Supporting Information

Cr,Yb-Codoped $Ca_2LaHf_2Al_3O_{12}$ Garnet Phosphor: Electronic Structure, Broadband NIR Emission and Energy Transfer Properties

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Table S1. Quantities of materials used for $Ca_2LaHf_2Al_3O_{12}$:xCr^{3+} (x = 0.003-0.05)

x (mmol)	$CaCO_3$ (g)	La_2O_3 (g)	HfO_2 (g)	Al_2O_3 (g)	CrO_2 (g)
0.003	0.2	0.1629	0.4197	0.1529	0.0002
0.004	0.2	0.1629	0.4192	0.1529	0.0003
0.005	0.2	0.1629	0.4188	0.1529	0.0004
0.01	0.2	0.1629	0.4168	0.1529	0.0008
0.015	0.2	0.1629	0.4147	0.1529	0.0011
0.02	0.2	0.1629	0.4127	0.1529	0.0015
0.03	0.2	0.1629	0.4084	0.1529	0.0022
0.04	0.2	0.1629	0.4041	0.1529	0.003
0.05	0.2	0.1629	0.3999	0.1529	0.0037

samples.

Table S2. Quantities of materials used for $Ca_2LaHf_2Al_3O_{12}$:0.01Cr^{3+},$y$$Yb^{3+}$ (y = 0.003-0.05) samples.

x (mmol)	$CaCO_3$ (g)	La_2O_3 (g)	HfO_2 (g)	Al_2O_3 (g)	CrO_2 (g)	Yb_2O_3 (g)
0.003	0.1996	0.1629	0.4168	0.1529	0.0022	0.0006
0.004	0.1994	0.1629	0.4168	0.1529	0.0022	0.0008
0.005	0.1992	0.1629	0.4168	0.1529	0.0022	0.001
0.01	0.1982	0.1629	0.4168	0.1529	0.0022	0.002
0.015	0.1972	0.1629	0.4168	0.1529	0.0022	0.003
0.02	0.1962	0.1629	0.4168	0.1529	0.0022	0.004
0.03	0.1942	0.1629	0.4168	0.1529	0.0022	0.006
0.04	0.1922	0.1629	0.4168	0.1529	0.0022	0.008
0.05	0.1902	0.1629	0.4168	0.1529	0.0022	0.01

Table S3. Crystallographic data for $Ca_2LaHf_2Al_3O_{12}$ and $Ca_2GdZr_2Al_3O_{12}$.

Formula	$Ca_2LaHf_2Al_3O_{12}$	$Ca_2GdZr_2Al_3O_{12}$
symmetry	Cubic	Cubic
space group	Ia-3d	Ia-3d
a/Å	12.604	12.5057
V/Å^3	2002.8	1955.79
Z	8	8
R_{wp} (%)	4.3	
R_p (%)	5.6	

Table S4. Variation of the average Hf-O bond lengths.

Cr^{3+} concentration (mmol)	Hf-O Bond Distances (Å)
0.003	1.939
0.004	1.942
0.005	1.946
0.01	1.952
0.015	1.961
0.02	1.970
0.03	1.976
0.04	1.983
0.05	1.990

Table S5. Energy transfer efficiencies and IQE as a function of the concentration.

x	η(T)(%)	IQE (xCr^{3+})(%)	IQE (0.01Cr^{3+},yYb^{4+})(%)
0.003	2	17	6
0.004	6	18	9
0.005	9	20	11
0.01	16	33	11
0.015	33	23	13
0.02	36	24	14
0.03	40	22	14
0.04	46	23	17
0.05	39	21	16

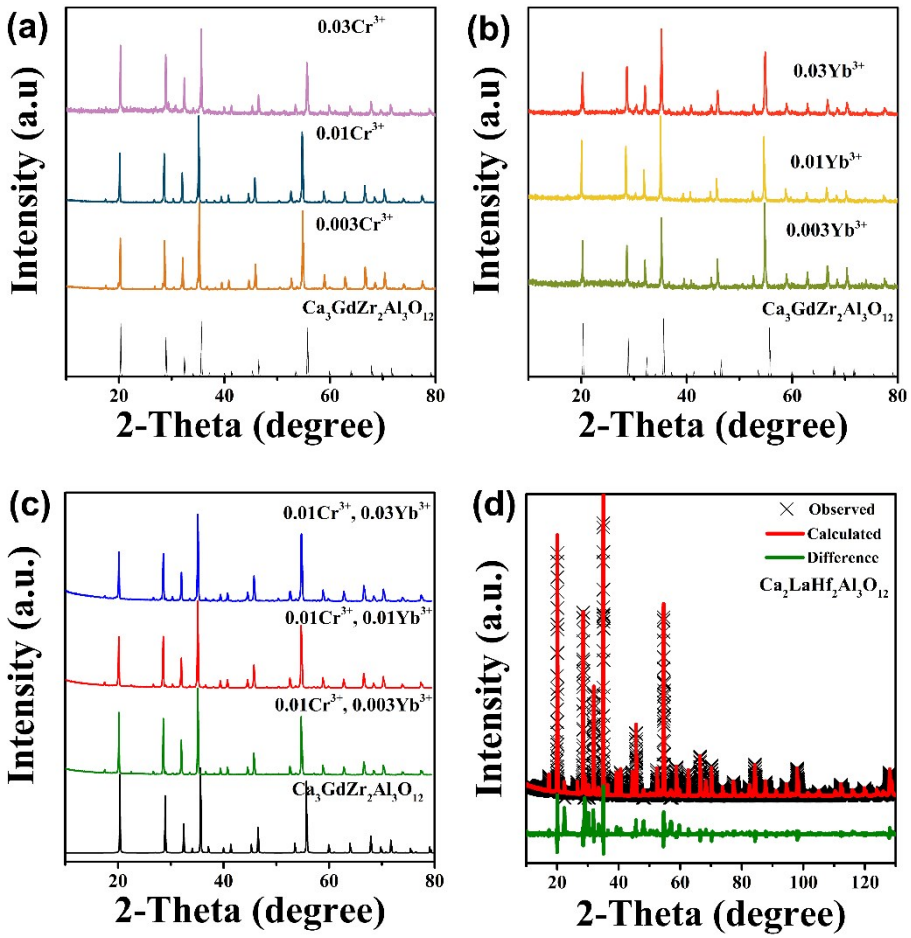

Figure S1. (a-c) XRD patterns of $Ca_2LaHf_2Al_3O_{12}$:$x$$Cr^{3+}$, $Ca_2LaHf_2Al_3O_{12}$:$y$$Yb^{3+}$ and $Ca_2LaHf_2Al_3O_{12}$:0.01Cr^{3+},$y$$Yb^{3+}$. (d) XRD Rietveld refinements of the host.

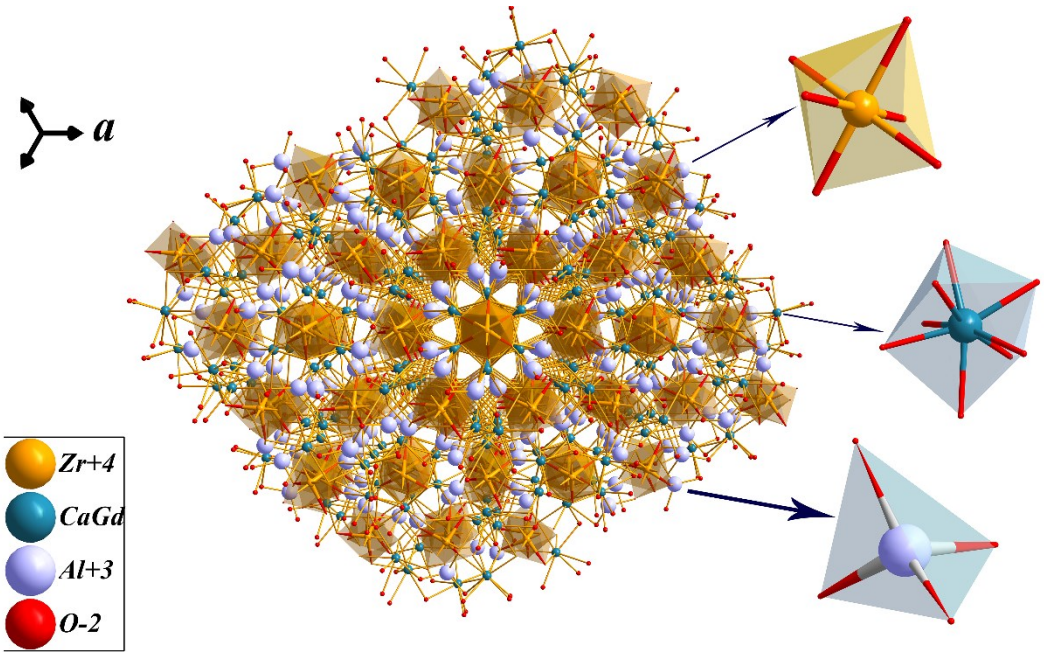

Figure S2. Structure diagram of $Ca_2GdZr_2Al_3O_{12}$ compound, and coordination environment of (Al/Zr/Gd/Ca) atoms.

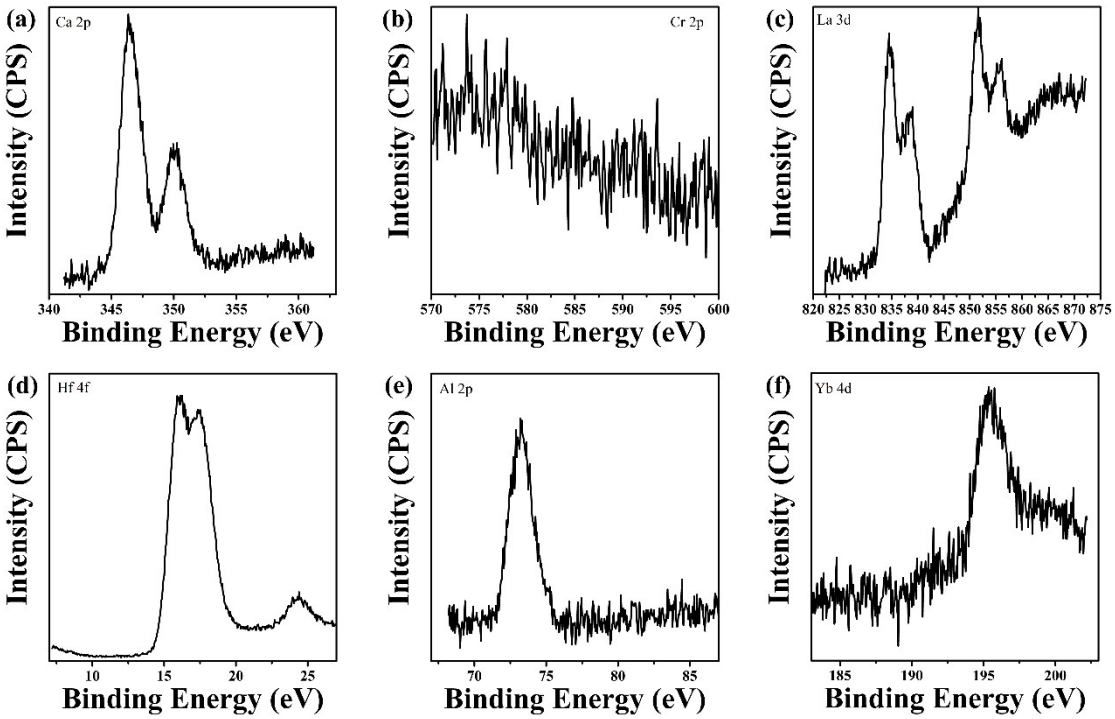

Figure S3. (a-f) Ca 2p, Cr 2p, La 3d, Hf 4f, Al 2p and Yb 4d XPS of $Ca_2LaHf_2Al_3O_{12}$:0.01Cr^{3+},0.01Yb^{3+} sample.

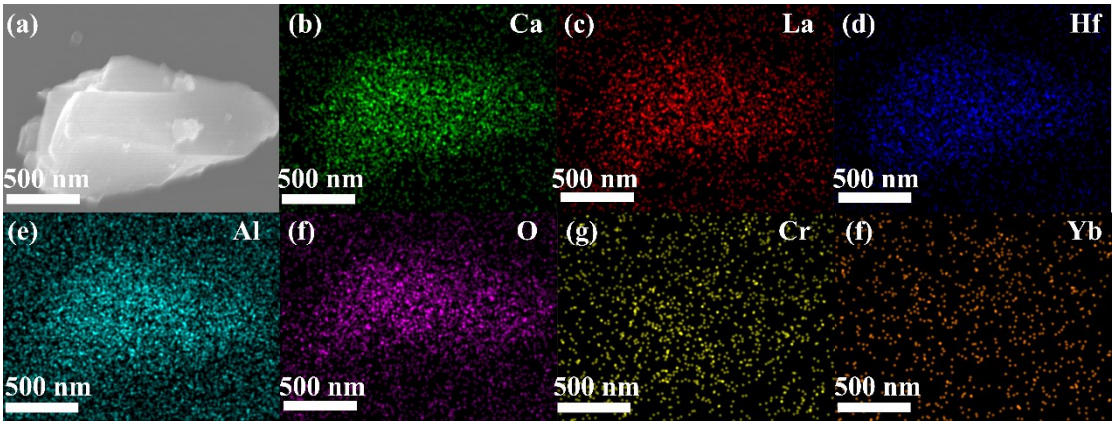

Figure S4. SEM image and mapping images of a $Ca_2LaHf_2Al_3O_{12}$:0.01Cr^{3+},0.01Yb^{3+} sample, and Ca, La, Hf, Al, O, Cr and Yb elemental mapping images of $Ca_2LaHf_2Al_3O_{12}$:0.01Cr^{3+},0.01Yb^{3+} sample.

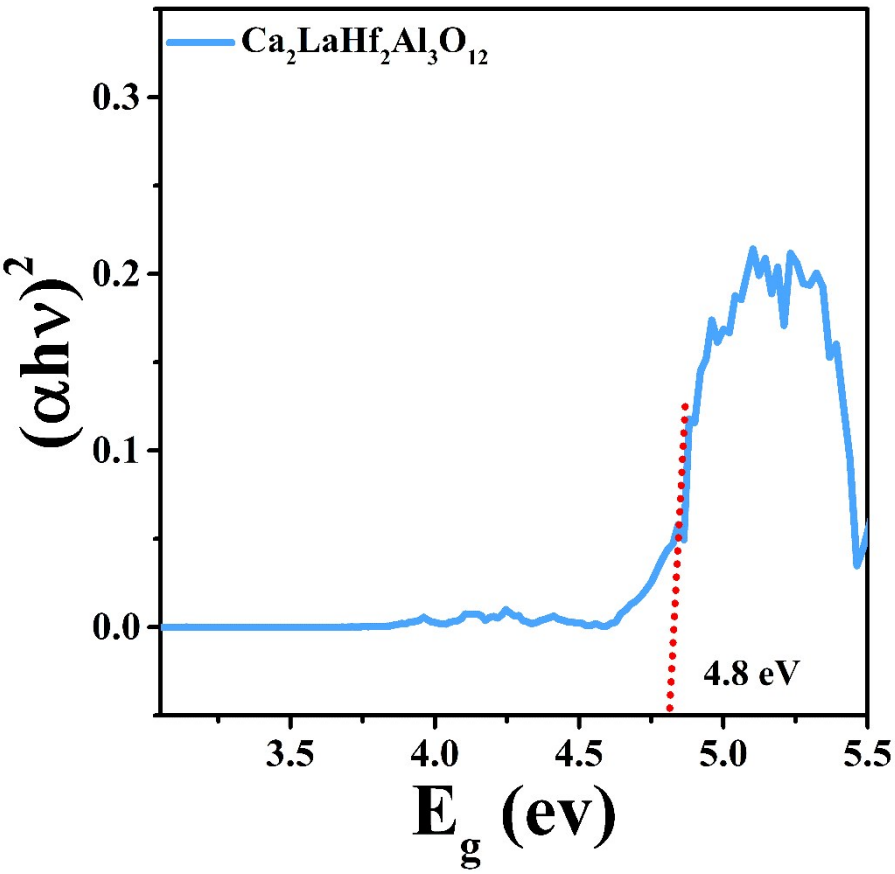

Figure S5. Relationship of $(\alpha hv)^2$ versus photon energy hv in the $Ca_2LaHf_2Al_3O_{12}$ sample.

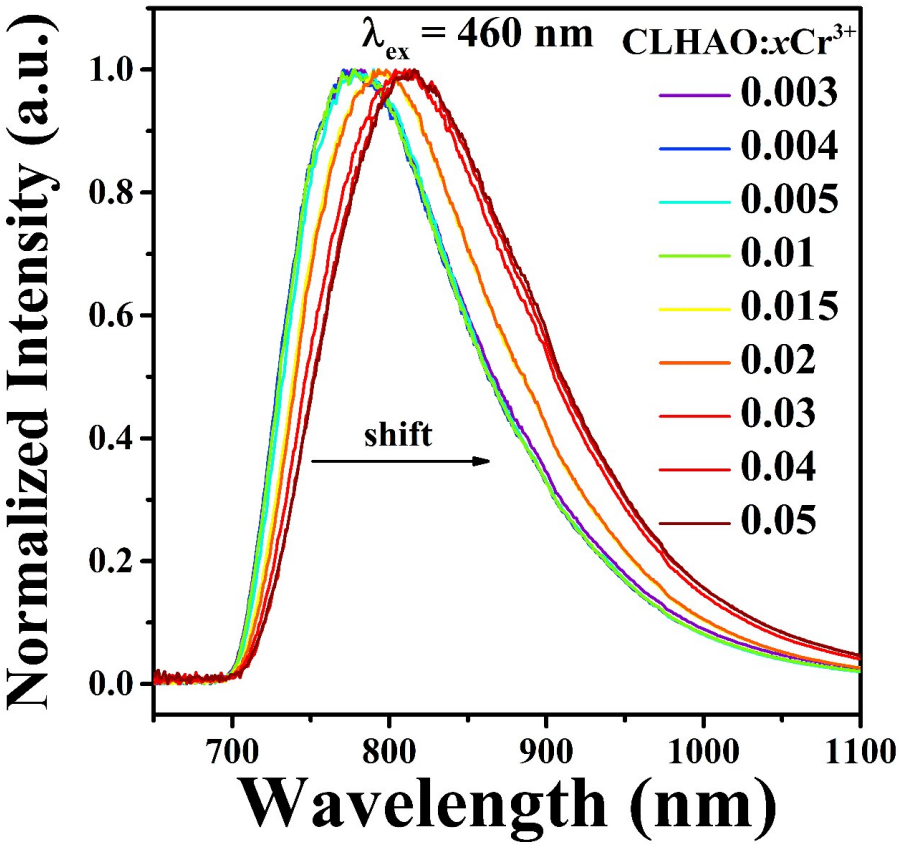

Figure S6. PL spectra of $Ca_2LaHf_2Al_3O_{12}$:$x$$Cr^{3+}$ (λ_{ex} = 460 nm).

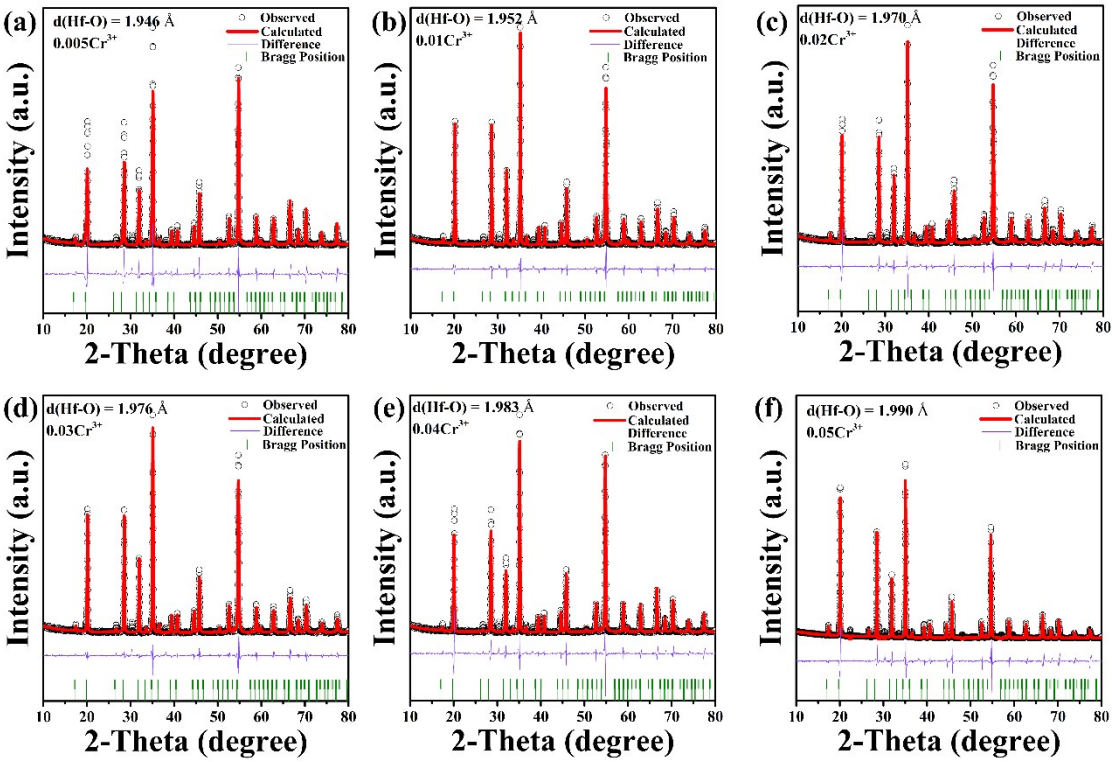

Figure S7. The Rietveld refinement fit of the XRD patterns of (a-f) $Ca_2LaHf_2Al_3O_{12}$:$x$$Cr^{3+}$ by using the GSAS program.

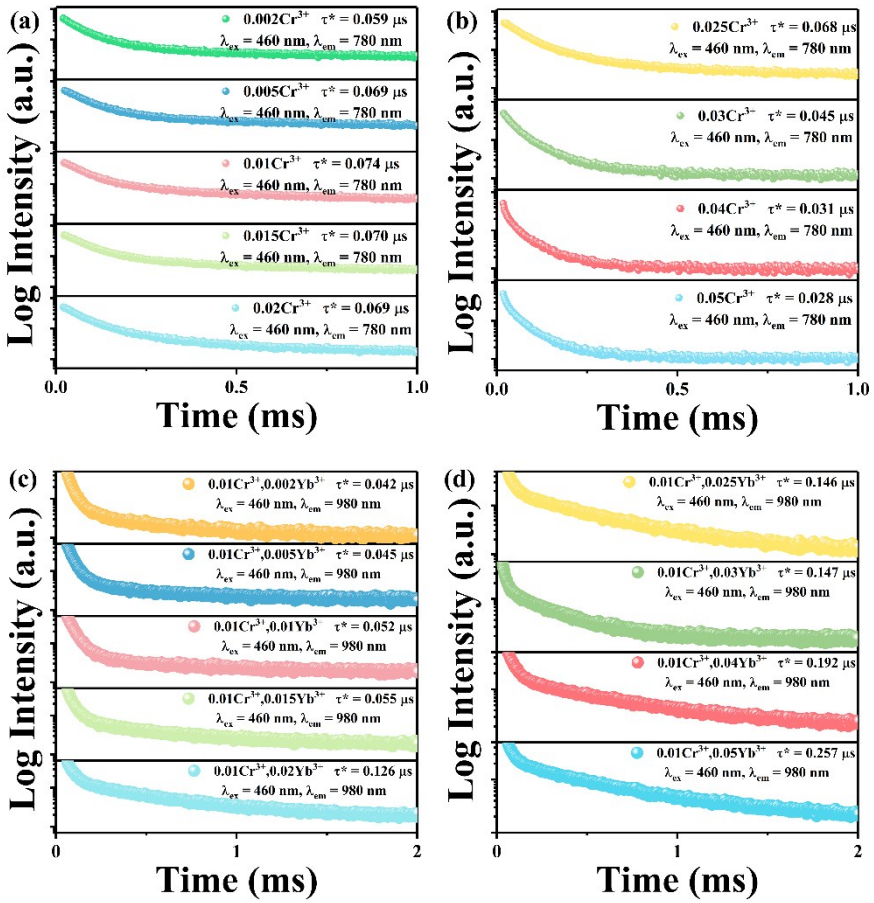

Figure S8. (a-b) Decay time of Cr^{3+} in $Ca_2LaHf_2Al_3O_{12}$:$x$$Cr^{3+}$ phosphors under excitation at 460 nm and monitored at 780 nm. (c-d) Decay time of Yb^{3+} in $Ca_2LaHf_2Al_3O_{12}$:0.01Cr^{3+},$y$$Yb^{3+}$ phosphors under excitation at 460 nm and monitored at 980 nm.

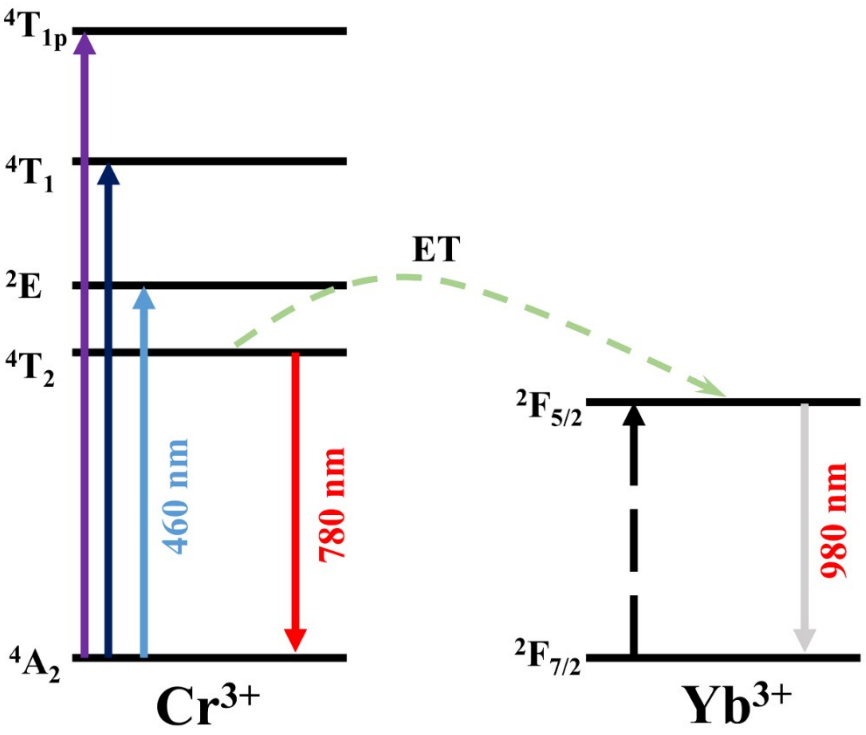

Figure S9. Schematic energy level diagrams of Cr^{3+} and Yb^{3+} involved ET process.

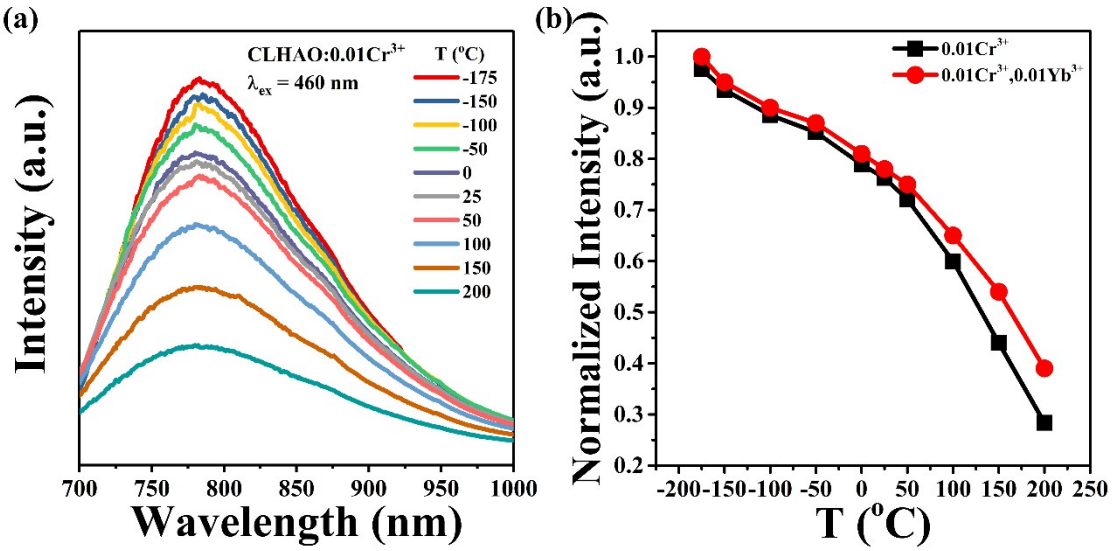

Figure S10. (a) Temperature-dependent PL spectra (-175~200 °C) and (b) Temperature dependence of the normalized intensity of $Ca_2LaHf_2Al_3O_{12}$:0.01Cr^{3+} and $Ca_2LaHf_2Al_3O_{12}$:0.01Cr^{3+},0.01Yb^{3+}.

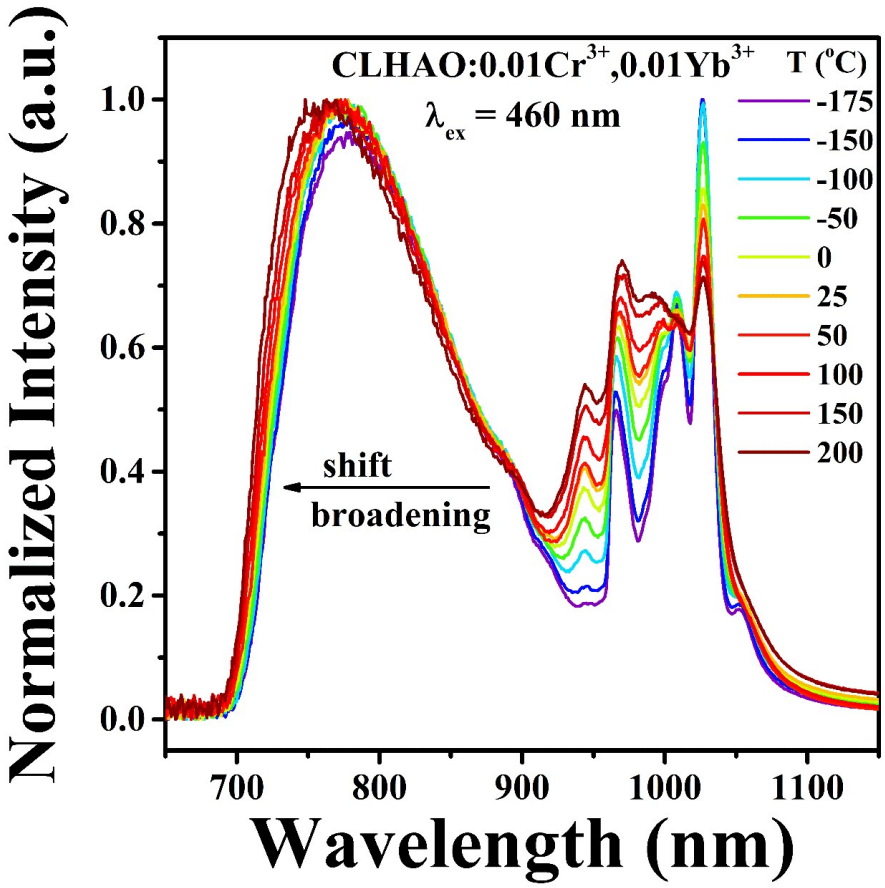

Figure S11. Temperature-dependent PL spectra (-175~200 °C) and normalized results of $Ca_2LaHf_2Al_3O_{12}$:0.01Cr^{3+},0.01Yb^{3+}.

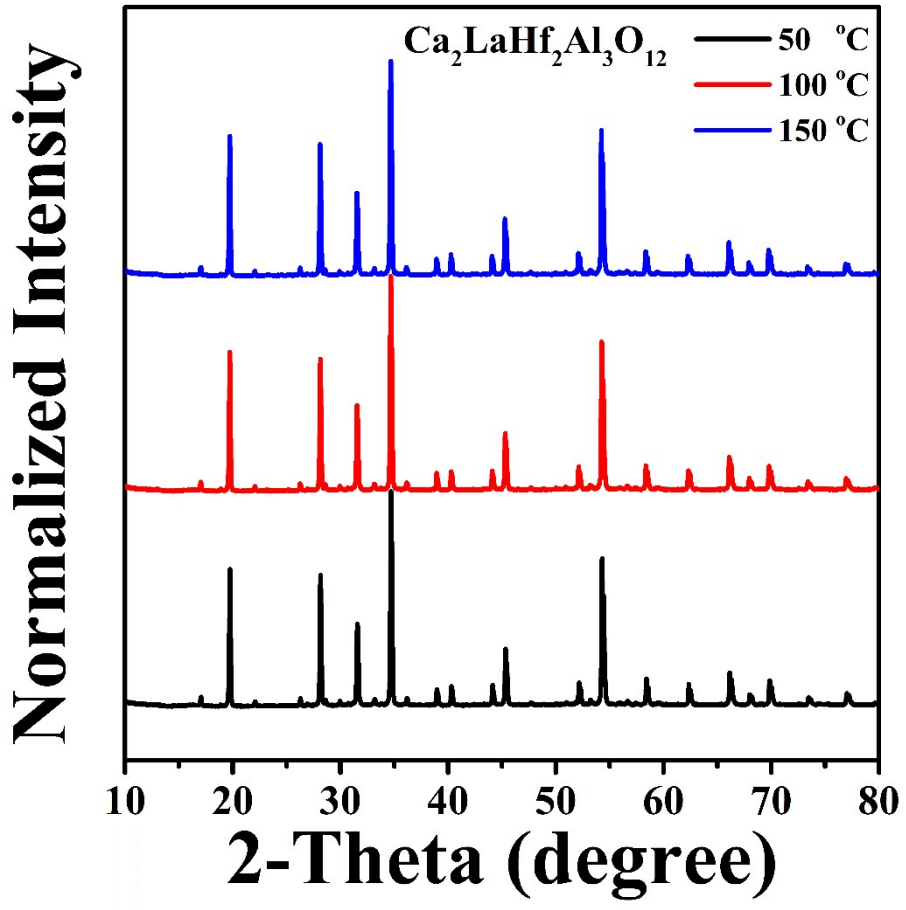

Figure S12. The dependent-temperature XRD patterns of $Ca_2LaHf_2Al_3O_{12}$ sample.

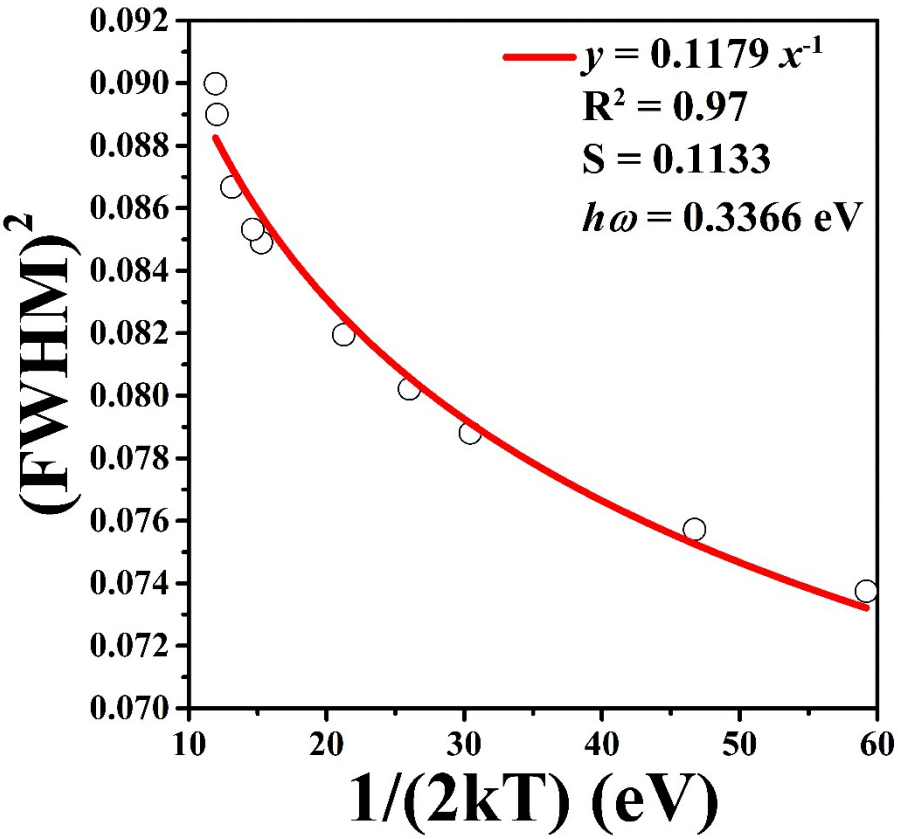

Figure S13. Fitting results of square of full width at half maximum ($FWHM^2$) as a function of 1/2kT.

The diffraction points in the red circle in SAED image correspond to the main diffraction lattice planes (0 2 4) and (2 3 3) of the $Ca_2LaHf_2Al_3O_{12}$ lattice, respectively, by selecting the largest diffraction point as the diffraction center. The planes (0 2 4) and (2 3 3) in a hexagonal system can be calculated by theoretical function.[1] The distance between adjacent crystal fringes is measured in crystal planes (0 2 4) and (2 3 3), and the d-spacing values are 0.2759 and 0.263 nm, respectively. The angle between the two crystal planes can be calculated by the following correlation function:

$$cos\varphi = \frac{\frac{h_1h_2}{a^2} + \frac{k_1k_2}{b^2} + \frac{l_1l_2}{c^2}}{\sqrt{\left(\frac{h_1^2}{a^2} + \frac{k_1^2}{b^2} + \frac{l_1^2}{c^2}\right)\left(\frac{h_2^2}{a^2} + \frac{k_2^2}{b^2} + \frac{l_2^2}{c^2}\right)}} \quad (1)$$

$a = b = c = 12.34$ represent the crystal lattice parameters of $Ca_2LaHf_2Al_3O_{12}$. h, k and l are indices of crystal planes (0 2 4) and (2 3 3), respectively. The crystal planes angle is 31° between (0 2 4) and (2 3 3) planes.

Its value is estimated through fitting the temperature-dependent full width at FWHM of emission peaks:[2, 3]

$$FWHM = 2.36\sqrt{S}\psi\omega\sqrt{coth\left(\frac{\psi\omega}{2kT}\right)} \quad (2)$$

In which k is the Boltzmann constant, ω is the phonon frequency, and

$$coth(x) = \frac{e^x + e^{-x}}{e^x - e^{-x}}$$

It can be converted to

$$FWHM^2 = 5.57 \times S \times (\psi\omega)^2\left(1 + \frac{1}{e^{\frac{\psi\omega}{kT}} - 1}\right) \quad (3)$$

According to $\frac{\psi\omega}{kT} \approx 10^{-3}$

Formula (3) is transformed into

$$FWHM^2 = 5.57 \times S \times (\psi\omega)^2\left(1 + \frac{1}{\frac{\psi\omega}{2kT}}\right) \quad (4)$$

Approximately equal to $$FWHM^2 = a + \frac{b}{\frac{1}{2kT}} \quad (5)$$

Where $a = 5.57 \times S \times (\psi\omega)^2$ and $b = 5.57 \times S \times (\psi\omega)$.

References

1 E. Hitzer, *Math. Meth. Appl. Sci.,* 2011, **34**, 1421-1429.

2 K. M. Mccall, C. C. Stoumpos, S. S. Kostina, M. G. Kanatzidis, B. W. Wessels, *Chem. Mater.,* 2017, **29**, 4129-4145.

3 J. J. Luo, X. M. Wang, S. R. Li, J. Liu, Y. M. Guo, G. D. Niu, L. Yao, Y. H. Fu, L. Gao, Q. S. Dong, C. Y. Zhao, M. Y. Leng, F. S. Ma, W. X. Liang, L. D. Wang, S. Y. Jin, J. B. Han, L. J. Zhang, J. Etheridge, J. B. Wang, Y. F. Yan, E. H. Sargent, J. Tang, *Nature*, 2018, **563**, 541-545.