Supplementary Information

Comparison of properties and performance of Eu^{2+}-doped $Ca_6BaP_4O_{17}$, $Ca_4Sr(PO_4)_3Cl$, $NaSrPO_4$ and $Sr_3Al_2O_5Cl_2$ thermometric phosphors

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Table S1. Atomic coordinates obtained by Rietveld refinement in CBP:Eu.

Atom	X	Y	Z	Occ.	Wyckoff
Ba	0.00000	0.00000	0.00000	1.00000	2a
Ca1	0.72210	0.00000	0.31501	1.00000	4i
Ca2	0.04999	0.76657	0.69955	1.00000	8j
P1	0.26010	0.00000	0.40024	1.00000	4i
P2	0.37110	0.00000	0.04795	1.00000	4i
O1	0.00000	0.00000	0.50000	1.00000	2c
O11	0.40220	0.00000	0.58521	1.00000	4i
O12	0.27410	-0.17490	0.33169	1.00000	8j
O13	0.12520	0.00000	0.36796	1.00000	4i
O21	0.29440	0.00000	0.10774	1.00000	4i
O22	0.24920	0.00000	-0.13966	1.00000	4i
O23	0.45010	-0.17968	0.11479	1.00000	8j

Table S2. Atomic coordinates obtained by Rietveld refinement in CSPC:Eu.

Atom	X	Y	Z	Occ.	Wyckoff
Ca1	0.33333	0.66667	0.00000	0.33300	4f
Ca2	0.25000	0.00000	0.25000	0.50000	6h
P	0.41700	0.36100	0.25000	0.50000	6h
O1	0.33333	0.50000	0.25000	0.50000	6h
O2	0.60100	0.46700	0.25000	0.50000	6h
O3	0.33330	0.25000	0.06500	1.00000	12i
Cl	0.00000	0.00000	0.00000	0.16700	2b

Table S3. Atomic coordinates obtained by Rietveld refinement in SAC:Eu.

Atom	X	Y	Z	Occ.	Wyckoff
Sr1	0.40729	0.99365	0.25387	1.00000	4a

Sr2	0.26156	0.41151	0.01071	1.00000	4a
Sr3	-0.00143	0.25618	0.40035	1.00000	4a
Al1	0.09755	0.10363	0.10586	1.00000	4a
Al2	0.64493	0.54724	0.68982	1.00000	4a
Cl1	0.30036	0.30119	0.31560	1.00000	4a
Cl2	0.79499	0.79401	0.83602	1.00000	4a
O1	1.00464	0.96303	0.00816	1.00000	4a
O2	0.51495	0.52064	0.43998	1.00000	4a
O3	0.08678	0.94930	0.38033	1.00000	4a
O4	0.21632	0.16422	1.02169	1.00000	4a
O5	0.98308	0.25427	0.08179	1.00000	4a

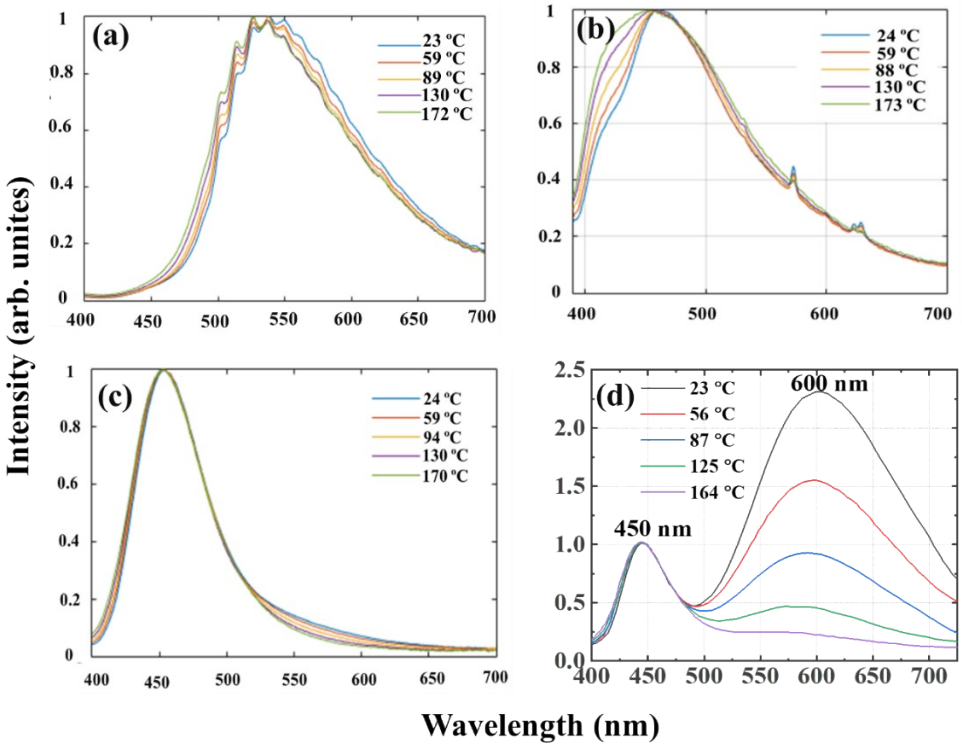

Figure S1. Normalized temperature-dependent luminescence of (a) CBP:Eu, (b) CSPC:Eu, NSP:Eu, and SAC:Eu excited at 355 nm.

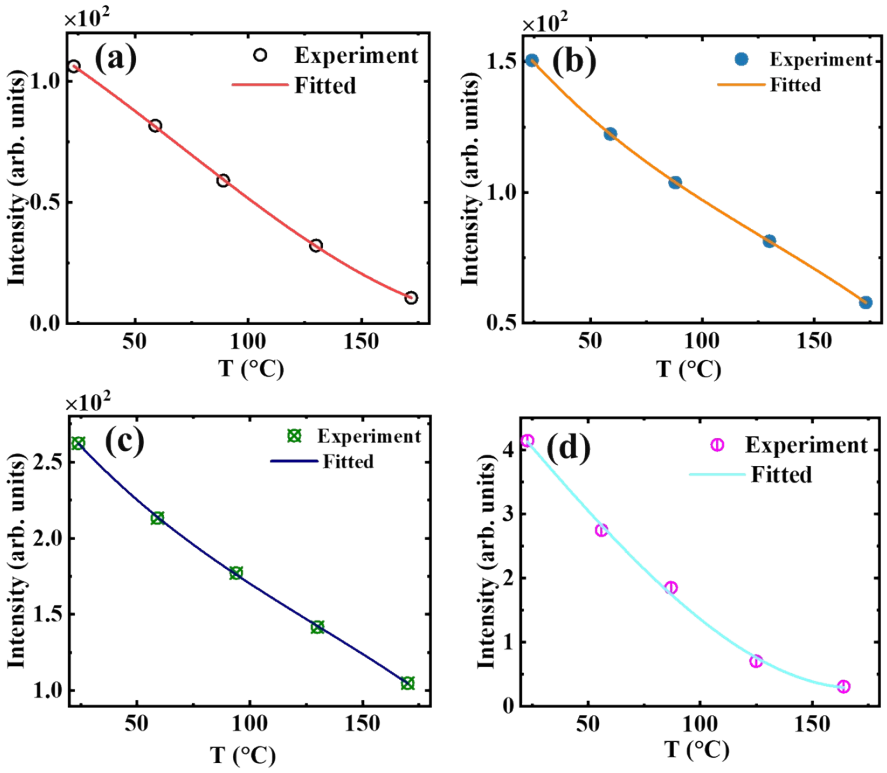

Figure S2. The plot of integrated emission intensity versus temperature for (a) CBP:Eu, (b) CSPC:Eu, NSP:Eu, and SAC:Eu.

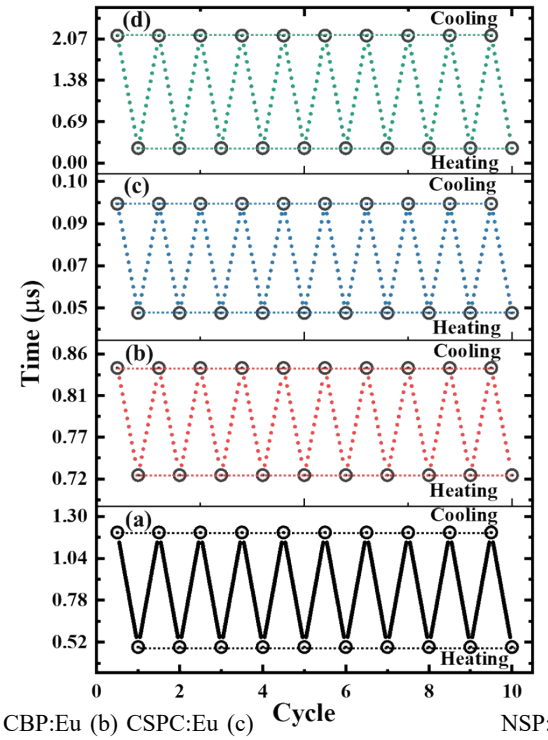

Figure S3. PL lifetime of (a) CBP:Eu (b) CSPC:Eu (c) NSP:Eu and SAC:Eu at 23 and 173 °C through multiple heating and cooling cycles.

S1. IMPURITY LEVEL MODEL FOR LANTHANIDES.

When trivalent lanthanide ions are doped in a host matrix, the lowest 4*f*–5*d* energy levels of the Ln^{3+} ions shift to a lower energy when compared to those of the Ln^{3+} free ions, $E_{fd}(Ln^{3+}, \text{free})$. According to Dorenbos's redshift model, the redshift value, $D(Ln^{3+}, host)$, is consistent across all lanthanides within the same compound, but it varies depending on the specific compound. It relates to the $E_{fd}(Ln^{3+}, \text{free})$ energies as described by Eq. (S1)[86,87].

$$E_{fd}(Ln^{3+}, host) = E_{fd}(Ln^{3+}, free) - D(Ln^{3+}, host) \quad \text{(S1)}$$

where $E_{fd}(Ln^{3+}, host)$ is the energy of the lowest 4*f*–5*d* excited state of the Ln^{3+} in a specific host. The values of $E_{fd}(Ln^{3+}, \text{free})$ for all lanthanides have been documented in the literature[88]. The energy level of 4*f*–5*d* for Ln^{3+} ions in a given host is typically expressed relative to that of Ce^{3+} [89]. The $E_{fd}(Ce^{3+}, CBP)$, $E_{fd}(Ce^{3+}, CSPC)$, $E_{fd}(Ce^{3+}, NSP)$ and $E_{fd}(Ce^{3+}, SAC)$ were determined from the PL excitation spectrum of each host doped with Ce^{3+} as 3.32, 3.91, 3.73 and 3.74 eV[90–92], respectively. Using Eq. (S1), the $D(Ln^{3+}, host)$ for CBP, CSPC, NSP and SAC are calculated to be 2.80, 2.21, 2.03, and 2.38, respectively. As stated previously, the value of the $D(Ln^{3+}, host)$ is identical for all lanthanides in the same host. Consequently, the $E_{fd}(Ln^{3+}, host)$ values for the other Ln^{3+} ions in the CBP, CSPC, NSP and SAC compounds can be calculated using Eq. (S1), along with the known values of $E_{fd}(Ln^{3+}, free)$ and $D(Ln^{3+}, host)$. The results are presented in Table S4.

Table S4. The energy of the lowest 4*f*–5*d* excited state of the Ln^{3+} in CBP, CSPC, NSP and SAC.

Ln	n	$E_{fd}(Ln^{3+}$, CBP)	$E_{fd}(Ln^{3+}$, CSPC)	$E_{fd}(Ln^{3+}$, NSP)	$E_{fd}(Ln^{3+}$, SAC)
La	0	–	–	–	–
Ce	1	3.32	3.91	3.73	3.74
Pr	2	4.83	5.42	5.24	5.25
Nd	3	6.12	6.71	6.53	6.54
Pm	4	6.44	7.03	6.85	6.86
Sm	5	6.54	7.13	6.95	6.96
Eu	6	7.70	8.29	8.11	8.12
Gd	7	9.00	9.59	9.41	9.42
Tb	8	4.98	5.57	5.39	5.40
Dy	9	6.45	7.04	6.86	6.87
Ho	10	7.30	7.89	7.71	7.72
Er	11	7.06	7.65	7.47	7.48
Tm	12	6.95	7.54	7.36	7.37
Yb	13	8.09	8.68	8.50	8.51
Lu	14	9.46	10.05	9.87	9.88

For Ln^{2+} ions, the energies, $E_{fd}(Ln^{2+}, host)$, of the lowest 4*f*–5*d* transitions are determined using a similar formula as $E_{fd}(Ln^{3+}, host)$, namely

$$E_{fd}(Ln^{2+}, host) = E_{fd}(Ln^{2+}, free) - D(Ln^{2+}, host) \quad \text{(S2)}$$

where the $D(Ln^{2+}, host)$ redshift is related to $D(Ln^{3+}, host)$ through Eq. (S3)[86]

$$D(Ln^{2+}, host) = 0.64D(Ln^{3+}, host) - 0.233\ eV \quad \text{(S3)}$$

The values of the $D(Ln^{2+}, host)$ were calculated to be 1.56, 1.18, 1.29, and 1.29 eV, for CBP, CSPC, NSP and SAC, respectively, using Eq. (S3). Then from the value of $E_{fd}(Ln^{2+}, free)$ reported in ref.[93] and Eq. (S2), the values of the $E_{fd}(Ln^{2+}, host)$ energies of all Ln^{2+} ions in CBP, CSPC, NSP, and SAC host lattices are calculated and listed in Table S5.

Table S5. The energy of the lowest 4*f*–5*d* excited state of the Ln^{2+} in CBP, CSPC, NSP and SAC.

Ln	n	$E_{fd}(Ln^{2+}$, CBP)	$E_{fd}(Ln^{2+}$, CSPC)	$E_{fd}(Ln^{2+}$, NSP)	$E_{fd}(Ln^{2+}$, SAC)
La	0	-2.49	-2.12	-2.23	-2.23
Ce	1	-1.18	-0.80	-0.91	-0.91
Pr	2	0.03	0.41	0.29	0.29
Nd	3	0.31	0.69	0.58	0.58
Pm	4	0.40	0.78	0.67	0.67
Sm	5	1.44	1.82	1.71	1.71
Eu	6	2.66	3.04	2.93	2.93
Gd	7	-1.76	-1.38	-1.49	-1.49
Tb	8	-0.37	0.01	-0.10	-0.10
Dy	9	0.61	0.99	0.88	0.88
Ho	10	0.69	1.07	0.96	0.96
Er	11	0.56	0.94	0.83	0.83
Tm	12	1.39	1.77	1.66	1.66
Yb	13	2.66	3.04	2.93	2.93
Lu	14	–	–	–	–

The charge transfer band, E^{CT}, is the energy required to transfer an electron from the valence band to a trivalent lanthanide impurity level in a compound. For any given compound, E^{CT} of a trivalent lanthanide ion reveals information about the position of the ground state of the corresponding divalent lanthanide ion in relation to the top of the valence band, and is expressed by Eq. (S4)

$$E_{Vf}(Ln^{2+},\ host) = E^{CT}(Ln^{3+},\ host) \tag{S4}$$

The E^{CT} values for CSPC and SAC were measured from the PL excitation spectra in Figure S3(a,b), respectively. The $E^{CT}(Eu^{3+},\ host)$ of Eu^{3+} doped CBP, CSPC, NSP and SAC are 3.73[58], 5.06, 3.88[59] and 4.16 eV. These values of the $E^{CT}(Eu^{3+},\ host)$ are equivalent to the energy $E_{Vf}(Eu^{2+},\ host)$ in each host.

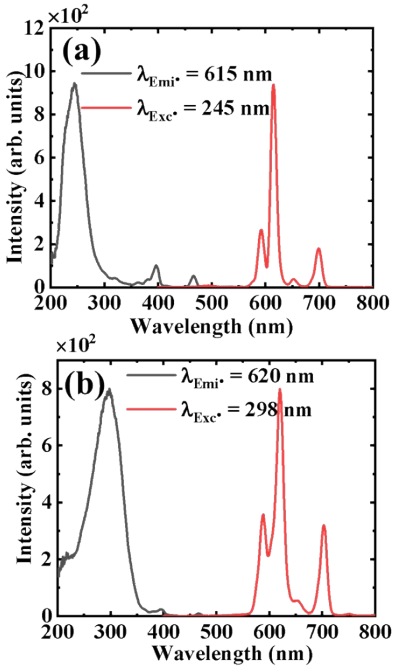

Figure S4. PL excitation and emission spectra of (a) CSPC:Eu^{3+} and (b) SAC:Eu^{3+}.

By comparing the $E_{Vf}(Eu^{2+},\ host)$ energy levels for CBP:Eu^{2+}, CSPC:Eu^{2+}, NSP:Eu^{2+} and SAC:Eu^{2+} to the known energy difference, $E_{Vf}(Ln^{2+},\ Eu^{2+})$, in ref.[94], the energy levels $E_{Vf}(Eu^{2+},\ host)$ for all divalent lanthanides in each host, can be found. The obtained values of $E_{Vf}(Eu^{2+},\ host)$ are listed in Table S6.

Table S6. The energy of the ground state, E_{vf}, of the Ln^{2+} in CBP, CSPC, NSP and SAC.

Ln	n	$E_{vf}(Ln^{2+}$, CBP)	$E_{vf}(Ln^{2+}$, CSPC)	$E_{vf}(Ln^{2+}$, NSP)	$E_{vf}(Ln^{2+}$, SAC)
La	0	9.42	10.75	9.49	9.85
Ce	1	7.80	9.13	8.01	8.23
Pr	2	6.56	7.89	6.75	6.99
Nd	3	6.23	7.56	6.31	6.66
Pm	4	6.05	7.38	6.22	6.48
Sm	5	4.97	6.30	5.13	5.40
Eu	6	3.73	5.06	3.88	4.16
Gd	7	8.40	9.73	8.44	8.83
Tb	8	6.96	8.29	7.09	7.39
Dy	9	6.03	7.36	6.15	6.46
Ho	10	6.17	7.50	6.28	6.60
Er	11	6.35	7.68	6.46	6.78
Tm	12	5.50	6.83	5.59	5.93
Yb	13	4.22	5.55	4.31	4.65
Lu	14	–	–	–	–

Just like the energy $E_{Vf}(Ln^{2+})$ of the divalent lanthanides, the energy of the ground states of trivalent lanthanides $E_{Vf}(Ln^{3+})$ can be determined by either measuring the E^{CT} energy of tetravalent lanthanide ions (Ln^{4+}) or with respect to the Coulomb correlation energy. There is currently insufficient information in the literature regarding the transitions of Ln^{4+} ions. Therefore, the energy $E_{Vf}(Ln^{3+})$ can be estimated using the Coulomb correlation energy U(6, host), which is defined as the difference in energy between the ground state of Eu^{2+} ions and that of Eu^{3+} ions[86].

$$U(6,\ host) = E_{Vf}(Eu^{2+},\ host) - E_{Vf}(Eu^{3+}, host) \tag{S5}$$

The $U(6,\ host)$ is also related to the centroid shift $\varepsilon_C(Ce^{3+},\ host)$ of Ce^{3+} ions in each host through Eq. (S6)

$$U(6, host) = 5.44 + 2.834 * e^{\frac{-\varepsilon_C(Ce^{3+},\ host)}{2.2}} \tag{S6}$$

The centroid shift refers to the change in the barycenter of the $5d_i$ levels of the Ce^{3+} ions in a host when compared to gaseous Ce^{3+} and it can be determined by Eq. (S7)[87]

$$\varepsilon_C(Ce^{3+}, host) = 6.35 - \frac{1}{n}\sum_{i=1}^{n} E_{fdi}(Ce^{3+}, host) \tag{S7}$$

where 6.35 eV is the average energy levels of $5d_i$ of gaseous Ce^{3+}, $n = 5$ is the number of the manifolds of Ce^{3+} excited states, and $E_{fdi}(Ce^{3+}, host)$ are the manifolds of the *f–d* excitation energy levels of Ce^{3+} ions in CSPC, CBP, NSP and SAC hosts obtained

from ref.[43, 95, 91, 96]. By combining Eq. (S6) and Eq. (S7), the values of $\varepsilon_C(Ce^{3+}, host)$ and $U(6, host)$ are determined to be 2.312 and 6.43 eV for CBP:Ce^{3+}, 1.67 and 6.77 eV for CSPC:Ce^{3+}, 1.76 and 6.71 eV for NSP:Ce^{3+}, and 1.746 and 6.72 eV for SAC:Ce^{3+}, respectively. Using Eq. (S5), the value of $E_{Vf}(Eu^{3+}, host)$ were calculated to be -2.69, -1.70, -2.84, and -2.56 eV, for CBP, CSPC, NSP and SAC, respectively. Using these values of $E_{Vf}(Eu^{3+}, host)$ and the energy difference between the 4*f* ground state of Ln^{3+} ions and that of Eu^{3+}, $E_{Vf}(Ln^{3+}, Eu^{3+})$ in ref.[93], we can predict the energies $E_{Vf}(Ln^{3+}, host)$ for all other Ln^{3+} ions in CBP, CSPC, NSP and SAC host lattices. This information is summarized in Table S7.

Table S7. The energy of the ground state, E_{vf}, of the Ln^{3+} in CBP, CSPC, NSP and SAC.

Ln	n	$E_{vf}(Ln^{3+}$, CBP)	$E_{vf}(Ln^{3+}$, CSPC)	$E_{vf}(Ln^{3+}$, NSP)	$E_{vf}(Ln^{3+}$, SAC)
La	0	–	–	–	–
Ce	1	2.54	3.54	2.40	2.68
Pr	2	0.69	1.69	0.55	0.83
Nd	3	-0.79	0.19	-0.94	-0.66
Pm	4	-1.24	-0.24	-1.38	-1.10
Sm	5	-1.43	-0.43	-1.57	-1.29
Eu	6	-2.69	-1.70	-2.84	-2.56
Gd	7	-4.04	-3.04	-4.18	-3.90
Tb	8	0.87	1.87	0.73	1.01
Dy	9	-0.55	0.45	-0.69	-0.41
Ho	10	-1.65	-0.65	-1.79	-1.51
Er	11	-1.58	-0.58	-1.72	-1.44
Tm	12	-1.42	-0.42	-1.56	-1.28
Yb	13	-2.46	-1.47	-2.60	-2.32
Lu	14	-3.72	-2.71	-3.85	-3.57

The energy level of the $E_{5d}(Ln^{2+}, host)$ lanthanide ions in the hosts can be obtained by adding the $E_{Vf}(Ln^{3+}, host)$ and $E_{fd}(Ln^{3+}, host)$ as expressed in Eq. (S8)

$$E_{5d}(Ln^{2+}, host) = E_{Vf}(Ln^{2+}, host) + E_{fd}(Ln^{2+}, host) \quad \text{S8}$$

The values of $E_{5d}(Ln^{2+}, host)$ for CBP, CSPC, NSP and SAC are listed in Table S8.

Table S8. The energy level of the 5d excited state of Ln^{2+} in CBP, CSPC, NSP and SAC.

Ln	n	$E_{5d}(Ln^{2+}$, CBP)	$E_{5d}(Ln^{2+}$, CSPC)	$E_{5d}(Ln^{2+}$, NSP)	$E_{5d}(Ln^{2+}$, SAC)
La	0	6.93	8.63	7.25	7.62
Ce	1	6.63	8.33	7.09	7.32
Pr	2	6.59	8.30	7.04	7.29
Nd	3	6.55	8.25	6.88	7.24
Pm	4	6.46	8.16	6.88	7.15
Sm	5	6.42	8.12	6.83	7.11
Eu	6	6.39	8.10	6.80	7.09
Gd	7	6.65	8.35	6.94	7.34
Tb	8	6.59	8.30	6.98	7.29

Dy	9	6.65	8.35	7.02	7.34
Ho	10	6.87	8.57	7.23	7.56
Er	11	6.92	8.62	7.28	7.61
Tm	12	6.89	8.60	7.25	7.59
Yb	13	6.89	8.59	7.23	7.58
Lu	14	–	–	–	–

In a manner similar to the $E_{5d}(Ln^{2+},\ host)$, the position of the *5d* levels for trivalent lanthanides in the different hosts, $E_{5d}(Ln^{3+},\ host)$, in relation to the top of the valence band, is also determined by Eq. (S8). The results are listed in Table S9.

The top of the valence band is set as the zero-energy level. The Host Referred Binding Energy (HRBE) diagram is constructed using the values of E_{Vf} and E_{5d} energies presented in Table S6, S7, S8 and S9. This diagram, shown in Figure 12, illustrates the positions of the $4f^n$ and $4f^{n-1}5d$ energy levels for all divalent and trivalent lanthanide impurities in relation to the top of the valence band of the host lattices. The E_g of CBP, CSPC, NSP and SAC are 6.63, 8.23, 6.80, and 7.20 eV, respectively [58,35,60,39], which allows to determine the energy difference between the lowest 5*d* state and the bottom of the conduction band, the thermal ionization energy (ΔE_i).

Table S9. The energy levels of the 5*d* excited states of Ln^{3+} in CBP, CSPC, NSP and SAC.

Ln	n	$E_{5d}(Ln^{3+}$, CBP)	$E_{5d}(Ln^{3+}$, CSPC)	$E_{5d}(Ln^{3+}$, NSP)	$E_{5d}(Ln^{3+}$, SAC)
La	0	–	–	–	–
Ce	1	5.86	7.45	6.14	6.42
Pr	2	5.52	7.11	5.79	6.08
Nd	3	5.32	6.91	5.59	5.88
Pm	4	5.20	6.79	5.48	5.76
Sm	5	5.11	6.69	5.39	5.67
Eu	6	5.00	6.59	5.28	5.56
Gd	7	4.96	6.55	5.24	5.52
Tb	8	5.85	7.44	6.13	6.41
Dy	9	5.90	7.49	6.18	6.46
Ho	10	5.65	7.24	5.93	6.21
Er	11	5.48	7.07	5.76	6.04

Tm	12	5.53	7.12	5.81	6.09
Yb	13	5.63	7.21	5.90	6.19
Lu	14	5.75	7.34	6.03	6.31

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