Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Controlling Europium Oxidation State in Diopside Through Flux Concentration

N. Górecka [a], T. Leśniewski [a], S. Mahlik [a], M. Łapiński [b], Y.-T. Tsai [c], A. Bielicka-Giełdoń [d] K. Szczodrowski *,[a]

[a]Institute of Experimental Physics, Faculty of Mathematics, Physics, and Informatics, University of Gdańsk, Wita Stwosza 57, 80-308 Gdańsk, Poland

[b]Institute of Nanotechnology and Materials Engineering, Gdansk University of Technology, Gabriela Narutowicza 11/12, 80-233 Gdansk, Poland

[c]Research Center for Applied Sciences, Academia Sinica, Taipei 11529, Taiwan

[d]Faculty of Chemistry, University of Gdańsk, Wita Stwosza 63, 80-308 Gdańsk, Poland

*Corresponding Author e-mail: karol.szczodrowski@ug.edu.pl

RESULTS

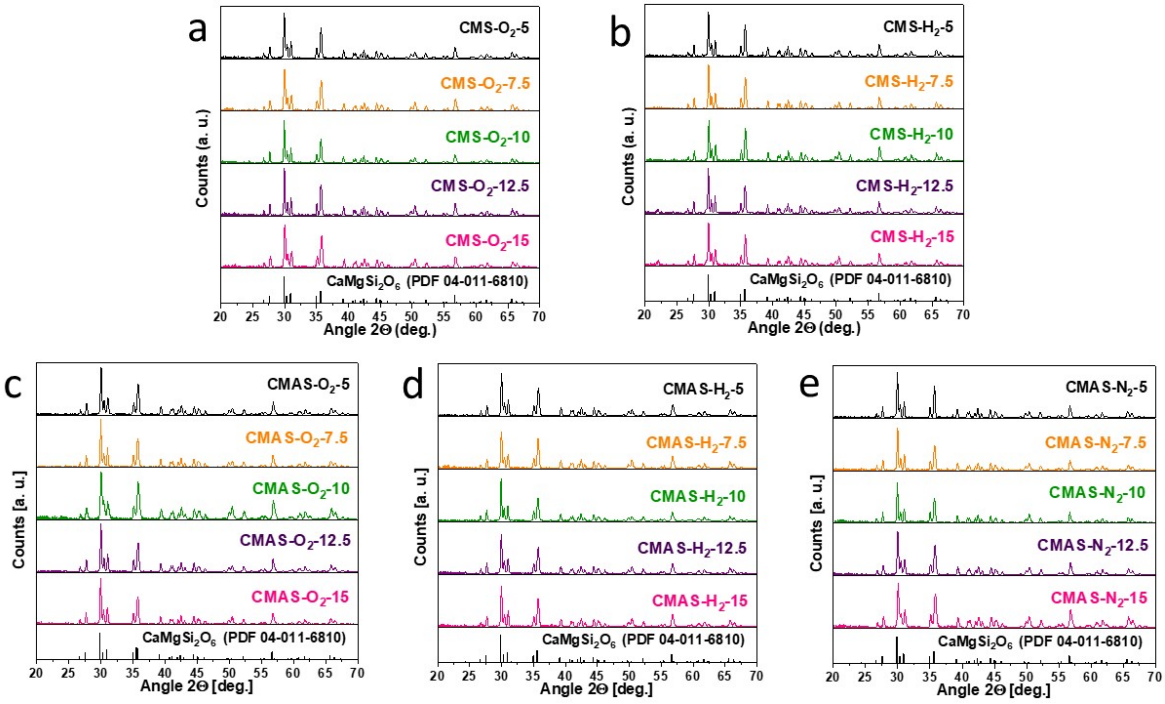

Figure S1. XRD patterns of samples: un-co-doped and obtained under (a) oxidative and (b) reductive atmosphere as well as co-doped with Al^{3+} and obtained under (c) oxidative, (d) reductive and (e) neutral atmosphere.

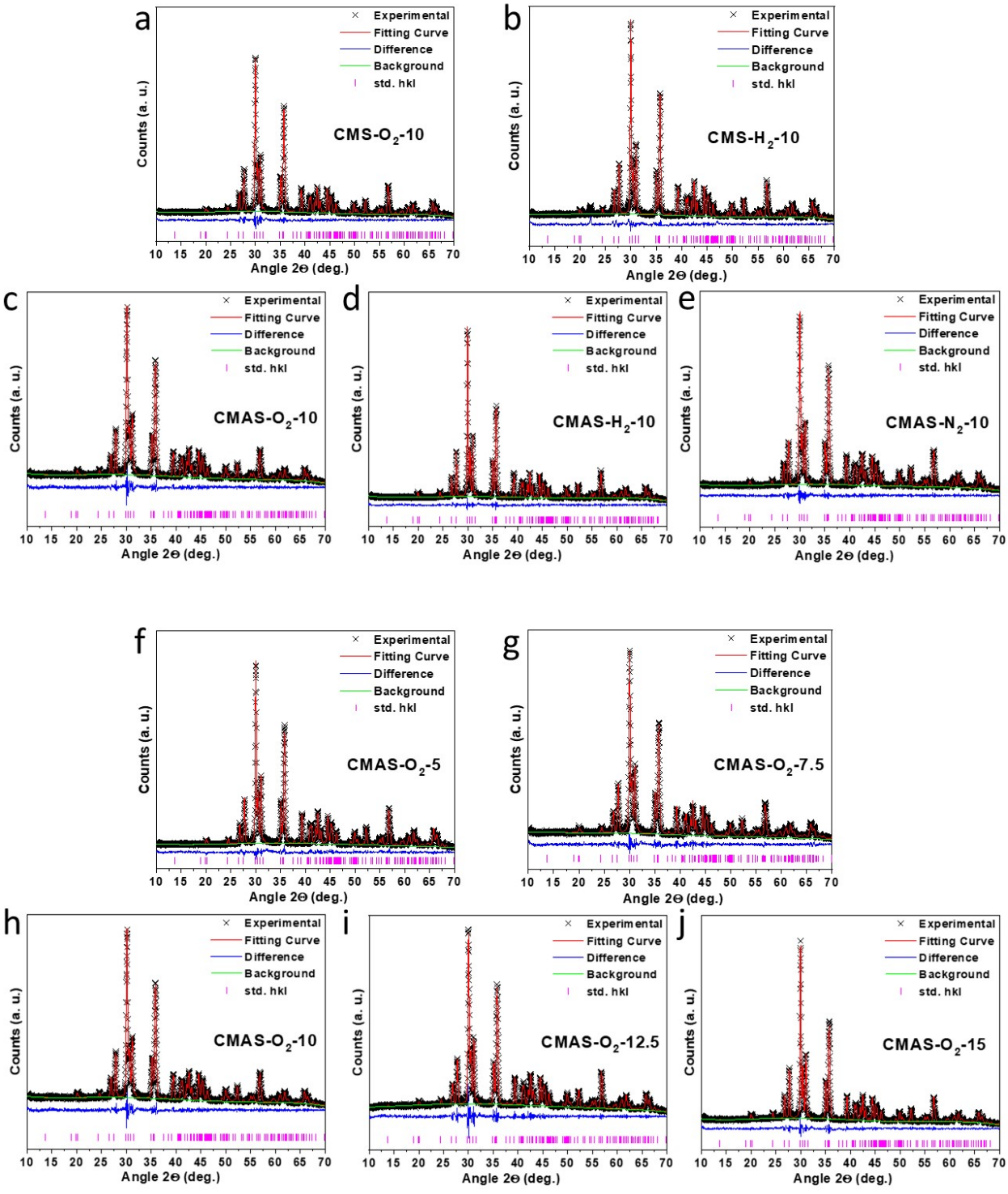

Figure S2. Rietveld refinement of high-quality XRD data collected for (a) CMS-O_2-10 sample, (b) CMS-H_2-10 sample, (c) CMAS-O_2-10 sample, (d) CMAS-H_2-10 sample, (e) CMAS-N_2-10 sample, (f) CMAS-O_2-5 sample, (g) CMAS-O_2-7.5 sample, (h) CMAS-O_2-10 sample, (i) CMAS-O_2-12.5 sample and (j) CMAS-O_2-15 sample.

The experimental and calculated data are represented by black crosses and solid red lines, respectively. The blue line denotes the difference between observed and computed data. The hkl reflection markers are referred to as the main phase as $CaMgSi_2O_6$ in the magenta vertical bars for clarity.

Table S1. Crystal lattice and the fitting parameters drawn out from the Rietveld refinement.

Sample	Length [Å]			Angle b [deg.]	Volume V [Å^3]	Rwp	Rp	GOF
	a	b	c					
CMS-O_2-10	9.7488	8.942	5.2512	105.895	440.26	5.80	4.47	1.37
CMS-H_2-10	9.7463	8.9436	5.2523	105.893	440.32	6.90	4.69	1.76
CMAS-O_2-10	9.7459	8.9444	5.2572	105.937	440.66	6.35	5.07	1.30
CMAS-H_2-10	9.7371	8.9328	5.2503	105.927	439.14	5.23	4.00	1.23
CMAS-N_2-10	9.7345	8.9352	5.2518	105.936	439.25	5.33	4.13	1.20
CMAS-O_2-5	9.7433	8.9418	5.2532	105.925	440.11	6.78	5.16	1.51
CMAS-O_2-7.5	9.7413	8.9387	5.2523	105.915	439.81	6.74	5.17	1.43
CMAS-O_2-10	9.7459	8.9444	5.2572	105.937	440.66	6.35	5.07	1.30
CMAS-O_2-12.5	9.7457	8.9393	5.2542	105.936	440.15	7.26	5.72	1.60
CMAS-O_2-15	9.7395	8.9338	5.2516	105.948	439.36	5.84	4.57	1.45

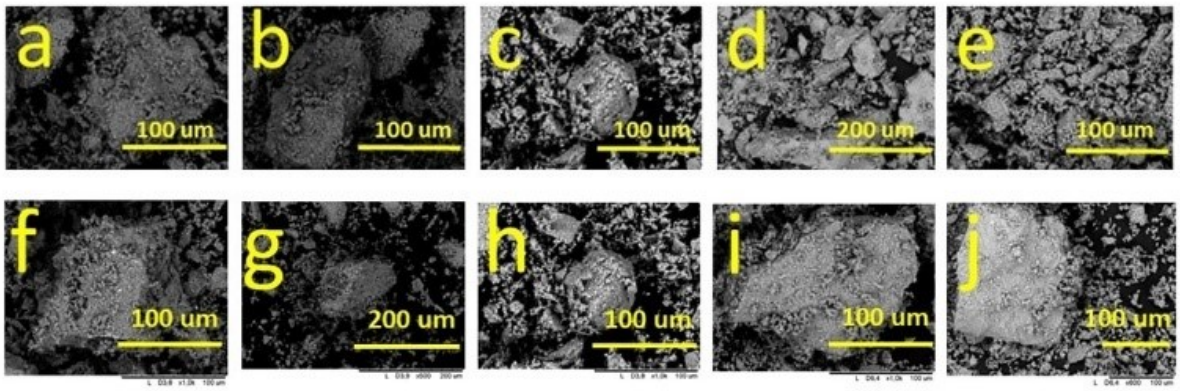

Figure S3. SEM micrographs for the samples: (a) CMS-O_2-10, (b) CMS-H_2-10, (c) CMAS-O_2-10, (d) CMAS-H_2-10, (e) CMAS-N_2-10, (f) CMAS-O_2-5, (g) CMAS-O_2-7.5, (h) CMAS-O_2-10, (i) CMAS-O_2-12.5, (j) CMAS-O_2-15.

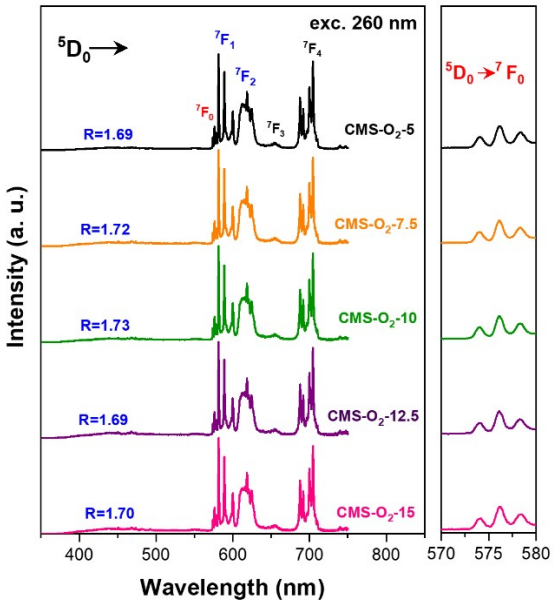

Figure S4. PL spectra collected at RT for materials of series CMS-O_2-z, excited at 260 nm. The structure of $^5D_0 \rightarrow ^7F_0$ emission is presented on the right.

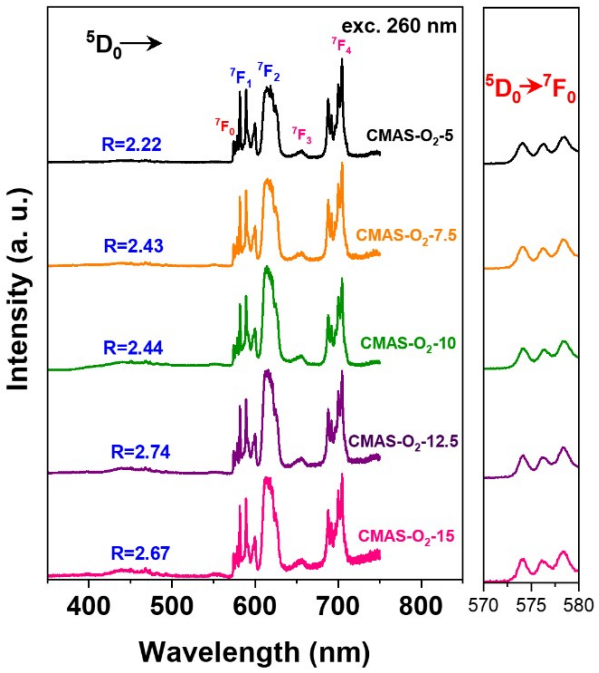

Figure S5. PL spectra collected at RT for materials of series CMAS-O_2-z, excited at 260 nm. The structure of $^5D_0 \rightarrow {}^7F_0$ emission is presented on the right.

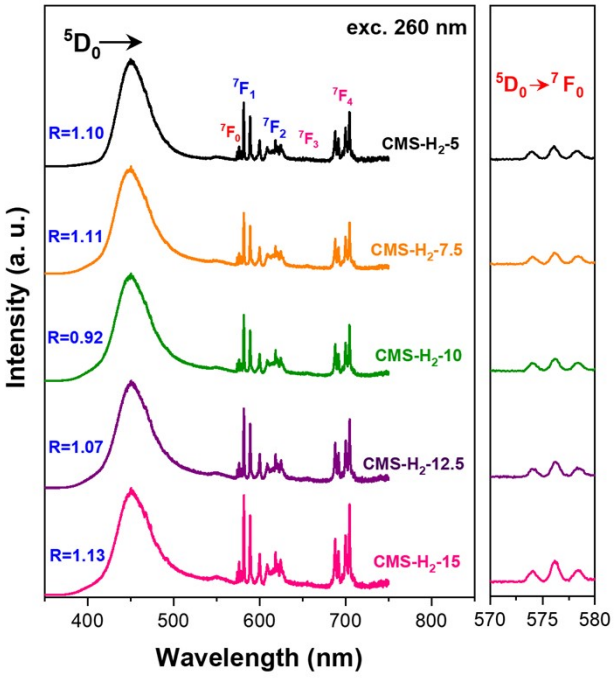

Figure S6. PL spectra collected at RT for materials of series CMS-H_2-z, excited at 260 nm. The structure of $^5D_0 \rightarrow {}^7F_0$ emission is presented on the right.

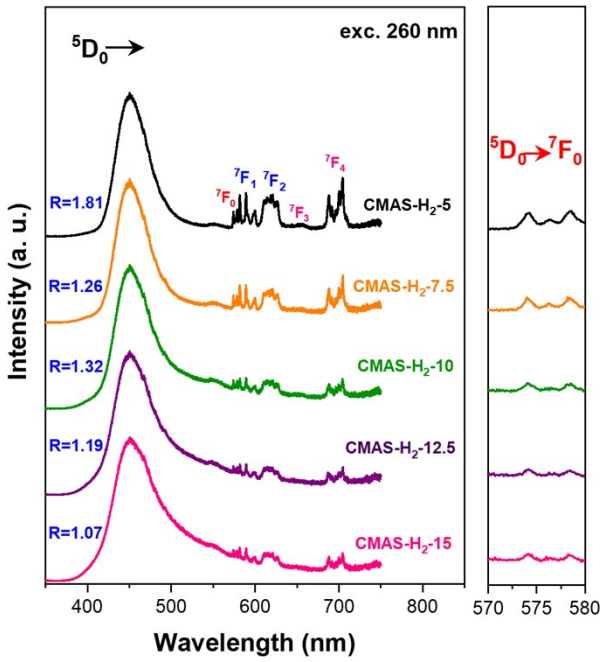

Figure S7. PL spectra collected at RT for materials of series CMAS-H_2-z, excited at 260 nm. The structure of $^5D_0 \rightarrow {}^7F_0$ emission is presented on the right.

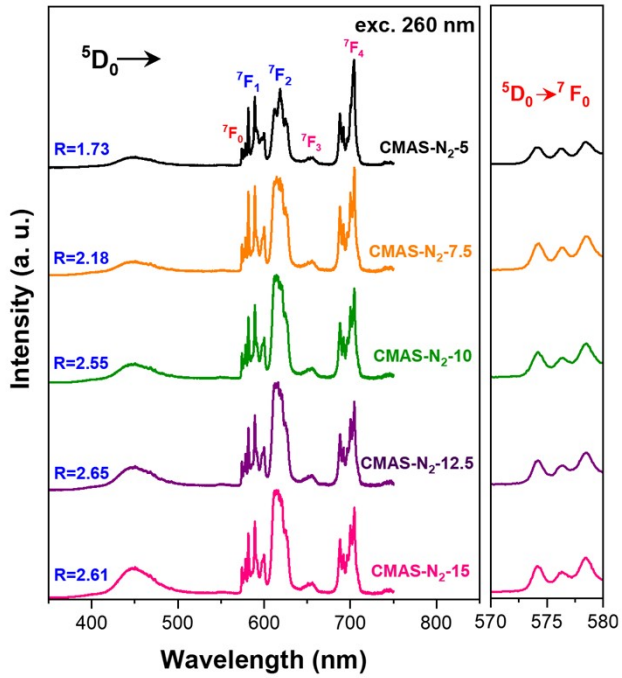

Figure S8. PL spectra collected at RT for materials of series CMAS-N_2-z, excited at 260 nm. The structure of $^5D_0 \rightarrow {}^7F_0$ emission is presented on the right.

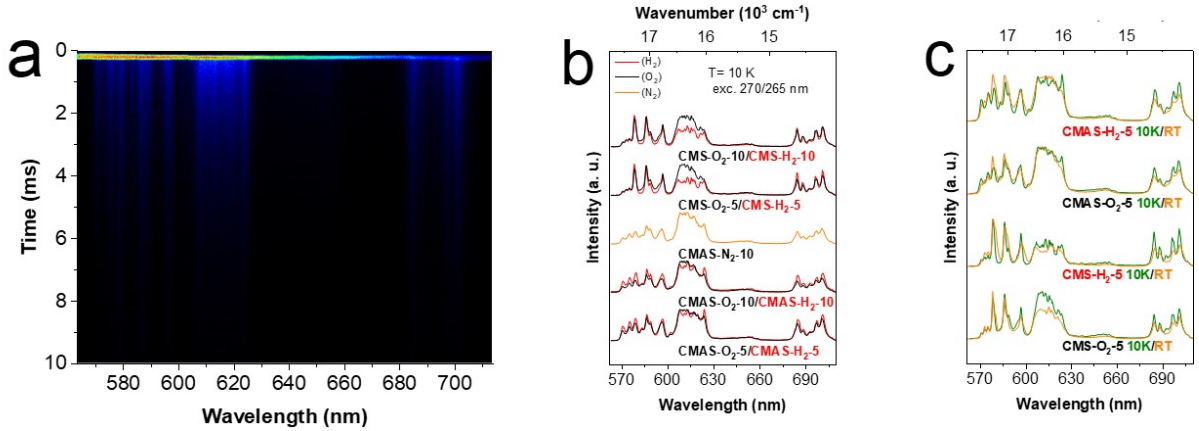

Figure S9. (a) Exemplary streak image of 10% Al modified sample (CMAS-H_2-10) measured in the 10 ms time range showing vast difference in decay time of Eu^{2+} luminescence (broad strip in the top of the graph) and Eu^{3+} luminescence (set of slowly decaying lines); (b) Time-resolved emission spectra of samples under O_2 , H_2 or N_2 atmosphere: CMS-O_2-z/CMS-H_2-z unmodified sample, CMAS-O_2-z/CMAS-H_2-z - 10% Al modified samples, CMAS-N_2-z - 10% Al modified sample, N_2 atmosphere; (c) Comparison of time-resolved emission spectra at low temperature (10K) and room temperature (300 K) for samples under O_2 or H_2 atmosphere: CMS-O_2-z/CMS-H_2-z - unmodified samples, CMAS-O_2-z/CMAS-H_2-z - 10% Al modified samples.