Supporting Information

Highly efficient and thermally stable single-activator white-emitting phosphor $K_2Ca(PO_4)F:Eu^{2+}$ for white light-emitting diodes

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Computational Methodology

The DFT calculations were performed using a generalized gradient approximation (GGA) functional in the Perdew-Burke-Ernzerhof (PBE) scheme, as implemented in the Vienna Ab-initio Simulation Package (VASP). A 2 × 2 × 2 supercell of K_2CaPO_4F (KCPOF), containing 288 atoms, was employed for the calculation of Eu^{2+}-substitution defect on one site of Ca^{2+}/K^+ cation. All the two kinds of Ca^{2+} sites and four K^+ sites were taken into consideration. Moreover, for the supercells with Eu^{2+} at a K^+ site, the nearest-neighbor (NN) Eu_{K1}-(V_{K4} or K_{Ca}), Eu_{K2}-(V_{K3} or K_{Ca}), Eu_{K3}-(V_{K2} or K_{Ca}), and Eu_{K4}-(V_{K1} or K_{Ca}), were modeled for defect charge balance.[1] The K($3s^23p^64s^1$), Ca($3s^23p^64s^2$), P($3s^23p^3$), O($2s^22p^4$), F($2s^22p^5$) and Eu($5s^25p^64f^76s^2$) were treated as valence electrons, and their interactions with the respective cores were described by the projected augmented wave (PAW) method. The geometries of the structures were fully optimized until the total energies and the Hellmann-Feynman forces on the atoms were converged to 10^{-4} eV and 0.05 eV·Å^{-1}, respectively. 2 × 2 × 1 *k*-point grid was used to sample the Brillouin zone. The cutoff energy for the plane wave basis was set to 400 eV, and the PREC-flag was set to accurate.

The defect formation energy (ΔE_f) in the charge state q was calculated by[2-4]

$$\Delta E_f[D^q] = E_{tot}[D^q] - E_{tot}[\text{perfect}] - \sum_A \Delta n_A \mu_A + qE_F + E_{corr} \qquad \text{(S1)}$$

where $E_{tot}[D^q]$ is the total energy derived from a supercell calculation containing the defect D, and E_{tot}[perfect] is the total energy for the perfect crystal using an equivalent supercell. The integer n_A indicates the number of atoms of type A (host atoms Ca/K or impurity atoms) that have been added to ($n_A > 0$) or removed from ($n_A < 0$) the supercell to form the defect, and the μ_A are the corresponding chemical potentials of these species. Chemical potentials represent the energy of the reservoirs with which atoms are being exchanged. The analog of the chemical potential for "charge" is given by the chemical potential of the electrons, i.e., the Fermi energy E_F. Finally, E_{corr} is a correction term for the electrostatic interactions of charged defects between supercells. For a neutral defective system (q = 0), the last two items E_F and E_{corr} are usually omitted.

The values of μ_A can be determined by thermodynamic equilibrium conditions of various phases containing the corresponding atomic species depending on the surface-annealing conditions. According to the experimental conditions, the KCPOF:Eu^{2+} crystals were grown from the melt in an oxygen-deficient atmosphere, the atomic chemical potentials of the metallic elements are set at the upper bounds by the formation of metallic bulks with the corresponding species:

$$\mu_K = \mu_{K\,(bulk)}, \qquad \mu_{Ca} = \mu_{Ca\,(bulk)}, \qquad \mu_{Eu} = \mu_{Eu\,(bulk)} \tag{S2}$$

In the above equilibrium state, the total energies of the bulk materials, K(bcc), Ca(fcc), and Eu(hcp) were calculated to determine the μ_A values.

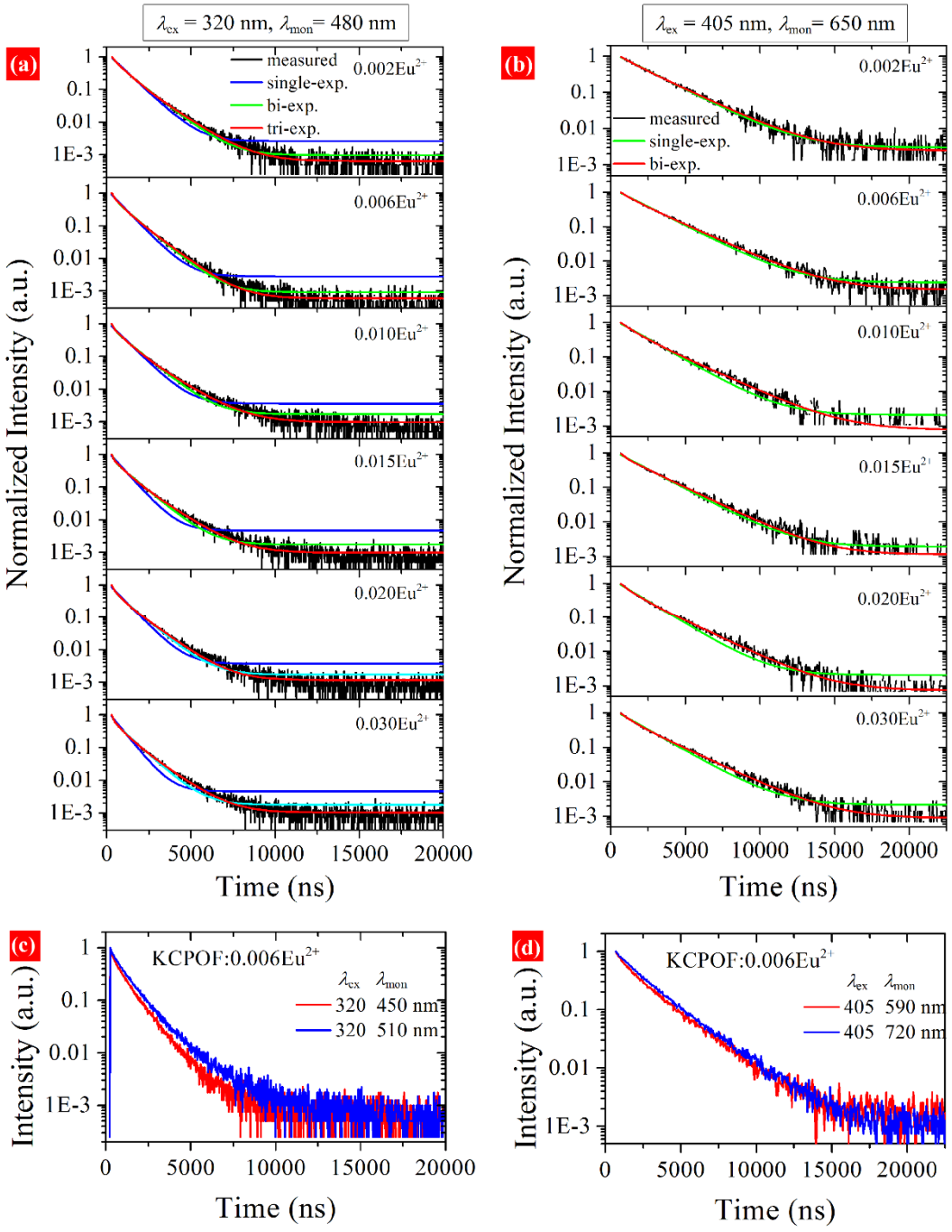

Figure S1. Fitting results of decay curves for KCPOF:xEu^{2+}. (a) Monitored at 480 nm, (b) monitored at 650 nm. Decay curves of KCPOF:0.006Eu^{2+} monitored at the sides of (e) cyan PL band and (f) red PL band.

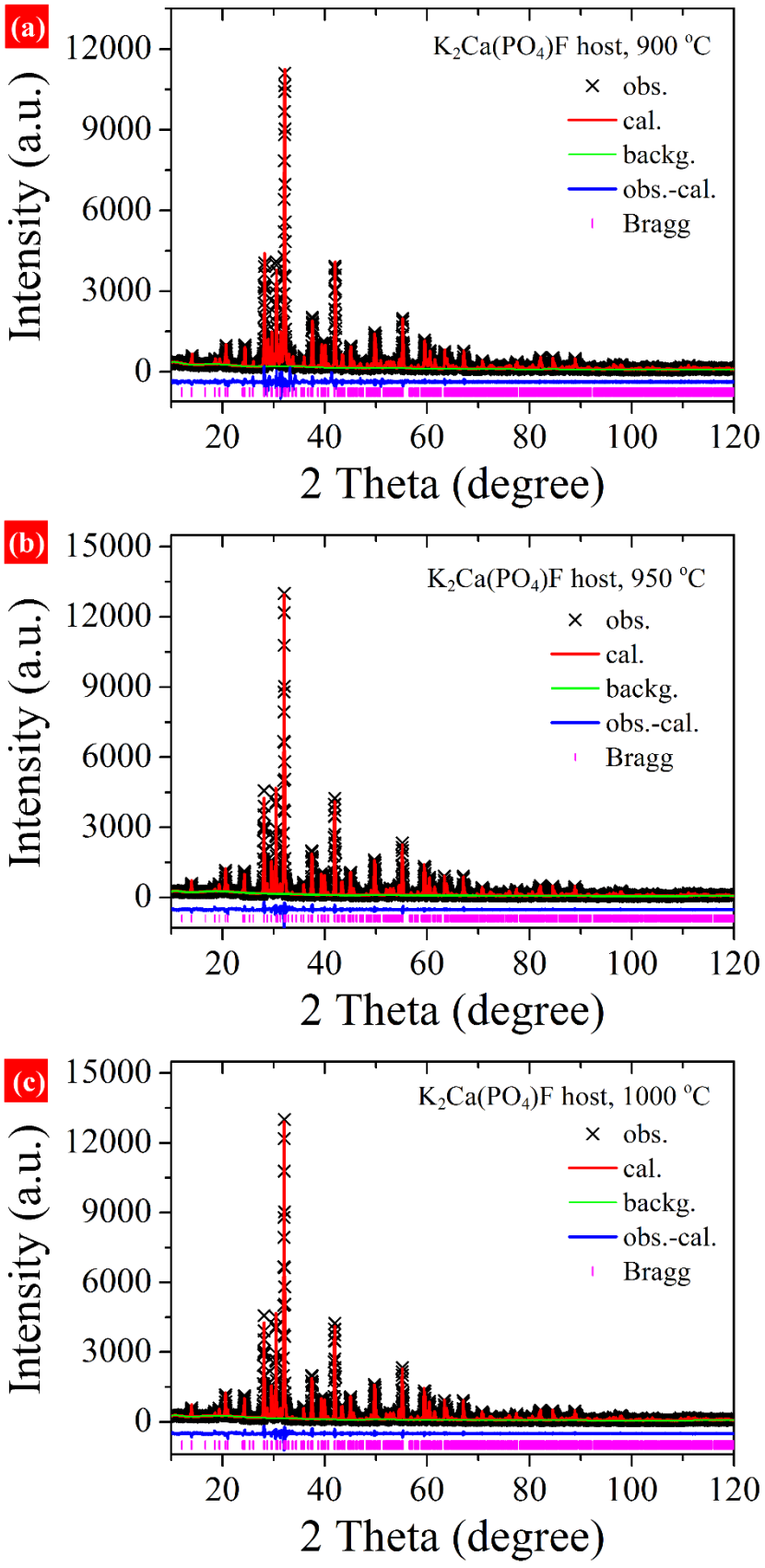

Figure S2. Refinement results of the hosts obtained at (a) 900, (b) 950, (c) 1000 °C.

Table S1. Crystallographic Data and Structure Refinement Parameters of the KCPOF hosts obtained at three temperatures

	900 °C	950 °C	1000 °C
unit cell	a = 7.3343(2) Å	a = 7.3332(1) Å	a = 7.3332(1) Å
	b = 5.8681(1) Å	b = 5.8667(0) Å	b = 5.8667(0) Å
	c = 12.6814(3) Å	c = 12.6779(1) Å	c = 12.6775(1) Å
	β = 90.22°	β = 90.22°	β = 90.22°
cell volume	V = 545.79(2) Å^3	V = 545.42(1) Å^3	V = 545.41(1) Å^3
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/m$	$P2_1/m$	$P2_1/m$
Z	4	4	4
R_{wp}	12.90%	8.73%	8.74%
R_p	7.88%	6.11%	6.09%
χ^2	4.433	1.636	1.637

Table S2. Atomic parameters of the KCPOF host obtained at 900 °C

Atom	**Wyckoff site**	**x/a**	**y/b**	**z/c**	**U [Å^2]**
Ca1	2e	0.79792	3/4	0.07811	0.0109
Ca2	2e	0.70617	3/4	0.56558	0.0109
K1	2e	0.78576	1/4	0.41942	0.0120
K2	2e	0.70766	1/4	0.93252	0.0129
K3	2e	0.51358	1/4	0.68828	0.0240
K4	2e	0.97746	3/4	0.81697	0.0108
P1	2e	0.98801	1/4	0.66151	0.0083
P2	2e	0.48553	3/4	0.84050	0.0208
F1	2a	0	1/2	0	0.0170
F2	2d	1/2	0	1/2	0.0006
O1	2e	0.65035	3/4	0.89511	0.0258
O2	2e	0.97799	3/4	0.21572	0.0188
O3	4f	0.88151	0.04448	0.62316	0.0062
O4	4f	0.37147	0.53109	0.85746	0.0104
O5	2e	0.53966	3/4	0.71576	0.0490
O6	2e	0.84506	3/4	0.40813	0.0146

Table S3. Atomic parameters of the KCPOF host obtained at 950 °C

Atom	Wyckoff site	x/a	y/b	z/c	U [Å²]
Ca1	2e	0.80186	3/4	0.07660	0.0098
Ca2	2e	0.70317	3/4	0.56457	0.0062
K1	2e	0.78638	1/4	0.42164	0.0150
K2	2e	0.70351	1/4	0.93107	0.0182
K3	2e	0.51029	1/4	0.68522	0.0148
K4	2e	0.97914	3/4	0.81474	0.0207
P1	2e	0.98931	1/4	0.66099	0.0153
P2	2e	0.48769	3/4	0.83847	0.0108
F1	2a	0	1/2	0	0.0120
F2	2d	1/2	0	1/2	0.0103
O1	2e	0.65512	3/4	0.90693	0.0213
O2	2e	0.99506	3/4	0.21968	0.0176
O3	4f	0.89105	0.03419	0.62516	0.0144
O4	4f	0.36560	0.53490	0.85897	0.0071
O5	2e	0.53812	3/4	0.71728	0.0146
O6	2e	0.82842	3/4	0.39720	0.0175

Table S4. Atomic parameters of the KCPOF host obtained at 1000 °C

Atom	Wyckoff site	x/a	y/b	z/c	U [Å²]
Ca1	2e	0.80262	3/4	0.07644	0.0106
Ca2	2e	0.70353	3/4	0.56483	0.0061
K1	2e	0.78702	1/4	0.42173	0.0136
K2	2e	0.70464	1/4	0.93121	0.0148
K3	2e	0.51004	1/4	0.68503	0.0119
K4	2e	0.97851	3/4	0.81496	0.0190
P1	2e	0.98889	1/4	0.66032	0.0145
P2	2e	0.48828	3/4	0.83815	0.0102
F1	2a	0	1/2	0	0.0115
F2	2d	1/2	0	1/2	0.0088
O1	2e	0.65256	3/4	0.90717	0.0207
O2	2e	0.99265	3/4	0.22066	0.0145
O3	4f	0.89146	0.03383	0.62501	0.0112
O4	4f	0.36507	0.53591	0.85911	0.0051
O5	2e	0.53685	3/4	0.71735	0.0123
O6	2e	0.82701	3/4	0.39642	0.0155

Table S5. The Ca-O/F and K-O/F distances based on the refinement of the KCPOF host obtained at 1000 °C

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Ca1-F1	2.27946(1)	Ca2-F2	2.24610(1)	K1-F2	2.75352(2)
Ca1-F1	2.27946(1)	Ca2-F2	2.24610(1)	K1-F2	2.75352(2)
Ca1-O1	2.40792(2)	Ca2-O3	2.29045(1)	K1-O3	2.97015(2)
Ca1-O2	2.29471(2)	Ca2-O3	2.29045(1)	K1-O3	2.97015(2)
Ca1-O4	2.23629(1)	Ca2-O5	2.29135(2)	K1-O3	2.94850(2)
Ca1-O4	2.23629(1)	Ca2-O6	2.32235(2)	K1-O3	2.94850(2)
				K1-O5	2.95256(3)
				K1-O6	2.96551(2)
				K1-O6	2.96551(2)
K2-F1	2.75474(2)	K3-F2	2.76722(2)	K4-F1	2.77061(2)
K2-F1	2.75474(2)	K3-F2	2.76722(2)	K4-F1	2.77061(2)
K2-O1	2.97364(2)	K3-O3	3.16652(3)	K4-O1	2.66482(3)
K2-O1	2.97364(2)	K3-O3	3.16652(3)	K4-O2	2.97556(2)
K2-O2	2.94408(3)	K3-O4	2.97182(2)	K4-O2	2.97556(2)
K2-O4	2.98586(2)	K3-O4	2.97182(2)	K4-O3	2.99453(2)
K2-O4	2.98586(2)	K3-O5	2.96826(2)	K4-O3	2.99453(2)
K2-O4	3.13568(2)	K3-O5	2.96826(2)	K4-O4	3.14874(3)
K2-O4	3.13568(2)	K3-O6	2.67507(3)	K4-O4	3.14874(3)

Table S6. Tri-exponential fitting results of decay curves for KCPOF:xEu^{2+} monitored at 480 nm.

x	τ_1/ns	A_1	τ_2/ns	A_2	τ_3/ns	A_3
0.002	**135.5**	0.704	677.6	0.827	1315.4	0.477
0.006	**121.7**	1.354	504.6	0.603	1140.9	0.651
0.010	**101.9**	2.671	665.5	0.480	1391.8	0.385
0.015	**81.3**	6.052	608.7	0.657	1303.3	0.450
0.020	**67.8**	8.835	464.7	0.680	1176.8	0.599
0.030	**75.1**	8.777	534.6	0.681	1201.7	0.463

Table S7. Bi-exponential fitting results of decay curves for KCPOF:xEu^{2+} monitored at 650 nm.

x	τ_1/ns	A_1	τ_2/ns	A_2	τ/ns*
0.002	901.1	0.276	2254.8	1.133	**2134.7**
0.006	695.8	0.497	2218.9	1.101	**2030.0**
0.010	817.6	0.769	2217.4	0.898	**1881.5**
0.015	301.3	1.641	2086.1	1.099	**1769.5**
0.020	720.3	0.858	2094.2	0.867	**1745.3**
0.030	652.0	0.789	2151.5	0.958	**1852.0**

* $\tau = \dfrac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$

Calculation of average distance between Eu^{2+} ions

The average distance R between the nearby Eu^{2+} ions can be estimated by the following equation[5,6]

$$R = 2\left(\frac{3V}{4\pi x_c N}\right)^{1/3} \qquad \text{(S3)}$$

where x_c is the concentration of Eu^{2+}, V represents the volume of the unit cell (545.41 $Å^3$ according to the refinement result), and N refers to the number of the cation sites occupied by activators per unit cell. x_cN stands for the number of Eu^{2+} ions per unit cell.

Table S8. Atomic parameters of the KCPOF host obtained at 900 °C after structural optimization with DFT theory

Atom	Wyckoff site	x/a	y/b	z/c
Ca1	2e	0.80058	3/4	0.07354
Ca2	2e	0.70581	3/4	0.56639
K1	2e	0.78671	1/4	0.42304
K2	2e	0.70447	1/4	0.93119
K3	2e	0.51240	1/4	0.68742
K4	2e	0.98996	3/4	0.81184
P1	2e	0.99157	1/4	0.66169
P2	2e	0.49013	3/4	0.83647
F1	2a	0	1/2	0
F2	2d	1/2	0	1/2
O1	2e	0.66829	3/4	0.90329
O2	2e	0.99564	3/4	0.21613
O3	4f	0.88627	0.03305	0.62585
O4	4f	0.37786	0.53315	0.86410
O5	2e	0.53161	3/4	0.71682
O6	2e	0.81856	3/4	0.39077

Table S9. Atomic parameters of the KCPOF host obtained at 1000 °C after structural optimization with DFT theory

Atom	Wyckoff site	x/a	y/b	z/c
Ca1	2e	0.80222	3/4	0.07524
Ca2	2e	0.70684	3/4	0.56500
K1	2e	0.78534	1/4	0.42130
K2	2e	0.70228	1/4	0.93298
K3	2e	0.51542	1/4	0.68754
K4	2e	0.98360	3/4	0.81162
P1	2e	0.99115	1/4	0.66130
P2	2e	0.48947	3/4	0.83618
F1	2a	0	1/2	0
F2	2d	1/2	0	1/2
O1	2e	0.66377	3/4	0.90651
O2	2e	0.00111	3/4	0.21626
O3	4f	0.88729	0.03301	0.62415
O4	4f	0.37574	0.53310	0.86169
O5	2e	0.53824	3/4	0.71749
O6	2e	0.81594	3/4	0.38867

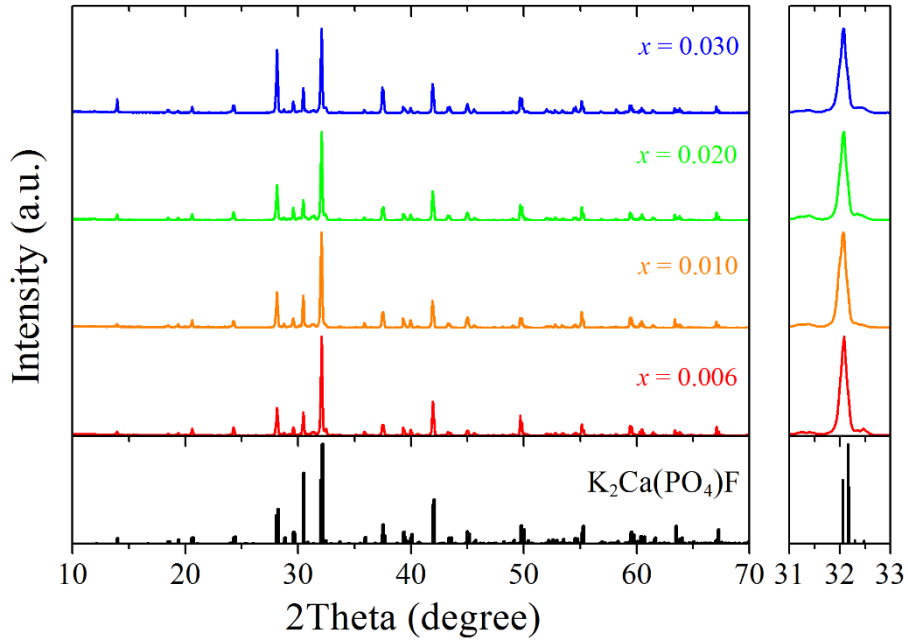

Figure S3. XRD patterns of KCPOF:xEu^{2+} (x = 0.006, 0.010, 0.020, and 0.030) prepared at 1000 °C.

Table S10. Internal and external quantum efficiencies of KCPOF: xEu^{2+} excited at 360 and 390 nm

x	λ_{ex} = 360 nm		λ_{ex} = 390 nm	
	IQE	EQE	IQE	EQE
0.002	94.0%	58.1%	97.8 %	37.0%
0.006	91.5%	66.9%	94.5 %	51.6%
0.010	92.9%	76.6%	76.4 %	46.5%
0.015	85.8%	68.6%	66.2 %	44.5%
0.020	80.5%	62.1%	72.0 %	51.7%
0.030	67.4%	55.1%	63.7 %	51.1%

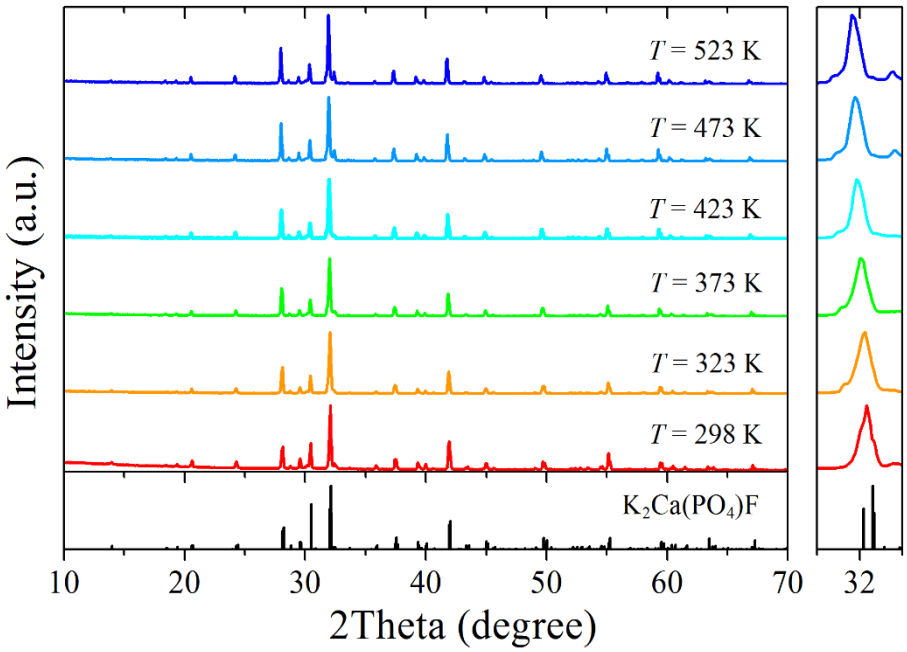

Figure S4. (a) XRD patterns of the samples KCPOF:0.006Eu^{2+} with various temperature ranging from 298 to 523 K.

Table S11. R1-R15 color rendering index values versus driving currents (*I*)

I/mA	R1	R2	R3	R4	R5	R6	R7	R8	**R9**	R10	R11	R12	R13	R14	R15
50	67	73	76	71	67	63	80	63	**3**	34	65	50	67	86	66
100	68	73	77	72	67	63	81	64	**5**	34	66	49	67	87	66
150	69	74	78	73	69	64	83	67	**12**	37	67	50	68	87	68
200	73	77	79	77	73	68	84	73	**27**	44	71	55	72	88	73
250	80	82	83	83	80	75	87	81	**48**	56	79	64	79	90	80
300	**89**	**88**	**86**	**89**	**88**	**83**	**90**	**89**	**75**	**70**	**88**	**77**	**88**	**92**	**90**
350	86	86	85	87	86	80	89	87	**66**	66	85	74	85	92	87

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