Electronic Supporting Information

Strong photoluminescence and sensing performance of nanosized Ca_{0.8}Ln_{0.1}Na_{0.1}WO₄ (Ln=Sm, Eu) compounds obtained by dry "top-down" grinding method

Germán E. Gomez,^{a*} Carlos A. López,^{a*} R. Lee Ayscue III,^b Karah E. Knope,^b M. del Rosario T. Deluigi,^c Griselda E. Narda^a

^a Instituto de Investigaciones en Tecnología Química (INTEQUI). Universidad Nacional de San Luis, CONICET, Almirante Brown 1455, 5700 San Luis, Argentina.

E-mails: gegomez@unsl.edu.ar, calopez@unsl.edu.ar

^b Georgetown University, Washington, D.C., USA.

^c Laboratorio de Microscopia Electrónica y Microanálisis (LABMEB), Facultad de Química, Bioquímica

y Farmacia, Universidad Nacional de San Luis, Ejército de los Andes 950, 5700 San Luis.

	CaWO ₄	Eu@CWO	Sm@CWO
a (Å)	5.2387(5)	5.2438(2)	5.2418(3)
<i>c</i> (Å)	11.378(1)	11.3799(5)	11.3817(8)
V (Å ³)	312.25(5)	312.91(2)	312.73(3)
A (8d) 0,1/4,5/8			
Occ (Ca/Ln)	1	0.804(8)/0.100(4)	0.81(1)/0.096(5)
B _{iso} (Å)	1.0(3)	1.5(5)	1.5(6)
W (8c) 0,1/4,1/8			
Occ	1	1	1
B _{iso} (Å)	0.8(1)	1.1(2)	0.9(2)
O(16f) x, y, z			
x	0.748(2)	0.755(3)	0.757(4)
y	0.412(3)	0.404(4)	0.413(5)
Z	0.049(1)	0.042(1)	0.042(2)
B _{iso} (Å)	2.5(5)	2.8(7)	3.9(9)
Occ	1	1	1
Reliability Factors			
Rp, Rwp, χ^2 , R _{Bragg}	10%, 15%, 5.6, 4.2%	12%, 19%, 1.4, 3.5%	16%, 24%, 1.6, 4.4%

Table S1: Main crystallographic parameter of crystalline samples of $CaWO_4$ and Eu and Sm doped phases (Eu@CWO and Sm@CWO).

Table S2: Cell and microstructural parameters of milled samples of Eu@CWO and Sm@CWO

.

	Eu@CWO	Sm@CWO
Cell parameters		
<i>a</i> (Å)	5.2455(9)	5.248(1)
c (Å)	11.373(2)	11.383(3)
V (Å ³)	312.9(1)	313.1(1)
Microstructural parameters		
Apparent size	17.51 nm	18.87 nm
Apparent strain	1.12 %	1.71 %
Reliability Factors		
$Rp, Rwp, \chi^2, R_{Bragg}$	14%, 18%, 1.1, 5.7%	14%, 19%, 1.1, 5.7%



Figure S1: SEM micrographs of CWO.



Figure S2: SEM micrographs of Eu@CWO before milling miniaturization.



Figure S3: SEM micrographs of Sm@CWO before milling miniaturization.



Figure S4: Excitation (black trace) and emission (blue trace) spectra of CWO.



Figure S5: Excitation (λ_{em} =616 nm) (black) and emission (red) (λ_{ex} =465 nm) spectra of Eu@CWO.



Figure S6: Emission spectra of Eu@CWO at λ_{ex} =395 and 535 nm.

				Eu@CWO				
	E	Excitation $\lambda_{exc}=39$	95 nm				Emission	
Label	λ (nm)	Energy (cm ⁻¹)	Transition		Label	λ (nm)	Energy (cm ⁻¹)	Transition
а	260-330	39063-30303	СТВ					
b	299	33445	${}^{5}I_{5}$, ${}^{5}H_{5}$ $\leftarrow {}^{7}F_{1}/ {}^{5}F_{5}$ $\leftarrow {}^{7}F_{0}$		А	418	23923	${}^{5}D_{3} \rightarrow {}^{7}F_{1}$
c	304	32895	${}^{5}F_{1} \leftarrow {}^{7}F_{1} / {}^{5}F_{2} \leftarrow {}^{7}F_{0}$		В	432	23148	${}^{5}D_{3} \rightarrow {}^{7}F_{2}$
d	319	31348	${}^{5}\mathrm{H}_{6}$ \leftarrow ${}^{7}\mathrm{F}_{0}$		С	446	22422	${}^{5}D_{3} \rightarrow {}^{7}F_{3}$
e	328	30488	${}^{5}\mathrm{H}_{7}$ \leftarrow ${}^{7}\mathrm{F}_{1}$		D	466	21459	${}^{5}D_{2} \rightarrow {}^{7}F_{0}$
f	362	27624	${}^{5}D_{4} \leftarrow {}^{7}F_{0}$		Е	470	21277	${}^{5}D_{2} \rightarrow {}^{7}F_{1}$
g	376	26596	${}^{5}G_{6} \leftarrow {}^{7}F_{0}$		F	488	20492	${}^{5}D_{2} \rightarrow {}^{7}F_{2}$
h	383	26110	⁵ G ₆ , ⁵ G ₅ , ⁵ G ₃ ← ⁷ F ₁		G	511	19569	${}^{5}D_{2} \rightarrow {}^{7}F_{3}$
i	395	25316	${}^{5}L_{6} \leftarrow {}^{7}F_{1}$		Н	527	18975	${}^{5}D_{1} \rightarrow {}^{7}F_{0}$
j	416	24038	${}^{5}D_{3} \leftarrow {}^{7}F_{1}$		Ι	537	18622	${}^{5}D_{1} \rightarrow {}^{7}F_{1}$
k	449	22272	${}^{5}D_{2} \leftarrow {}^{7}F_{0}$		J	556	17986	${}^{5}D_{1} \rightarrow {}^{7}F_{2}$
1	465	21505	${}^{5}D_{2} \leftarrow {}^{7}F_{0}$		K	580	17241	${}^{5}D_{0} \rightarrow {}^{7}F_{0}$
m	473	21142	${}^{5}D_{2} \leftarrow {}^{7}F_{1}$		L	592	16892	${}^{5}D_{0} \rightarrow {}^{7}F_{1}$
n	527	18975	${}^{5}D_{1} \leftarrow {}^{7}F_{0}$		М	616	16234	${}^{5}D_{0} \rightarrow {}^{7}F_{2}$
0	536	18657	${}^{5}D_{1} \leftarrow {}^{7}F_{0}$		Ν	655	15267	${}^{5}D_{0} \rightarrow {}^{7}F_{3}$
р	554	18051	${}^{5}D_{1} \leftarrow {}^{7}F_{0}$		0	702	14245	${}^{5}D_{0} \rightarrow {}^{7}F_{4}$
q	579	17271	${}^{5}D_{0} \leftarrow {}^{7}F_{0}$		Р	746	13405	${}^{5}D_{0} \rightarrow {}^{7}F_{5}$
r	591	16920	${}^{5}D_{0} \leftarrow {}^{7}F_{1}$		Q	792	12626	${}^{5}D_{0} \rightarrow {}^{7}F_{6}$
				Sm@CWO				
	E	Excitation					Emission	
Label	λ (nm)	Energy (cm ⁻¹)	Transition		Label	λ (nm)	Energy (cm ⁻¹)	Transition
a	260-330	39063-30303	CTB					10 (11
b	306	32680	${}^{4}\mathrm{P}_{5/2} \leftarrow {}^{4}\mathrm{H}_{15/2}$		А	564	17730	${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$
с	318	31447	${}^{4}P_{3/2} \leftarrow {}^{4}H_{15/2}$		В	608	16447	${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$
d	333	30030	${}^{4}G_{9/2} \leftarrow {}^{4}H_{15/2}$		С	646	15480	${}^4\text{G}_{5/2} {\longrightarrow} {}^6\text{H}_{9/2}$
e	346	28902	${}^{4}D_{7/2} \leftarrow {}^{4}H_{15/2}$		D	706	14164	${}^{4}G_{5/2} \rightarrow {}^{6}H_{11/2}$
f	363	27548	${}^{4}D_{5/2}, {}^{6}P_{5/2} {\leftarrow} {}^{4}H_{15/2}$					
g	377	26525	${}^{6}\mathrm{P}_{7/2} \leftarrow {}^{4}\mathrm{H}_{15/2}$					
h	392	25510	${}^{4}L_{15/2} \leftarrow {}^{4}H_{15/2}$					
i	405	24691	${}^{6}P_{3/2} \leftarrow {}^{4}H_{15/2}$					

 Table S3. Assignment of the 4f-4f transitions in the excitation and emission spectra of Eu@CWO and Sm@CWO nanoparticles.

j	420	23810	⁶ P _{5/2} , ⁴ P _{5/2} ← ⁴ H _{15/2}	
k	440	22727	${}^{4}G_{9/2}, {}^{4}M_{17/2} \leftarrow {}^{4}H_{15/2}$	
1	452	22124	⁴ I _{13/2} , ⁴ I _{11/2} ← ⁴ H _{15/2}	
m	464	21552	⁴ I _{13/2} , ⁴ I _{11/2} ← ⁴ H _{15/2}	
n	470	21277	${}^{4}I_{13/2}, {}^{4}I_{11/2} \leftarrow {}^{4}H_{15/2}$	
0	482	20747	⁴ I _{13/2} , ⁴ I _{11/2} ← ⁴ H _{15/2}	
р	490	20408	⁴ I _{13/2} , ⁴ I _{11/2} ← ⁴ H _{15/2}	
q	500	20000	${}^4G_{5/2} \leftarrow {}^4H_{15/2}$	
r	530	18868	${}^4F_{3/2} \leftarrow {}^4H_{15/2}$	
S	562	17794	${}^{4}F_{3/2} - {}^{4}H_{15/2}$	



Figure S7: Lifetime profile Eu@CWO (left) and Sm@CWO (right) with λ_{ex} of 395 and 405 nm respectively. The red and blue traces represent the best fitting profiles.