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

Supporting Information

Title: Development of ultraviolet-B long persistent phosphors in Pr^{3+}-doped garnets

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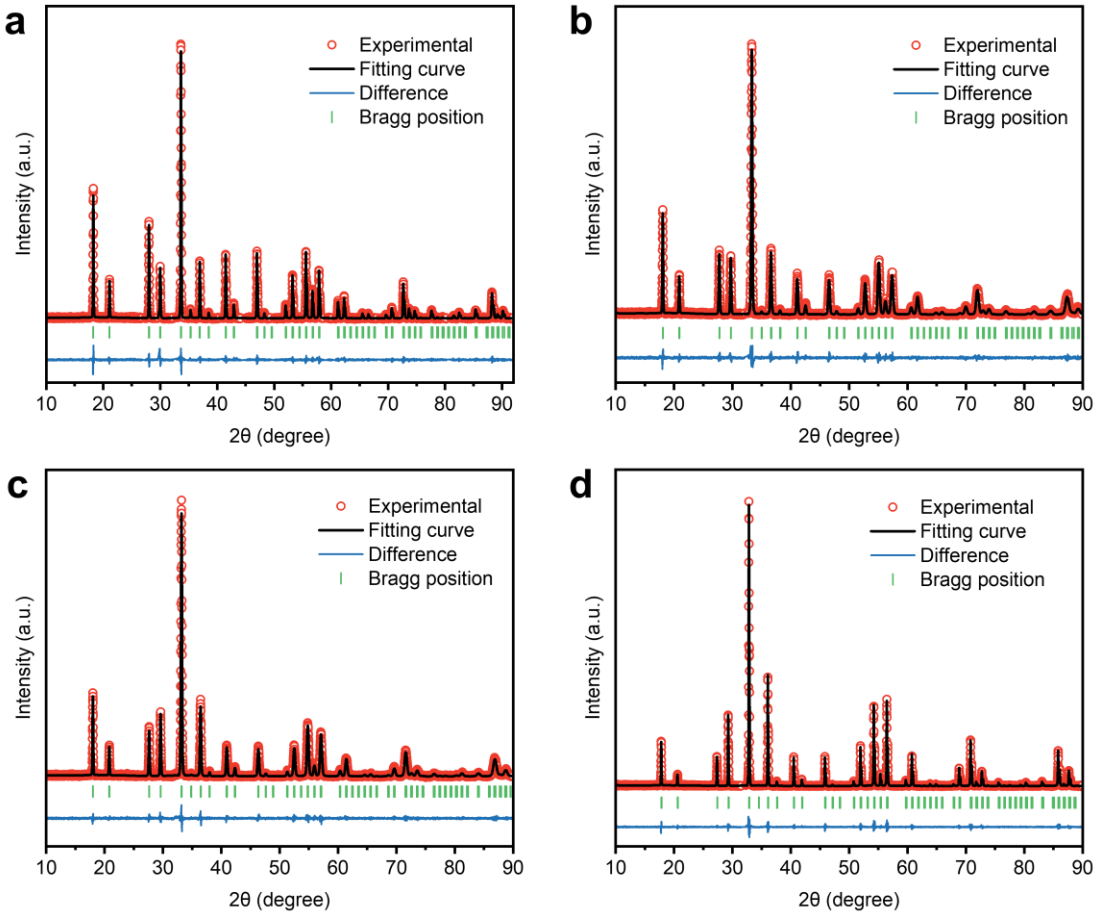

Fig. S1 The Rietveld refinement of the powder XRD pattern of $Lu_3Al_5O_{12}$:0.5%Pr^{3+} (a), $Lu_3Al_3Ga_2O_{12}$:0.5%Pr^{3+} (b), $Lu_3Al_2Ga_3O_{12}$:0.5%Pr^{3+} (c), and $Lu_3Ga_5O_{12}$:0.5%Pr^{3+} (d).

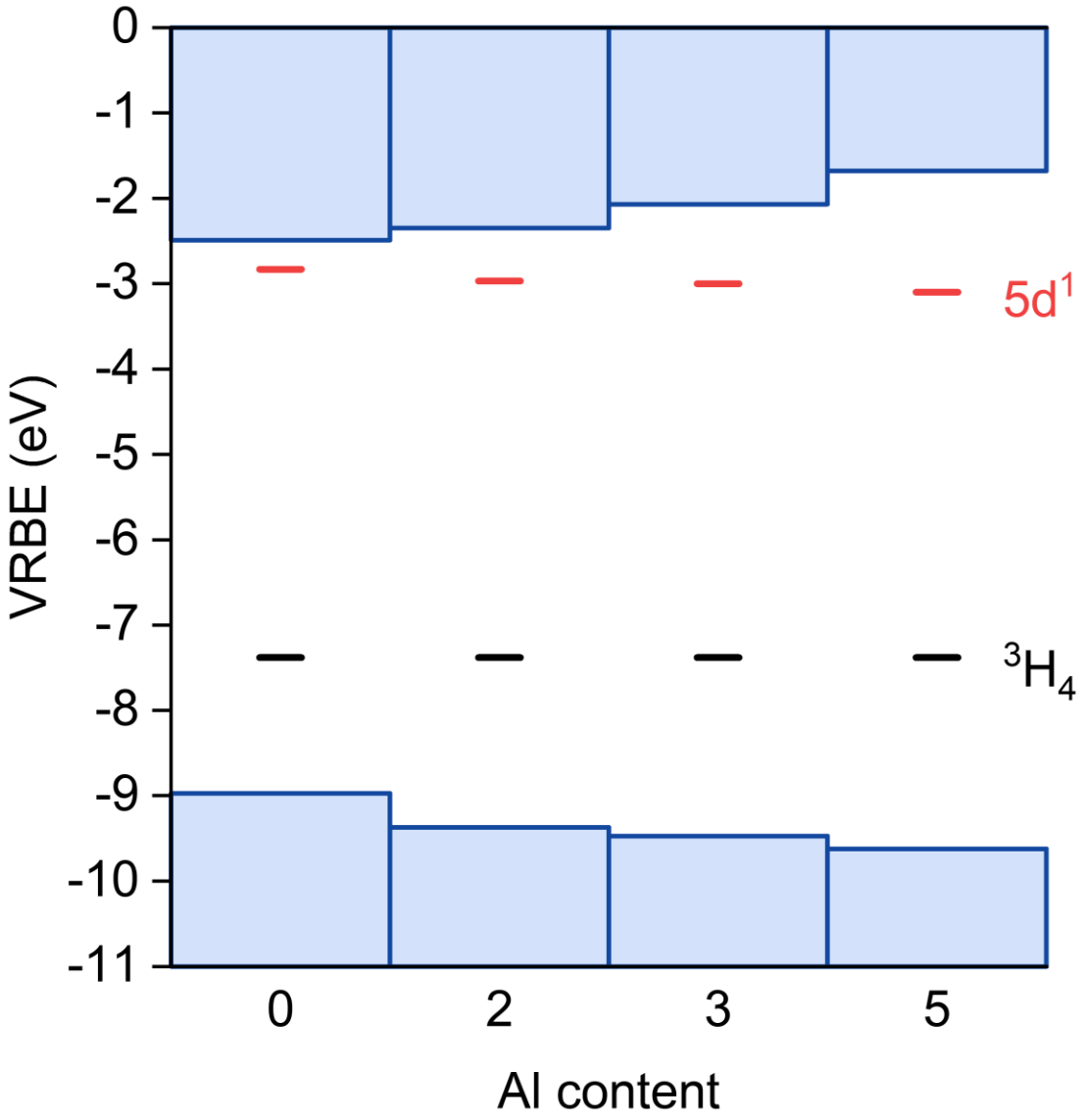

Fig. S2 Effect of the Al/Ga ratio on the VRBE scheme in $Lu_3Al_xGa_{5-x}O_{12}:Pr^{3+}$ (x = 0, 2, 3, 5) garnet compounds.

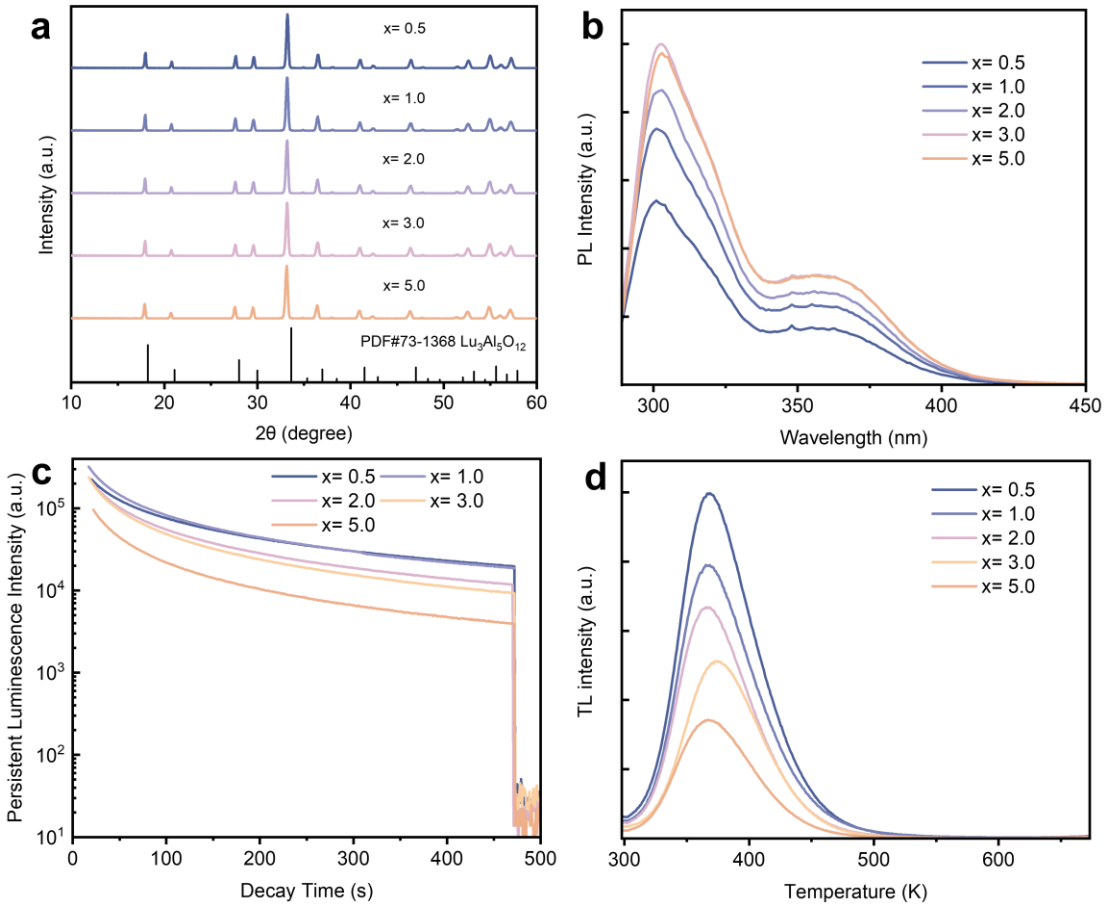

Fig. S3 (a) XRD patterns of $Lu_3Al_3Ga_2O_{12}$:x%Pr^{3+} (x = 0.5, 1, 2, 3, 5). (b) Photoluminescence emission spectra of $Lu_3Al_3Ga_2O_{12}$:x%Pr^{3+} (x = 0.5, 1, 2, 3, 5). The emission spectra were obtained upon 279 nm excitation. (c) Persistent luminescence decay curves of $Lu_3Al_3Ga_2O_{12}$:x%Pr^{3+} (x = 0.5, 1, 2, 3, 5) phosphors at room temperature. The decay curves were monitored at 302 nm after irradiation by a 254 nm UV lamp for 10 min. (d) TL curves of $Lu_3Al_3Ga_2O_{12}$:x%Pr^{3+} (x = 0.5, 1, 2, 3, 5). The samples were pre-irradiated by 254 nm UV lamp for 10 min.

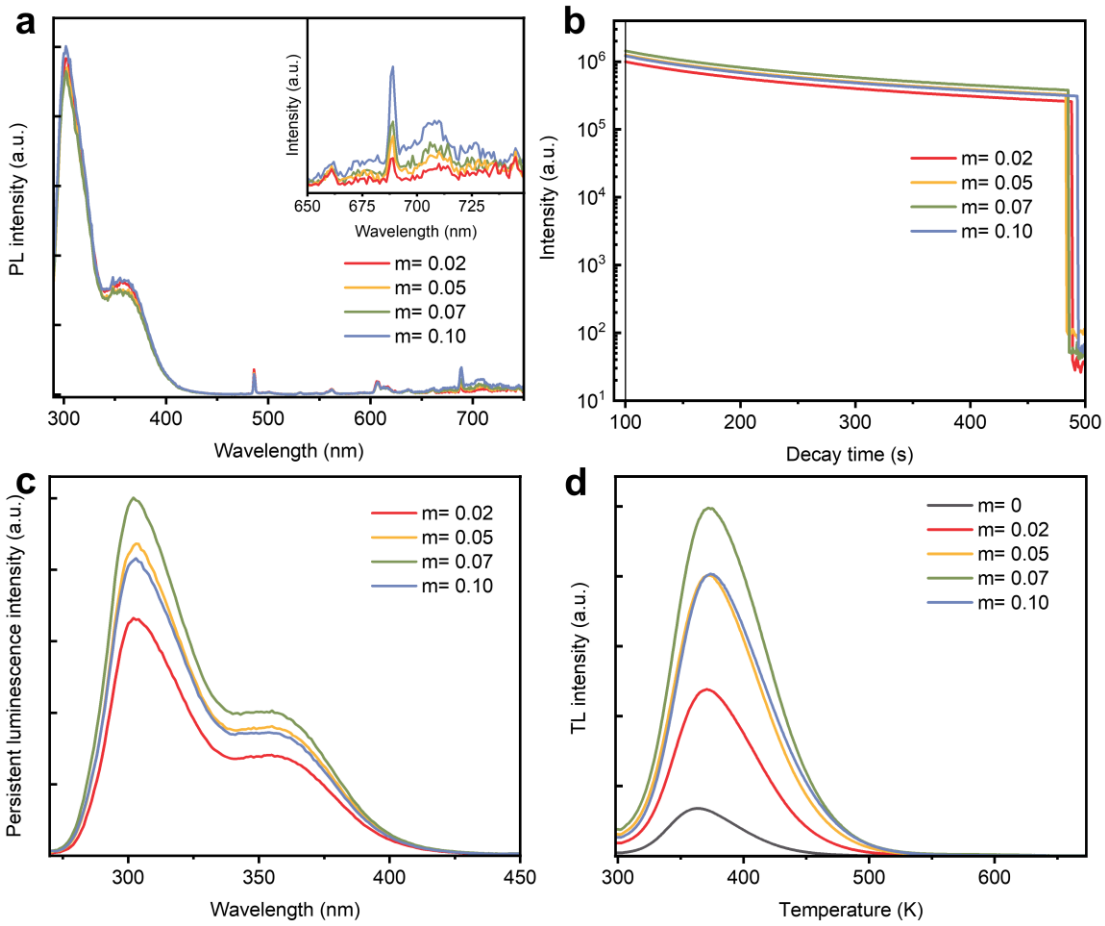

Fig. S4 (a) Emission spectra of $Lu_3Al_3Ga_2O_{12}$:0.5%Pr^{3+},*m*%Cr^{3+} (*m* = 0.02, 0.05, 0.07, 0.10). All the emission spectra were obtained with the excitation wavelength of 279 nm light. (b, c) Persistent luminescence decay curves and persistent luminescence emission spectra of $Lu_3Al_3Ga_2O_{12}$:0.5%Pr^{3+}, *m*%Cr^{3+} (*m* = 0.02, 0.05, 0.07, 0.10). The discs were monitored at 302 nm after pre-irradiated by 254 nm UV lamp for 10 min. The persistent luminescence emission spectra were obtained after 10 min decay. (d) Thermoluminescence curves of $Lu_3Al_3Ga_2O_{12}$:0.5%Pr^{3+},*m*%Cr^{3+} (*m* = 0, 0.02, 0.05, 0.07, 0.10).

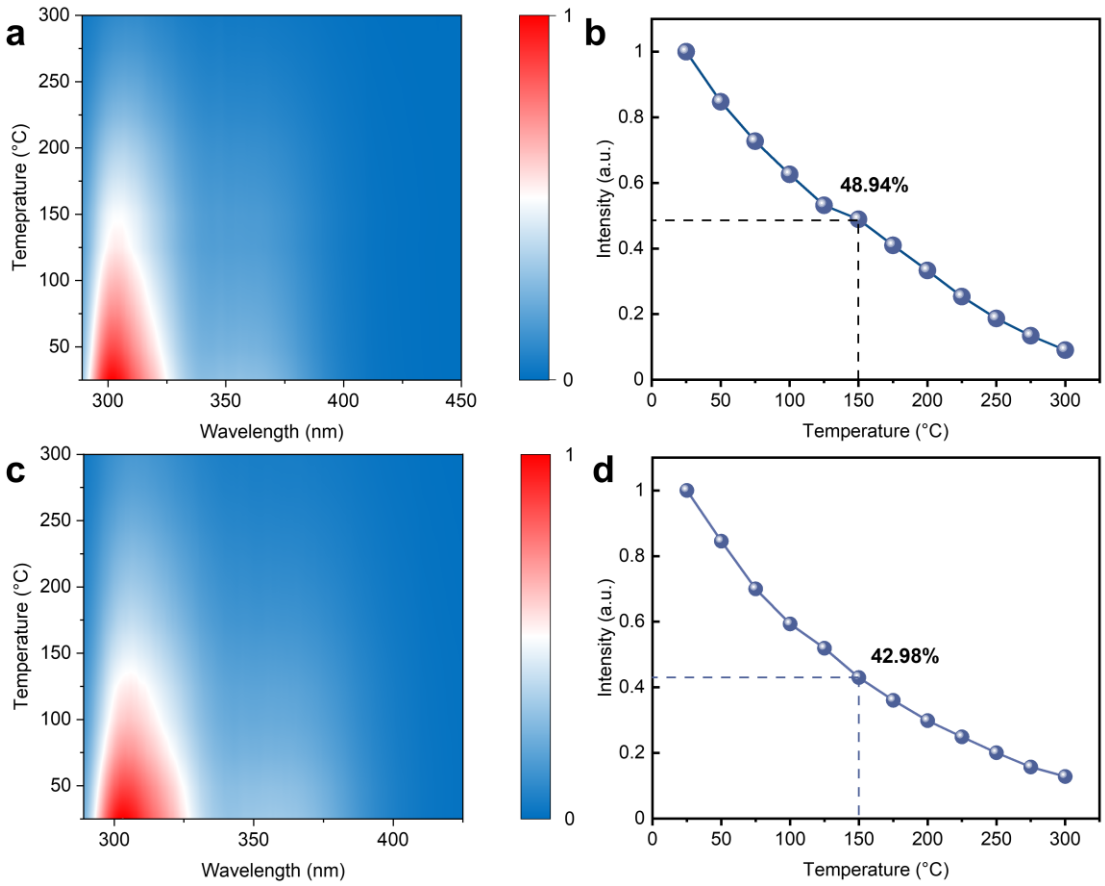

Fig. S5 (a) 2D color maps of temperature-dependent emission spectra of LAGG:Pr phosphor. (b) Normalized emission intensities of LAGG:Pr monitored at 302 nm as a function of temperature. (c) 2D color maps of temperature-dependent emission spectra of LAGG:Pr,Cr phosphor. (d) Normalized emission intensities of LAGG:Pr,Cr monitored at 302 nm as a function of temperature.

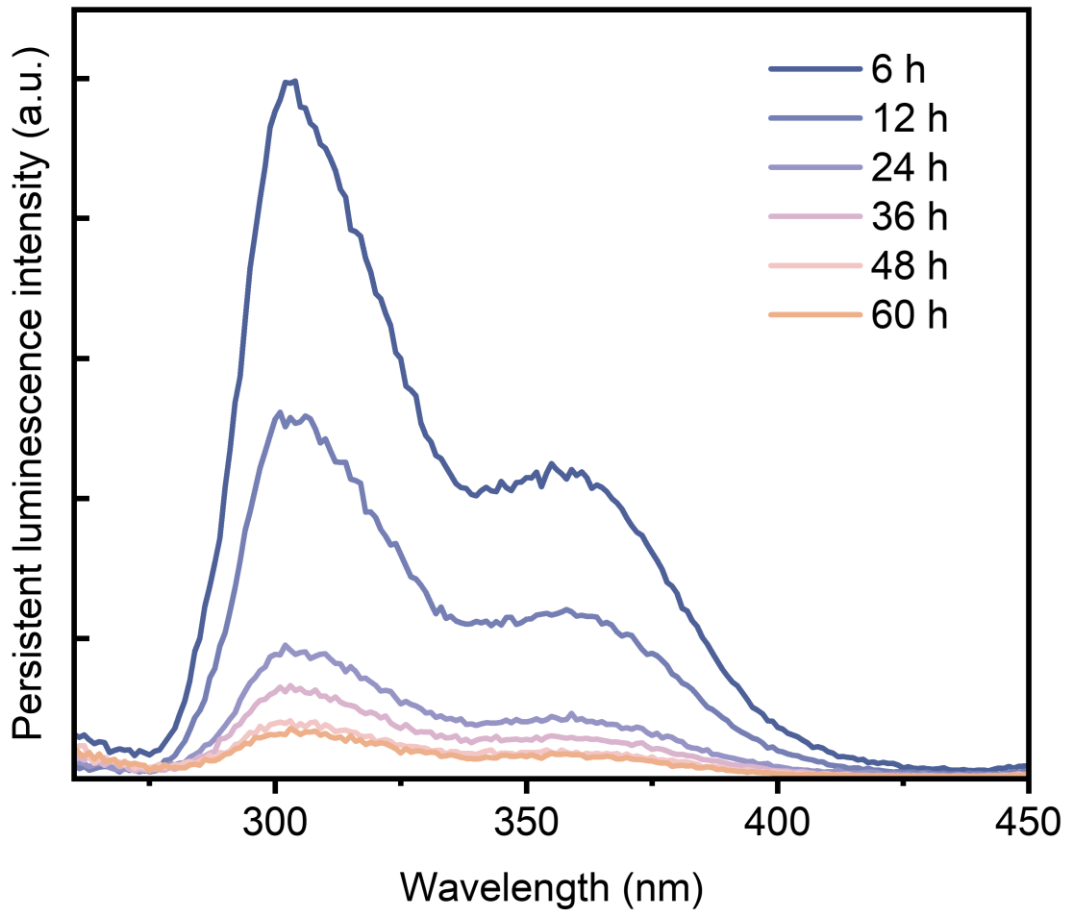

Fig. S6 Persistent luminescence emission spectra of LAGG:Pr,Cr phosphor at different decay time. The sample was pre-irradiated by 254 nm UV lamp for 15 min.

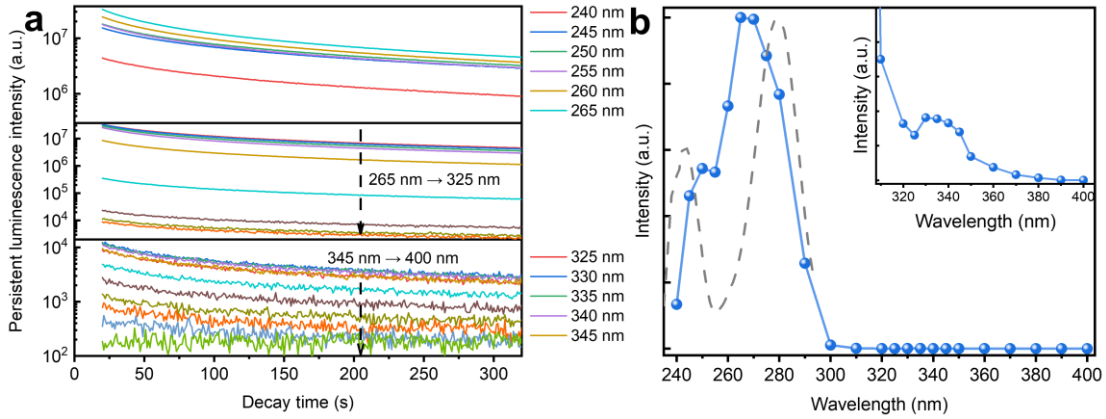

Fig. S7 (a) Room temperature persistent luminescence decay curves of LAGG:Pr,Cr phosphor irradiated by monochromatic light between 240–400 nm for 5 min. The monitoring wavelength is 302 nm. The persistent luminescence intensity at 20 s was used to plot the persistent luminescence intensity as a function of excitation wavelength shown in Fig. S7b. (b) Persistent luminescence excitation spectrum (blue ball curve) and photoluminescence excitation spectrum (grey dash curve) of LAGG:Pr,Cr. The upper inset is the zoom-in spectrum between 310–400 nm.

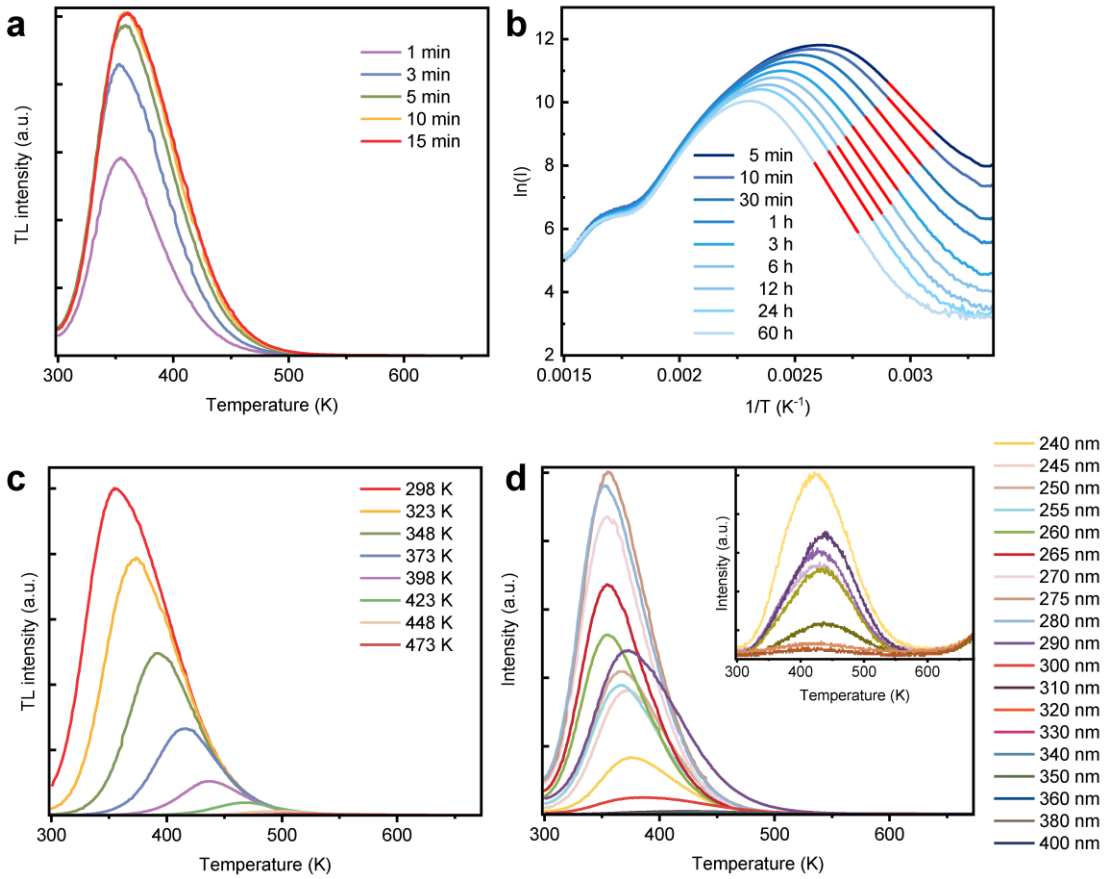

Fig. S8 (a) Thermoluminescence curves of LAGG:Pr,Cr after pre-irradiated by 254 nm UV lamp for different times. (b) TL curves analyzed by the initial rise method in the LAGG:Pr,Cr phosphor. The depth of the shallowest occupied trap for each curve was estimated according to the slope of fitting red straight lines. (c) Thermoluminescence curves obtained on the LAGG:Pr,Cr sample underwent thermal cleaning at different temperatures. (d) Thermoluminescence curves with an excitation wavelength from 240 to 400 nm of LAGG:Pr,Cr. The sample was pre-irradiated for 10 min at each measured wavelength using a xenon arc lamp.

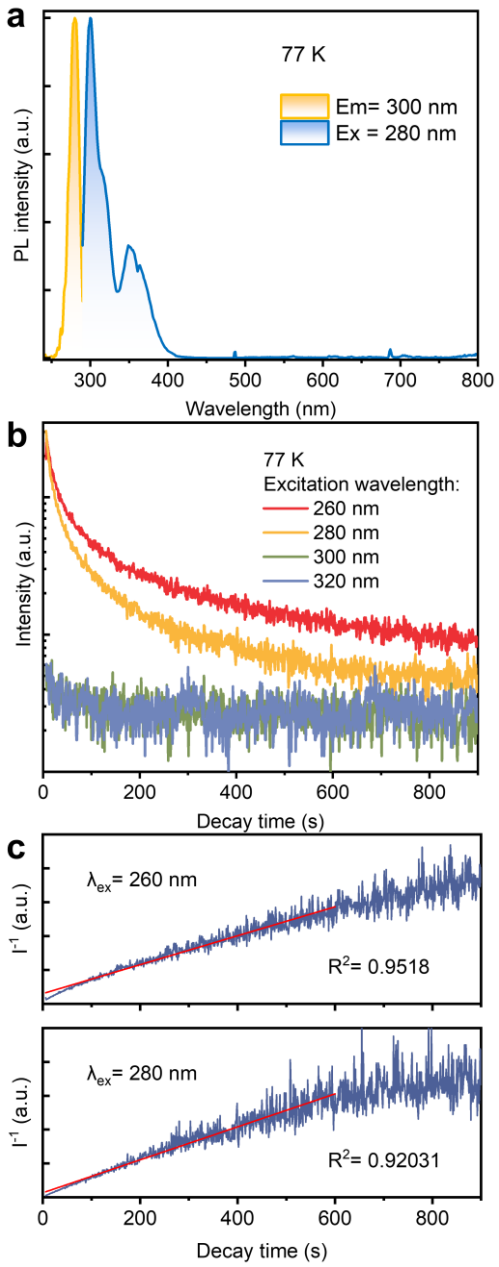

Fig. S9 (a) Photoluminescence excitation and emission spectra of LAGG:Pr,Cr phosphor at 77K. (b) Persistent luminescence decay curves of LAGG:Pr,Cr at 77 K after pre-irradiated by the monochromic light (260, 280, 300 nm, and 320 nm) for 10 min at 77 K. (c) The reciprocal of the persistent luminescence intensity (I^{1}) *versus* decay time (t) after irradiation by 260 nm and 280 nm UV light for 15 min at 77 K.

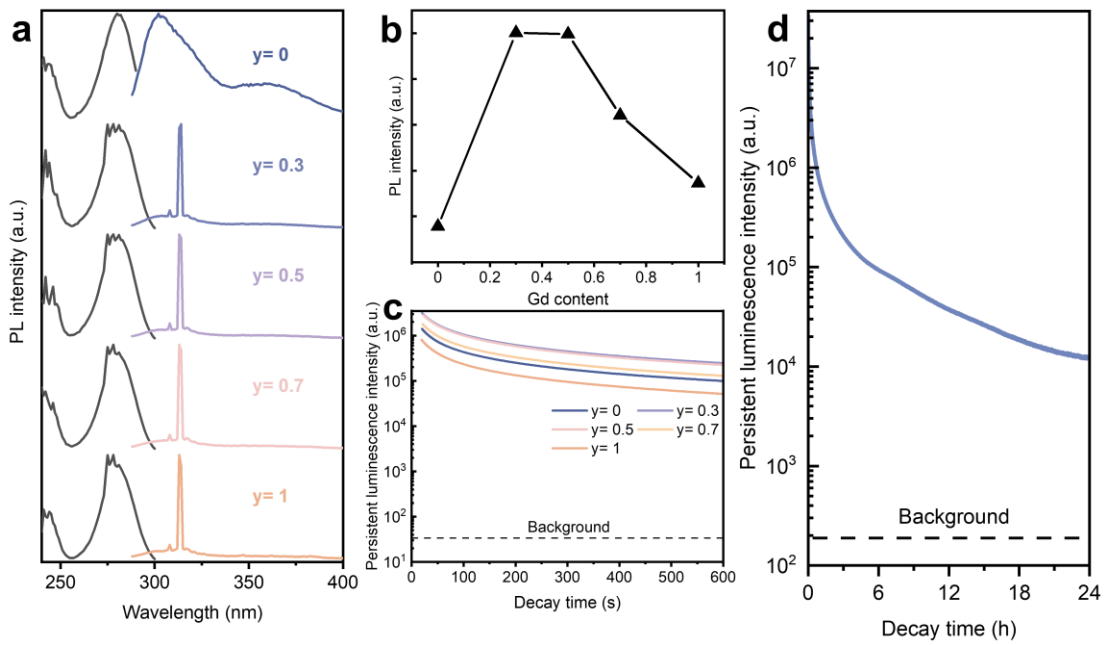

Fig. S10 (a) Normalized photoluminescence excitation and emission spectra of $Lu_{3-y}Gd_yAl_3Ga_2O_{12}$:0.5%$Pr^{3+}$,0.07%$Cr^{3+}$ (y = 0, 0.3, 0.5, 0.7, 1). (b) Emission intensity at 313 nm as a function of Gd contents. (c) Persistent luminescence decay curves of $Lu_{3-y}Gd_yAl_3Ga_2O_{12}$:0.5%$Pr^{3+}$,0.07%$Cr^{3+}$ (y = 0, 0.3, 0.5, 0.7, 1). The discs were pre-irradiated by a 254 nm UV lamp for 10 min. (d) Long-lasting persistent luminescence decay curve of $Lu_{2.7}Gd_{0.3}Al_3Ga_2O_{12}$:0.5%$Pr^{3+}$,0.07%$Cr^{3+}$ phosphor. Before measurement, the sample was irradiated by 254 nm UV lamp for 15 min to fully fill the traps.

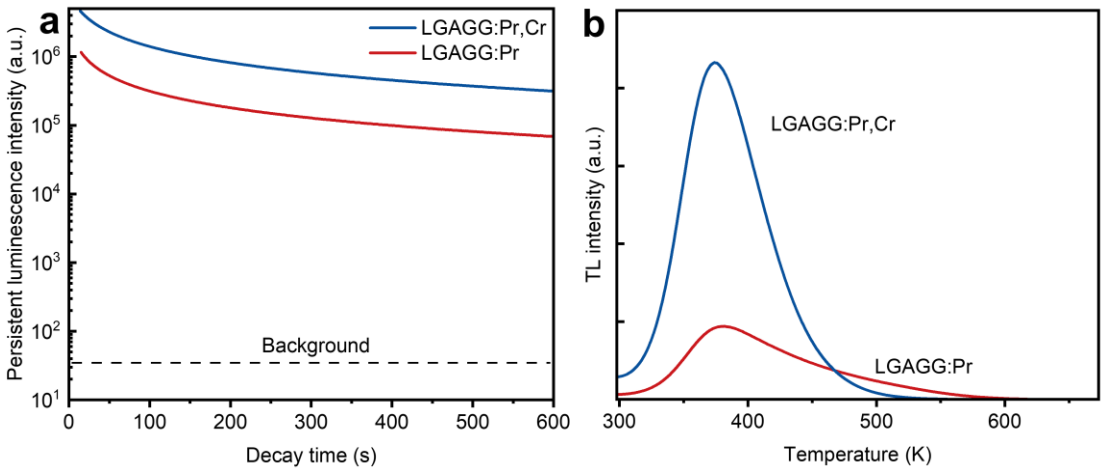

Fig. S11 (a) Persistent luminescence decay curves monitored at 313 nm for LGAGG:Pr and LGAGG:Pr,Cr phosphors. The samples were pre-irradiated by a 254 nm UV lamp for 10 min. (b) TL curves of LGAGG:Pr and LGAGG:Pr,Cr phosphors after being irradiated by a 254 nm UV lamp for 10 min.

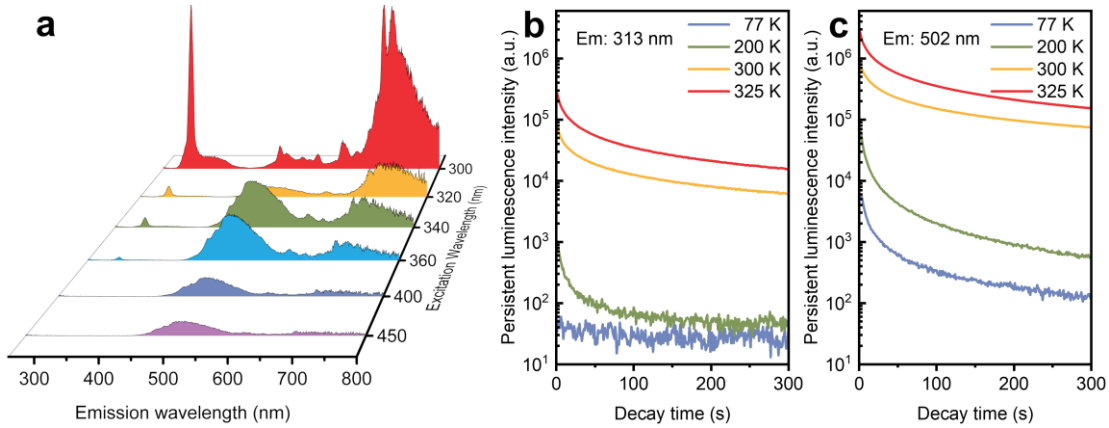

Fig. S12 (a) Persistent luminescence emission spectra of LGAGG:Pr,Cr phosphor after irradiated by different monochromic light for 10 min. (b, c) Persistent luminescence decay curves of LGAGG:Pr,Cr measured at different temperatures from 77 K to 325 K. The curves were monitored at 313 nm (b) and 502 nm (c) after irradiation by 340 nm monochromic light for 10 min.

Table S1 Experimental and computational data used to construct the VRBE diagram of the $Lu_3(Al,Ga)_5O_{12}$ series garnet compounds (in eV).

Host lattice	U(6,A)	$E^{4f}_{Eu^{2+}}$	$E^{4f}_{Eu^{3+}}$	$E_{Eu^{3+},CT}$	E_V	E^{ex}	E_{CV}	E_C	$E^{4f}_{Pr^{3+}}$	$E^{5d}_{Pr^{3+}}$
$Lu_3Al_5O_{12}$	6.8	-3.97	-10.77	5.65	-9.62	7.35	7.94	-1.68	-7.38	-3.10
$Lu_3Al_3Ga_2O_{12}$	6.8	-3.97	-10.77	5.49	-9.46	6.85	7.40	-2.07	-7.38	-3.00
$Lu_3Al_2Ga_3O_{12}$	6.8	-3.97	-10.77	5.40	-9.37	6.50	7.02	-2.35	-7.38	-2.97
$Lu_3Ga_5O_{12}$	6.8	-3.97	-10.77	5.00	-8.97	6.00	6.48	-2.49	-7.38	-2.83

Table S2 Rietveld refinement parameters of $Lu_3Al_xGa_{5-x}O_{12}$:0.5%Pr^{3+} (x= 0, 2, 3, 5) phosphors.

Sample	$Lu_3Al_5O_{12}:Pr^{3+}$	$Lu_3Al_3Ga_2O_{12}:Pr^{3+}$	$Lu_3Al_2Ga_3O_{12}:Pr^{3+}$	$Lu_3Ga_5O_{12}:Pr^{3+}$
Space group	Ia-3d	Ia-3d	Ia-3d	Ia-3d
α= β= γ (°)	90	90	90	90
a= b= c (Å)	11.92026(4)	12.02269(8)	12.08188(7)	12.187200(26)
V (Å^3)	1693.779(10)	1737.823(20)	1763.613(17)	1810.138(7)
R_{wp}	13.31%	12.94%	12.42%	14.20%
R_p	9.17%	9.31%	8.58%	10.11%
χ^2	1.309	1.240	1.181	1.491

Table S3 UVB persistent luminescence power intensities measured by Newport power meter.

Decay time (s)	Intensity (mW m^{-2})
5	19.76
10	14.00
30	7.41
60	4.62
180	2.06
300	1.31
600	0.65
900	0.44

Table S4 Comparison of the reported UV persistent phosphors.

Material	Maximum emission	Irradiance	Ref. (in text)
$Ca_2Al_2SiO_7:Pr^{3+}$	268 nm	4.8 mW m^{-2} at 10 s	1
$Y_3Ga_5O_{12}:Bi^{3+}$	313 nm	5.7 mW m^{-2} at 10 s	2
$LiYGeO_4:Bi^{3+}$	365 nm	11.83 mW m^{-2} at 10 s	3
$Cs_2NaYF_6:Pr^{3+}$	270 nm	14.9 mW m^{-2} at 30 s	4
$Lu_2SiO_5:Pr^{3+}$	270 nm	6.98 mW m^{-2} at 15s	5
$Lu_3Al_3Ga_2O_{12}:Pr^{3+},Cr^{3+}$	302 nm	14.00 mW m^{-2} at 10 s	This work

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