Supporting Information

Luminescence spectra simulation of Ce^{3+}-activated phosphors by accumulating emission lines along first-principles molecular dynamics trajectories

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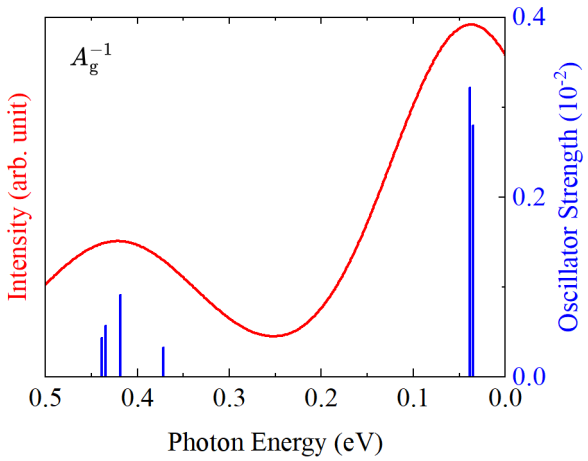

Figure S1. Calculated absorption spectra of YAG:Ce structure model (red curve) using TDM from the lowest Ce 4f level to higher levels in A_g^{-1} states. Blue bars indicate the calculated transition energies and the oscillator strengths.

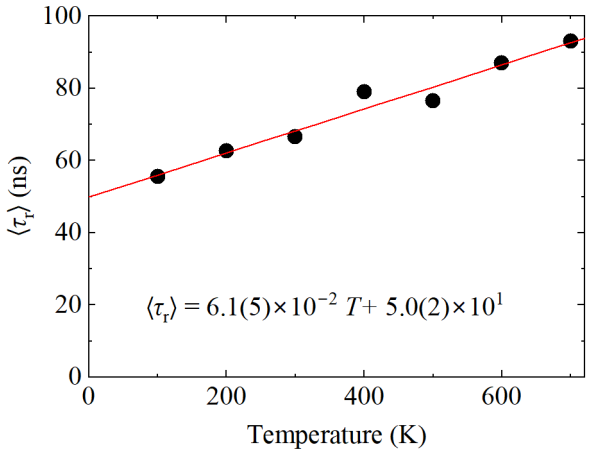

Figure S2. Average radiative lifetime ‹τ_r› as a function of temperature calculated along the trajectory of FPMD for YAG:Ce structure model.

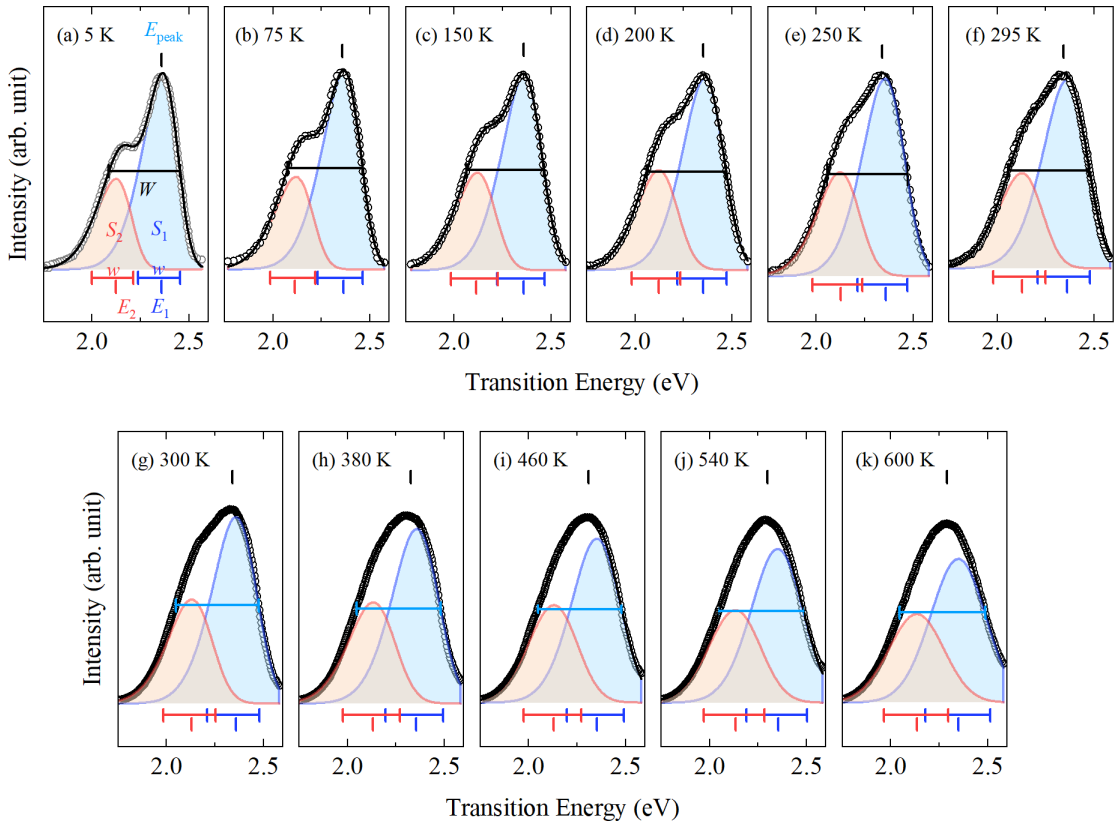

Figure S3. Evaluation of emission peak positions and FWHMs in experimental luminescence emission spectra of YAG:Ce at 5-600 K taken from literature.[S1] The spectral intensity $\rho(\lambda)$ in the wavelength domain was converted to the spectral intensity $\rho(\epsilon)$ in the energy domain by the equation $\rho(\epsilon) = (\lambda^2/hc)\,\rho(\lambda)$. In the reference, the YAG:Ce luminescence spectra were measured below 295 K and above 300 K using different spectrophotometers. Because the sensitivity curves of the two spectrometers are different, the spectra above 300 K were corrected using the intensity ratio of the spectra at 300 K and 295 K; $\rho_{corr}(\epsilon) = \rho_{294}(\epsilon) / \rho_{300}(\epsilon)\,\rho(\epsilon)$.

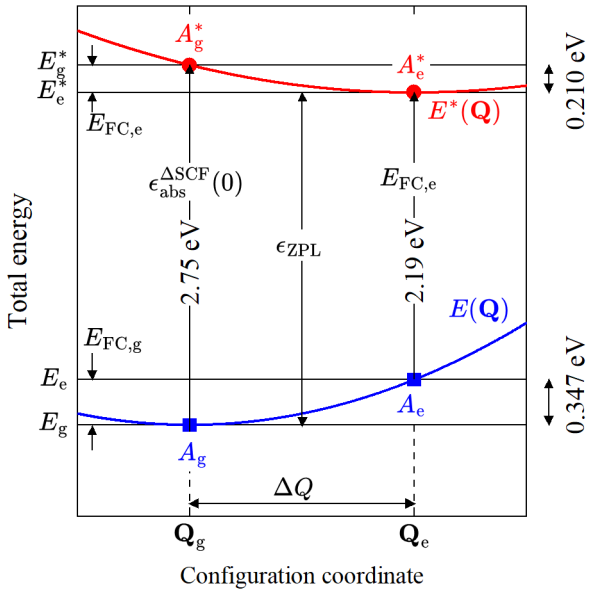

Figure S4. Configuration coordinate diagram of total energy for the $CeY_{23}Al_{40}O_{96}$ structure model obtained by the ΔSCF approach.

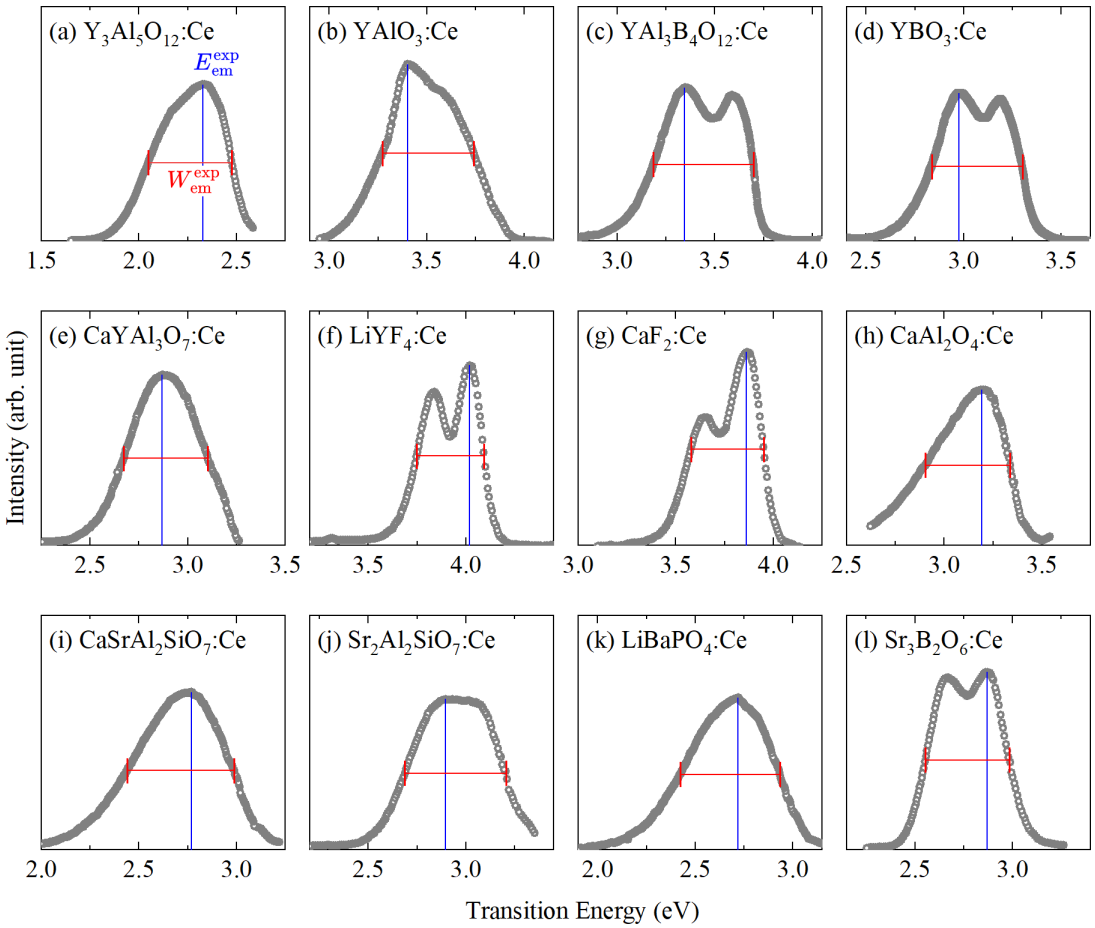

Figure S5. Evaluation of emission peak positions and FWHMs in experimental luminescence emission spectra of 12 known Ce^{3+}-activated phosphors measured at 300 K, taken from the literature. (a)$Y_3Al_5O_{12}$:Ce,[S1] (b) $YAlO_3$:Ce,[S2] (c) $YAl_3B_4O_{12}$:Ce,[S3] (d) YBO_3:Ce,[S3] (e) $CaYAl_3O_7$:Ce,[S4] (f) $LiYF_4$:Ce,[S5] (g) CaF_2:Ce,[S6] (h) $CaAl_2O_4$:Ce[S7] (i), $CaSrAl_2O_7$:Ce[S8] (j), $Sr_2Al_2O_7$:Ce,[S9] (k) $LiBaPO_4$:Ce,[S10] and (l) $Sr_3B_2O_6$:Ce[S11].

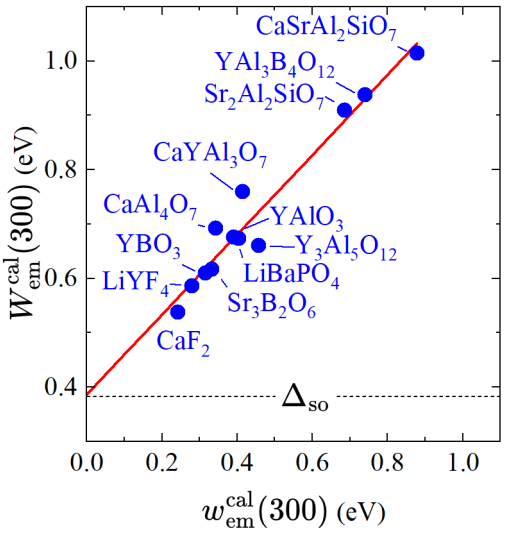

Figure S6. Relation between the FWHM $\boldsymbol{W_{em}^{cal}}$ of whole emission band and the FWHMs $\boldsymbol{w_{em}^{cal}}$ of $5d_1 \rightarrow {}^2F_{5/2}$ and $5d_1 \rightarrow {}^2F_{7/2}$ bands in the spectra at 300 K in the Ce^{3+}-activated phosphor series.

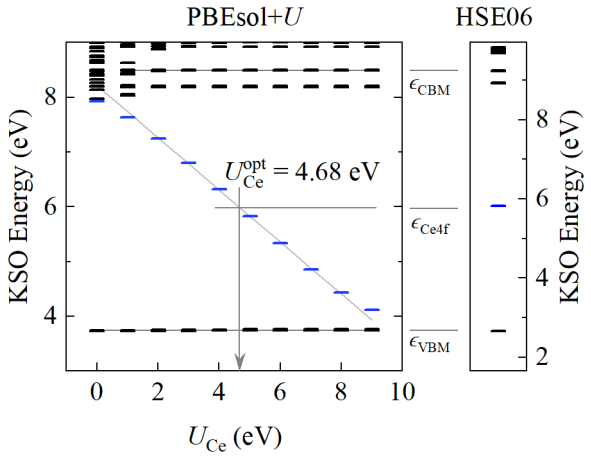

Figure S7. KSO energies as functions of U_{Ce} obtained by PBEsol+U calculation for $CeY_{23}Al_{40}O_{96}$ model, compared with KSO energies calculated by HSE06 hybrid functional.

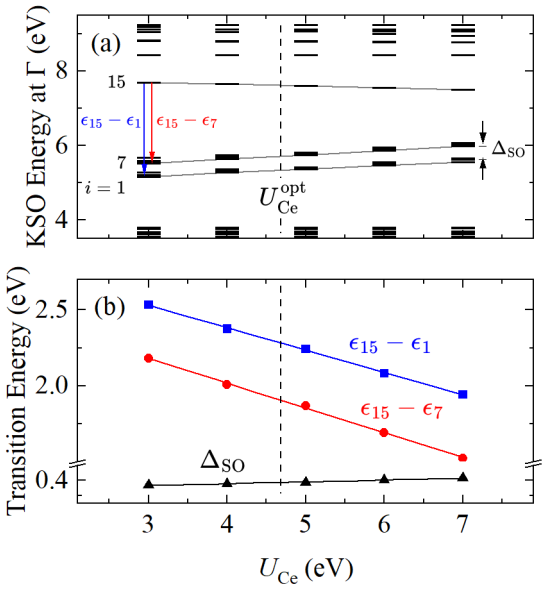

Figure S8. (a) KSO energies at Γ, (b) $\epsilon_{15} - \epsilon_1$ and $\epsilon_{15} - \epsilon_7$ transition energies and spin-orbit splitting Δ_{SO} for A_e^{-1} state in YAG:Ce model as a function of U_{Ce}.

Table S1. List of Ce^{3+}-activated phosphor systems with U_{Ce}^{opt} used for structure optimization and total energy calculation and ΔSCF parameters, absorption energy at 0 K ($\epsilon_{abs}^{\Delta SCF}(0)$, eV), emission energy at 0 K ($\epsilon_{em}^{\Delta SCF}(0)$, eV), Stoks shift at 0 K ($\Delta S(0)$, eV) Franck–Condon shifts for GS ($E_{FS,g}$) and ES ($E_{FS,e}$) electronic states, and total normal coordinate change (ΔQ, $amu^{1/2}$Å).

Compounds	U_{Ce}^{opt}	$\epsilon_{abs}^{\Delta SCF}(0)$	$\epsilon_{em}^{\Delta SCF}(0)$	$\Delta S(0)$	$E_{FS,g}$	$E_{FS,e}$	ΔQ
$Y_3Al_5O_{12}$:Ce	4.68	2.751	2.194	0.557	0.347	0.210	1.423
$YAlO_3$:Ce	3.83	4.114	3.672	0.442	0.285	0.157	1.231
$YAl_3B_4O_{12}$:Ce	3.51	4.045	3.126	0.919	0.701	0.218	2.026
YBO_3:Ce	3.77	3.646	3.211	0.435	0.263	0.172	1.132
$CaYAl_3O_7$:Ce	3.84	3.466	2.352	1.114	0.768	0.347	1.473
$LiYF_4$:Ce	3.71	4.642	4.485	0.157	0.087	0.070	0.226
CaF_2:Ce, F	3.40	4.180	3.993	0.187	0.106	0.081	0.895
$CaAl_4O_7$:Ce, Na	3.61	4.089	3.067	1.022	0.693	0.329	2.188
$CaSrAl_2SiO_7$:Ce, Na	3.61	3.799	2.703	1.096	0.821	0.275	1.626
$Sr_2Al_2SiO_7$:Ce, Na	3.73	3.702	2.810	0.892	0.632	0.261	2.179
$LiBaPO_4$:Ce,Na	3.50	4.264	3.581	0.683	0.390	0.294	2.349
$Sr_3B_2O_6$:Ce,Na	3.53	3.558	2.943	0.615	0.358	0.256	2.514

Table S2. Parameters obtained by harmonic oscillator model analysis of ΔSCF data: Associated effective vibrational energies for GS ($\hbar\Omega_g$, meV) and ES ($\hbar\Omega_e$, meV) electronic states, Huang-Rhys parameters for GS (S_g) and ES (S_e) states, emission energy at 300 K ($\epsilon_{em}^{\Delta SCF}(300)$, eV) and FWHM of emission peak at 300 K ($\epsilon_{em}^{\Delta SCF}(300)$, eV).

System	$\hbar\Omega_g$	$\hbar\Omega_e$	S_g	S_e	$\epsilon_{em}^{\Delta SCF}(300)$	$w_{em}^{\Delta SCF}(300)$
$Y_3Al_5O_{12}$:Ce	37.8	29.4	9.17	7.13	2.265	0.426
$YAlO_3$:Ce	39.6	29.4	7.19	5.34	3.722	0.405
$YAl_3B_4O_{12}$:Ce	37.8	21.1	18.55	10.35	3.332	0.826
YBO_3:Ce	41.4	33.5	6.35	5.14	3.251	0.362
$CaYAl_3O_7$:Ce	54.4	36.6	14.12	9.49	2.533	0.752
$LiYF_4$:Ce	119.3	107.0	0.73	0.65	4.496	0.257
CaF_2:Ce,F	33.3	29.1	3.19	2.79	4.008	0.209
$CaAl_4O_7$:Ce,Na	34.8	24.0	19.92	13.73	3.194	0.669
$CaSrAl_2SiO_7$:Ce,Na	50.9	29.5	16.12	9.33	2.942	0.882
$Sr_2Al_2SiO_7$:Ce,Na	33.4	21.4	18.95	12.18	2.959	0.681
$LiBaPO_4$:Ce,Na	24.3	21.1	16.05	13.93	3.619	0.396
$Sr_3B_2O_6$:Ce,Na	21.8	18.4	16.45	13.91	2.989	0.387

Table S3. Peak energies ($\epsilon_{5/2}^{\mathrm{cal}}$ and $\epsilon_{7/2}^{\mathrm{cal}}$, eV), SO splitting ($\Delta_{\mathrm{SO}}^{\mathrm{cal}}$, eV), FWHMs ($w_{5/2}^{\mathrm{cal}}$ and $w_{7/2}^{\mathrm{cal}}$, eV) and areal intensity ratio ($s_{7/2}^{\mathrm{cal}}/s_{5/2}^{\mathrm{cal}}$) of $5d_1 \rightarrow {}^2F_{5/2}$ and $5d_1 \rightarrow {}^2F_{7/2}$ emission bands from peak fitting for emission spectra obtained by FPMD spectra accumulation method $I_{5/2}(\epsilon)$ and $I_{7/2}(\epsilon)$ at 300 K.

System	$\epsilon_{5/2}^{\mathrm{cal}}$	$\epsilon_{7/2}^{\mathrm{cal}}$	$\Delta_{\mathrm{SO}}^{\mathrm{cal}}$	$w_{5/2}^{\mathrm{cal}}$	$w_{7/2}^{\mathrm{cal}}$	$s_{7/2}^{\mathrm{cal}}/s_{5/2}^{\mathrm{cal}}$
$Y_3Al_5O_{12}$:Ce	2.226	1.856	0.370	0.455	0.458	0.524
$YAlO_3$:Ce	3.512	3.132	0.380	0.388	0.393	0.627
$YAl_3B_4O_{12}$:Ce	3.196	2.816	0.380	0.750	0.731	0.599
YBO_3:Ce	3.269	2.898	0.371	0.314	0.316	0.636
$CaYAl_3O_7$:Ce	2.578	2.198	0.380	0.491	0.482	0.630
$LiYF_4$:Ce	4.648	4.278	0.370	0.279	0.280	0.642
CaF_2:Ce,F	4.375	4.005	0.370	0.243	0.243	0.602
$CaAl_4O_7$:Ce,Na	2.918	2.528	0.390	0.360	0.337	0.707
$CaSrAl_2SiO_7$:Ce,Na	2.813	2.443	0.370	0.885	0.875	0.659
$Sr_2Al_2SiO_7$:Ce,Na	3.187	2.817	0.370	0.670	0.712	0.667
$LiBaPO_4$:Ce,Na	3.374	2.924	0.450	0.384	0.399	0.526
$Sr_3B_2O_6$:Ce,Na	2.910	2.530	0.380	0.334	0.333	0.576

Table S4. Peak energy ($E_{\mathrm{em}}^{\mathrm{cal}}$, eV) and FWHM ($W_{\mathrm{em}}^{\mathrm{cal}}$, eV) of calculated whole emission spectrum $I(\epsilon)$ at 300 K compared with their experimental values ($E_{\mathrm{em}}^{\mathrm{exp}}$and $W_{\mathrm{em}}^{\mathrm{exp}}$, eV) taken from literature.

System	$E_{\mathrm{em}}^{\mathrm{cal}}$	$W_{\mathrm{em}}^{\mathrm{cal}}$	$E_{\mathrm{em}}^{\mathrm{exp}}$	$W_{\mathrm{em}}^{\mathrm{exp}}$
$Y_3Al_5O_{12}$:Ce	2.186	0.660	2.339	0.427
$YAlO_3$:Ce	3.492	0.676	3.455	0.488
$YAl_3B_4O_{12}$:Ce	2.946	0.938	3.590	0.513
YBO_3:Ce	3.269	0.609	3.189	0.464
$CaYAl_3O_7$:Ce	2.508	0.759	2.876	0.435
$LiYF_4$:Ce	4.648	0.586	4.024	0.347
CaF_2:Ce,F	4.375	0.537	3.863	0.368
$CaAl_4O_7$:Ce,Na	2.908	0.692	3.203	0.431
$CaSrAl_2SiO_7$:Ce,Na	2.673	1.014	2.748	0.542
$Sr_2Al_2SiO_7$:Ce,Na	2.837	0.909	2.989	0.515
$LiBaPO_4$:Ce,Na	3.374	0.673	2.709	0.514
$Sr_3B_2O_6$:Ce,Na	2.900	0.616	2.866	0.432

Table S5. Statistical analyses of ΔSCF emission energy $\epsilon_{\mathrm{em}}^{\Delta\mathrm{SCF}}$ against calculated emission peak energy $\epsilon_{5/2}^{\mathrm{cal}}$ and ΔSCF emission band FWHM against calculated emission FWHM $w_{5/2}^{\mathrm{cal}}$ at 300 K. ME (eV), MAE (eV), MRE (%) and MARE (%) stand for the mean error, mean absolute error, mean relative error, and mean absolute relative error, respectively. The slope, intercept and coefficient of determination (R^2) correspond to the linear fitting. The number in parentheses indicates the standard deviation.

	$\epsilon_{5/2}^{\mathrm{cal}}$ vs $\epsilon_{\mathrm{em}}^{\Delta\mathrm{SCF}}$	$w_{5/2}^{\mathrm{cal}}$ vs $w_{\mathrm{em}}^{\Delta\mathrm{SCF}}$
ME (eV)	−0.03(20)	−0.06(11)
MAE (eV)	0.16(11)	0.07(10)
MRE (%)	0(6)	−8(18)
MARE (%)	5(3)	13(14)
Slope	1.07(10)	0.77(14)
Intercept (eV)	−0.25(33)	0.06(8)
R^2	0.91	0.76

Table S6. Statistical analysis of peak energy E_{em} and FWHM W_{em} of whole emission spectra of Ce^{3+}-activated phosphors calculated by FPMD spectra accumulation method. ME (eV), MAE (eV), MRE (%) and MARE (%) stand for the mean error, mean absolute error, mean relative error, and mean absolute relative error, respectively. The slope, intercept (eV) and coefficient of determination (R^2) correspond to the linear fitting. The number in parentheses indicates the standard deviation.

	E_{em}	W_{em}	$W_{\mathrm{em}} - \Delta_{\mathrm{SO}}$
ME	0.07(37)	0.27(11)	0.18(11)
MAE	0.30(22)	0.27(11)	0.18(11)
MRE	2(12)	58(19)	113(65)
MARE	9(7)	58(19)	113(65)
Slope	1.31(22)	2.02(47)	2.02(47)
Intercept	−0.89(69)	−0.19(22)	0.00(8)
R^2	0.78	0.65	0.65

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