The local environment of the activator ions in the solid state lighting phosphor $Y_{3-x}Ce_xAl_5O_{12}$[†]

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Supporting Information Available

Optical measurements. To confirm the properties of $Y_{3-x}Ce_xAl_5O_{12}$, photoluminescence and photoluminescence quantum yield (PLQY) were measured. Photoluminescence spectra were obtained on a Perkin Elmer LS55 spectrophotometer, scanning a wavelength range from 300 nm to 800 nm. The samples were thoroughly mixed and finely ground with KBr (99%, FT-IR grade, Sigma-Aldrich) and subsequently pressed into a pellet (diameter = 13 mm, KBr:sample ratio approximately 10:1 by mass). Two-dimensional spectra were collected for each excitation wavelength in steps of 1 nm. PLQY was measured with 457 nm excitation using an argon laser and an experimental protocol as described by Greenham et al.[1]

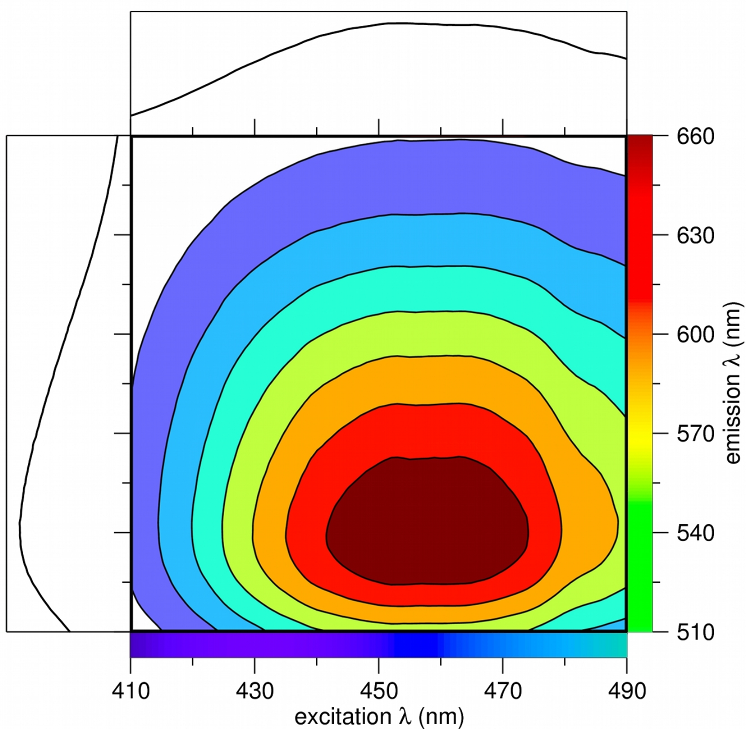

Figure S1: Two-dimensional contour plot of fluorimetry of $Y_{2.94}Ce_{0.06}Al_5O_{12}$, with the maximum excitation/emission spectra shown opposite the axis labels. The corresponding colors for the wavelength ranges are shown below the excitation axis and to the right of the emission axis. Contour lines are drawn at intervals of 100 (arbitrary units).

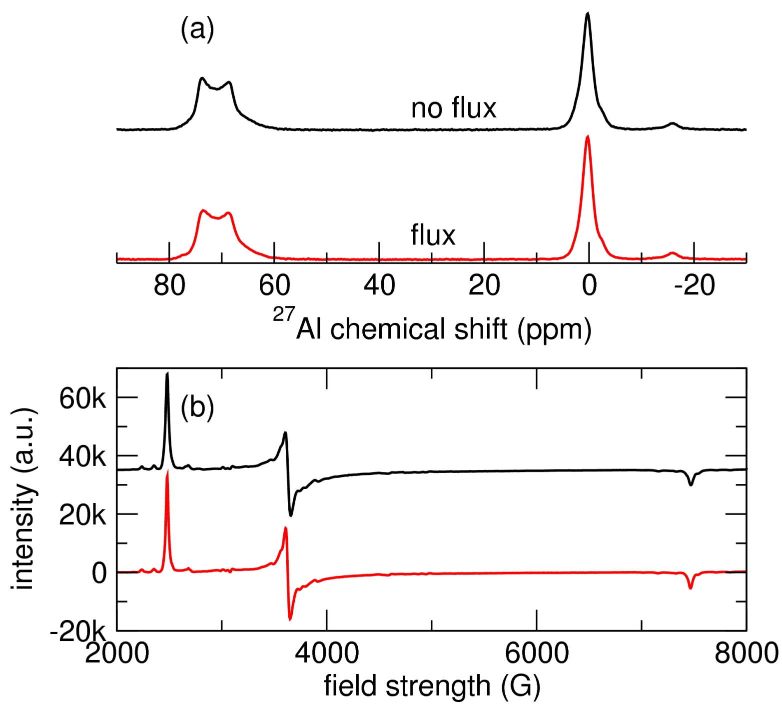

Figure S2: (a) 1D solid-state single-pulse ^{27}Al NMR spectra (24 kHz MAS) of $Y_{2.94}Ce_{0.06}Al_5O_{12}$ taken at 293 K and 18.8 T, made without and with BaF_2 and NH_4F fluxes. (b) Solid-state EPR spectra of $Y_{2.94}Ce_{0.06}Al_5O_{12}$ taken at 4 K and 9.4 GHz, made without and with BaF_2 and NH_4F fluxes.

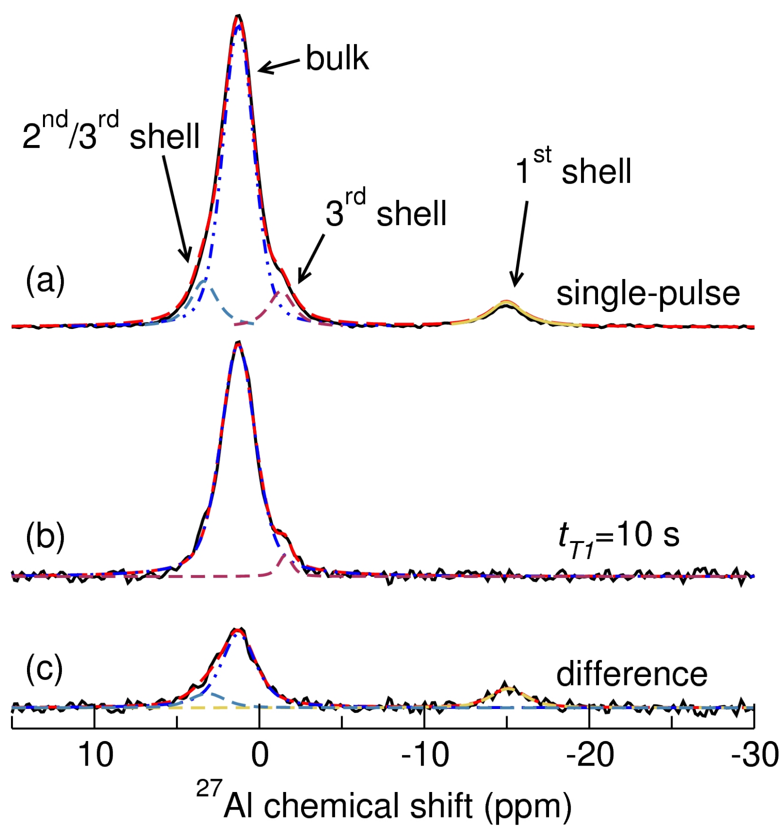

Figure S3: The octahedral region of (a) 1D solid-state single pulse and (b) T_1-filtered ^{27}Al NMR spectra (24 kHz MAS) of $Y_{2.94}Ce_{0.06}Al_5O_{12}$ taken at 293 K and 18.8 T, and (c) the difference of (a) and (b). Fits to the data are shown, which have identical δ_{iso}s to the fit in Figure 7(b). The results of the T_1-filtered experiment confirm the model in Figure 7(b).

Table S1: U_{xx} atomic displacement parameters of $Y_{3-x}Ce_xAl_5O_{12}$ from Rietveld refinement of 11-BM synchrotron X-ray/HIPD neutron and NPDF neutron scattering data.[a]

Temperature	15 K	15 K	295 K	295 K	295 K
Beamline(s)	NPDF	NPDF	11-BM, HIPD	11-BM, HIPD	NPDF
nominal Ce_x	0	0.08	0	0.06	0.09
Y/Ce $U_{11} \times 100$ (Å^2)	0.24(2)	0.26(2)	0.107(7)	0.162(7)	0.39(1)
Y/Ce $U_{22} \times 100$ (Å^2)	0.20(1)	0.25(1)	0.237(7)	0.349(4)	0.496(9)
Y/Ce $U_{33} \times 100$ (Å^2)	0.20(1)	0.25(1)	0.237(7)	0.349(4)	0.496(9)
Y/Ce $U_{12} \times 100$ (Å^2)	0	0	0	0	0
Y/Ce $U_{13} \times 100$ (Å^2)	0.02(2)	0	0	0	0
Y/Ce $U_{23} \times 100$ (Å^2)	0	0.01(1)	0.069(4)	0.061(5)	0.06(1)
Al(6) $U_{11} \times 100$ (Å^2)	0.15(1)	0.24(1)	0.217(6)	0.317(6)	0.42(1)
Al(6) $U_{22} \times 100$ (Å^2)	0.15(1)	0.24(1)	0.217(6)	0.317(6)	0.42(1)
Al(6) $U_{33} \times 100$ (Å^2)	0.15(1)	0.24(1)	0.217(6)	0.317(6)	0.42(1)
Al(6) $U_{12} \times 100$ (Å^2)	0.03(2)	−0.01(2)	−0.07(1)	−0.07(1)	−0.01(2)
Al(6) $U_{13} \times 100$ (Å^2)	0.03(2)	−0.01(2)	−0.07(1)	−0.07(1)	−0.01(2)
Al(6) $U_{23} \times 100$ (Å^2)	0.03(2)	−0.01(2)	−0.07(1)	−0.07(1)	−0.01(2)
Al(4) $U_{11} \times 100$ (Å^2)	0.30(3)	0.15(4)	0.22(3)	0.11(2)	0.29(3)
Al(4) $U_{22} \times 100$ (Å^2)	0.17(5)	0.37(2)	0.24(1)	0.37(1)	0.49(2)
Al(4) $U_{33} \times 100$ (Å^2)	0.28(3)	0.37(2)	0.24(1)	0.37(1)	0.49(2)
Al(4) $U_{12} \times 100$ (Å^2)	0	0	0	0	0
Al(4) $U_{13} \times 100$ (Å^2)	0	0	0	0	0
Al(4) $U_{23} \times 100$ (Å^2)	0	0	0	0	0
O $U_{11} \times 100$ (Å^2)	0.28(1)	0.35(1)	0.22(2)	0.305(7)	0.506(9)
O $U_{22} \times 100$ (Å^2)	0.28(1)	0.35(1)	0.31(2)	0.352(7)	0.48(1)
O $U_{33} \times 100$ (Å^2)	0.40(1)	0.44(1)	0.24(3)	0.463(7)	0.63(1)
O $U_{12} \times 100$ (Å^2)	0.03(1)	0.041(7)	0.20(2)	0.099(5)	0.057(6)
O $U_{13} \times 100$ (Å^2)	0.03(1)	0.002(7)	0.09(2)	−0.063(5)	0.008(6)
O $U_{23} \times 100$ (Å^2)	0.01(1)	−0.01(1)	0.05(2)	−0.012(5)	0.022(7)

[a] Ce_x refers to the amount of Ce in $Y_{3-x}Ce_xAl_5O_{12}$. Estimated standard deviations for the last digit of parameters are given in parenthesis.

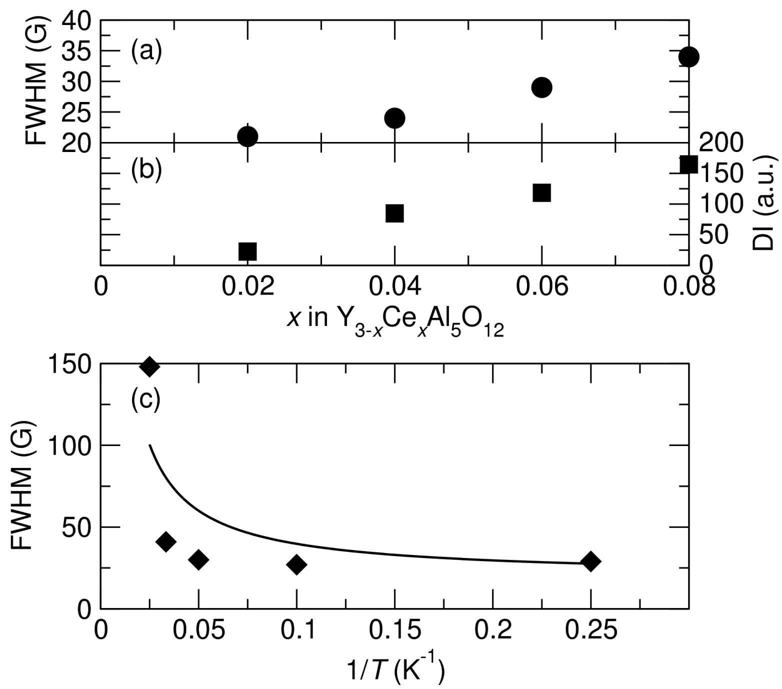

Figure S4: (a) FWHM (Γ) of the peak at 2480 G and (b) double integration (DI) values from solid-state EPR spectra at 4 K and 9.4 GHz of $Y_{3-x}Ce_xAl_5O_{12}$. (c) Γ of the 2480 G signal of EPR spectra of $Y_{2.94}Ce_{0.06}Al_5O_{12}$ for temperatures from 4 K to 40 K. The line in (c) shows the fit to the data from the Orbach equation (see text for more details).

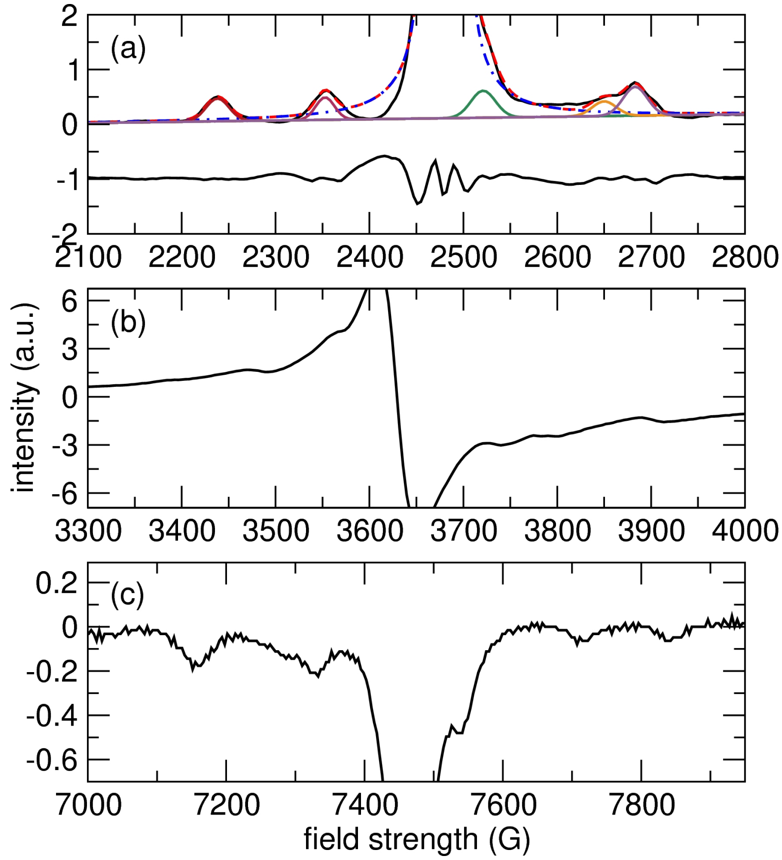

Figure S5: Solid-state EPR spectra taken at 4 K and 9.4 GHz of $Y_{2.94}Ce_{0.06}Al_5O_{12}$, showing an expanded view of the (a) g_x, (b) g_y, and (c) g_z regions. The g_x region (a) has been fit with 6 distinct peaks, with the difference curve shown at the bottom of (a). The small satellite signals are due to Ce^{3+} ions in distinct environments in YAG:Ce.

References

(1) Greenham, N. C.; Samuel, I. D. W.; Hayes, G. R.; Phillips, R. T.; Kessener, Y. A. R. R.; Moratti, S. C.; Holmes, A. B.; Friend, R. H. *Chem. Phys. Lett.* **1995**, *241*, 89 – 96.

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