Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Fundamental luminescent properties of Mn^{4+} activated $Ca_{14}Al_{10}Zn_6O_{35}$ phosphor

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Table S1. Atom parameters of $Ca_{14}Al_{10}Zn_6O_{35}$ host.

Atom	x	y	z	B_{eff}, Å^2	multiplicity
Ca1	0.21405	0.00000	0.00000	0.306	24f
Ca2	0.61335	0.61335	0.61335	0.100	16e
Ca3	0.38734	0.38734	0.38734	0.100	16e
Zn1	0.17236	0.17236	0.17236	0.380	16e
Zn2	0.00000	0.00000	0.00000	0.100	4a
Al1	0.00000	0.00000	0.00000	0.100	4a
Zn3	-0.00230	0.25000	0.25000	0.100	24g
Al2	-0.00230	0.25000	0.25000	0.100	24g
Zn4	0.50000	0.50000	0.50000	0.120	4b
Al3	0.50000	0.50000	0.50000	0.120	4b
Zn5	0.85725	0.8571025	0.85725	0.130	16e
Al4	0.85725	0.8571025	0.85725	0.130	16e
O1	0.25000	0.25000	0.25000	0.460	4c
O2	0.36866	0.00000	0.00000	0.100	24f
O3	-0.06593	-0.06593	-0.06593	0.560	16e
O4	0.06688	0.25747	0.34915	0.570	48h
O5	0.15329	0.25575	0.56745	0.640	48h

Table S2. Atom parameters of CAZO:2.5%Mn phosphor.

Atom	x	y	z	B_{eff}, Å^2	multiplicity
Ca1	0.21420	0.00000	0.00000	0.306	24f
Ca2	0.61310	0.61310	0.61310	0.100	16e
Ca3	0.38760	0.38760	0.38760	0.100	16e
Zn1	0.17240	0.17240	0.17240	0.380	16e
Zn2	0.00000	0.00000	0.00000	0.100	4a
Al1	0.00000	0.00000	0.00000	0.100	4a
Zn3	-0.00230	0.25000	0.25000	0.100	24g
Al2	-0.00230	0.25000	0.25000	0.100	24g
Zn4	0.50000	0.50000	0.50000	0.120	4b
Al3	0.50000	0.50000	0.50000	0.120	4b
Mn1	0.50000	0.50000	0.50000	0.120	4b
Zn5	0.85710	0.85710	0.85710	0.130	16e
Al4	0.85710	0.85710	0.85710	0.130	16e
O1	0.25000	0.25000	0.25000	0.460	4c
O2	0.36980	0.00000	0.00000	0.100	24f
O3	-0.06670	-0.06670	-0.06670	0.560	16e
O4	0.06590	0.25610	0.34970	0.570	48h
O5	0.15040	0.25540	0.56960	0.640	48h

Table S3. Crystallographic data and refinement parameters of CAZO and CAZO:2.5%Mn.

Parameters	$Ca_{14}Al_{10}Zn_6O_{35}$	$Ca_{14}Al_{9.5}Zn_{6.25}Mn_{0.25}O_{35}$
a = b = c (Å)	14.89497	14.90359
$\alpha = \beta = \gamma$ (°)	90	90
V (Å^3)	3304.599	3310.340
R_p (%)	6.10	5.96
R_{wp} (%)	7.93	7.75
R_{exp} (%)	7.21	7.29
χ^2	1.21	1.13

The refinement parameters R_p, R_{wp}, and R_{exp} represent the profile R factor, the weighted profile R factor, and the expected R factor, respectively, while χ^2 means the fitting degree.

Table S4. Summary of the ZPL emission energies (in cm^{-1}; 1 eV = 8068 cm^{-1}), crystal-field, Racah and nephelauxetic parameters for CAZO:Mn^{4+} (this work) and some other Mn^{4+}-activated oxide and fluoride phosphors (#)

Host crystal	^2E_g (cm^{-1})	D_q (cm^{-1})	B (cm^{-1})	C (cm^{-1})	Dq/B	β_1	4B+3C (cm^{-1})	7B+3.1C (cm^{-1})
$Ca_{14}Al_{10}Zn_6O_{35}$	14388	1887	644	3179	2.930	0.924	12113	14363
$Ca_3Al_4ZnO_{10}$	14329	1825	495	3500	3.687	0.919	12480	14315
$CaMg_2Al_{16}O_{27}$	15216	1790	495	3785	3.616	0.978	13335	15199
$Sr_2MgAl_{22}O_{36}$	15208	1720	565	3635	3.044	0.975	13165	15224
$BaZnAl_{10}O_{17}$	15063	1815	675	3345	2.689	0.971	12735	15095
$MgAl_2O_4$	15370	1870	600	3600	3.117	0.984	13200	15360
$Ca_3La_2W_2O_{12}$	14119	1640	540	3335	3.037	0.904	12165	14119
$K_2BaGe_8O_{18}$	15345	1825	695	3395	2.626	0.991	12965	15390
$CaMgYSbO_6$	14563	1620	655	3235	2.473	0.940	12325	14614
La_2LiTaO_6	14426	1785	480	3565	3.719	0.926	12615	14412
$Lu_3Al_5O_{12}$	15281	1895	475	3855	3.989	0.985	13465	15276
$Mg_6As_2O_{11}$	15620	1790	710	3455	2.521	1.010	13205	15681
$Sr_3SiAl_{10}O_{20}$	15119	1695	720	3270	2.354	0.981	12690	15177
$CaTiO_3$	14143	1805	605	3190	2.983	0.906	11990	14124
K_2TiF_6	16063	2000	495	4055	4.040	1.034	14145	16036
Na_2SiF_6	16192	1970	540	4000	3.648	1.040	14160	16180
Li_2SiF_6	16136	2009	505	4060	3.978	1.039	14200	16121
$(NH_4)_2GeF_6$	16023	1975	515	4000	3.835	1.030	14060	16005
$BaTiF_6$	15975	1950	565	3875	3.451	1.024	13885	15968
K_3HfF_7	16104	1865	605	3830	3.083	1.032	13910	16108
Na_3ZrF_7	16088	2009	525	3995	3.827	1.033	14085	16060
Na_3TaF_8	16152	1960	545	3980	3.596	1.037	14120	16153
$Na_5Zr_2F_{13}$	16225	1975	555	3980	3.559	1.041	14160	16223
K_2NbF_7	16152	1880	475	4140	3.958	1.046	14320	16159
$KTeF_5$	16120	1975	615	3805	3.211	1.031	13875	16101
Cs_2SnF_6	16047	1920	475	4105	4.042	1.038	14215	16051
Rb_2KAlF_6	16152	1930	480	4130	4.021	1.045	14310	16163

Cited from Ref. [S. Adachi, Review-Mn^{4+}-Activated Red and Deep Red-Emitting Phosphors, *ECS J. Solid State Sci. Technol.,* 2019, **9**, 016001].

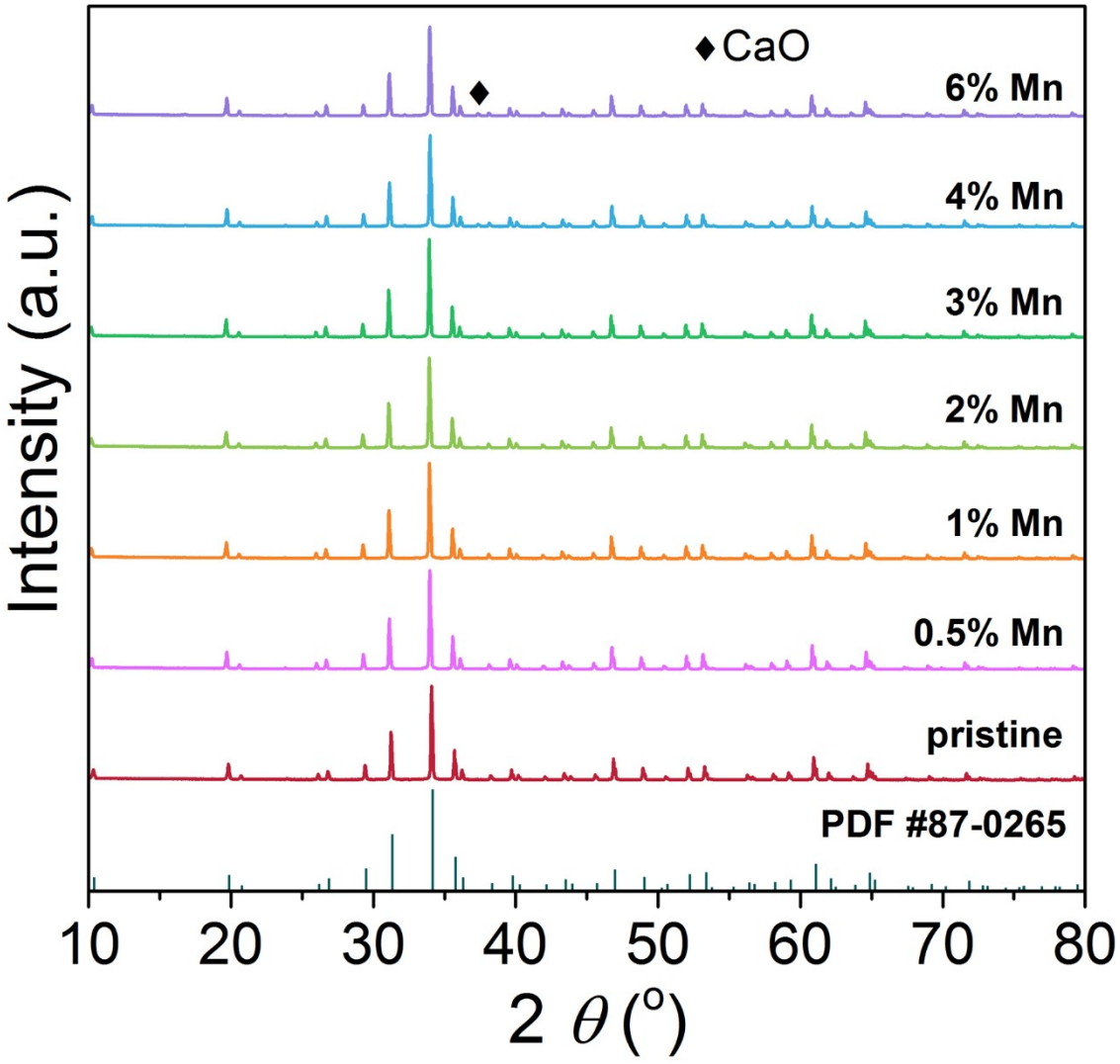

Fig.S1 XRD patterns of the pristine and Mn-doped $Ca_{14}Al_{10}Zn_6O_{35}$ powders.

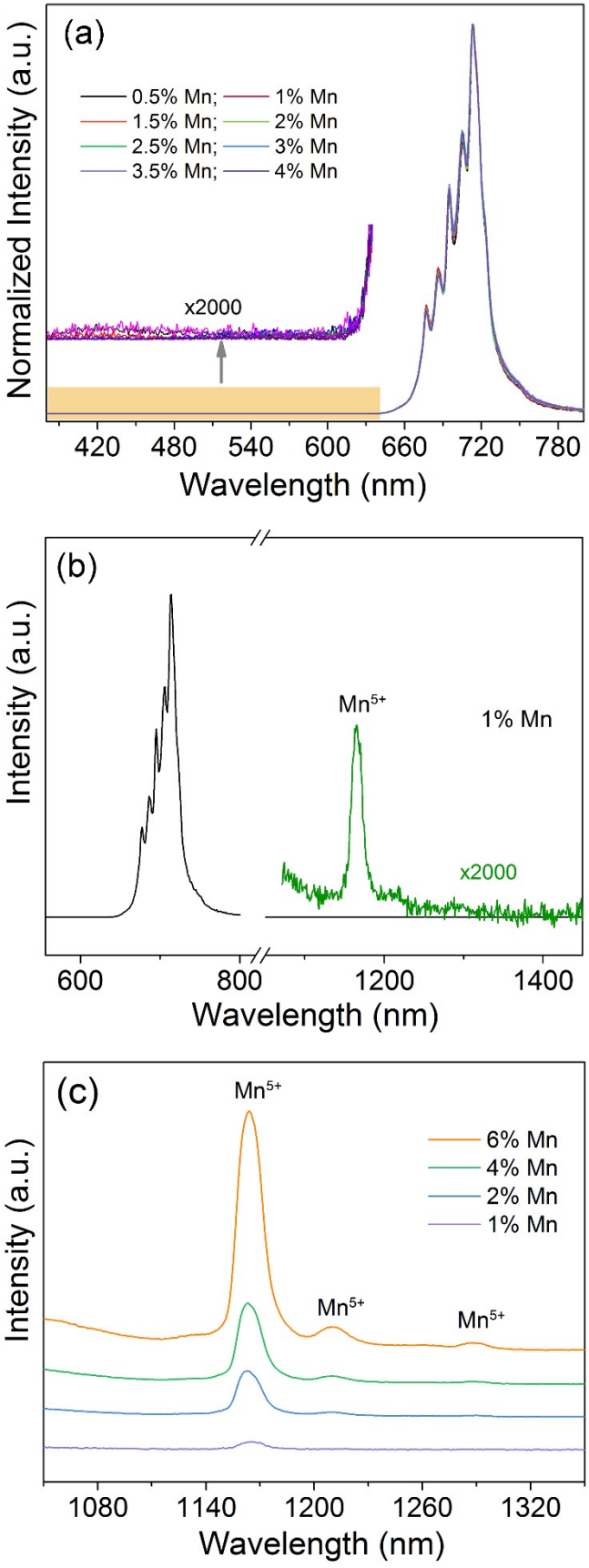

Fig. S2 PL (λ_{ex} = 340 nm) spectra of (a) CAZO:Mn^{4+} with different doping concentrations in the visible region

(emission wavelength range: 380-820 nm), (b) CAZO:1%Mn with emission wavelength range of 550-800 nm and 1050-1450 nm (the green line shows the enlarged spectrum in the wavelength range of 1070-1450 nm), and (c) CAZO:Mn^{4+} with different doping concentrations in the infrared region (emission wavelength range: 1050-1350 nm).

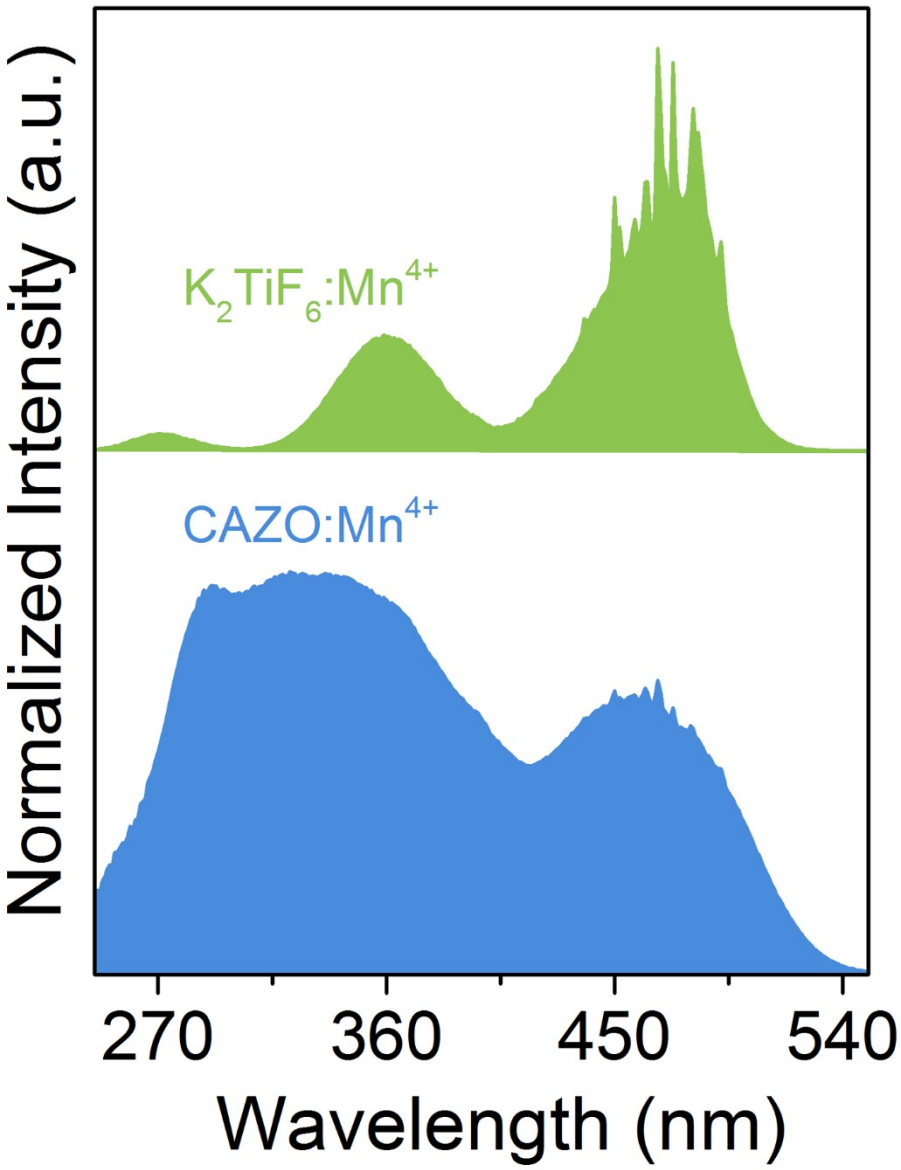

Fig. S3 Comparison of the PLE spectra of CAZO:Mn^{4+} and K_2TiF_6:Mn^{4+} at 300 K.

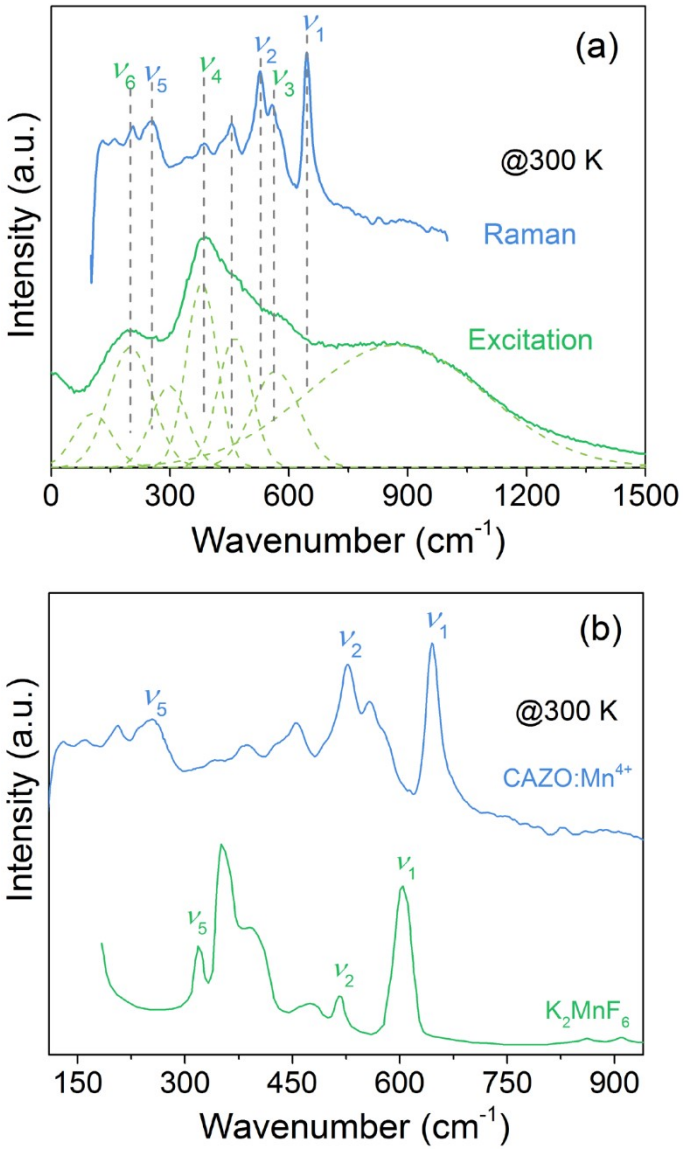

Fig. S4 Comparison of (a) the PLE and Raman spectra of CAZO:Mn^{4+}, (b) Raman spectra of CAZO:Mn^{4+} and K_2MnF_6.

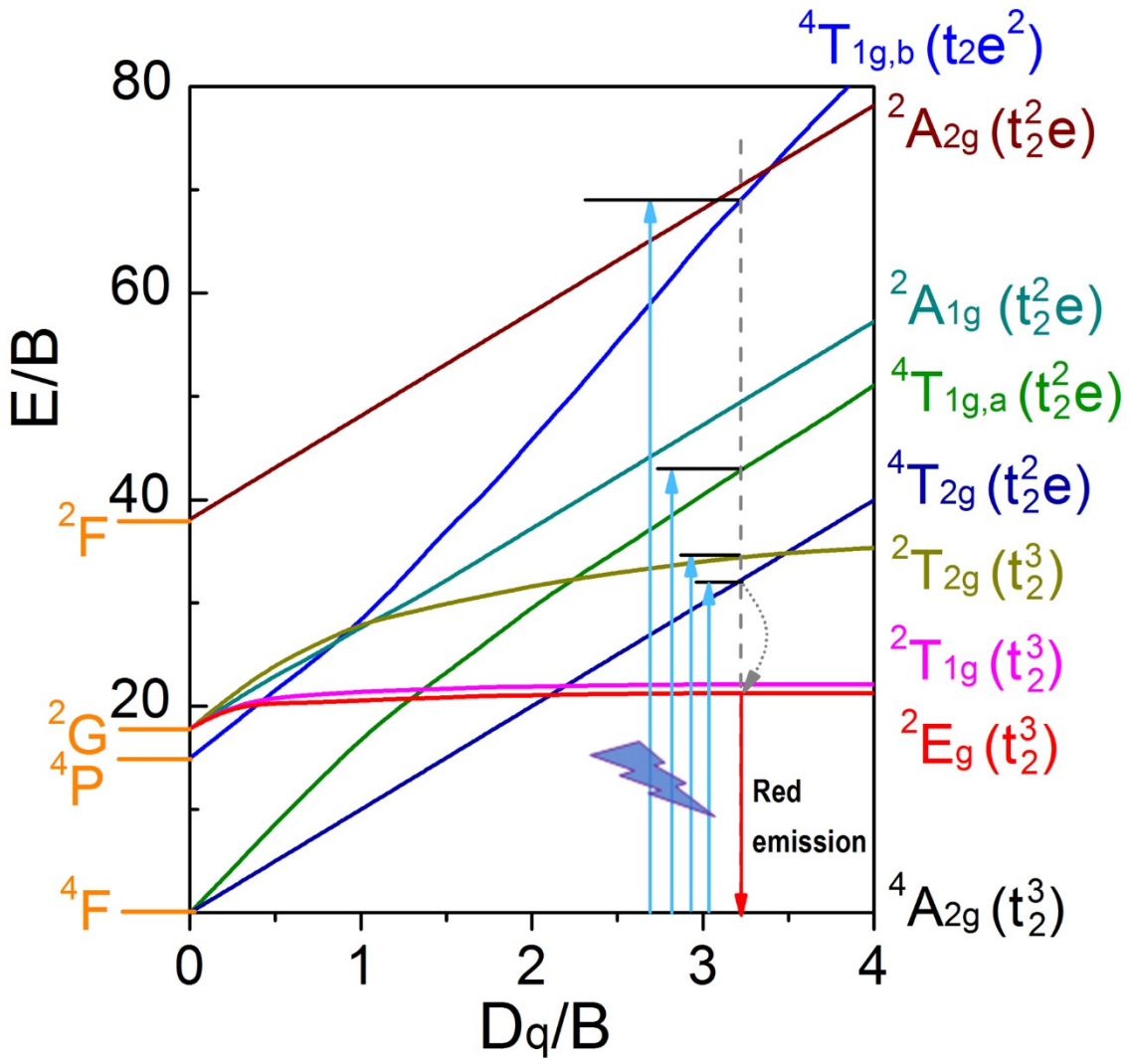

Fig. S5 Tanabe-Sugano energy-level diagram for Mn^{4+} in octahedral symmetry.

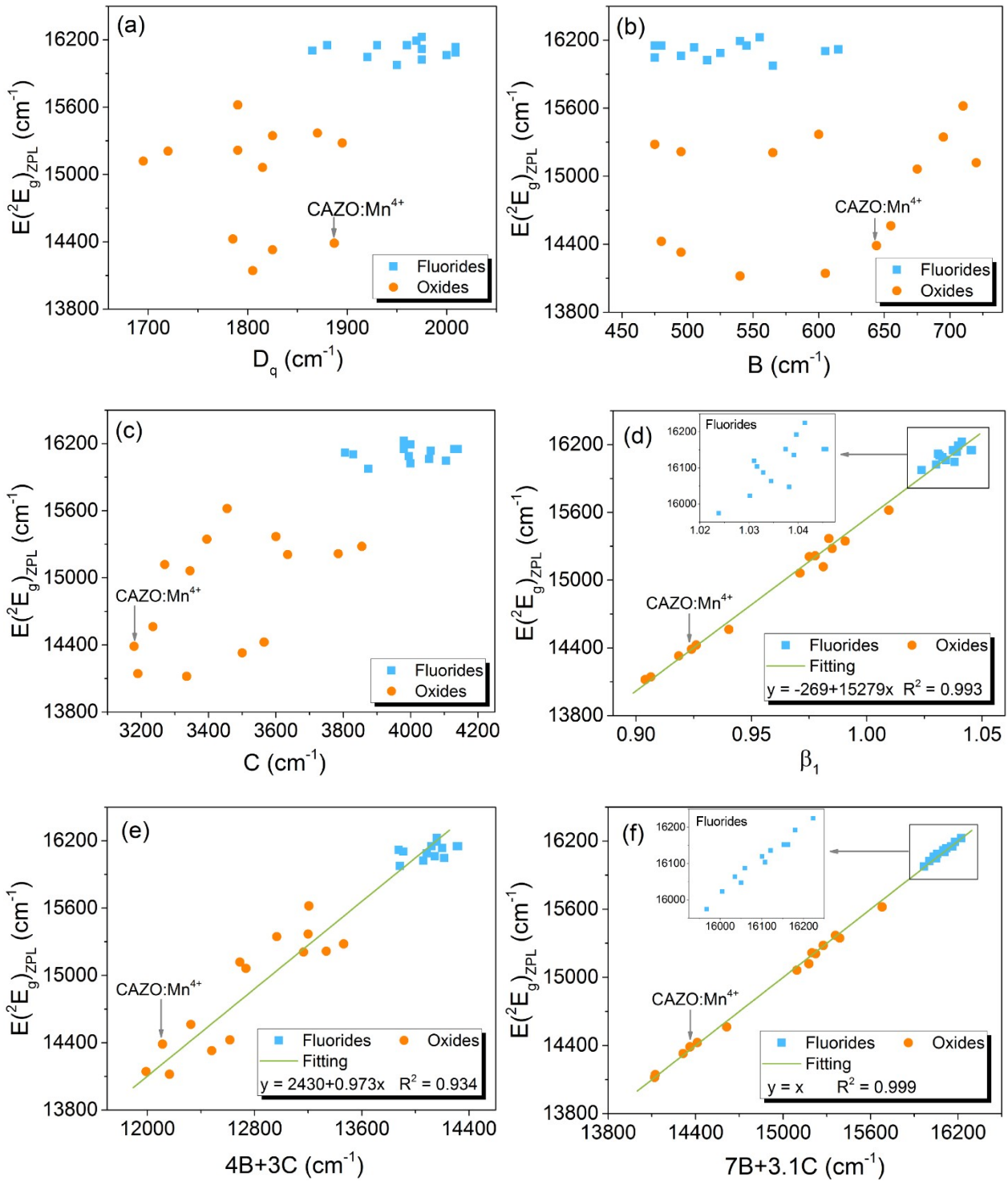

Fig. S6 Dependence of the ZPL emission Energy $E(^2E_g)_{ZPL}$ on the crystal field, Racah and nephelauxetic parameters.

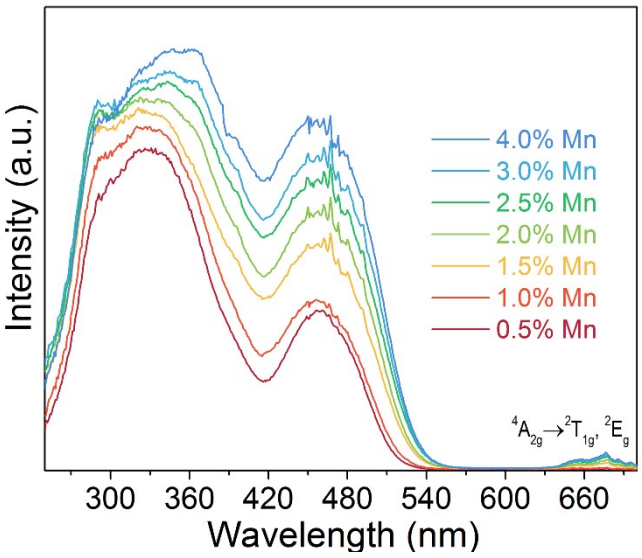

Fig. S7 Excitation spectra of the CAZO:Mn^{4+} phosphors (λ_{em} = 713 nm).

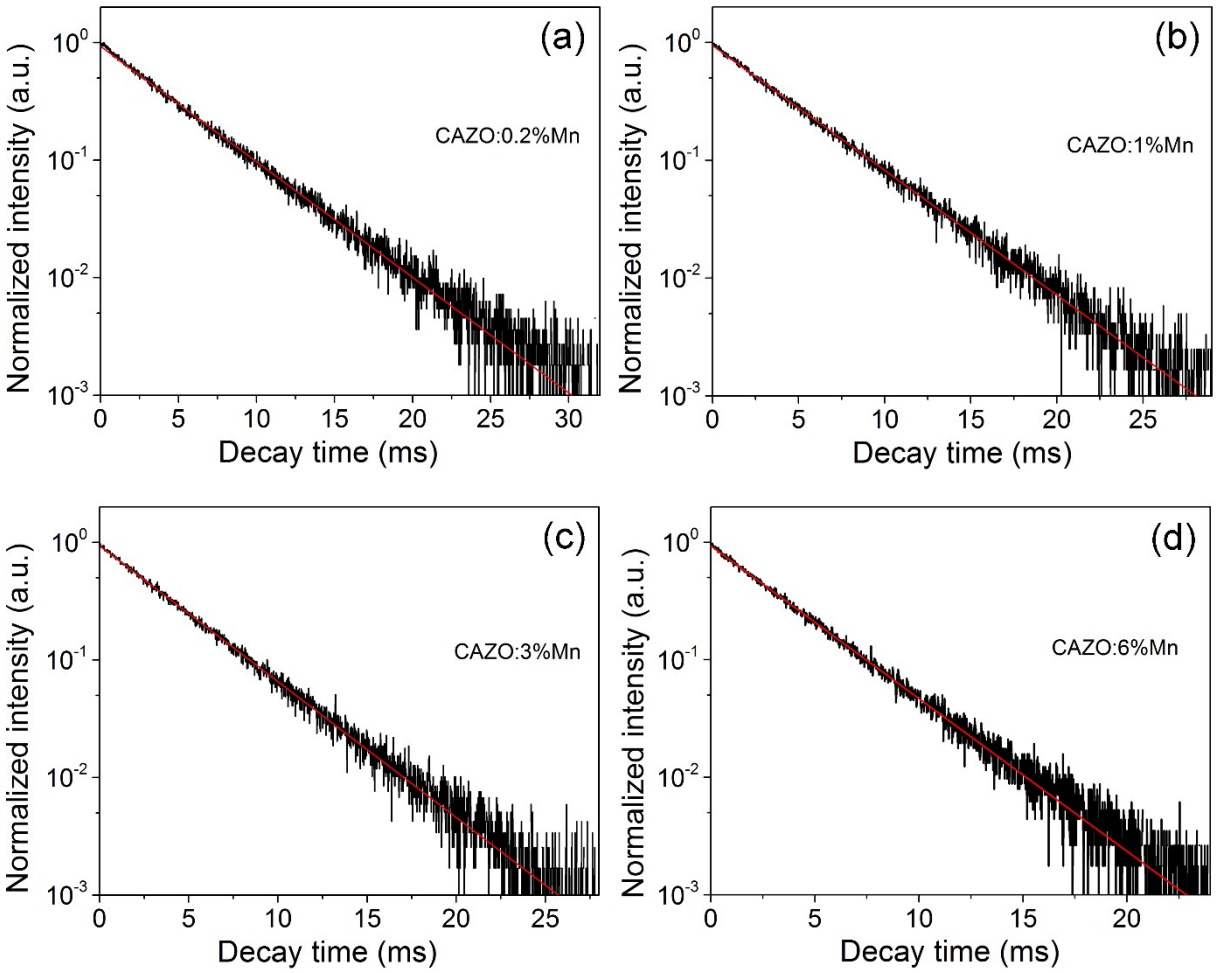

Fig. S8 PL decay curves and the corresponding mono-exponential fitting (red lines) of CAZO:Mn^{4+} phosphors at 300 K (λ_{ex} = 325 nm, λ_{em} = 713 nm).

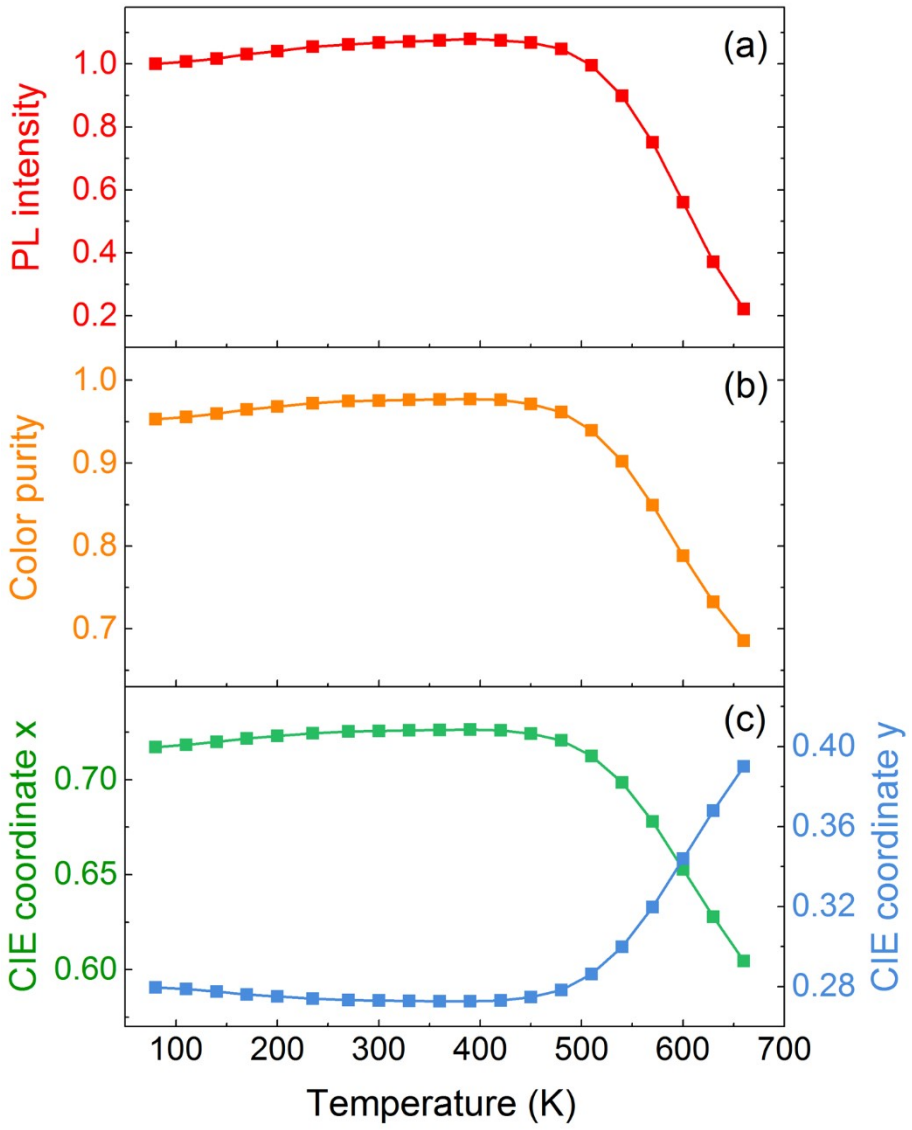

Fig. S9 Dependence of the emission intensity (a), color purity (b) and CIE chromaticity coordinates (c) of CAZO:0.5%Mn on temperature.

The color purity was calculated by using the following equation:

$$Color\ purity = \frac{\sqrt{(x - x_i)^2 + (y - y_i)^2}}{\sqrt{(x_d - x_i)^2 + (y_d - y_i)^2}} \times 100\%$$

where (x, y), (x_i, y_i), and (x_d, y_d) are the CIE chromaticity coordinates of the sample, the standard white illumination with a value of (0.33, 0.33), and the dominated wavelength, respectively.

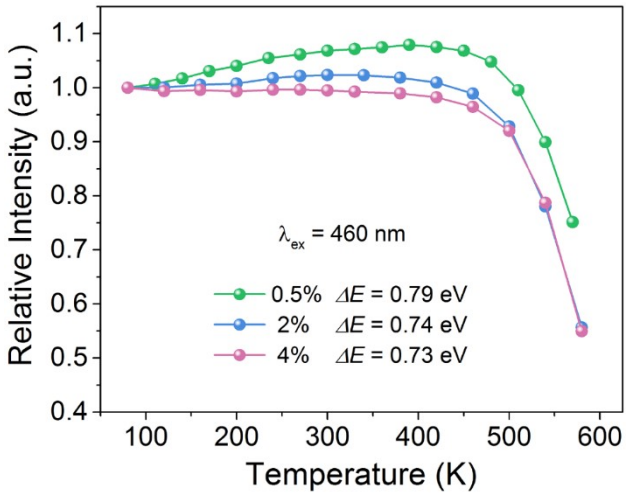

Fig. S10 Comparison of the temperature-dependent emission intensity for CAZO: Mn^{4+} phosphors with different Mn-doping concentration under excitation at 460nm.

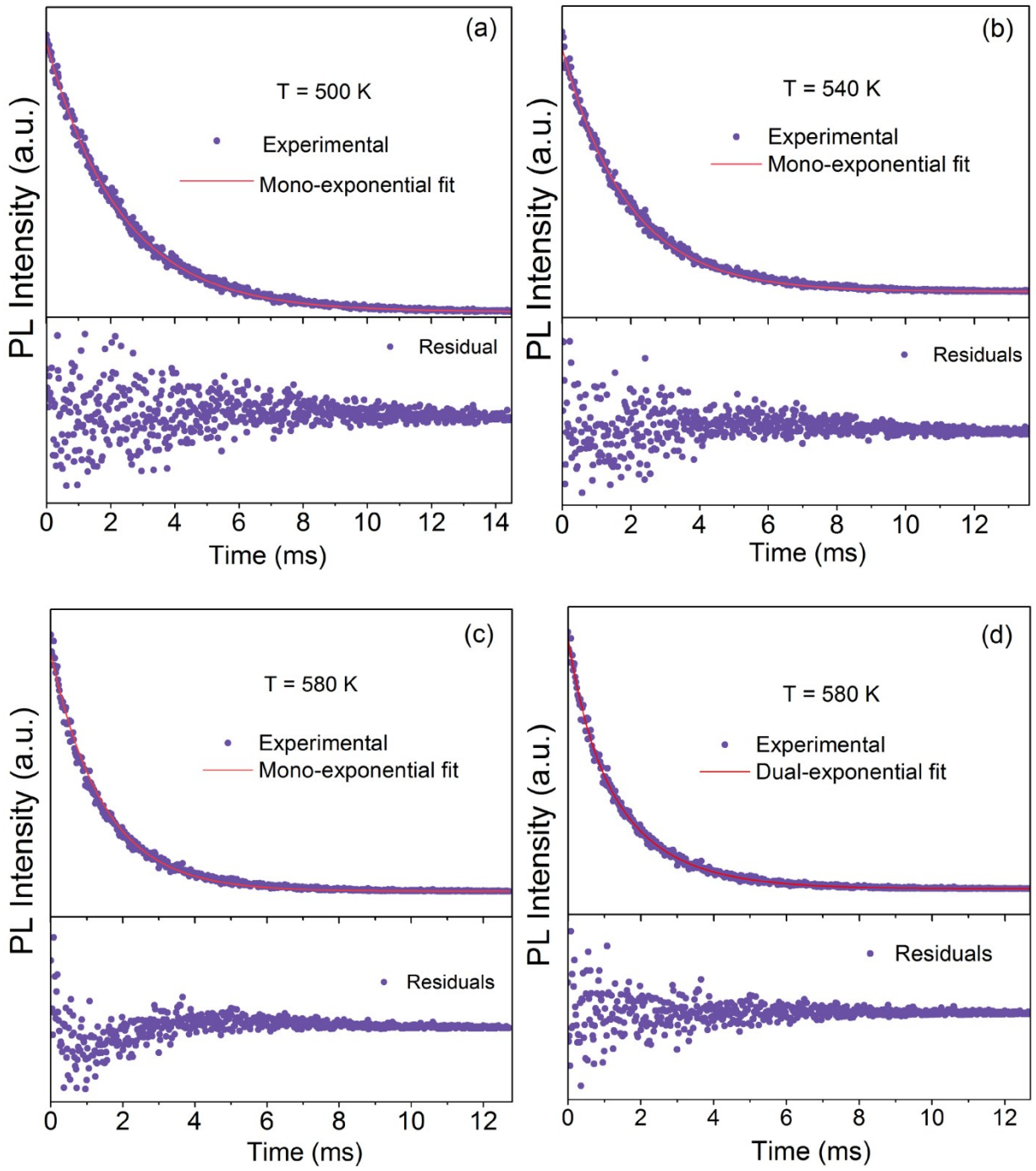

Fig. S11 Decay curves of CAZO:0.5%Mn phosphor (λ_{ex} = 460 nm, λ_{em} = 713 nm) at T = 500 K (a), 540 K (b) and 580 K (c, d). The upper panel shows the mono-exponential fit of the experimental data, and the bottom panel shows the fit residuals.