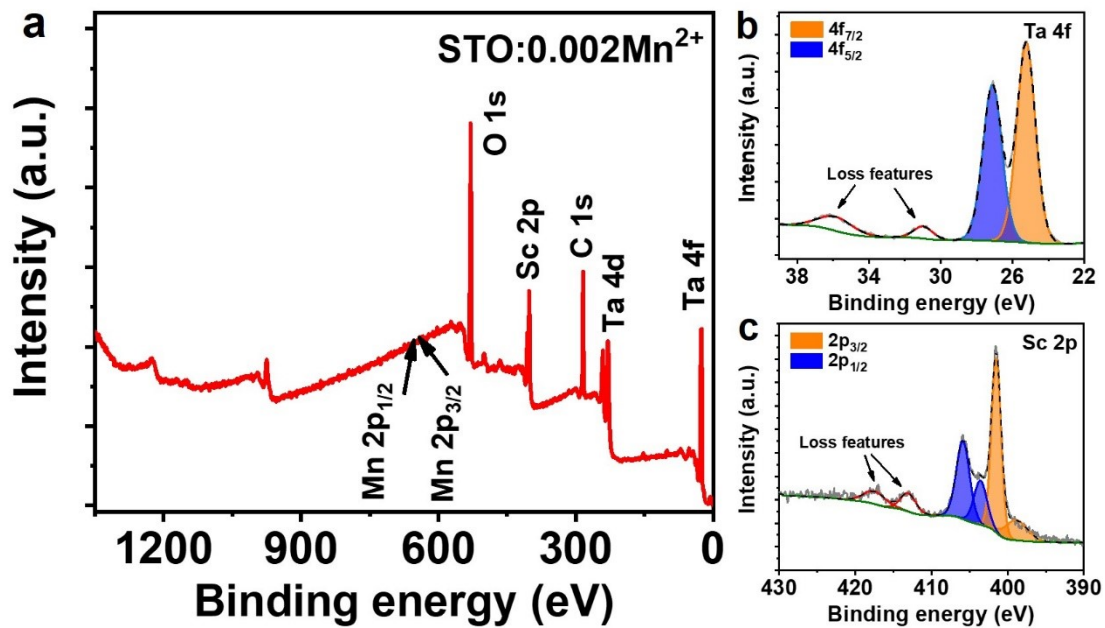

Fig. S1 (a) XPS survey spectra of STO:0.002Mn^{2+}, (b) HR-XPS core spectra of Ta 4f orbital and (c) HR-XPS core spectra of Sc 2p orbital.
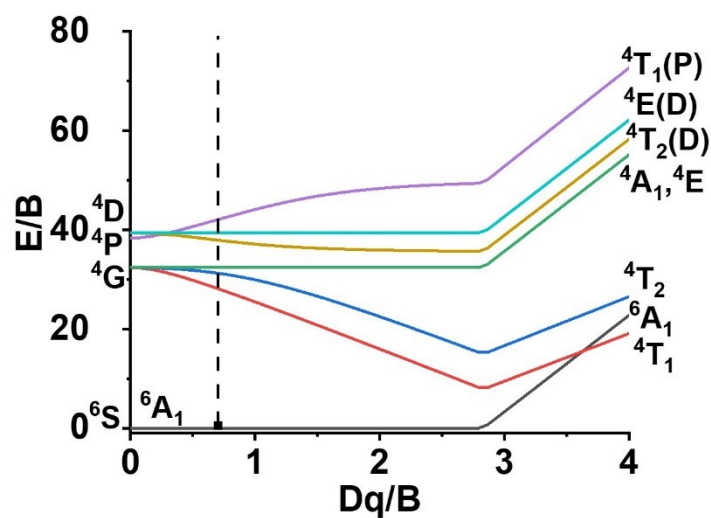

Fig. S2 Tanable–Sugano diagram of 3d^5 electronic configuration of Mn^{2+} ions.

Details calculation for the Dq and Dq/B for the STO:0.002Mn^{2+}: Four excitation bands

around at 27324.04cm^{-1}(366nm), 23530.82cm^{-1}(425nm), 22473.26cm^{-1}(445nm), and 21098.31cm^{-1}(474nm) are corresponding to the transitions of $^6A_1(^6S) \rightarrow ^4E(^4D)$, $^6A_1(^6S) \rightarrow ^4T_2(^4D)$, $^6A_1(^6S) \rightarrow ^4E, ^4A_1(^4G)$, and $^6A_1(^6S) \rightarrow ^4T_2(^4G)$ of Mn^{2+} ions by utilizing the Tanabe–Sugano energy level diagram for the 3d^5 configuration of Mn^{2+}. The transitions of $^4E(^4D) \rightarrow ^6A_1(^6S)$ and $^4E, ^4A_1(^4G) \rightarrow ^6A_1(^6S)$ are parity- and spin-forbidden. The ground state ^6S level is set to zero, the coordination of ^4G and ^4D energies of octahedron Mn^{2+} depends on the Racah parameter values of B and C, which can be calculated follow the equations:

$$^6A_1(^6S) \rightarrow ^4E, ^4A_1(^4G) = 10B + 5C \quad (S1)$$

$$^6A_1(^6S) \rightarrow ^4E, (^4D) = 17B + 5C \quad (S1)$$

$$E\,^4E, ^4A_1(^4G) + E\,^4E, (^4D) = 10Dq \quad (S3)$$

where B and C are Racah parameters, Dq is the cubic-field splitting parameter. The $Dq = 485$ cm^{-1}, $B = 693$, $C = 3109$, $Dq/B = 0.7$.
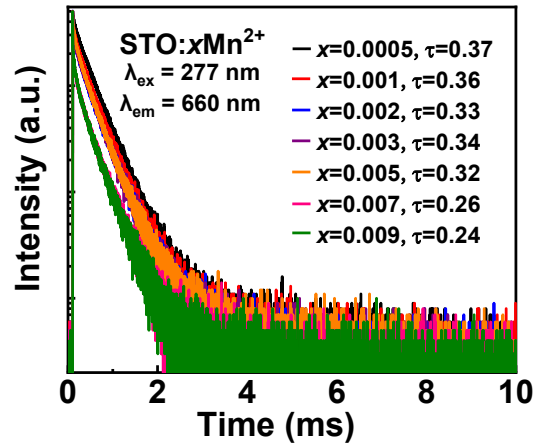

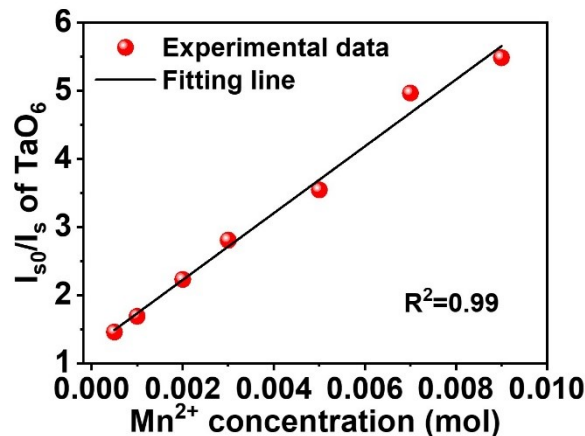Fig. S3 Decay curves of STO:xMn^{2+} phosphors by monitoring the emission at 660 nm

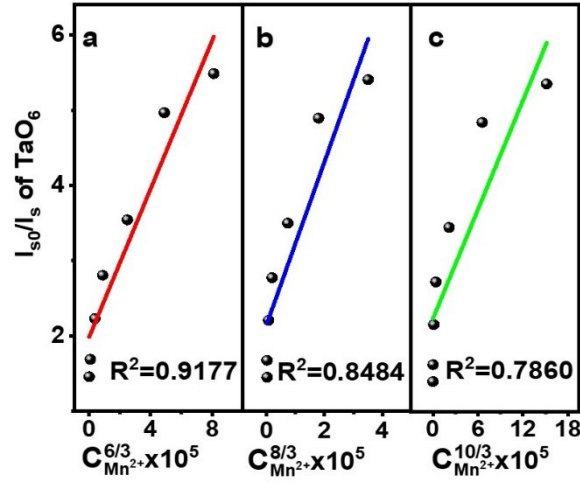Fig. S4 Relationship between the intensity ratio I_{s0}/I_s of [TaO$_6$] groups and Mn^{2+} doping concentrations

Fig. S5 Dependence of I_{s0}/I_s of host on $C_{Mn^{2+}}^{6/3}$ (a), $C_{Mn^{2+}}^{8/3}$ (b), and $C_{Mn^{2+}}^{10/3}$ (c).

Details for the energy transfer process: The relationship between the intensity ratio I_{s0}/I_s of [TaO$_6$] groups and Mn^{2+} doping concentrations are shown in Fig. S4. Where I_s and I_{s0} represent the emission intensity of [TaO$_6$] groups with and without Mn^{2+} ions, respectively. As the doping Mn^{2+} ion concentration increase, the value of I_{s0}/I_s for TaO$_6$ groups monotonically increases, which further suggests that there's an effective energy transfer path existing between [TaO$_6$] groups and Mn^{2+} ions. The energy transfer process from [TaO$_6$] groups to Mn^{2+} in STO:Mn^{2+} in STO should occurs via a multipolar interaction according to the Dexter's energy transfer expression and Reisfeld's approximation. The following relation can be given: S1,S2

$$\eta_0/\eta \propto C^{\alpha/3} \quad \text{(S4)}$$

where η_0 and η represent emission quantum efficiencies of the host without and with Mn^{2+} ions, respectively; C is the concentration of Mn^{2+}; and the α = 6, 8, 10 corresponding to dipole-dipole, dipole-quadrupole and quadrupole-quadrupole

interaction, respectively. The value of η_0/η can be approximately estimated by the emission intensity ratio (I_{s0}/I_s) as follow: S1,S2

$$I_{s0}/I_s \propto C^{\alpha/3} \quad (S5)$$

The dependence of I_{s0}/I_s for $C_{Mn^{2+}}^{\alpha/3}$ ($\alpha = 6, 8, 10$ respectively) are exhibited in Fig. S5. The linear fitting is found to give a best match when $\alpha = 6$, with a correlation coefficient $R^2=0.9177$. Indicating that the dominant energy transfer mechanism from [TaO$_6$] groups to Mn^{2+} in STO is a dipole-dipole interaction.

Table S2　　The CIE coordinates of STO:xMn^{2+} ($x = 0 \sim 0.009$) samples

Mn^{2+} concentration	CIE coordinate (x, y)
0.000	(0.222, 0.302)
0.0005	(0.374, 0.329)
0.001	(0.418, 0.306)
0.002	(0.475, 0.307)
0.003	(0.502, 0.305)
0.005	(0.516, 0.303)
0.007	(0.538, 0.303)
0.009	(0.543, 0.305)

Table S3　　CIE chromaticity coordinates of STO:0.0005Mn^{2+} sample at various temperatures

Temperature (K)	CIE coordinate (x, y)
298	(0.374, 0.329)
323	(0.367, 0.332)
348	(0.343, 0.331)
373	(0.330, 0.330)
398	(0.318, 0.329)
423	(0.310, 0.327)
448	(0.295, 0.325)
473	(0.279, 0.322)

523	(0.258, 0.310)

The temperature uncertainty δT (thermal resolution) could be calculated follow the equation:

$$\delta T = \frac{1}{S_r} \frac{\delta LIR}{LIR} \qquad (S6)$$

where δLIR is the uncertainty in LIR, considering the uncertainty in the measurement of the influence intensity, $\frac{\delta LIR}{LIR}$ can be calculated according to the equation:

$$\frac{\delta LIR}{LIR} = \sqrt{\left(\frac{\delta I_{host}}{I_{host}}\right)^2 + \left(\frac{\delta I_{Mn^{2+}}}{I_{Mn^{2+}}}\right)^2} \qquad (S7)$$

For each transition, we can assume that:

$$\frac{\delta I_{host}}{I_{host}} = \frac{\delta I_{bl}}{\langle I \rangle} \qquad (S8)$$

Where δI_{bl} is the uncertainty determined by the fluctuations of the baseline readout, and $\langle I \rangle$ denotes the average intensity and evaluated over whole emission spectral region $(E_0 \leq E \leq E_1)$ by the equation:

$$\langle I \rangle = \frac{\displaystyle\int_{E_0}^{E_1} I(E)dE}{E_1 - E_0} \qquad (S9)$$

Combine above equation (S6-S9), the temperature δT could be calculated.
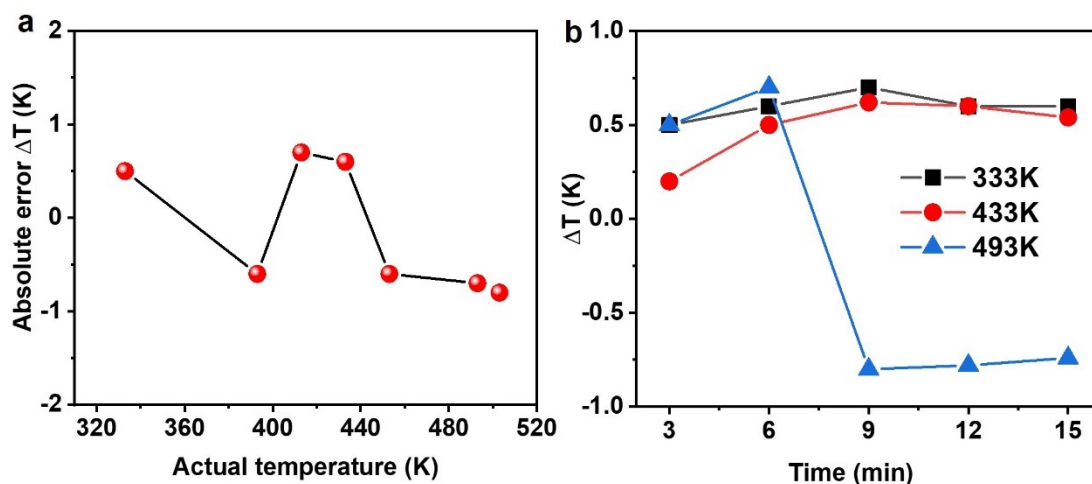
Fig. S6　(a) Absolute error at different temperature and (b) the repeatability of the optical fiber thermometry prototype.
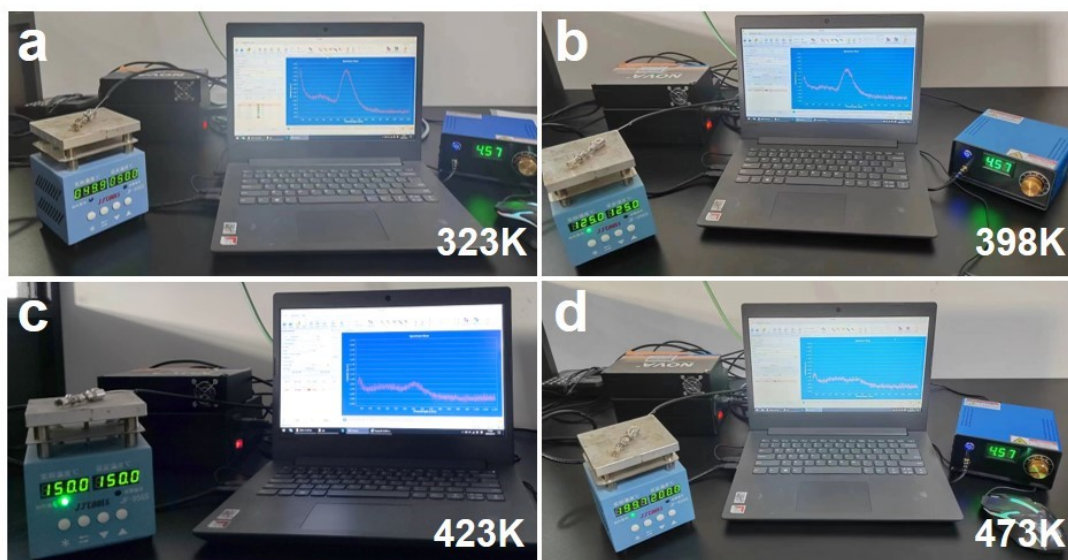

Fig. S7　The actual application using a heating stage and measuring the temperature with the prototype at 323 K (a), 398 K (b), 423 K (c) and 473 K (d).

References

1　D. L. Dexter and J. H. Schulman, J. Chem. Phys., 1954, 22, 6: 1063-1070.

2　Blasse, G. Phys. Lett. A 1968, 28, 444−445.