Electronic Supplementary Information

Origin of Green Persistent Luminescence of Eu-Doped SrAl₂O₄ from Multiconfigurational *Ab Initio* Study of $4f^7 \rightarrow 4f^65d^1$ Transitions

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Computational Methodology

The Eu²⁺-doped SrAl₂O₄ was modelled by incorporating a Eu in a periodic $\sqrt{2} \times \sqrt{2} \times 2$ supercell containing 112 atoms. The atomic structures were fully optimized by minimizing the total energy and Hellmann–Feynman forces to convergence of 10^{-6} eV and 0.01 eV Å⁻¹, respectively. Hybrid DFT calculations were performed in the PBE0 scheme,¹ where the fraction of Hartree-Fock exchange was set at 31% in order to match the calculated band gap with the experimental data,² as implemented in the VASP package.^{3,4} The Sr(4s²4p⁶5s²), Al(3s²3p¹), O(2s²2p⁴), and Eu(5s²5p⁶4f⁷6s²) were treated as valence electrons, and their interactions with the respective cores were described by the projected augmented wave method.⁵ Due to the large size of the systems and the high computational cost of hybrid DFT, one k-point Γ was used to sample the Brillouin zone, with a cutoff energy of 530 eV for the plane wave basis.

The 4f \rightarrow 5d transition energies of Eu²⁺ located at the Sr1 and Sr2 sites of SrAl₂O₄ were calculated by using a wave function-based embedded cluster approach. Eu-centered clusters, $(Eu_{Sr1}O_9)^{16-}$ and $(Eu_{Sr2}O_9)^{16-}$, were first constructed on the basis of the DFT-optimized supercell structures, each comprising the central Eu²⁺ and the O²⁻ ions in the first coordination shell. Their immediate crystalline surroundings within a sphere of radius 10 Å were modelled respectively by 725 and 712 *ab initio* model potentials (AIMPs)⁶ with the remaining surroundings represented by 80 913 and 80 925 point charges at lattice sites. These AIMPS and point charges were generated using the method by Lepetit,⁷ to account for the electrostatic, exchange, and Pauli interactions of the clusters with their surroundings.

For the two embedded clusters, state-average complete active space self-consistent field (SA-CASSCF) calculations were carried out. The CAS is formed by distributing 7 electrons in 19 active molecular orbitals, with main characters of Eu^{2+} 4f, 5d, and 5f orbitals. Test calculations indicated that the inclusion of the Eu^{2+} 6s orbital in the CAS is not important in the present calculations. We have studied all the 36 high-spin octet states in the 4f⁷ and 4f⁶5d¹ configurations, including the 4f⁷(⁸S) ground state and the excited states derived from 4f⁶5d¹ (⁸P, ⁸D, ⁸F, ⁸G, and ⁸H) terms. We have also studied the 35 lowest-energy spin sextet states, to evaluate the effect of these states on the energy levels of spin octet states *via* spin-orbit interaction. The molecular orbitals were optimized by minimizing the average energy of all the spin-octet (or sextet) states. Since no symmetry (i.e. *C*₁ site symmetry) is present for the Eu_{Sr1} or the Eu_{Sr2} site, these states will be arranged in order of increasing energy.

With the SA-CASSCF wavefunctions and the occupied and virtual orbitals, CASPT2 calculations were then carried out, where dynamic correlation effects of the Eu^{2+} 5s, 5p, 4f and 5d electrons and the O^{2-} 2s and 2p electrons were taken into account. Based on the CASSCF wavefunctions and CASPT2 energies, spin-orbit coupling was further taken into consideration by using a restricted active space state-interaction spin–orbit (RASSI-SO) method.⁸ These calculations were performed using the program MOLCAS.⁹ A [Kr] core relativistic effective core potential with the (14s10p10d8f3g)/[6s5p6d4f1g] Gaussian valence basis set was used for Eu,¹⁰ and a [He] core effective core potential with the (5s6p1d)/[2s4p1d] valence basis set was used for oxygen.¹¹ An extra basis set (11s8p)/[1s1p] has been used for the 11 Al atoms closest to the embedded clusters to improve the cluster-host orthogonality.

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	M = Sr1	$M = E u_{Sr1} \\$	M = Sr2	$M=Eu_{Sr2} \\$
Bond length (Å)				
M-O1	2.509	2.511	2.515	2.512
M-O2	2.533	2.538	2.522	2.529
M-O3	2.600	2.599	2.535	2.530
M–O4	2.614	2.615	2.615	2.620
M–O5	2.656	2.655	2.722	2.736
M-06	2.703	2.703	2.772	2.784
М-О7	3.109	3.109	3.014	3.010
M-08	3.572	3.567	3.207	3.206
M-09	3.624	3.623	3.560	3.560
Average bond length (Å)	2.880	2.880	2.832	2.829
Polyhedral volume (Å ³)	41.242	41.231	39.979	39.843
Distortion index D	0.128	0.128	0.100	0.102

Table S1 Calculated individual and average bond lengths from the dopant site (M) to the coordinating oxygen atoms, and the volumes and distortion indexes of the coordination polyhedra.

The distortion index is defined by $D = \frac{1}{n} \sum_{i=1}^{n} \frac{|d_i - d_{av}|}{d_{av}}$, where d_i is the bond length to the *i*th coordinating O atom and d_{av} is the average bond length.

Table S2 Calculated energy levels (cm⁻¹) for spin octet states in the $4f^{6}5d^{1}$ configuration of Eu²⁺ located at the Sr1 site of SrAl₂O₄. The numbers of the energy levels are 35 and 140 without and with spin-orbit coupling (SO), respectively. The $4f^{7}(^{8}S \text{ or } ^{8}S_{7/2})$ ground levels were aligned at the same energy of 0 cm⁻¹.

Wit	hout SO		With SO						
No.	Energy	No.	Energy	No.	Energy	No.	Energy	No.	Energy
1	27542	1	24964	36	30273	71	35403	106	40115
2	27748	2	25282	37	30364	72	35729	107	40533
3	27820	3	25558	38	30461	73	35906	108	40638
4	28403	4	25778	39	30589	74	36020	109	40703
5	28536	5	25861	40	30673	75	36081	110	40776
6	28745	6	26210	41	30852	76	36229	111	40790
7	28756	7	26442	42	31002	77	36502	112	40865
8	29610	8	26601	43	31084	78	36558	113	40916
9	29702	9	26695	44	31147	79	36677	114	41053
10	30046	10	26933	45	31332	80	36721	115	41204
11	30385	11	27206	46	31458	81	36806	116	41430
12	30972	12	27364	47	31523	82	36889	117	41539
13	31645	13	27463	48	31640	83	37047	118	41915
14	31759	14	27583	49	31750	84	37099	119	42103
15	34275	15	27750	50	32100	85	37178	120	42224
16	34498	16	27957	51	32141	86	37306	121	42351
17	35261	17	28073	52	32214	87	37553	122	42750
18	35777	18	28172	53	32515	88	37641	123	43052
19	35839	19	28299	54	32691	89	37701	124	43106
20	36108	20	28434	55	32762	90	37779	125	43180
21	36438	21	28620	56	32878	91	37891	126	43325
22	38000	22	28668	57	33023	92	38000	127	43476
23	38086	23	28753	58	33246	93	38060	128	43934
24	38723	24	28941	59	33329	94	38208	129	44211
25	38888	25	29046	60	33475	95	38412	130	44400
26	38892	26	29156	61	33643	96	38492	131	44449
27	39082	27	29283	62	33815	97	38644	132	44548
28	39309	28	29375	63	34108	98	38810	133	44584
29	42483	29	29564	64	34319	99	38921	134	44740
30	42688	30	29667	65	34435	100	39231	135	45284
31	43270	31	29778	66	34619	101	39409	136	45498
32	43367	32	29856	67	34898	102	39497	137	45778
33	43418	33	29954	68	35017	103	39576	138	46109
34	44607	34	30066	69	35189	104	39758	139	46448
35	44650	35	30199	70	35310	105	39847	140	46781

Table S3 Calculated energy levels (cm⁻¹) for spin octet states in the $4f^{6}5d^{1}$ configuration of Eu²⁺ located at the Sr2 site of SrAl₂O₄. The numbers of the energy levels are 35 and 140 without and with spin-orbit coupling (SO), respectively. The $4f^{7}(^{8}S \text{ or } ^{8}S_{7/2})$ ground levels were aligned at the same energy of 0 cm⁻¹.

Wit	hout SO		With SO						
No.	Energy	No	. Energy	No.	Energy	No.	Energy	No.	Energy
1	26231	1	23596	36	29836	71	34985	106	42580
2	26448	2	23917	37	29956	72	35208	107	42663
3	26503	3	24249	38	30208	73	35585	108	42765
4	26975	4	24505	39	30403	74	35724	109	42849
5	27033	5	24532	40	30534	75	35754	110	42915
6	27544	ϵ	25109	41	30790	76	35911	111	43090
7	27575	7	25242	42	30858	77	35982	112	43247
8	30103	8	25373	43	31012	78	36109	113	43348
9	30251	9	25489	44	31159	79	36742	114	43440
10	30785	10	25833	45	31425	80	36898	115	43685
11	31013	11	26196	46	31537	81	37166	116	43800
12	31237	12	26454	47	31619	82	37469	117	43895
13	31758	13	26493	48	31727	83	37813	118	44007
14	31829	14	26584	49	31854	84	38171	119	44121
15	33475	15	26637	50	31946	85	39127	120	44217
16	33686	16	27391	51	32169	86	39303	121	44314
17	34688	17	27430	52	32385	87	39513	122	44418
18	34750	18	27514	53	32554	88	39774	123	44543
19	34964	19	27667	54	32695	89	39917	124	44667
20	36203	20	27782	55	32751	90	40123	125	44780
21	36253	21	27874	56	32849	91	40372	126	44872
22	40910	22	27960	57	32947	92	40538	127	44964
23	41032	23	28323	58	33035	93	40720	128	45068
24	41262	24	28579	59	33158	94	40930	129	45439
25	41532	25	28774	60	33232	95	41087	130	45732
26	41973	26	28828	61	33354	96	41356	131	45963
27	42639	27	28915	62	33471	97	41486	132	46049
28	42948	28	28988	63	33575	98	41510	133	46276
29	43499	29	29039	64	33775	99	41637	134	46324
30	43503	30	29161	65	33857	100	41811	135	46642
31	44557	31	29265	66	34161	101	41951	136	47188
32	45302	32	29356	67	34265	102	42201	137	47506
33	45558	33	29471	68	34480	103	42297	138	47697
34	45792	34	29582	69	34551	104	42364	139	47847
35	46001	35	29700	70	34768	105	42529	140	47946



Figure S1. Calculated energy levels for spin octet and sextet states in the $4f^{6}5d^{1}$ configuration of Eu²⁺ located at the Sr1 and Sr2 sites of SrAl₂O₄. The numbers of the energy levels are 35 and 140 without and with spin-orbit coupling (SO), respectively. The $4f^{7}(^{8}S \text{ or } ^{8}S_{7/2})$ ground levels were aligned at the same energy of 0 cm⁻¹, and the energies of the lowest $4f^{6}5d^{1}$ level are indicated.



Figure S2. Schematic diagram for the calculated energies and relative oscillator strengths of the 4f \rightarrow 5d transitions from the 4f⁷(⁸S_{7/2}) ground level to the energy levels (including the effect of spin-sextets on the spin-octets) in the 4f⁶5d¹ configuration of Eu_{Sr1}²⁺ and Eu_{Sr2}²⁺ in SrAl₂O₄. The experimental excitation spectra adapted from ref. 9 are also included for comparison.