Defects induced deep red luminescence of $CaGdAlO_4$-type layered perovskite: multi-cationic sites partial/full substitution and application in pc-LED and plant lighting

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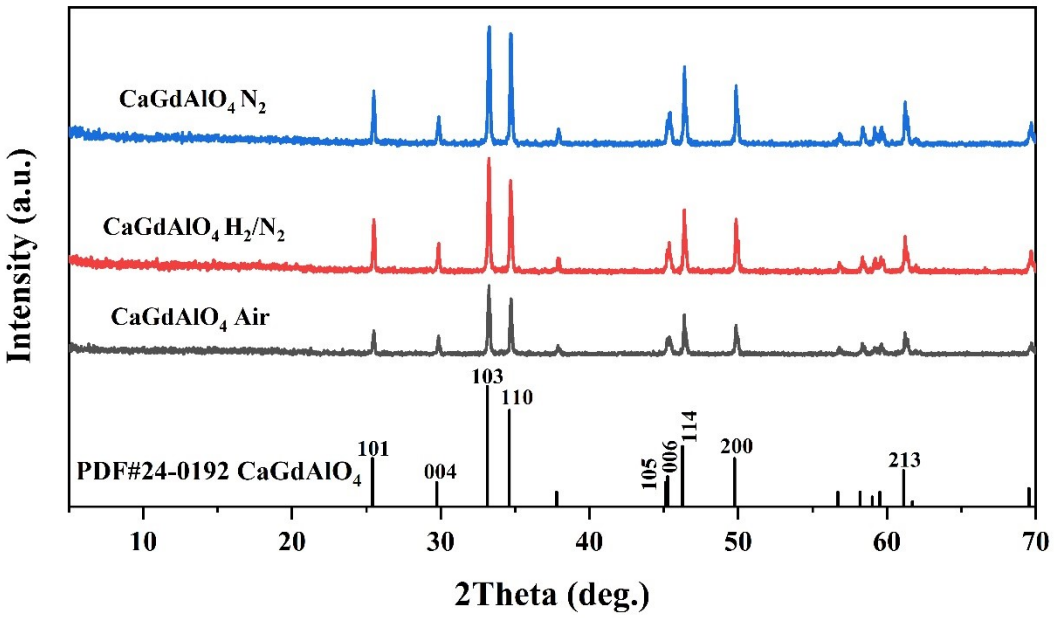

Fig. S1 XRD patterns of the $CaGdAlO_4$ samples synthesized in different atmospheres.

Table S1 A summary of O_i:V_o ratios in intensity and in area of the XPS peaks for the $CaGdAlO_4$ samples calcined in different atmospheres.

	O_i:V_o (in intensity)	O_i:V_o (in area)
Air	1.93	3.45
N_2	2.54	3.64
H_2+N_2	1.57	2.33

Table S2 A summary of the sub-peak position/intensity, trap depth (E_T) and trap density (N_0), which were obtained from the thermoluminescence spectra of the $CaGdAlO_4$ samples calcined in different atmospheres.

Atmosphere	T_1/(℃)	$Intensity_1$	E_{T1}/(eV)	N_{01}	T_2/(℃)	$Intensity_2$	E_{T2}/(eV)	N_{02}
Air	108.93	83.128	0.766	735.608	233.01	235.781	1.014	2086.451
N_2	113.85	84.953	0.776	810.075	261.63	450.009	1.072	4291.089
N_2+H_2	-	-	-	-	240.36	510.338	1.029	3290.449

Table S3 A summary of the results of fluorescence decay analysis for the samples synthesized with different Ca:Gd atomic ratios.

Ca:Gd	A_1	A_2	$\tau_1(\mu s)$	$\tau_2(\mu s)$	χ^2	$\tau_{av}(ms)$
0.990:1.010	12977.86	427.28	3.56	1775.63	1.399	1.652
0.995:1.005	13192.77	353.03	3.56	1865.95	1.112	1.764
1.000:1.000	14202.86	334.06	3.54	1741.39	1.178	1.603
1.005:0.995	12123.35	336.85	3.78	1751.51	1.106	1.626
1.010:0.990	11935.05	304.36	3.78	1721.49	1.204	1.585

Table S4 A summary of the sub-peak position/intensity, trap depth (E_T) and trap density (N_0), which were obtained from the thermoluminescence spectra of the $CaGdAlO_4$ samples synthesized with varying Ca:Gd atomic ratio.

Ca:Gd	T_1/(℃)	$Intensity_1$	E_{T1}/(eV)	N_{01}	T_2/(℃)	$Intensity_2$	E_{T2}/(eV)	N_{02}
0.990:1.010	101.85	95.903	0.752	858.471	274.57	357.297	1.097	3198.327
0.995:1.005	109.10	134.508	0.767	1213.905	258.13	478.185	1.065	4315.512
1.000:1.000	108.93	83.128	0.766	735.608	233.01	235.781	1.014	2086.451
1.005:0.995	109.53	48.225	0.767	429.02	204.89	106.192	0.958	944.707
1.010:0.990	111.58	114.638	0.771	932.708	185.33	183.596	0.919	1493.758

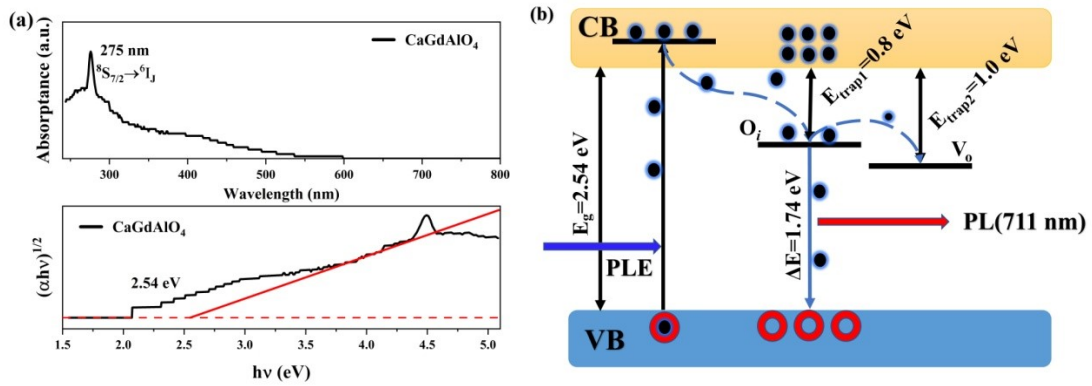

Fig. S2 UV-vis absorption spectrum and $(\alpha h\nu)^2$ vs $h\nu$ plot for $CaGdAlO_4$ (a), and a scheme for the proposed mechanism of luminescence (b).

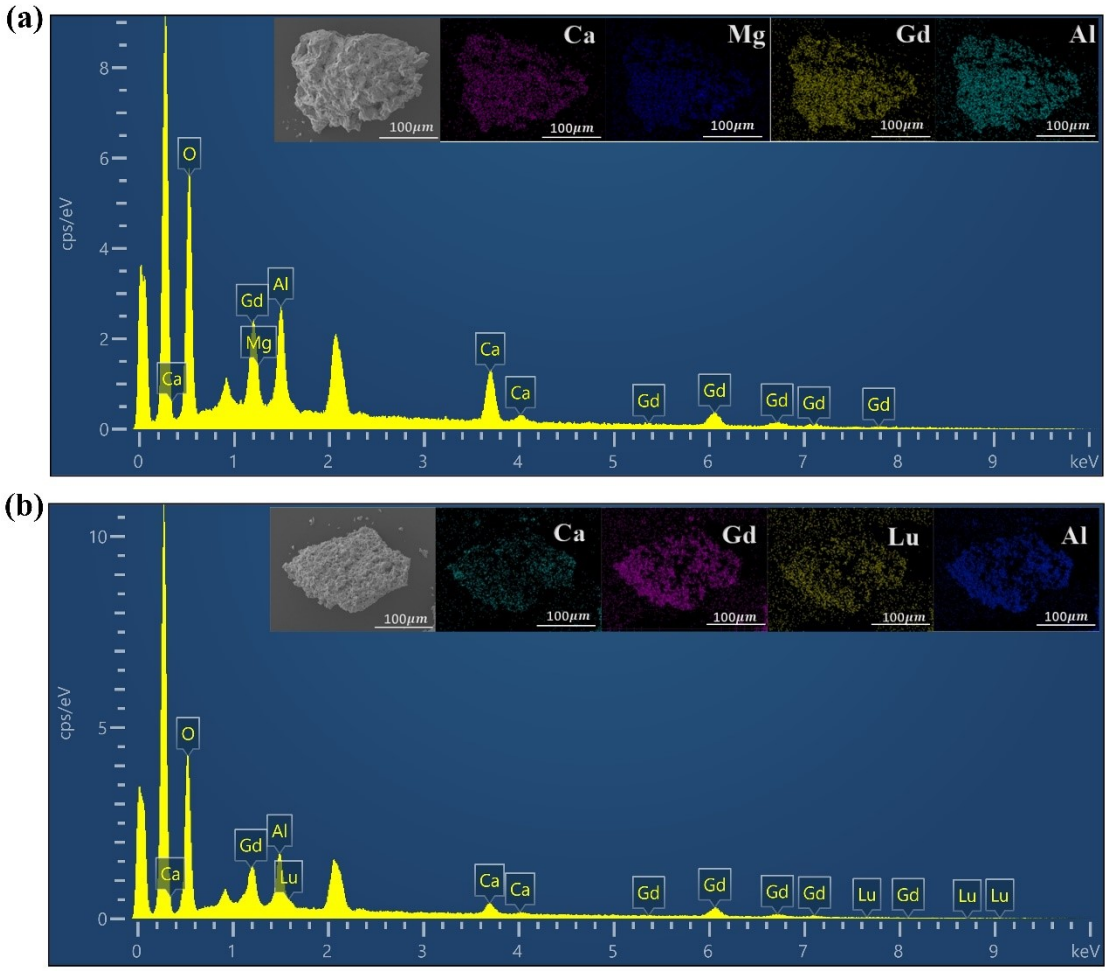

Fig. S3 EDS spectra and the results of elemental mapping for samples partially substituted with Mg^{2+} (a) and Lu^{3+} (b).

Table S5 A summary of ionic radius and the relative difference in ionic radius for Ca^{2+}, Gd^{3+} and the substituting ions.

Cation	$R_{CN=9}$	D_r
Ca^{2+}	1.180	-
Mg^{2+}	0.890	−24.6%
Sr^{2+}	1.310	9.9%
Ba^{2+}	1.470	19.7%
Gd^{3+}	1.107	-
La^{3+}	1.216	8.9%
Y^{3+}	1.075	−2.9%
Lu^{3+}	1.032	−6.8%

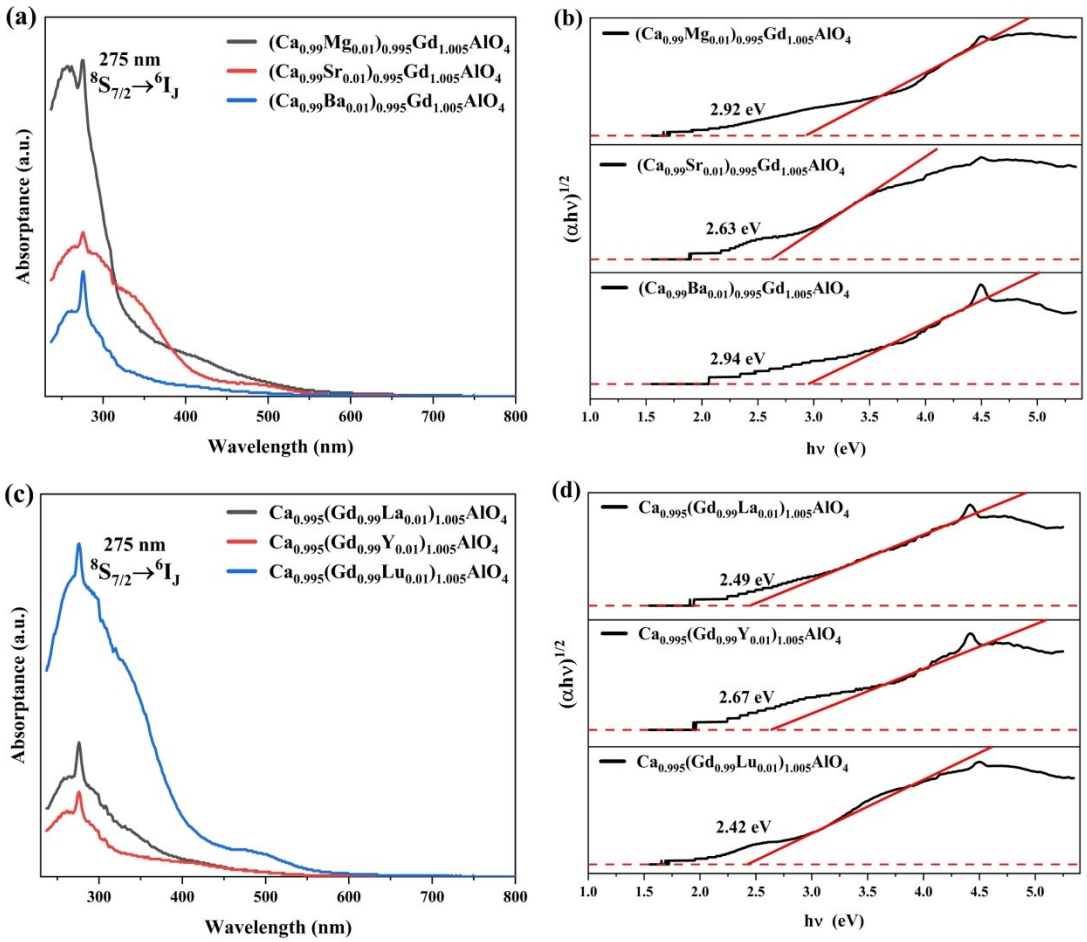

Fig. S4 UV-vis absorption spectra (a, c) and the determination of bandgap energies (b, d) for Ca-site and Gd-site partially substituted products. The *A* in the Y-axis title of parts (b) and (d) represents absorbance, which is proportional to the absorption coefficient α.

Table S6 A summery of the results of fluorescence decay analysis for the samples with Ca and Gd sites partially substituted.

Substituting ion	A_1	A_2	$\tau_1(\mu s)$	$\tau_2(\mu s)$	χ^2	$\tau_{av}(ms)$
Mg^{2+}	115.76	244.15	336.9	1792.64	1.049	1.673
Sr^{2+}	14058.08	241.78	3.48	1701.47	1.220	1.521
Ba^{2+}	14269.57	277.07	3.45	1768.34	1.298	1.607
La^{3+}	12125.22	204.46	3.71	1691.74	0.962	1.497
Y^{3+}	15487.45	242.78	3.36	1737.46	0.998	1.547
Lu^{3+}	881.37	1099.93	559.33	2043.01	1.791	1.776

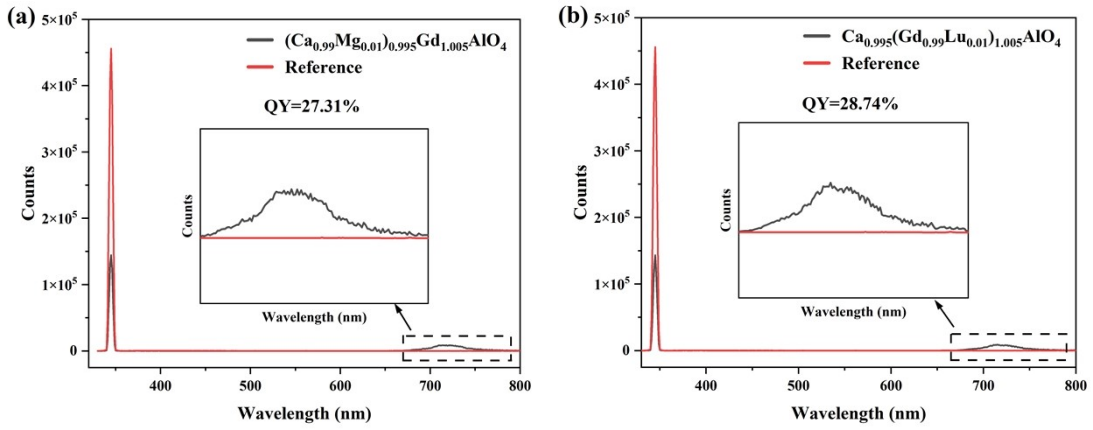

Fig. S5 Quantum yield analysis for the products partially substituted by Mg^{2+} and Lu^{3+}.

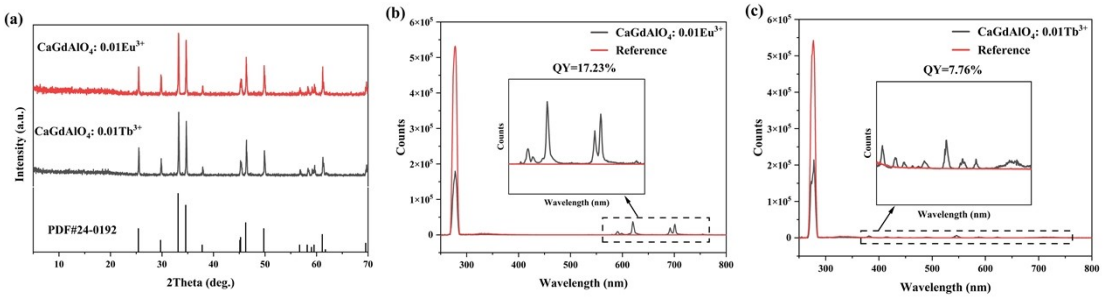

Fig. S6 The XRD patterns of $CaGdAlO_4$:$0.01Tb^{3+}$ and $CaGdAlO_4$:$0.01Eu^{3+}$ (a), and quantum yield analysis for $CaGdAlO_4$:$0.01Eu^{3+}$ (b) and $CaGdAlO_4$:$0.01Tb^{3+}$ (c).

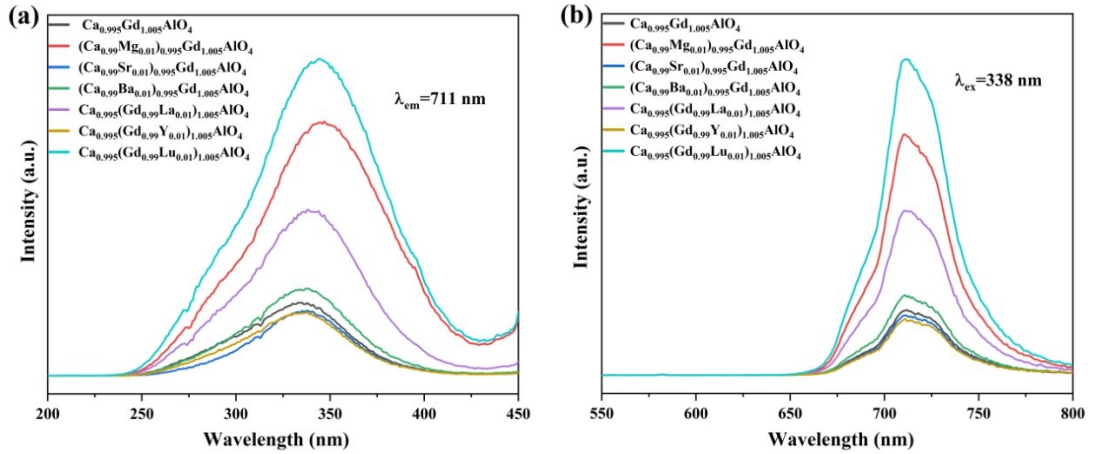

Fig. S7 Photoluminescence spectra of the $CaGdAlO_4$ products, whose Ca and Gd sites were partially substituted.

Table S7 A summary of the results of fluorescence decay analysis for $CaYAlO_4$ and $CaGdAlO_4$.

Compound	A_1	A_2	$\tau_1(\mu s)$	$\tau_2(\mu s)$	χ^2	$\tau_{av}(ms)$
$CaGdAlO_4$	14202.86	334.06	3.54	1741.39	1.178	1.603
$CaYAlO_4$	355.13	438.98	911.3	2758.42	1.691	2.369

Table S8 A summary of the sub-peak position/intensity, trap depth (E_T) and trap density (N_0), which were obtained from the thermoluminescence spectra of $CaYAlO_4$ and $CaGdAlO_4$.

Compound	T_1/(℃)	$Intensity_1$	E_{T1}/(eV)	N_{01}	T_2/(℃)	$Intensity_2$	E_{T2}/(eV)	N_{02}
$CaGdAlO_4$	108.93	83.128	0.766	735.608	233.01	235.781	1.014	2086.451
$CaYAlO_4$	110.75	268.534	0.770	2363.337	215.99	198.957	0.980	1750.998

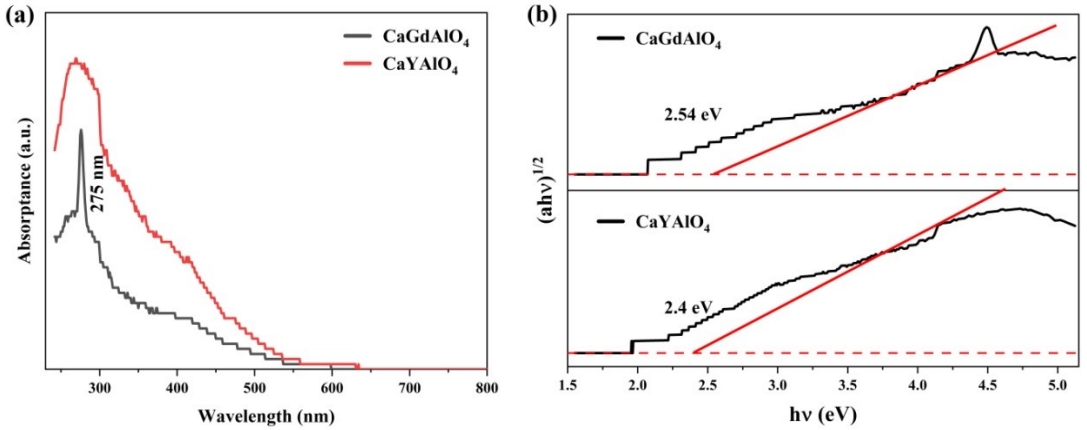

Fig. S8 UV-vis absorption spectra (a) and the determination of bandgap energies (b) for $CaGaAlO_4$ and $CaYAlO_4$. The *A* in the Y-axis title of part (b) represents absorbance, which is proportional to the absorption coefficient α.