

## Supplementary Information

### Research on Quantum Confinement Effect and Enhanced Luminescence of Red-emitting Phosphors P<sup>5+</sup>-doped CaAl<sub>12</sub>O<sub>19</sub>:Mn<sup>4+</sup>,Mg<sup>2+</sup>

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**Table S1.** Rietveld Refinement Data and Crystallographic Parameter of  $\text{CaAl}_{12-m}\text{P}_m\text{O}_{19+m}:0.01\text{Mn}^{4+},0.2\text{Mg}^{2+}$  ( $m=0-0.15$ ) phosphors.

Formula	m=0	m=0.02	m=0.04	m=0.07	m=0.10	m=0.13	m=0.15
cryst syst	Hexagon						
2 $\theta$ range(deg)	5-80	5-80	5-80	5-80	5-80	5-80	5-80
space group	<i>P63/mmc</i>						
a=b (Å)	5.566	5.562	5.561	5.561	5.560	5.560	5.559
c (Å)	21.925	21.904	21.907	21.904	21.899	21.900	21.899
$\alpha=\beta$ (deg)	90	90	90	90	90	90	90
$\gamma$ (deg)	120	120	120	120	120	120	120
V (Å <sup>3</sup> )	588.34	586.82	586.6	586.6	586.22	586.33	586.18
R <sub>wp</sub> (%)	9.26	9.58	9.86	9.57	9.83	9.62	9.95
R <sub>p</sub> (%)	6.89	7.25	7.63	7.22	7.31	7.28	7.84
Z	2	2	2	2	2	2	2
$\chi^2$	2.358	2.671	2.264	3.027	2.951	2.587	2.216

**Table S2.** Ionic radii difference percentage ( $D_r$ ) between host cations and doped ions.

Ions	Coordination		$D_r/\%$			
	number (CN)	Radius/Å	Ca <sup>2+</sup> 1.34* (CN = 12)	Al <sup>3+</sup> 0.39* (CN = 4)	Al <sup>3+</sup> 0.48* (CN = 5)	Al <sup>3+</sup> 0.535* (CN = 6)
Mn <sup>4+</sup>	6	0.53	/	-35.90	-10.41	0.93
Mn <sup>2+</sup>	6	0.67	/	-71.79	-39.58	-25.23
Mg <sup>2+</sup>	4	0.57	/	-41.65	-18.75	-6.54
Mg <sup>2+</sup>	6	0.72		-84.62	-50.00	-34.58
P <sup>5+</sup>	4	0.38		2.56	20.83	28.97

\* Ionic radius. “/” refers to no mention in the literature.

**Table S3.** Wyckoff positions, atomic coordinates and occupancy for  $\text{CaAl}_{11.90}\text{P}_{0.1}\text{O}_{19.10}:0.01\text{Mn}^{4+},0.2\text{Mg}^{2+}$ .

Atom	Wyck.	x	y	z	Occ.
Ca1	2d	0.6667	0.3333	0.2500	1.0
Al1	2a	0	0	0	1.0
Al2	4e	0	0	0.2891	0.1854
P1	4e	0	0	0.2891	0.3146
Al3	4f	0.3333	0.6667	0.0281	1.0
Al4	4f	0.3333	0.6667	0.1910	1.0
Al5	12k	0.1686	0.3371	-0.1091	1.0
O1	4e	0	0	0.1491	1.0
O2	4f	0.6667	0.3333	0.0546	1.0
O3	6h	0.1811	0.3621	0.2500	1.0
O4	12k	0.1551	0.3101	0.0521	1.0
O5	12k	0.5033	1.0065	0.1491	1.0

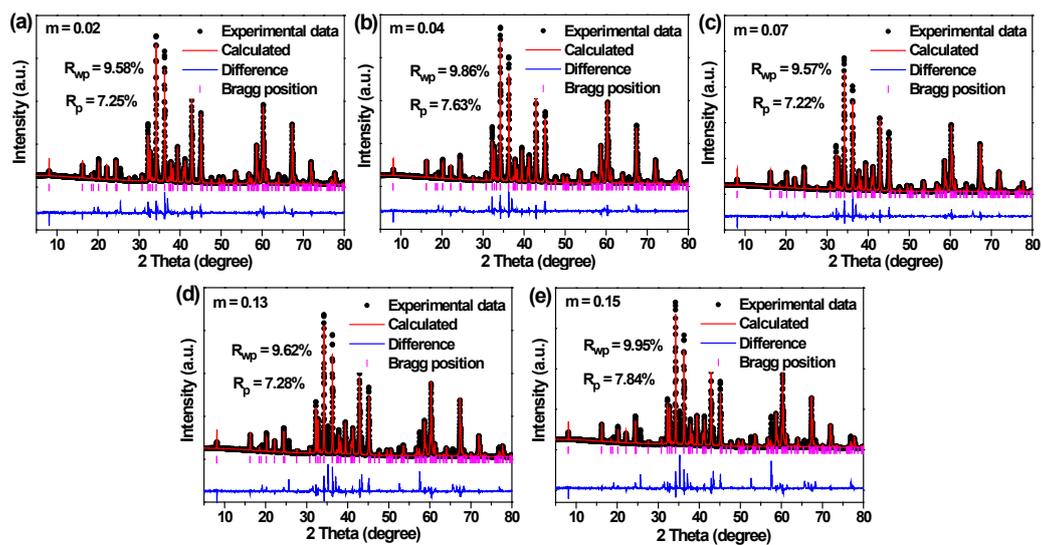
**Table S4.** P site occupancy of  $\text{CaAl}_{12-m}\text{P}_m\text{O}_{19+m}:0.01\text{Mn}^{4+},0.2\text{Mg}^{2+}$  ( $m=0.02-0.15$ ).

Atom \ Occ.	m = 0.02	m = 0.04	m = 0.07	m = 0.10	m = 0.13	m = 0.15
Al2	0.3931	0.3392	0.2605	0.1854	0.1999	0.2086
P1	0.1069	0.1608	0.2395	0.3146	0.3001	0.2914

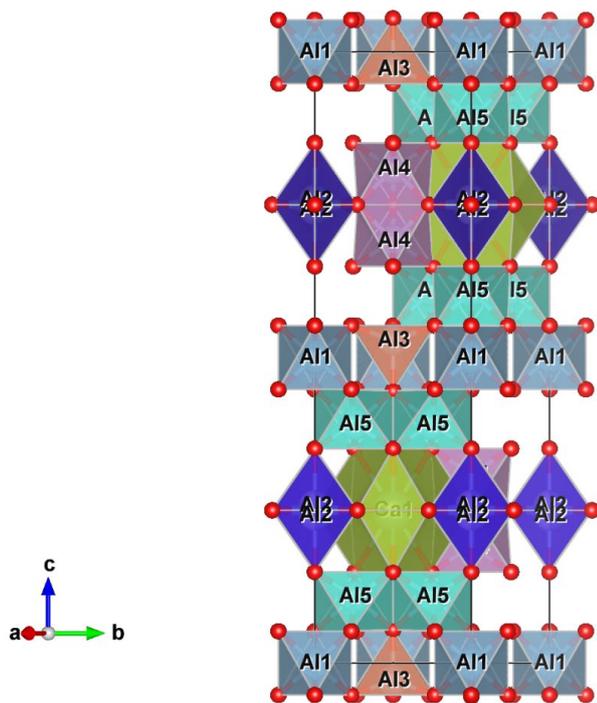
\* P site occupancy+Al (2) site occupancy=0.5000

**Table S5.** The fluorescence lifetime, CIE and PLQY of  $\text{CaAl}_{12-m}\text{P}_m\text{O}_{19+m}:\text{0.01Mn}^{4+},\text{0.2Mg}^{2+}$  ( $m=0\text{--}0.15$ ) phosphors.

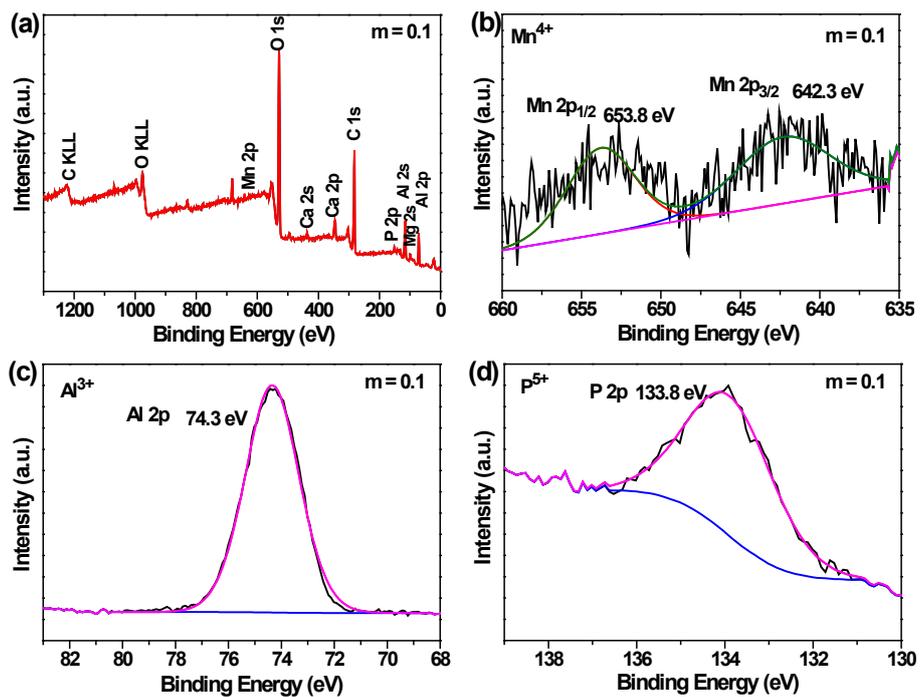
Sample	CIE (chromaticity coordinates)		$\tau$ (ms)	PLQY (%)
	under 396 nm excitation			
	x	y		
m=0	0.6438	0.3549	0.9165	9.8
m=0.02	0.7191	0.2809	0.9514	30.7
m=0.04	0.7191	0.2808	0.9529	32.8
m=0.07	0.7190	0.2809	0.9543	41.2
m=0.10	0.7193	0.2807	0.9567	70.2
m=0.13	0.7191	0.2808	0.9526	41.6
m=0.15	0.7192	0.2808	0.9316	38.9



**Fig. S1** XRD Rietveld refinement results of  $\text{CaAl}_{12-m}\text{P}_m\text{O}_{19+m}:\text{0.01Mn}^{4+},\text{0.2Mg}^{2+}$  ( $m=0.02, 0.04, 0.07, 0.13, 0.15$ ) phosphors. (a)  $m=0.02$ , (b)  $m=0.04$ , (c)  $m=0.07$ , (d)  $m=0.13$ , (e)  $m=0.15$ .



**Fig. S2** Crystal structure of  $\text{CaAl}_{12}\text{O}_{19}$  (hexagonal,  $P63/mmc$ ).



**Fig. S3** XPS spectra of  $\text{CaAl}_{11.90}\text{P}_{0.1}\text{O}_{19.10}:0.01\text{Mn}^{4+}, 0.2\text{Mg}^{2+}$  (a) survey, (b) Mn 2p, (c) Al 2p and (d) P 2p.

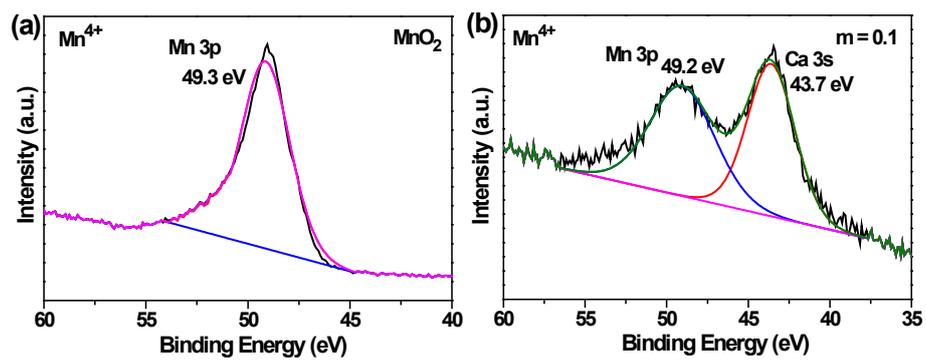
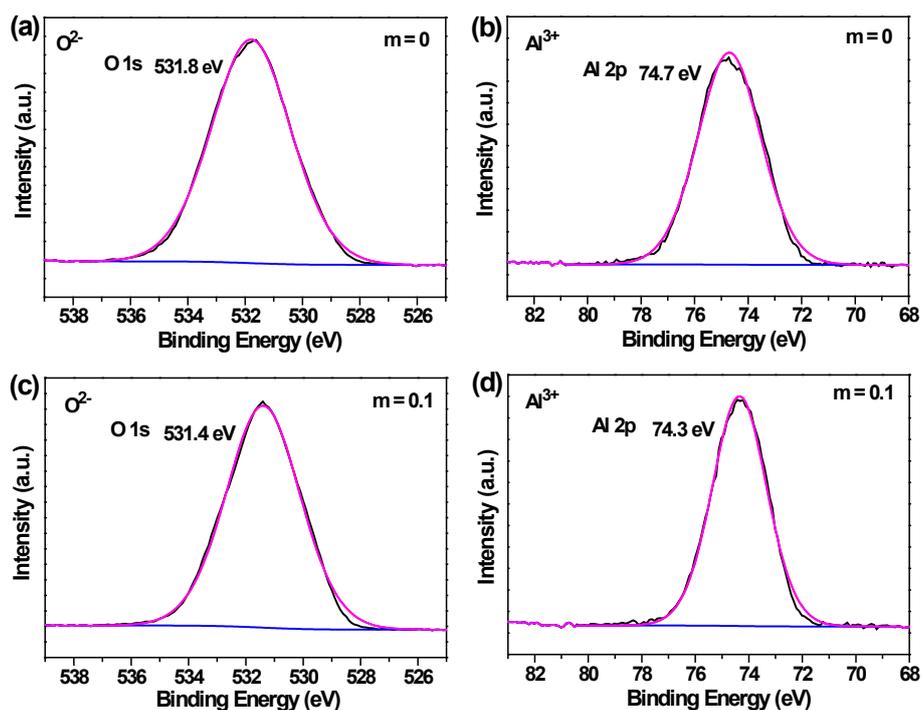
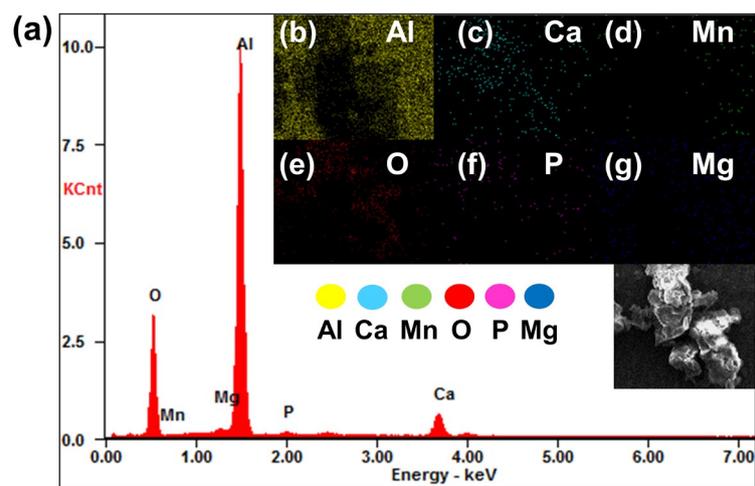


Fig. S4 Mn 3p of MnO<sub>2</sub> and CaAl<sub>11.90</sub>P<sub>0.1</sub>O<sub>19.10</sub>:0.01Mn<sup>4+</sup>,0.2Mg<sup>2+</sup>.

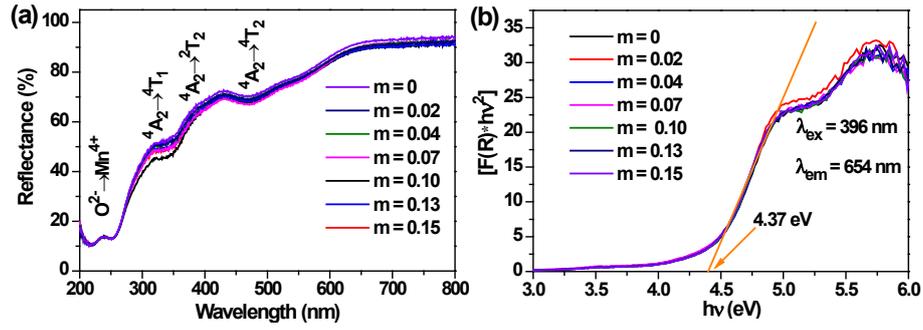


**Fig. S5** XPS spectra of  $\text{CaAl}_{12}\text{O}_{19}:0.01\text{Mn}^{4+},0.2\text{Mg}^{2+}$  phosphor (a) Al 2p and (b) O 1s and  $\text{CaAl}_{11.90}\text{P}_{0.1}\text{O}_{19.10}:0.01\text{Mn}^{4+},0.2\text{Mg}^{2+}$  phosphor (c) Al 2p and (d) O 1s.

In the  $\text{CaAl}_{12}\text{O}_{19}:0.01\text{Mn}^{4+},0.2\text{Mg}^{2+}$  ( $m=0$ ) and  $\text{CaAl}_{11.90}\text{P}_{0.1}\text{O}_{19.10}:0.01\text{Mn}^{4+},0.2\text{Mg}^{2+}$  ( $m=0.1$ ) phosphors, the binding energy of Al 2p orbital and O 1s orbital are located at 74.70 eV, 74.33 eV and 531.79 eV, 531.39 eV, respectively. Compared with the undoped  $\text{P}^{5+}$ , it is found that when the doping amount of  $\text{P}^{5+}$  is 0.1, the peak of O 1s moved  $\sim 0.4$  eV towards the low binding energy. Combined with the analysis of crystal structure of the sample, it shows that there is a shallow electron trap caused by oxygen vacancies in  $\text{CaAl}_{11.90}\text{P}_{0.1}\text{O}_{19.10}:0.01\text{Mn}^{4+},0.2\text{Mg}^{2+}$  ( $m=0.1$ ) phosphor, which can confine photo-generated electrons in the traps, resulting in an increase in the electron cloud density, thereby causing a decrease in the binding energy of electrons. Therefore, we speculate that the existence of oxygen vacancies and electron traps is extremely important to improve the luminescence performance of phosphors.



**Fig. S6** The EDS spectrum and element mapping images of  $\text{CaAl}_{11.90}\text{P}_{0.1}\text{O}_{19.10}:0.01\text{Mn}^{4+},0.2\text{Mg}^{2+}$  phosphor.

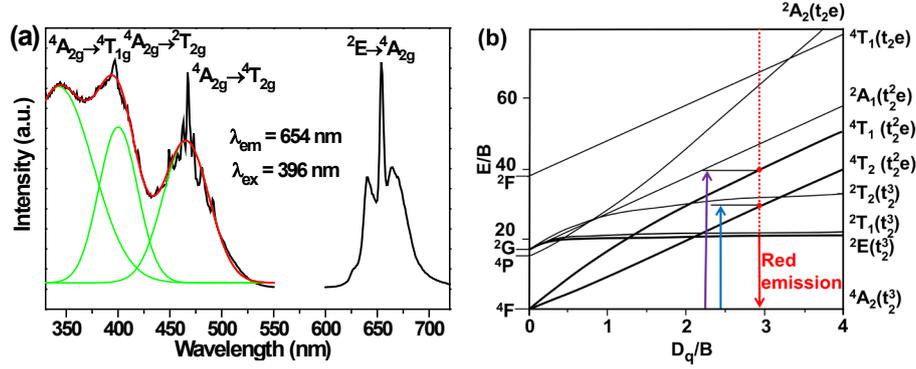


**Fig. S7** (a) Diffuse reflectance spectra of  $\text{CaAl}_{12-m}\text{P}_m\text{O}_{19+m}:\text{0.01Mn}^{4+},\text{0.2Mg}^{2+}$  ( $m=0-0.15$ ) phosphors. (b) Relationship of  $[F(R)hv]^2$  versus photon energy  $hv$  in  $\text{CaAl}_{12-m}\text{P}_m\text{O}_{19+m}:\text{0.01Mn}^{4+},\text{0.2Mg}^{2+}$  ( $m=0-0.15$ ) phosphors.

The diffuse reflectance spectrum of  $\text{CaAl}_{12-m}\text{P}_m\text{O}_{19+m}:\text{0.01Mn}^{4+},\text{0.2Mg}^{2+}$  ( $m=0-0.15$ ) phosphors with different  $\text{PO}_4^{3-}$  concentrations are depicted in Fig. S7a. Obviously, As the content of  $\text{PO}_4^{3-}$  increases, the reflection rate decreases slightly, phosphors begin to absorb light from 600nm, and strong light absorption is observed in the n-ultraviolet (n-UV) region in the range of 200–350 nm, which is attributed to the charge transfer transition of  $\text{O}^{2-}\rightarrow\text{Mn}^{4+}$  (CTB). Furthermore, the energy bands between 300–400 nm and 430–500 nm are attributed to the  ${}^4\text{A}_{2g}\rightarrow{}^4\text{T}_{1g}$ ,  ${}^4\text{A}_{2g}\rightarrow{}^2\text{T}_{2g}$  and  ${}^4\text{A}_{2g}\rightarrow{}^4\text{T}_{2g}$  transitions of  $\text{Mn}^{4+}$ , respectively. The band gap energy can be obtained by the Tauc-Plot method:<sup>1</sup>

$$[F(R)hv]^n = A(hv - E_g) \quad (1)$$

where  $F(R)$  is the absorption coefficient,  $R$  is the reflectance coefficient,  $hv$  is the photon energy,  $A$  represents the absorption constant, and  $E_g$  is the optical band gap value.  $n = 1/2$  and 2 correspond to the direct band gap and the indirect band gap, respectively. According to the calculation of the electronic structure,  $\text{CaAl}_{12}\text{O}_{19}$  is a direct band gap semiconductor, so  $n = 1/2$ . Fig. S7b displays the relationship between  $[F(R)hv]^2$  and  $hv$ . The band gap values of  $\text{CaAl}_{11.90}\text{P}_{0.10}\text{O}_{19.10}:\text{0.01Mn}^{4+},\text{0.2Mg}^{2+}$  phosphors remains unchanged with the increase of  $\text{PO}_4^{3-}$  content, indicating that the addition of  $\text{PO}_4^{3-}$  only enhances the crystal field without changing the band structure.



**Fig. S8** (a) PLE and PL spectra of  $\text{CaAl}_{11.90}\text{P}_{0.1}\text{O}_{19.10}:0.01\text{Mn}^{4+},0.2\text{Mg}^{2+}$  phosphor ( $\lambda_{\text{ex}} = 396$  nm,  $\lambda_{\text{em}} = 654$  nm). (b) Tanabe-Sugano energy level diagram of  $\text{Mn}^{4+}$  ( $3d^3$ ) in an octahedral crystal field.

The Tanabe-Sugano energy-level diagram illustrates the luminescence behavior of  $\text{Mn}^{4+}$  ions in the octahedral crystal field in phosphor host, as shown in Fig. S8b. The values of  $D_q$  and  $B$  can be calculated from the following equations:<sup>2,3</sup>

$$D_q = E(4A_{2g} \rightarrow 4T_{2g}) / 10 \quad (2)$$

$$\frac{D_q}{B} = \frac{15(x-8)}{x^2-10x} \quad (3)$$

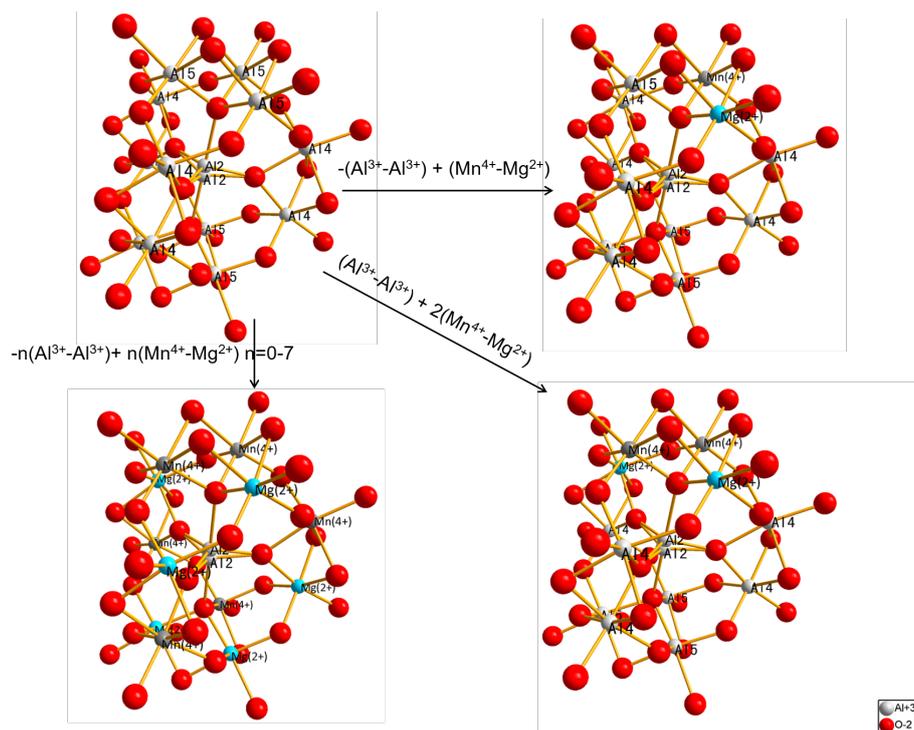
where the parameter  $x$  is defined by the following formula:

$$x = \frac{E(4A_{2g} \rightarrow 4T_{1g}) - E(4A_{2g} \rightarrow 4T_{2g})}{D_q} \quad (4)$$

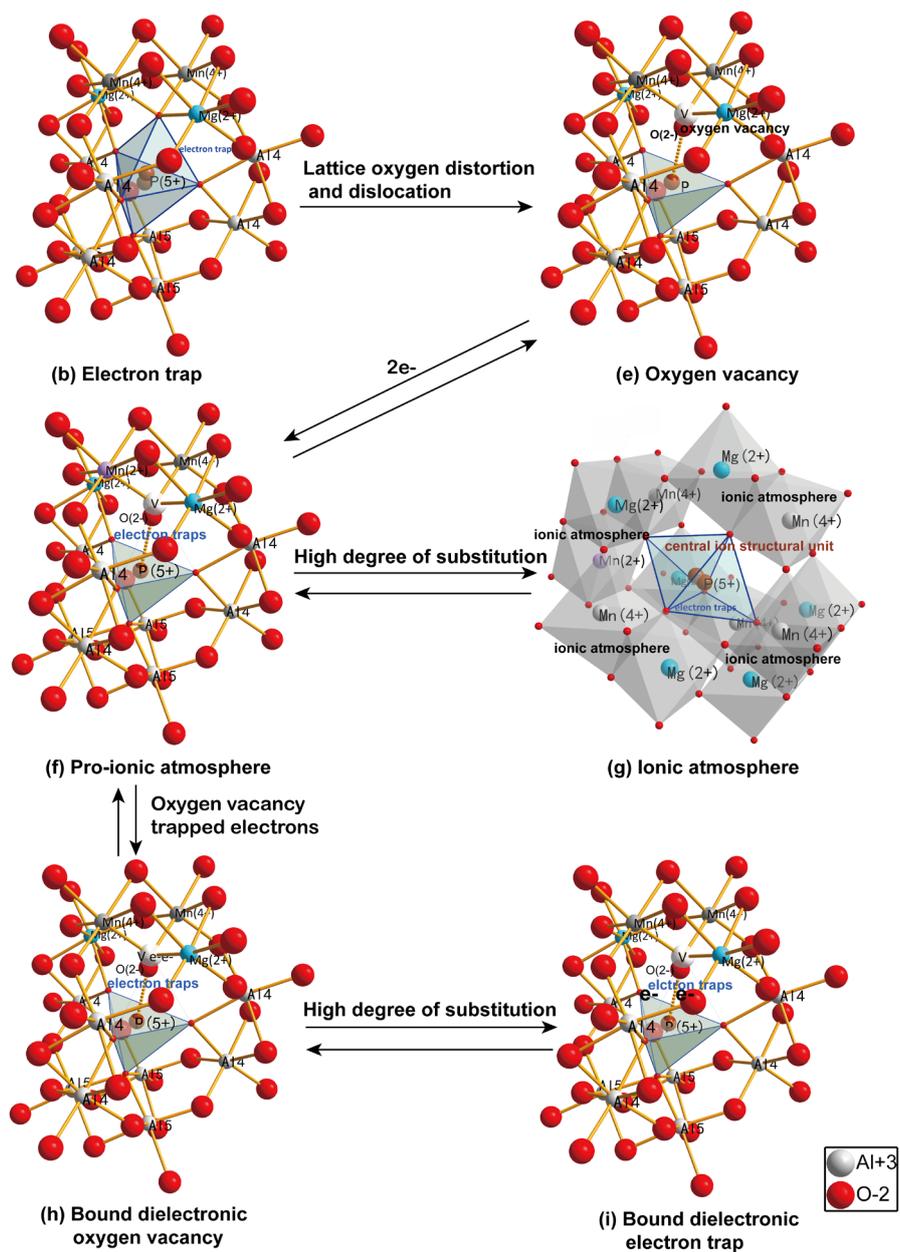
Based on the peak energy of  ${}^2E_g \rightarrow {}^4A_{2g}$  transition ( $15291 \text{ cm}^{-1}$ ) obtained from the emission spectrum, the Racah parameter  $C$  can be calculated by the following expression:<sup>4</sup>

$$\frac{E({}^2E_g \rightarrow {}^4A_{2g})}{B} = \frac{3.05C}{B} + 7.9 - \frac{1.8B}{D_q} \quad (5)$$

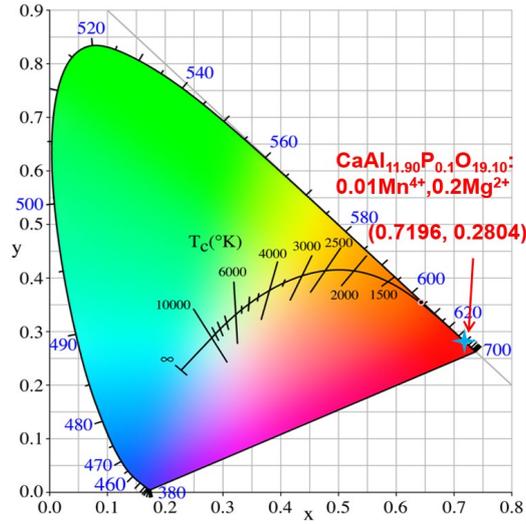
The crystal field parameters  $D_q$ ,  $B$  and  $C$  of  $\text{CaAl}_{11.90}\text{P}_{0.1}\text{O}_{19.10}:0.01\text{Mn}^{4+},0.2\text{Mg}^{2+}$  are 2141, 742 and  $3642 \text{ cm}^{-1}$ , respectively.  $D_q/B$  is equal to  $\sim 2.88$ , indicating that there is a strong crystal field of  $\text{Mn}^{4+}$  ions in phosphor host.



**Fig. S9** The substitution process of ion pairs in the crystal structure.



**Fig. S10** The formation of oxygen vacancy and ionic atmosphere, and their binding state of electrons.

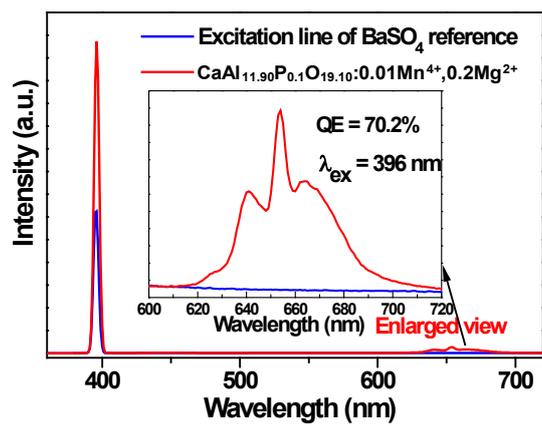


**Fig. S11** CIE chromaticity diagram of  $\text{CaAl}_{11.90}\text{P}_{0.1}\text{O}_{19.10}:\text{0.01Mn}^{4+},\text{0.2Mg}^{2+}$  phosphor.

The color purity is calculated by the following formula:<sup>5</sup>

$$\text{Color purity} = \frac{\sqrt{(x - x_i)^2 + (y - y_i)^2}}{\sqrt{(x_d - x_i)^2 + (y_d - y_i)^2}} \times 100\% \quad (6)$$

where  $(x_d, y_d)$  is the color coordinate corresponding to the dominant wavelength of the light source (0.7320, 0.2680),  $(x, y)$  is the color coordinate of  $\text{CaAl}_{11.90}\text{P}_{0.1}\text{O}_{19.10}:\text{0.01Mn}^{4+},\text{0.2Mg}^{2+}$  sample (0.7196, 0.2804),  $(x_i, y_i)$  is the standard color coordinates (0.310, 0.316) specified by the National Television Standards Committee (NTSC). Based on the above equation, the color purity of  $\text{CaAl}_{11.90}\text{P}_{0.1}\text{O}_{19.10}:\text{0.01Mn}^{4+},\text{0.2Mg}^{2+}$  phosphor is calculated to be 96.8%.



**Fig. S12** The measurement of PLQY of CaAl<sub>11.90</sub>P<sub>0.1</sub>O<sub>19.10</sub>:0.01Mn<sup>4+</sup>,0.2Mg<sup>2+</sup> phosphor, and the inset is the enlarged pattern ranging from 600 nm to 720 nm.

## **Supporting videos**

**SV1:** The substitution process of  $\text{Mn}^{4+}$ - $\text{Mg}^{2+}$  ion pairs in the crystal structure.

**SV2:** The formation of electron trap and its capture of foreign electrons.

**SV3 and SV4:** The formation of oxygen vacancy and ionic atmosphere, and their binding state of electrons.

**SV5:** The formation process of luminescence center and electron trap between the (012) crystal plane.

## References

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