Supporting Information

Long-lasting far-UVC persistent luminescence for solar-blind optical tagging

Xihui Shan, Yi Zhang, Xulong Lv and Yanjie Liang*

Key Laboratory for Liquid-Solid Structure Evolution and Processing of Materials, Ministry of Education, Shandong University, Jinan 250061, P. R. China

*Corresponding author: Yanjie Liang
E-mail: yanjie.liang@sdu.edu.cn

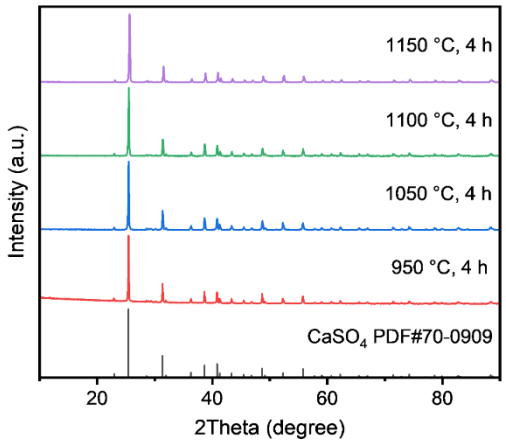

Fig. S1 XRD patterns of the $CaSO_4$:1%Pr^{3+} phosphor sintered at different temperatures from 950 to 1150 ºC (without prefiring).

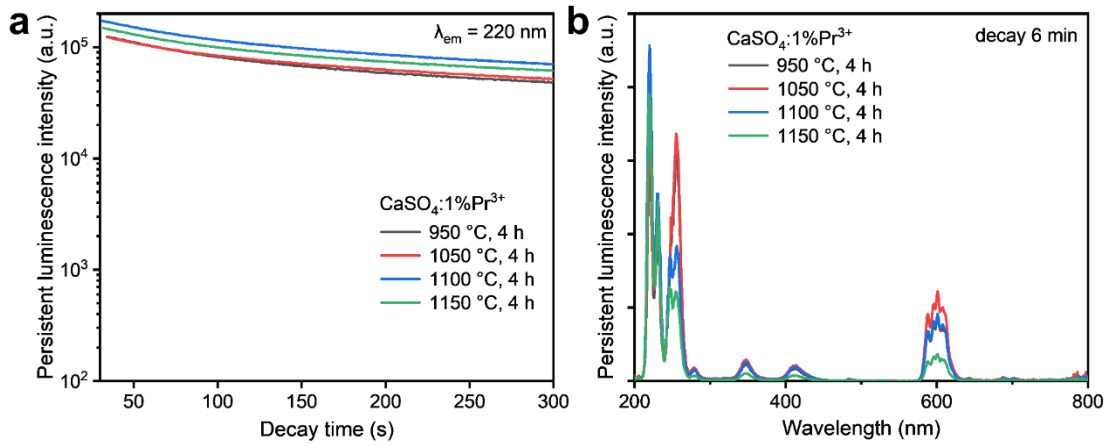

Fig. S2 (a) Far-UVC persistent luminescence decay curves of the $CaSO_4$:1%Pr^{3+} phosphor sintered at different temperatures (without prefiring) monitored at 220 nm after irradiation by an X-ray beam. (b) Persistent luminescence emission spectra recorded at 6 min decay after the stoppage of X-ray irradiation.

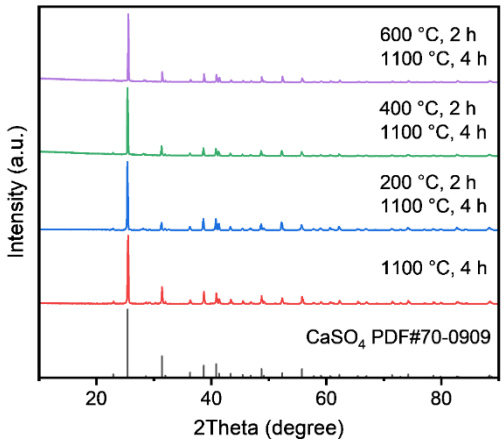

Fig. S3 XRD patterns of the $CaSO_4$:1%Pr^{3+} phosphor sintered at 1100 ºC in the absence and presence of prefiring at different temperatures.

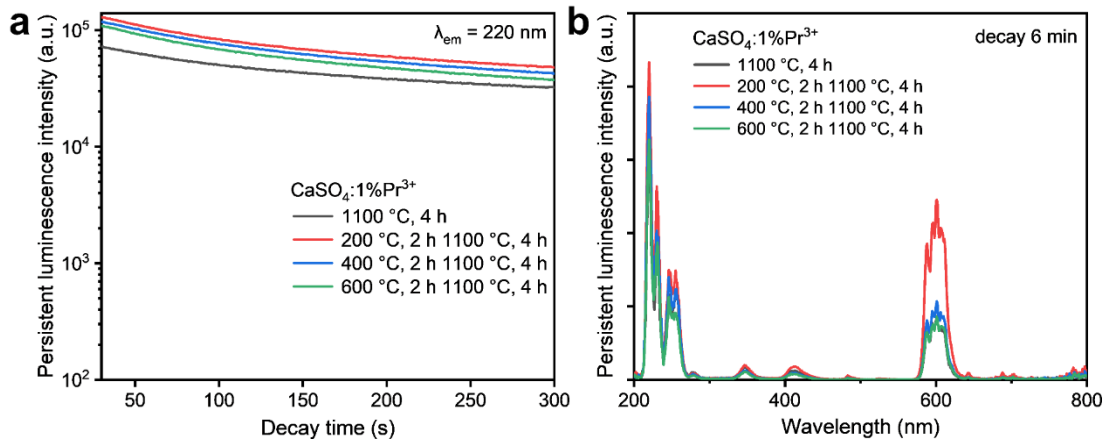

Fig. S4 (a) Far-UVC persistent luminescence decay curves of the $CaSO_4$:1%Pr^{3+} phosphor sintered at 1100 ºC in the absence and presence of prefiring at different temperatures monitored at 220 nm after irradiation by an X-ray beam. (b) Persistent luminescence emission spectra recorded at 6 min decay after stopping X-ray irradiation.

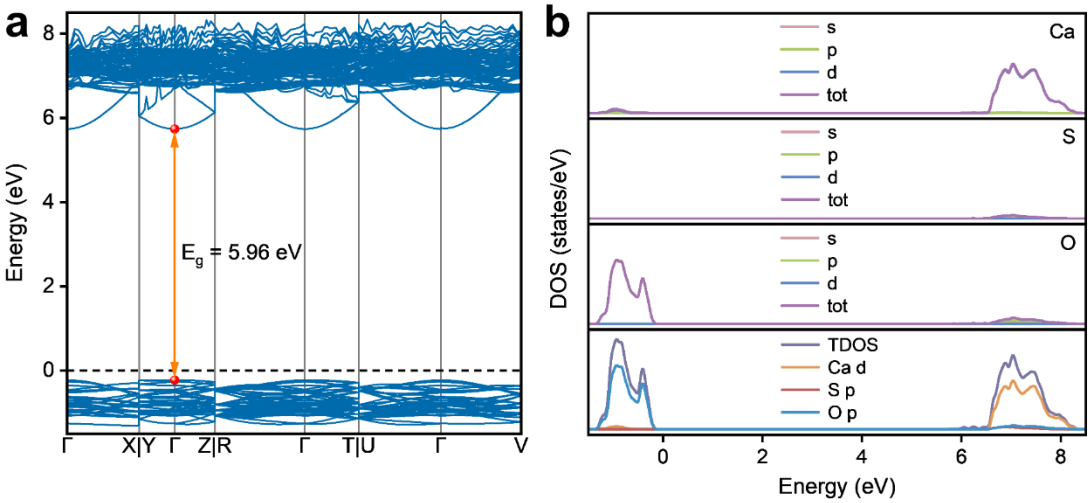

Fig. S5 (a) Band structure and (b) total DOS and partial DOS of the $CaSO_4$ host.

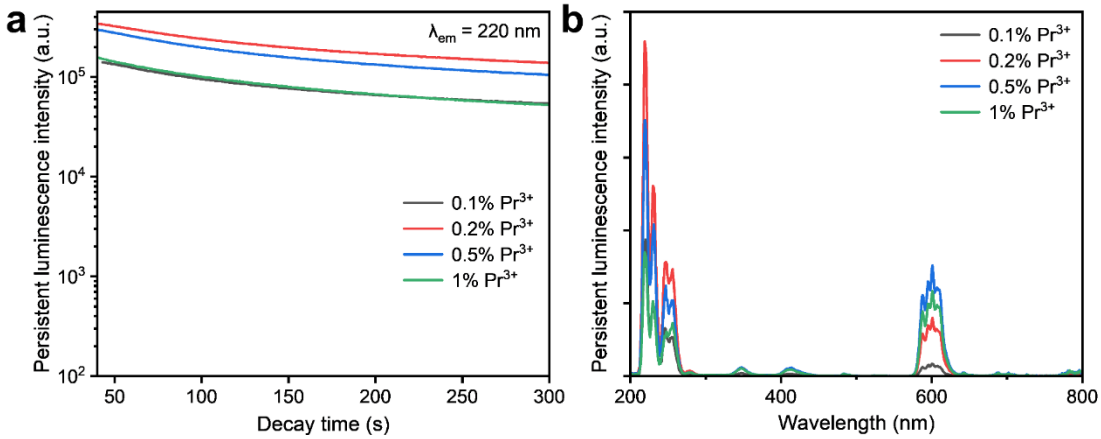

Fig. S6 (a) Concentration-dependent persistent luminescence decay curves of the $CaSO_4$:x%Pr^{3+} (x = 0.1, 0.2, 0.5, and 1) phosphors monitored at 220 nm in the dark after irradiation with an X-ray tube for 5 min (dose rate: 208.20 mGy/s). (b) Concentration-dependent persistent luminescence emission spectra recorded at 6 min decay after ceasing X-ray irradiation.

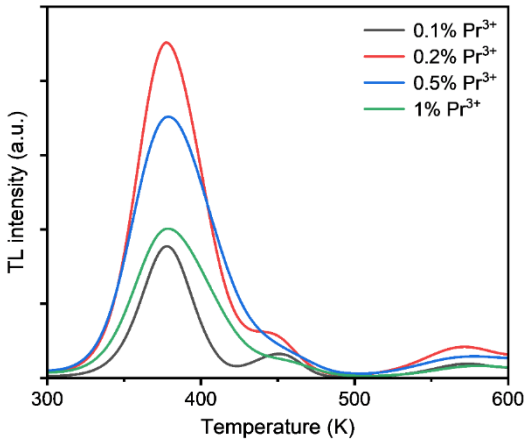

Fig. S7 TL curves of the $CaSO_4$:x%Pr^{3+} (x = 0.1, 0.2, 0.5, and 1) phosphors after irradiation with an X-ray tube for 5 min (dose rate: 208.20 mGy/s). TL curves were acquired after 1 min decay.

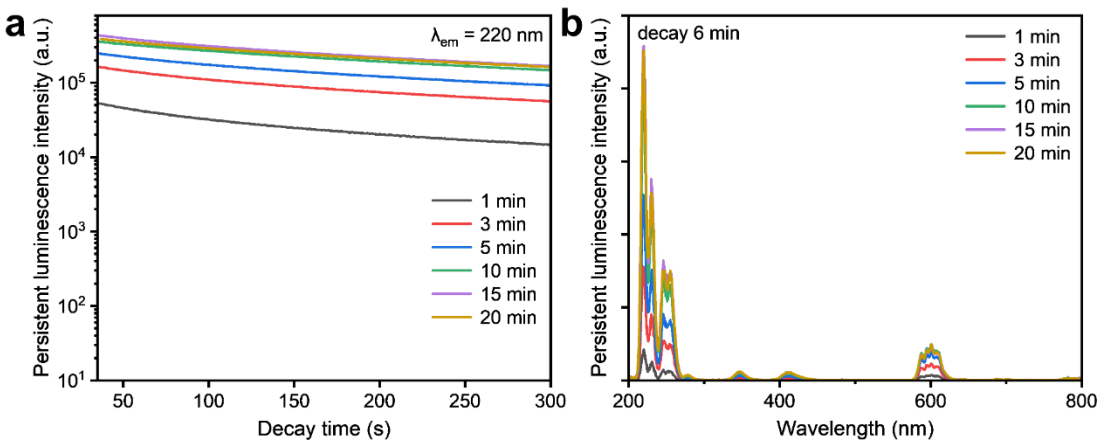

Fig. S8 (a) Persistent luminescence decay curves of the $CaSO_4$:0.2%Pr^{3+} phosphor monitored at 220 nm in the dark by varying the X-ray irradiation time (dose rate: 208.20 mGy/s). (b) Persistent luminescence emission spectra measured at 6 min decay after stopping X-ray irradiation.

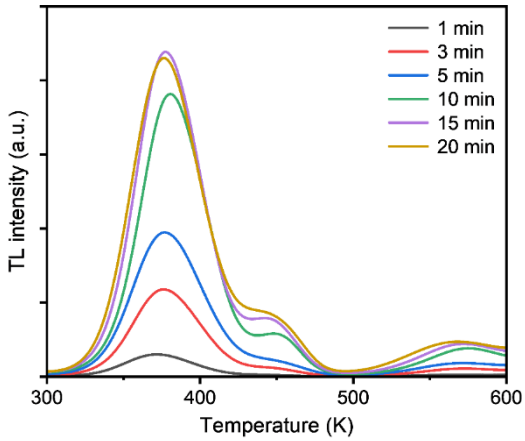

Fig. S9 TL curves of the $CaSO_4$:0.2%Pr^{3+} phosphor with varying the excitation duration from 1 to 20 min (dose rate: 208.20 mGy/s). TL curves were obtained after 1 min decay.

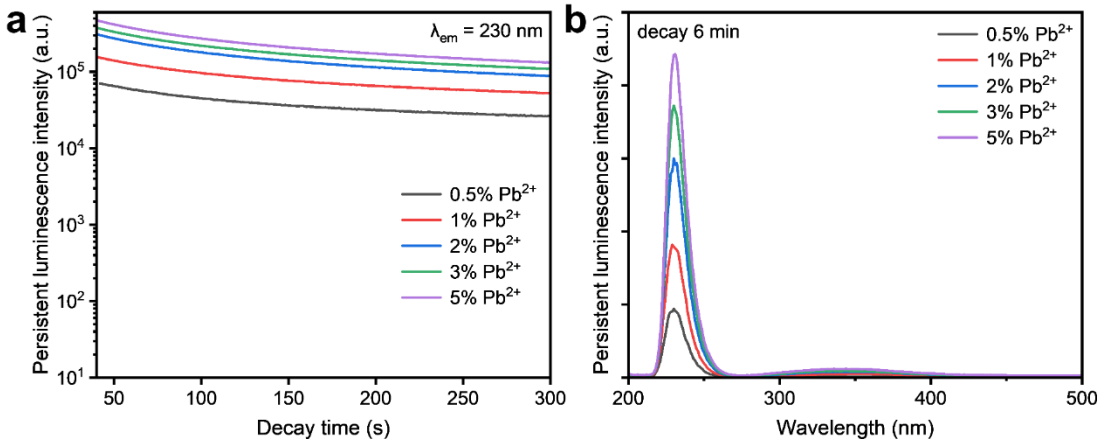

Fig. S10 (a) Concentration-dependent afterglow decay curves of the $CaSO_4$:x%Pb^{2+} (x = 0.5, 1, 2, 3 and 5) phosphors monitored at 230 nm in the dark after irradiation with an X-ray tube for 3 min (dose rate: 290.30 mGy/s). (b) Concentration-dependent afterglow emission spectra recorded at 6 min decay after the stoppage of X-ray irradiation.

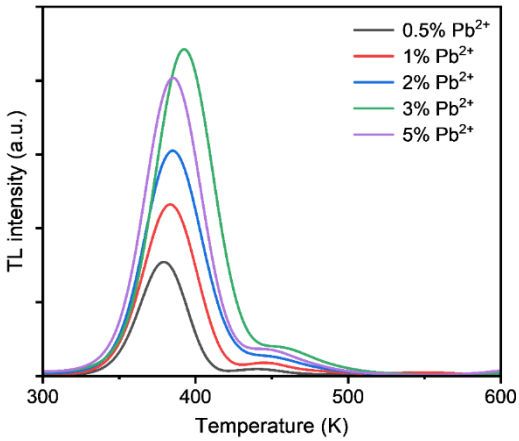

Fig. S11 TL curves of the $CaSO_4$:x%Pb^{2+} (x = 0.5, 1, 2, 3 and 5) phosphors after irradiation with an X-ray tube for 3 min (dose rate: 290.30 mGy/s). TL curves were obtained after 1 min decay.

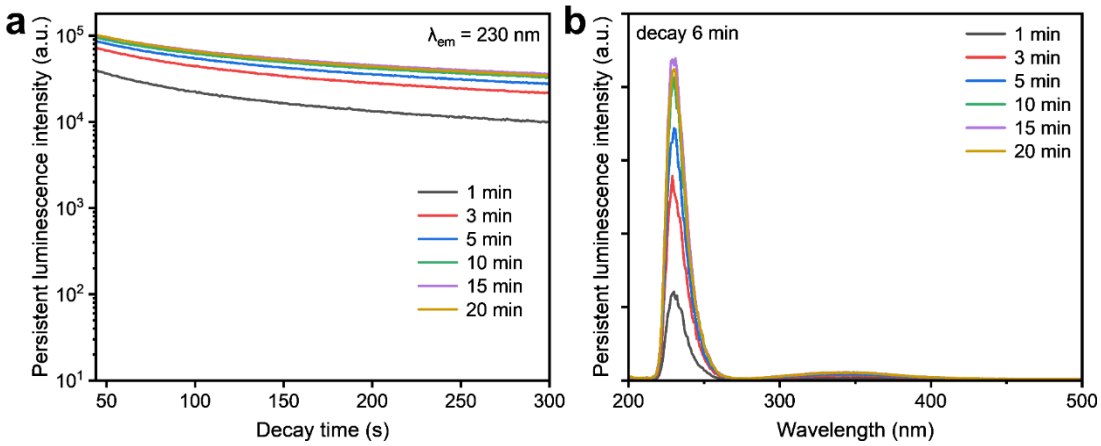

Fig. S12 (a) Persistent luminescence decay curves of the $CaSO_4$:3%Pb^{2+} phosphor monitored at 230 nm in the dark by varying the X-ray irradiation time (dose rate: 290.30 mGy/s). (b) Persistent luminescence emission spectra obtained at 6 min decay after ceasing X-ray irradiation.

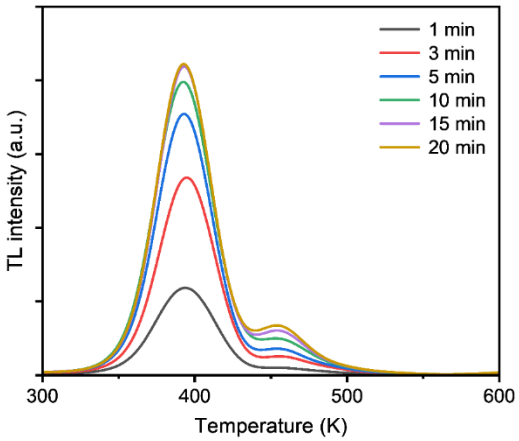

Fig. S13 TL curves of the $CaSO_4$:3%Pb^{2+} phosphor with varying the excitation duration from 1 to 20 min (dose rate: 290.30 mGy/s). TL curves were recorded after 1 min decay.

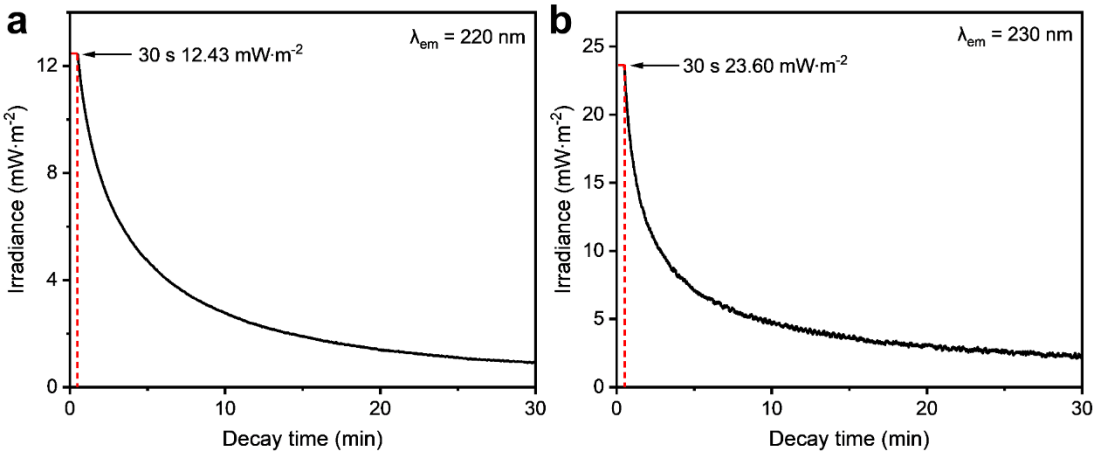

Fig. S14 Far-UVC persistent luminescence power density decay curves of the pre-irradiated (a) $CaSO_4$:0.2%Pr^{3+} and (b) $CaSO_4$:3%Pb^{2+} phosphors measured by Newport power meter.

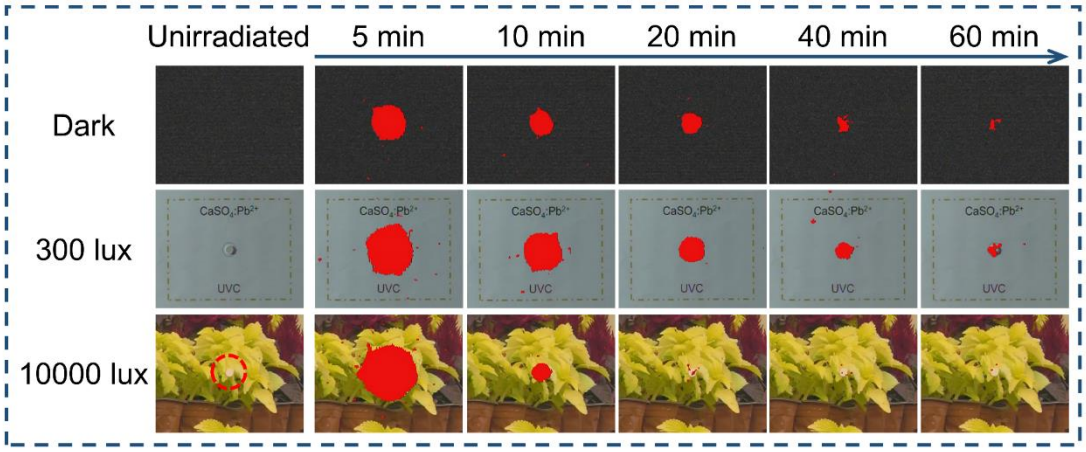

Fig. S15 UVC persistent luminescence images of the charged $CaSO_4$:3%Pb^{2+} phosphor disc at different decay instants in dark, in an indoor LED lighting environment (300 lux), and in an outdoor sunlight environment (~10000 lux), respectively. The phosphor disc was pre-irradiated by 290.30 mGy/s X-ray for 15 min.

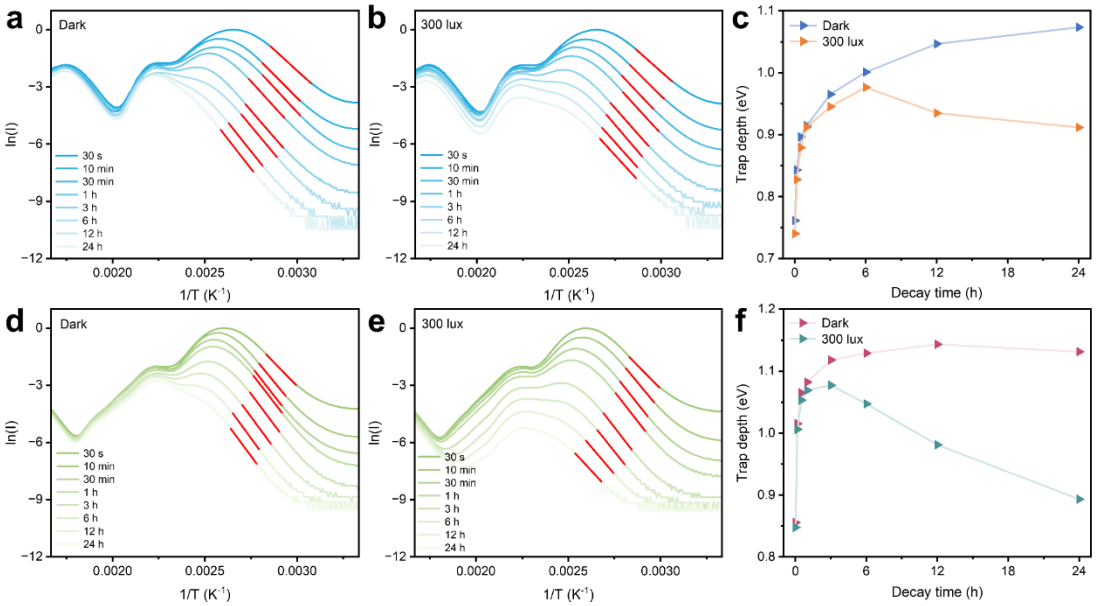

Fig. S16 (a,b) Initial rising analysis for the TL curves of the pre-irradiated $CaSO_4$:0.2%Pr^{3+} phosphor at different decay instants in dark and bright (300 lux) indoor environments. (c) The depth of the shallowest occupied trap for each curve of the $CaSO_4$:0.2%Pr^{3+} phosphor was estimated according to the slope of fitting red straight line. (d,e) Initial rising analysis for the TL curves of the pre-irradiated $CaSO_4$:3%Pb^{2+} phosphor at different decay times in dark and bright (300 lux) indoor environments. (f) The depth of the shallowest occupied trap for each curve of the $CaSO_4$:3%Pb^{2+} phosphor was estimated according to the slope of fitting red straight line.

The initial rise method assumes that the initial low-temperature side of the TL peak adheres to the Arrhenius equation:

$$I = C\exp(-\Delta E/kT)$$

where I denotes the TL intensity, C is a fitting constant incorporating a frequency factor, ΔE represents the trap depth, k is the Boltzmann constant, and T is the temperature. Based on this equation, the initial rise part of the glow curve is represented by a straight line with a slope of $-\Delta E/k$ if $\ln(I)$ is plotted as a function of $1/T$. The fittings of the selected glow curves are depicted by the red solid lines.

Table S1 Rietveld refinement parameters of the $CaSO_4$:0.2%Pr^{3+} and $CaSO_4$:3%Pb^{2+} phosphors.

Sample	$CaSO_4$:0.2%Pr^{3+}	$CaSO_4$:3%Pb^{2+}
Space group	Bmmb (63)	Bmmb (63)
a (Å)	6.99049(6)	6.99071(5)
b (Å)	6.99866(8)	7.00146(11)
c (Å)	6.24056(7)	6.23985(7)
α=β=γ (°)	90	90
Volume (Å^3)	305.313(6)	305.411(6)
R_{wp}	9.75%	10.90%
R_p	6.72%	7.63%
χ^2	2.65	4.645

Table S2 Far-UVC persistent luminescence power intensities of the $CaSO_4$:0.2%Pr^{3+} and $CaSO_4$:3%Pb^{2+} phosphors measured by the power meter.

Decay time (s)	$CaSO_4$:0.2%Pr^{3+} Irradiance ($mW \cdot m^{-2}$)	$CaSO_4$:3%Pb^{2+} Irradiance ($mW \cdot m^{-2}$)
30	12.43	23.60
60	10.21	16.94
90	8.81	13.72
120	7.80	11.90
150	6.99	10.68
300	4.73	7.04
600	2.77	4.61
900	1.89	3.62

Table S3 Persistent luminescence irradiance comparison with the other reported UVC persistent phosphors.

Material	Emission wavelength (nm)	Irradiance (mW m^{-2})	Ref. (in text)
$Ca_2Al_2SiO_7:Pr^{3+}$	268	4.8 (10 s)	9
$Sr_2P_2O_7:Pr^{3+}$	222	35.42 (30 s)	29
$Cs_2NaYF_6:Pr^{3+}$	270	14.9 (30 s)	32
$Lu_2SiO_5:Pr^{3+}$	270	6.98 (15 s)	34
$LiLuSiO_4:Pr^{3+}$	280	12.47 (10 s)	35
$CaSO_4:Pr^{3+}$	220	12.43 (30 s)	This work
$CaSO_4:Pb^{2+}$	230	23.60 (30 s)	This work