Electronic Supporting Information

Lanthanide-dependent photoluminescence and thin film fabrication of host CaWO₄ micro-materials for potential indoor plant growth applications

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Figure S1: SEM images of Tb@CWO particles.



Figure S2: SEM images of Eu,Tb@CWO particles.



Figure S3: EDS profiles for a) Eu@CWO, b) Tb@CWO and c) Eu,Tb@CWO





Figure S4: Observed (red points), calculated (black full line) and difference (bottom) Rietveld profiles for a) **CWO**, b) **Gd@CWO**, c) **Tb@CWO**, d) **Eu,Gd@CWO**, e) **Eu,Tb@CWO**,f) **Gd,Tb@CWO**and g) **Eu,Gd,Tb@CWO** at room temperature. Theoretical profile of pristine **CWO** phase (ICSD collection code: 060551)¹ (h).

ABO ₄	$Ca_{0.8}Eu_{0.05}Tb_{0.05}Na_{0.1}$	$Ca_{0.8}Eu_{0.05}Gd_{0.05}Na_{0.1}$	$Ca_{0.8}Tb_{0.05}Gd_{0.05}Na_{0.1}$	$Ca_{0.8}Eu_{0.033}Tb_{0.033}Gd_{0.033}Na_{0.1}\\$
a (Å)	5.2480(2)	5.2470(2)	5.2456(2)	5.2436(2)
<i>c</i> (Å)	11.3779(5)	11.3799(2)	11.3752(5)	11.3726(5)
V (Å ³)	313.36(2)	313.30(2)	313.0(2)	312.7(2)
A (8d) 0,1/4,5/8				
Occ (Ca/Ln)	0.820(4)/0.088(4)	0.808(4)/0.096(4)	0.828(4)/0.088(4)	0.772/0.108(5)
U ^{iso} (Ų)	0.009(2)	0.013(2)	0.009(2)	0.014(2)
W (8 <i>c</i>) 0,1/4,1/8				
Occ	1	1	1	1
U ^{iso} (Ų)	0.0095(5)	0.0095(5)	0.0095(6)	0.0096(5)
O (16ƒ) x,y,z				
X	0.762(2)	0.762(2)	0.760(2)	0.760(2)
Y	0.399(1)	0.400(2)	0.400(2)	0.401(2)
Z	0.0413(6)	0.0415(1)	0.0413(1)	0.0416(7)
U ^{iso} (Å ²)	0.019(4)	0.026(4)	0.018(4)	0.021(4)
Осс	1	1	1	1
Reliability Factors				
Rp, Rwp,	5.6%, 7.4%,	5.2%, 7.0%,	5.2%, 7.0%,	5.2%, 7.1%,
χ^2 , R _{Bragg}	0.6, 1.3%	0.5, 1.1%	0.5, 1.2%	0.5, 1.1%

Table S1: Main crystallographic parameter of crystalline samples of co-doped phases.



Figure S5: Comparison between isotropic (a) and anisotropic (b) models for Eu@CWO.

			Siz	e (nm)			Strain
							(%%)
sample	Formula	Apparent	[001]	[100]	[110]	[111]	
CWO	CaWO ₄	27(2)	24.5	28.5	29.5	28.3	7.23(1)
Eu@CWO	Ca _{0.8} Eu _{0.1} Na _{0.1} WO ₄	29(2)	30.0	29.7	30.5	29.1	25.81(2)
Gd@CWO	Ca _{0.8} Gd _{0.1} Na _{0.1} WO ₄	23(1)	22.4	23.5	23.7	23.2	18.21(2)
Tb@CWO	Ca _{0.8} Tb _{0.1} Na _{0.1} WO ₄	28(2)	29.5	28.0	30.2	28.6	28.70(5)
Eu,Gd@CWO	Ca _{0.8} Eu _{0.05} Gd _{0.05} Na _{0.1} WO ₄	25(1)	23.9	25.4	25.9	25.0	14.87(1)
Eu,Tb@CWO	Ca _{0.8} Eu _{0.05} Tb _{0.05} Na _{0.1} WO ₄	29(2)	30.7	28.6	30.0	29.0	26.50(1)
Tb,Gd@CWO	Ca _{0.8} Gd _{0.05} Tb _{0.05} Na _{0.1} WO ₄	23(1)	22.7	23.4	24.0	23.0	16.61(3)
Eu,Gd,Tb@CWO	$Ca_{0.8}Eu_{0.03}Gd_{0.03}Tb_{0.03}Na_{0.1}WO_{4}$	27(1)	25.7	29.0	27.9	27.1	15.31(2)

Table S2: Main Microstructural parameters.



Figure S6: Excitation (λ_{em} = 470 nm) and emission spectra (λ_{exc} = 340 nm) of CWO matrix.

Table S3. Assignment of the 4f-4f transitions in the excitation and emission spectra of all the compounds.

				cwo				
	Excitation 2	λ _{em} =470 nm			Emiss	ionλ _{exc} =:	340 nm	
Label	λ (nm)	Energy (cm ⁻¹)	Transition		Label	λ (nm)	Energy (cm ⁻¹)	Transition
а	340	29412	СТВ		A	470	21277	O ²⁻ ligandto W ⁶⁺
				Gd@CWO				
Excitation λem	=470 nm				Emiss	ionλ _{exc} =:	380 nm	
Excitation λ _{em} Label	<mark>=470 nm</mark> λ (nm)	Energy (cm ⁻¹)	Transition		Emiss Label	ionλ _{exc} =: λ (nm)	380 nm Energy (cm ⁻¹)	Transition
Excitation λ _{em} Label	=470 nm <u>λ (nm)</u> 380	Energy (cm ⁻¹) 26316	Transition CTB		Emiss Label A	<mark>ionλ_{exc}=: λ (nm)</mark> 470	380 nm Energy (cm ⁻¹) 21277	Transition O ²⁻ ligandto W ⁶⁺
Excitation λ _{em} Label a	=470 nm <u>λ (nm)</u> 380	Energy (cm ⁻¹) 26316	Transition CTB	Eu@CWO	Emiss Label A	ionλ _{exc} =3 <u>λ (nm)</u> 470	380 nm Energy (cm ⁻¹) 21277	Transition O ²⁻ ligandto W ⁶⁺
Excitation λem	=470 nm λ (nm) 380 =615 nm	Energy (cm ⁻¹) 26316	Transition CTB	Eu@CWO	Emiss Label A Emiss	ionλ _{exc} =: <u>λ (nm)</u> 470 ionλ _{exc} =4	380 nm Energy (cm ⁻¹) 21277 463 nm	Transition O ²⁻ ligandto W ⁶⁺

а	276	36232	СТВ		Α	511	19569	${}^{5}D_{2} {\rightarrow}^{7}F_{3}$
b	301	33223	${}^{5}I_{5}, {}^{5}H_{5} \leftarrow {}^{7}F_{1} / {}^{5}F_{5} \leftarrow {}^{7}F_{0}$		в	521	19194	${}^{5}D_{1} \rightarrow {}^{7}F_{0}$
с	317	31546	⁵ H ₆ ← ⁷ F₀		С	537	18622	$^{5}D_{1}{\rightarrow}^{7}F_{1}$
d	360	27778	⁵ D₄← ⁷ F₀		D	555	18018	$^{5}D_{1}{\rightarrow}^{7}F_{2}$
е	375	26667	⁵ G ₆ ← ⁷ F₀		Е	579	17271	$^{5}\text{D}_{0} {\rightarrow}^{7}\text{F}_{0}$
f	380	26316	⁵ G ₆ , ⁵ G ₅ , ⁵ G ₃ ← ⁷ F ₁		F	591	16920	$^{5}\text{D}_{0} {\rightarrow}^{7}\text{F}_{1}$
g	393	25445	${}^{5}L_{6} \leftarrow {}^{7}F_{1}$		G	615	16260	$^{5}\text{D}_{0} {\rightarrow}^{7}\text{F}_{2}$
h	414	24155	⁵ D ₃ ← ⁷ F ₁		н	654	15291	$^{5}\text{D}_{0} {\rightarrow}^{7}\text{F}_{3}$
i	463	21598	⁵ D ₂ ← ⁷ F ₀		Т	702	14245	$^{5}D_{0}{\rightarrow}^{7}F_{4}$
j	471	21231	⁵ D ₂ ← ⁷ F ₁		J	746	13405	${}^{5}D_{0} \rightarrow {}^{7}F_{5}$
				Tb@CWO				
Excitation λ _{em} =	=544 nm				Emiss	ion λ _{exc} =	360 nm	
Excitation λ _{em} = Label	= <mark>544 nm</mark> λ (nm)	Energy (cm ⁻¹)	Transition		Emiss Label	i <mark>on λ_{exc}=</mark> λ (nm)	<mark>360 nm</mark> Energy (cm⁻¹)	Transition
Excitation λ _{em} = Label	=544 nm <u>λ (nm)</u> 261	Energy (cm ⁻¹) 38314	Transition CTB		Emiss Label A	<mark>ion λ_{exc}=</mark> <u>λ (nm)</u> 488	<mark>360 nm Energy (cm⁻¹)</mark> 20492	Transition ⁵ D₄→ ⁷ F ₆
<u>Excitation λem</u> = Label a b	-544 nm <u>λ (nm)</u> 261 350	Energy (cm ⁻¹) 38314 28571	Transition CTB ⁵L9← ⁷ F6		Emiss Label A B	<mark>ion λ_{exc}= <u>λ (nm)</u> 488 544</mark>	360 nm Energy (cm ⁻¹) 20492 18382	Transition ⁵ D₄→ ⁷ F ₆ ⁵ D₄→ ⁷ F₅
Excitation λ _{em} = Label a b c	-544 nm <u>λ (nm)</u> 261 350 360	Energy (cm ⁻¹) 38314 28571 27778	Transition CTB ⁵ L9← ⁷ F6 ⁵ G₅← ⁷ F6		Emiss Label A B C	ion λ _{exc} = <u>λ (nm)</u> 488 544 587	360 nm Energy (cm ⁻¹) 20492 18382 17036	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$
Excitation λ _{em} = Label a b c d	-544 nm λ (nm) 261 350 360 367	Energy (cm ⁻¹) 38314 28571 27778 27248	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$		Emiss Label A B C D	<mark>ion λ_{exc}=</mark> <u>λ (nm)</u> 488 544 587 621	360 nm Energy (cm ⁻¹) 20492 18382 17036 16103	$\begin{tabular}{c} \hline Transition \\ $^5D_4 $\rightarrow 7F_6 \\ $^5D_4 $\rightarrow 7F_5 \\ $^5D_4 $\rightarrow 7F_4 \\ $^5D_4 $\rightarrow 7F_3 \end{tabular}$
Excitation λ _{em} = Label a b c d e	- 544 nm λ (nm) 261 350 360 367 376	Energy (cm ⁻¹) 38314 28571 27778 27248 26596	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$		Emiss Label A B C D	ion λ _{exc} = <u>λ (nm)</u> 488 544 587 621	360 nm Energy (cm ⁻¹) 20492 18382 17036 16103	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$

				Eu,Gd@CWO				
Excitation λ _{em}	-=615 nm				Emiss	ionλ _{exc} =4	463 nm	
Label	λ (nm)	Energy (cm ⁻¹)	Transition	_	Label	λ (nm)	Energy (cm ⁻¹)	Transition
а	279	35842	СТВ		Α	591	16920	$^{5}\text{D}_{0} {\rightarrow}^{7}\text{F}_{1}$
b	297	33670	⁵ I ₅ , ⁵ H ₅ ← ⁷ F ₁ / ⁵ F ₅ ← ⁷ F ₀		в	615	16260	$^5\text{D}_0 {\rightarrow} ^7\text{F}_2$
с	317	31546	⁵ H ₆ ← ⁷ F₀		с	654	15291	$^5\text{D}_0 {\rightarrow} ^7\text{F}_3$
d	360	27778	⁵ D₄← ⁷ F₀		D	702	14245	$^5\text{D}_0 {\rightarrow} ^7\text{F}_4$
е	375	26667	⁵ G ₆ ← ⁷ F₀					
f	380	26316	⁵ G ₆ , ⁵ G ₅ , ⁵ G ₃ ← ⁷ F ₁					
g	393	25445	${}^{5}L_{6} \leftarrow {}^{7}F_{1}$					
h	414	24155	⁵ D ₃ ← ⁷ F ₁					
i	463	21598	⁵ D₂← ⁷ F₀					
i	471	21231	⁵ D₂← ⁷ F₁					
				Tb,Gd@CWO				

Excitation λ _{em}	=544 nm				Emiss	ion λ _{exc} =	263 nm	
Label	λ (nm)	Energy (cm ⁻¹)	Transition		Label	λ (nm)	Energy (cm ⁻¹)	Transition
а	263	38023	СТВ		Α	488	20492	${}^{5}\text{D}_{4} \rightarrow {}^{7}\text{F}_{6}$
b	283	35336	⁵ I ₈ ← ⁷ F ₆		в	544	18382	$^5\text{D}_4 {\rightarrow} ^7\text{F}_5$
с	302	33113	⁵ H ₆ ← ⁷ F ₆		с	587	17036	$^{5}\text{D}_{4} {\rightarrow} ^{7}\text{F}_{4}$
d	317	31546	⁵ H ₆ , ⁵ D ₀ ← ⁷ F ₆		D	621	16103	$^5\text{D}_4 {\rightarrow} ^7\text{F}_3$
е	336	29762	⁵ L ₈ , ⁵ L ₇ ← ⁷ F ₆					
f	357	28011	⁵ G₅← ⁷ F ₆					
g	367	27248	⁵ L ₁₀ ← ⁷ F ₆					
h	376	26596	⁵ G ₆ ← ⁷ F ₆					
				Eu,Tb@CWO				
Excitation λ _{em}	=615 nm				Emiss	ionλ _{exc} =4	463 nm	
Label	λ (nm)	Energy (cm ⁻¹)	Transition		Label	λ (nm)	Energy (cm ⁻¹)	Transition
а	260	38462	СТВ		Α	488	20492	${}^{5}D_{4}{ ightarrow}^{7}F_{6}\ (Tb^{3+})$
b	317	31546	⁵ H ₆ ← ⁷ F ₀ (Eu ³⁺)		в	544	18382	${}^5\text{D}_4{\rightarrow}{}^7\text{F}_5 \text{ (Tb}^{3+}\text{)}$
с	338	29586	$(Tb^{3+}) {}^{5}L_{8}, {}^{5}L_{7} \leftarrow {}^{7}F_{6}$		С	591	16920	${}^{5}D_{0}{\rightarrow}^{7}F_{1}$ (Eu ³⁺)
d	350	28571	⁵ D₄← ⁷ F₀ (Eu ³⁺)		D	615	16260	${}^{5}D_{0} {\rightarrow} {}^{7}F_{2}$ (Eu ³⁺)
е	360	27778	⁵ D₄← ⁷ F₀ (Eu ³⁺)		Е	654	15291	${}^{5}D_{0}{\rightarrow}^{7}F_{3}$ (Eu ³⁺)
f	370	27027	⁵ G ₆ ← ⁷ F₀ (Eu ³⁺)		F	701	14265	${}^{5}D_{0}{\rightarrow}^{7}F_{4}$ (Eu ³⁺)
g	377	26525	⁵ G ₆ , ⁵ G ₅ , ⁵ G ₃ ← ⁷ F ₁ (Eu ³⁺)					

				Eu,Tb,Gd@CWO				
Excitation λer	_m =615 nm				Emiss	ionλ _{exc} =4	463 nm	
Label	λ (nm)	Energy (cm ⁻¹)	Transition		Label	λ (nm)	Energy (cm ⁻¹)	Transition
а	273	36630	СТВ		Α	488	20492	${}^{5}\text{D}_{4} {\rightarrow} {}^{7}\text{F}_{6} \text{ (Tb}^{3+}\text{)}$
b	297	33670	${}^{5}I_{5}, {}^{5}H_{5} \leftarrow {}^{7}F_{1} / {}^{5}F_{5} \leftarrow {}^{7}F_{0} (Eu^{3+})$		в	544	18382	${}^{5}D_{4}{ ightarrow}{}^{7}F_{5}\ (Tb^{3^{+}})$
с	302	33113	⁵ H ₆ ← ⁷ F ₆ (Tb ³⁺)		с	591	16920	${}^{5}D_{0}{\rightarrow}^{7}F_{1}$ (Eu ³⁺)
d	317	31546	⁵ H ₆ ← ⁷ F₀ (Eu ³⁺)		D	615	16260	${}^{5}\text{D}_{0}{\rightarrow}^{7}\text{F}_{2}$ (Eu $^{3+}$)
е	360	27778	⁵ D₄← ⁷ F₀ (Eu ³⁺)		Е	654	15291	${}^{5}D_{0}{\rightarrow}^{7}F_{3}\ (Eu^{3^{+}})$
f	375	26667	⁵ G ₆ ← ⁷ F₀ (Eu ³⁺)		F	702	14245	${}^{5}D_{0}{\rightarrow}^{7}F_{4}\ (Eu^{3^{+}})$
g	380	26316	${}^{5}G_{6}, {}^{5}G_{5}, {}^{5}G_{3} \leftarrow {}^{7}F_{1} (Eu^{3+})$					
h	393	25445	⁵ L ₆ ← ⁷ F ₁ (Eu ³⁺)					
i	414	24155	⁵ D ₃ ← ⁷ F ₁ (Eu ³⁺)					
j	463	21598	⁵ D ₂ ← ⁷ F ₀ (Eu ³⁺)					





Figure S7: Decay profiles of the studied compounds (black dots) and the corresponding monoexponential fitting (red or green traces) for a) **Eu@CWO**, b) **Tb@CWO**, c) **Eu,Tb@CWO**, d) **Eu,Gd@CWO**,e) **Tb,Gd@CWO** and f) **Eu,Tb,Gd@CWO**

 Table S4. Assignment of the 4f-4f transitions in emission spectra of the selected films.

Eu@CWO - Film Emission λ _{exc} = 277 nm						
Label	λ (nm)	Energy (cm ⁻¹)	Transition			
Α	591	16920	$^5\text{D}_0 {\rightarrow} ^7\text{F}_1$			
в	614	16287	$^5\text{D}_0\!\!\rightarrow^7\!\!F_2$			
с	653	15314	$^5\text{D}_0 {\rightarrow} ^7\text{F}_3$			

Eu,Gd@CWO - Film Emission λ _{exc} = 277 nm					
Label	λ (nm)	Energy (cm ⁻¹)	Transition		
Α	592	16892	$^{5}\text{D}_{0}{\rightarrow}^{7}\text{F}_{1}$		
В	614	16287	$^5\text{D}_0 {\rightarrow} ^7\text{F}_2$		

Eu,Tb@CWO - Film Emission λεχς=260 nm					
Label	λ (nm)	Energy (cm ⁻¹)	Transition		
Α	545	18349	${}^5\text{D}_4 {\rightarrow} {}^7\text{F}_5 \text{ (Tb}^{3+}\text{)}$		
В	591	16920	${}^{5}D_{0}{\rightarrow}{}^{7}F_{1}$ (Eu ³⁺)		
С	614	16287	${}^{5}\text{D}_{0}{\rightarrow}{}^{7}\text{F}_{2}$ (Eu ³⁺)		

Eu,Tb,Gd@CWO - Film Emissionλ _{exc} = 261 nm						
Label λ (nm) Energy (cm ⁻¹) Transition						

Α	488	20492	${}^{5}D_{4} \rightarrow {}^{7}F_{6} (Tb^{3+})$
В	545	18349	${}^{5}\text{D}_{4}{\rightarrow}^{7}\text{F}_{5}$ (Tb $^{3+}$)
С	590	16949	${}^{5}D_{0} {\rightarrow} {}^{7}F_{1}$ (Eu $^{3+}$)
D	614	16287	${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (Eu ³⁺)

¹ R. M. Hazen, L. W. Finger, and J. W. E. Mariathasan, "High pressure crystal chemistry of Scheelite-type tungstates and molybdates", J. Phys. Chem. Sol., 1985, 46, 253 - 263.