Supporting information

Site-selective and cooperative doping of $Gd_3Al_5O_{12}$:Ce garnet for structure stabilization and warm w-LED lighting of low CCT and high CRI

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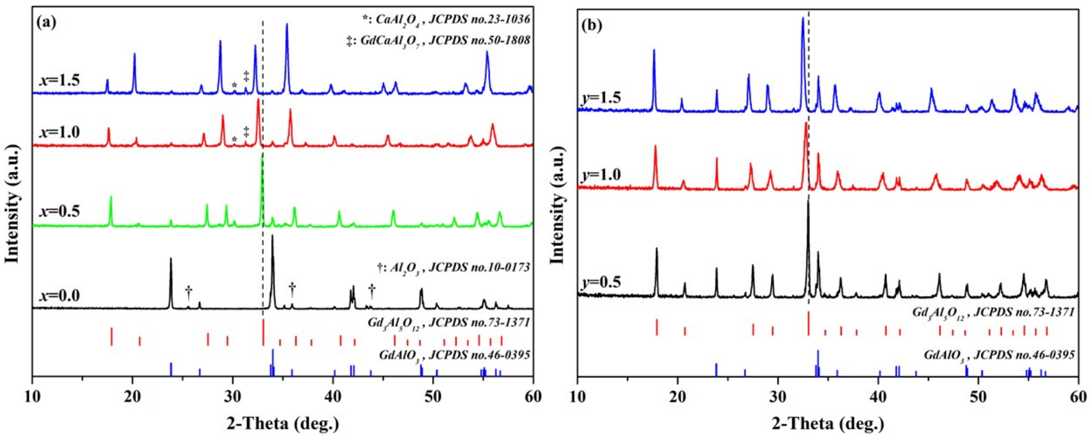

Fig. S1 XRD patterns of the $Gd_{3-x}Ca_xHf_xAl_{5-x}O_{12}$ (x = 0−1.5; part a) and $Gd_3Sc_yAl_{5-y}O_{12}$ (y = 0.5−1.5; part b) powders obtained by calcining in air at 1550 °C for 6 h. The red and blue vertical bars donate the standard diffraction of $Gd_3Al_5O_{12}$ (JCPDS No. 73-1371) and $GdAlO_3$ (JCPDS No. 46-0395), respectively. The symbols †, ‡ and * in (a) denote ɑ-Al_2O_3, $GdCaAl_3O_7$ and $CaAl_2O_4$, respectively.

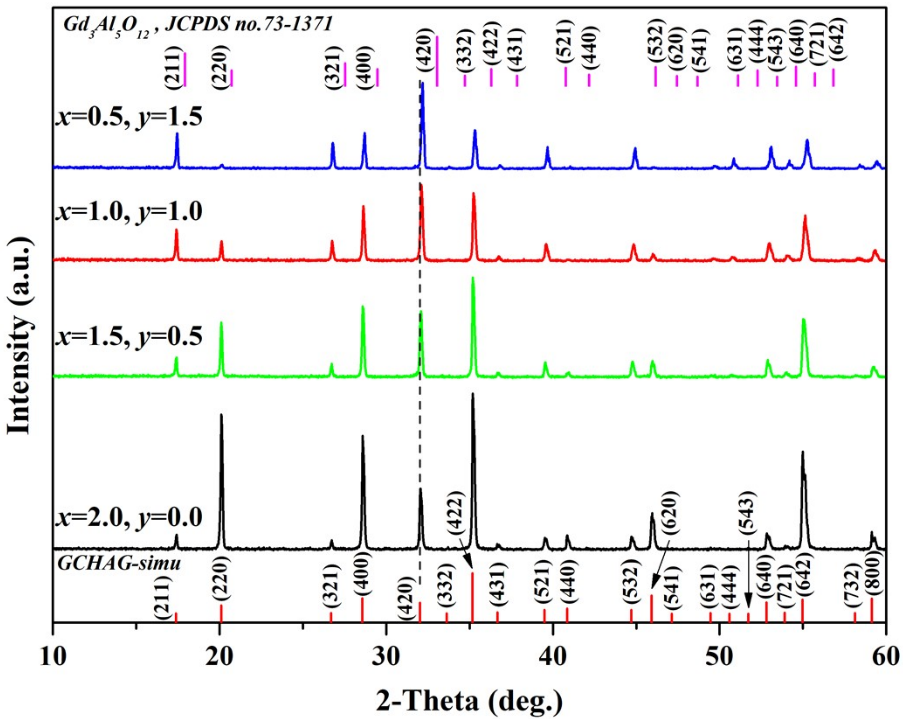

Fig. S2 XRD patterns of the $Gd_{3-x}Ca_xHf_xSc_yAl_3O_{12}$ powders (x = 0.5−2.0, y = 0.0−1.5, $x + y$ = 2.0). The red and pink vertical bars donate the simulated diffractions of $GdCa_2Hf_2Al_3O_{12}$ (x = 2.0, y = 0) and the standard diffractions of $Gd_3Al_5O_{12}$ (JCPDS No. 73-1371), respectively.

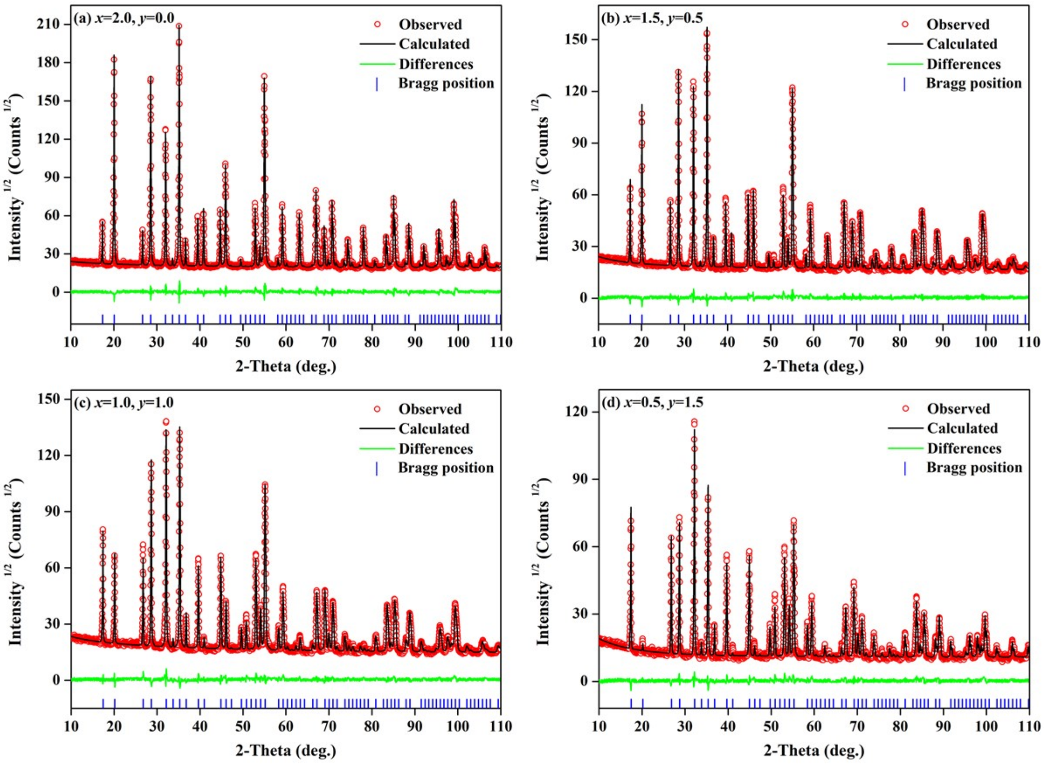

Fig. S3 The results of Rietveld refinement of XRD pattern for the $Gd_{3-x}Ca_xHf_xSc_yAl_3O_{12}$ powders (x = 0.5−2.0, y = 0.0−1.5, $x + y$ = 2.0).

Table S1 Crystallographic data, atomic coordinates (x, y, z), atomic occupancy (Occ.) and isotropic displacement parameter (Å^2) for the $Gd_{3-x}Ca_xHf_xSc_yAl_3O_{12}$ garnets (x = 0.5−2.0, y = 0.0−1.5, $x + y$ = 2.0).

x=2.0, y=0.0	Atom	Position	x	y	z	Occ.	B_{iso}
$GdCa_2Hf_2Al_3O_{12}$	Gd	24c	1/8	0	1/4	0.333	0.21(4)
$a = b = c$ = 12.4885(2) Å	Ca	24c	1/8	0	1/4	0.667	0.21(4)
R_{wp} = 9.08%	Hf	16a	0	0	0	1	0.25(2)
R_p = 6.72%	Al	24d	3/8	0	1/4	1	0.25(1)
χ^2 = 2.70	O	96h	0.9636(3)	0.0511(3)	0.1598(3)	1	0.20(1)
x=1.5, y=0.5							
$Gd_{1.5}Ca_{1.5}Hf_{1.5}Sc_{0.5}Al_3O_{12}$	Gd	24c	1/8	0	1/4	0.5	0.22(3)
$a = b = c$ = 12.4695(3) Å	Ca	24c	1/8	0	1/4	0.5	0.22(3)
R_{wp} = 8.16%	Hf	16a	0	0	0	0.75	0.08(2)
R_p = 6.26%	Sc	16a	0	0	0	0.25	0.08(2)
χ^2 = 2.05	Al	24d	3/8	0	1/4	1	0.21(8)
	O	96h	0.9631(2)	0.0522(3)	0.1603(2)	1	0.40(1)

x=1.0, y=1.0							
$Gd_2CaHfScAl_3O_{12}$	Gd	24c	1/8	0	1/4	0.667	0.18(3)
$a = b = c$ = 12.4509(2) Å	Ca	24c	1/8	0	1/4	0.333	0.18(3)
R_{wp} = 8.88%	Hf	16a	0	0	0	0.5	0.27(3)
R_p = 6.70%	Sc	16a	0	0	0	0.5	0.27(3)
χ^2 = 2.12	Al	24d	3/8	0	1/4	1	0.08(7)
	O	96h	0.9627(2)	0.0536(3)	0.1605(3)	1	0.04(1)
x=0.5, y=1.5							
$Gd_{2.5}Ca_{0.5}Hf_{0.5}Sc_{1.5}Al_3O_{12}$	Gd	24c	1/8	0	1/4	0.833	0.22(3)
$a = b = c$ = 12.4217(1) Å	Ca	24c	1/8	0	1/4	0.167	0.22(3)
R_{wp} = 11.32%	Hf	16a	0	0	0	0.25	0.46(5)
R_p = 8.70%	Sc	16a	0	0	0	0.75	0.46(5)
χ^2 = 1.92	Al	24d	3/8	0	1/4	1	0.29(9)
	O	96h	0.9621(3)	0.0548(4)	0.1610(4)	1	0.22(1)

χ^2 was defined as R_{wp}/R_{exp} in the Users' Manual of TOPAS V4.2 software. R_p, R_{wp} and R_{exp} are pattern reliability factor, weighted profile reliability factor and expected reliability factor, respectively.

Table S2 The bond distances of d_4, d_6, d_{82}, d_{84}, d_{av}, d_{88} and d_{81} for the $Gd_{3-x}Ca_xHf_xSc_yAl_3O_{12}$ garnets (x = 0.5−2.0, y = 0.0−1.5, $x + y$ = 2.0).

	d_4	d_6	d_{82}	d_{84}	d_{av}	d_{88}	d_{81}
x=2.0, y=0.0	1.7035(4)	2.1434(4)	2.3952(4)	2.5627(4)	2.4790	2.8999	2.9998
x=1.5, y=0.5	1.6973(3)	2.1520(3)	2.3986(3)	2.5473(4)	2.4730	2.8782	2.9697
x=1.0, y=1.0	1.6968(3)	2.1575(3)	2.4015(3)	2.5285(4)	2.4650	2.8537	2.9391
x=0.5, y=1.5	1.6903(5)	2.1646(5)	2.4038(4)	2.5097(5)	2.4568	2.8356	2.9114

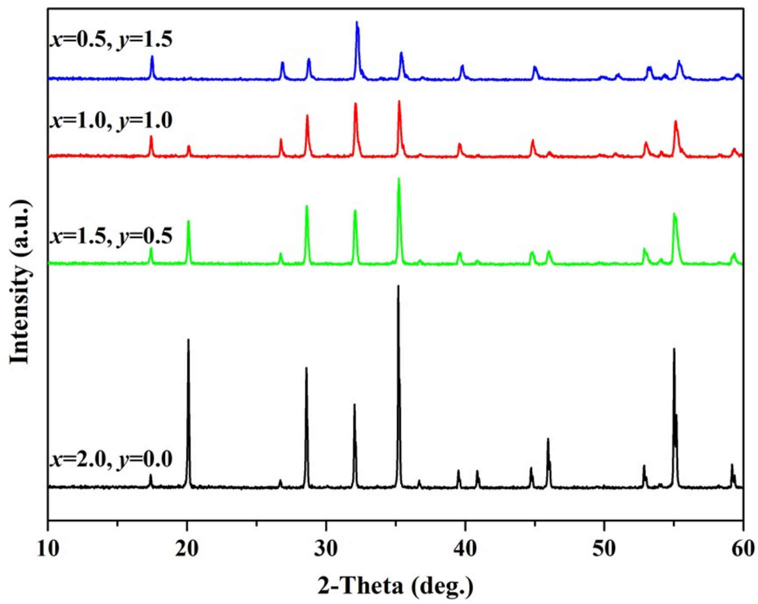

Fig. S4 XRD patterns of the $Gd_{2.97-x}Ca_xHf_xSc_yAl_3O_{12}$:0.03Ce phosphors ($x$ = 0.5−2.0, y = 0.0−1.5, $x + y$ = 2.0).

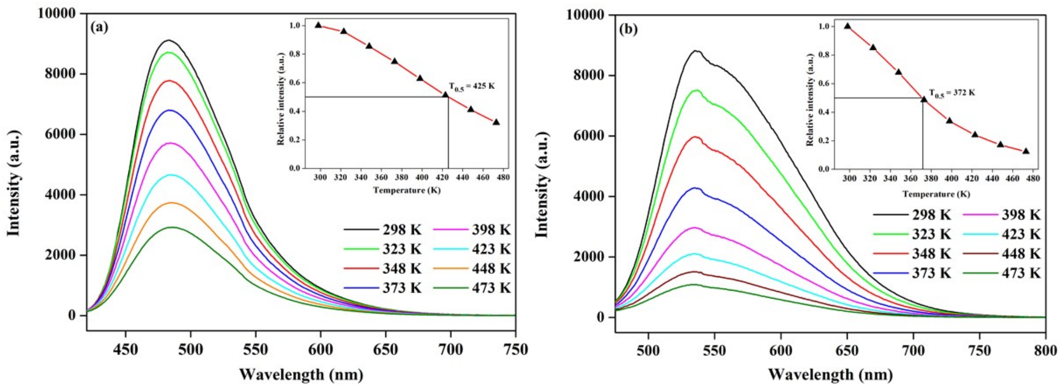

Fig. S5 Temperature-dependent photoluminescence spectra for $Gd_{0.97}Ca_2Hf_2Al_3O_{12}$:0.03Ce (a, λ_{ex} = 408 nm) and $Gd_{2.47}Ca_{0.5}Hf_{0.5}Sc_{1.5}Al_3O_{12}$:0.03Ce (b, λ_{ex} = 452 nm). The inset in (a) and (b) present the relative intensity of emission as a function of the measurement temperature.