Electronic Supplementary Information for

Structural investigation of the *A*-site vacancy in Scheelites and the luminescence behaviors of two continuous solid solutions $A_{1-1.5x}Eu_x\square_{0.5x}WO_4$ and $A_{0.64-0.5y}Eu_{0.24}Li_y\square_{0.12-0.5y}WO_4$ (*A* = Ca, Sr; □ = vacancy)

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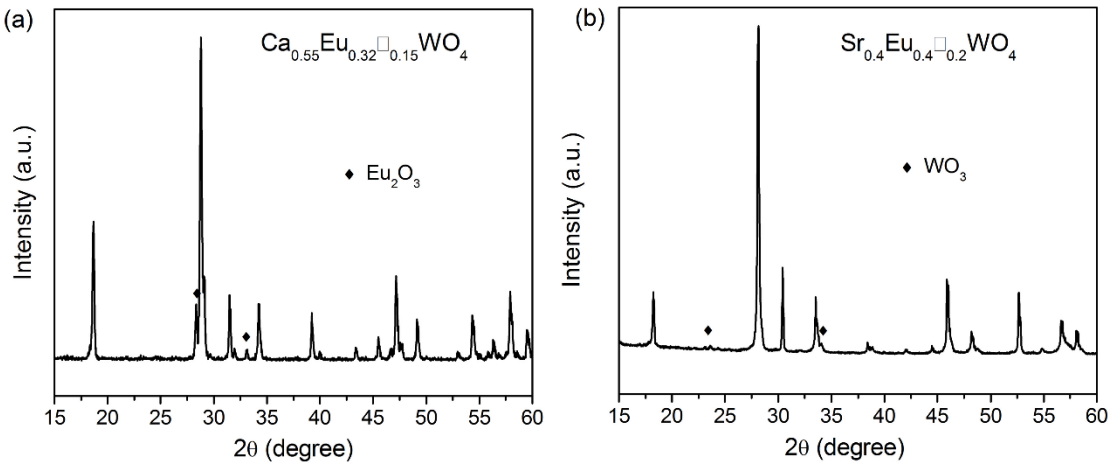


Fig. S1 XRD patterns for "$Ca_{0.55}Eu_{0.32}\square_{0.15}WO_4$" and "$Sr_{0.4}Eu_{0.4}\square_{0.2}WO_4$" samples prepared by high temperature solid state reactions. Other than the major phase of Scheelite, minor impurity peaks appear as marked in above figures, either belong to Eu_2O_3 or WO_3. There supposed to be other impurities, however, probably their diffraction peaks are overlapped with the major phase, it is hard to identify all of them. Nevertheless, our experiments show that the assumed compositions "$Ca_{0.55}Eu_{0.32}\square_{0.15}WO_4$" and "$Sr_{0.4}Eu_{0.4}\square_{0.2}WO_4$" cannot be annealed to be phase-pure.

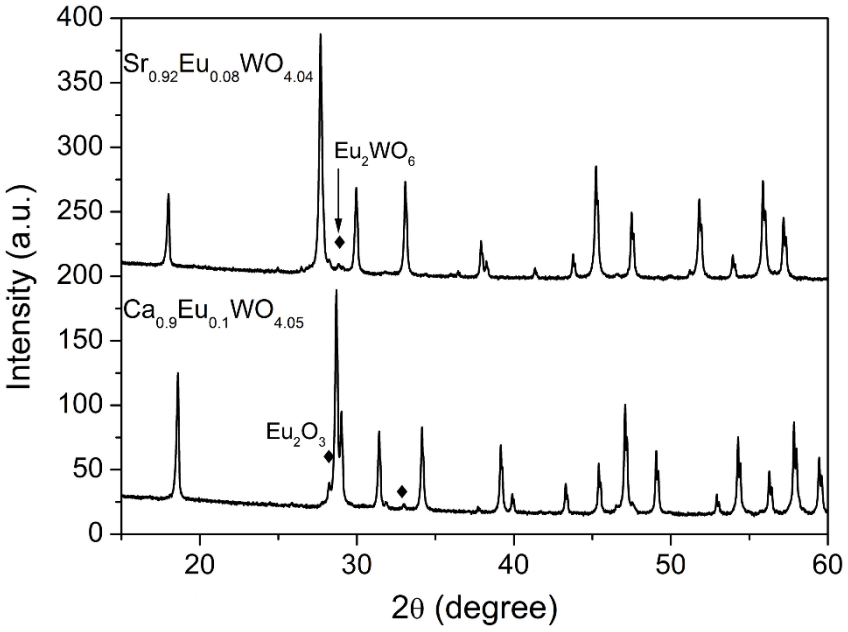


Fig. S2 XRD patterns of $Sr_{0.92}Eu_{0.08}WO_{4.04}$ and $Ca_{0.90}Eu_{0.10}WO_{4.05}$. The dark diamond in the figure represents the diffraction peaks of the impurity phases.

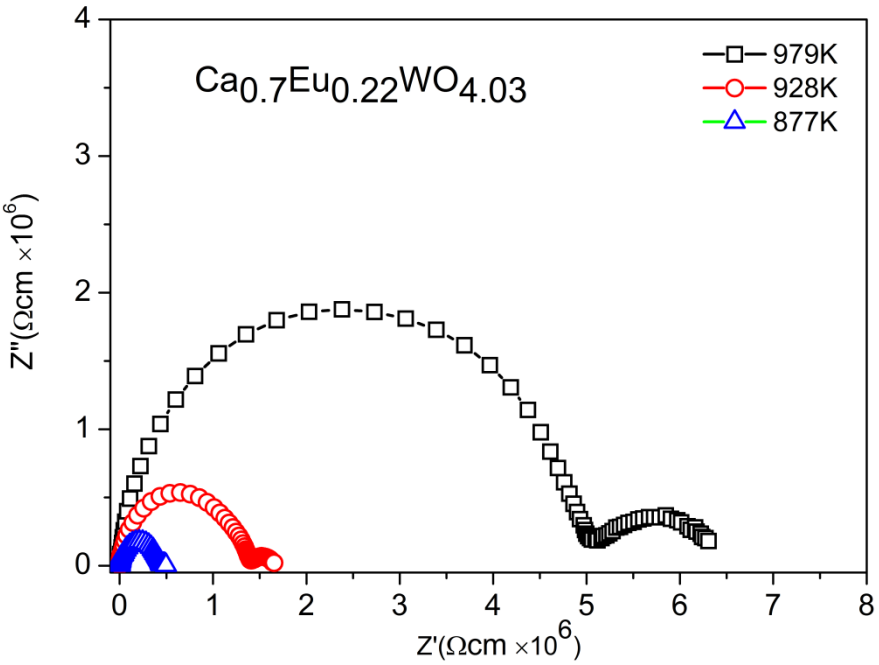
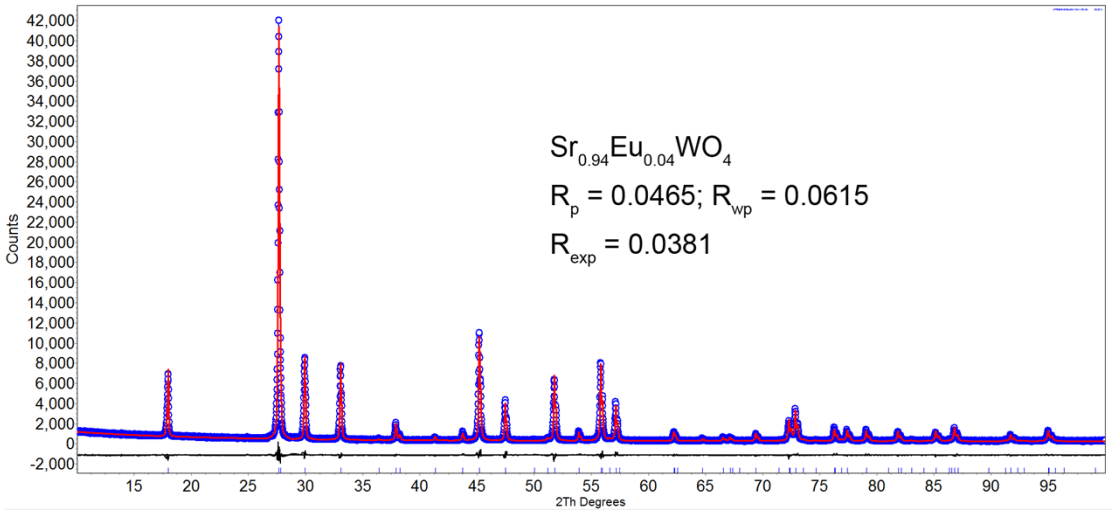
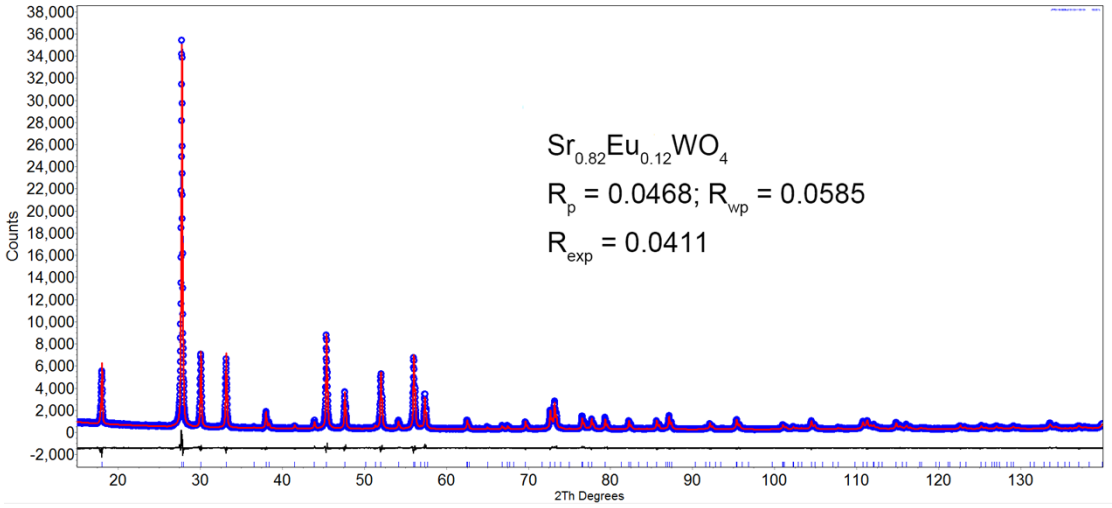


Fig. S3 Complex AC impedance spectra at 600, 650 and 705 °C, which comprise one broad and one narrow semi-circles. The broad and narrow semi-circle assign to the bulk and grain boundary contribution, respectively, and no electrode response or ionic conductivity was observed.




Counts
2Th Degrees
$Sr_{0.82}Eu_{0.12}WO_4$
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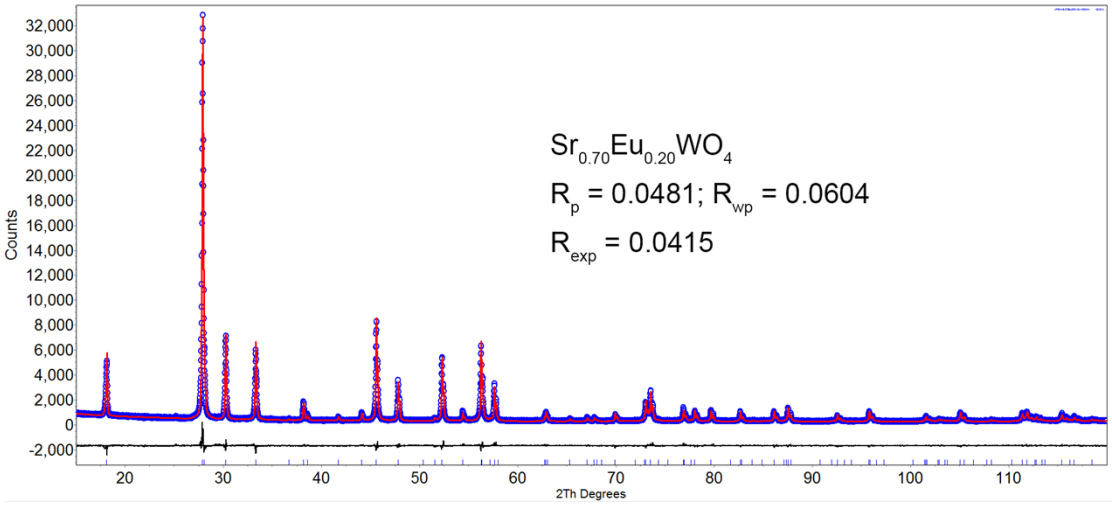
R_{exp} = 0.0411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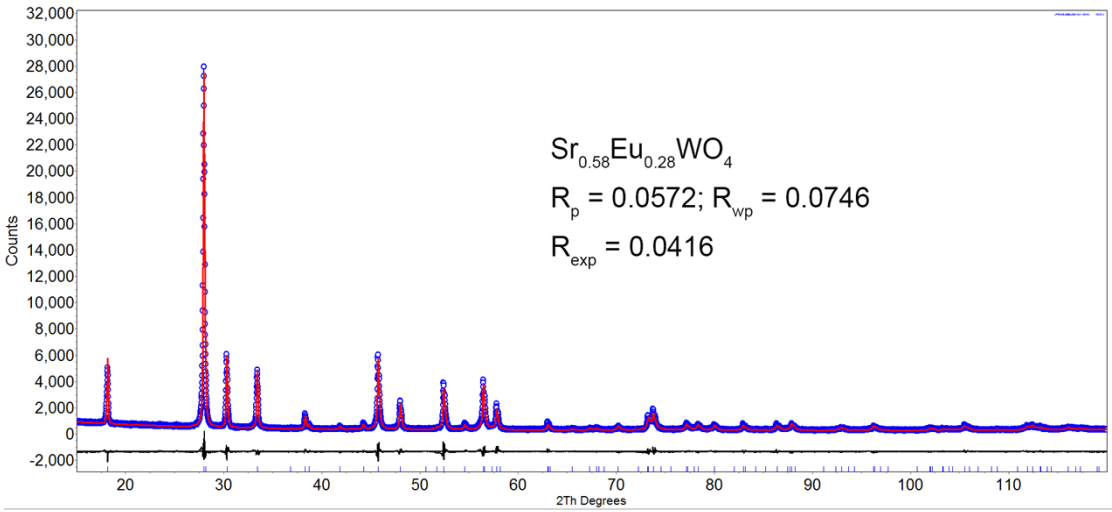
$Sr_{0.70}Eu_{0.20}WO_4$
R_p = 0.0481; R_{wp} = 0.0604
R_{exp} = 0.0415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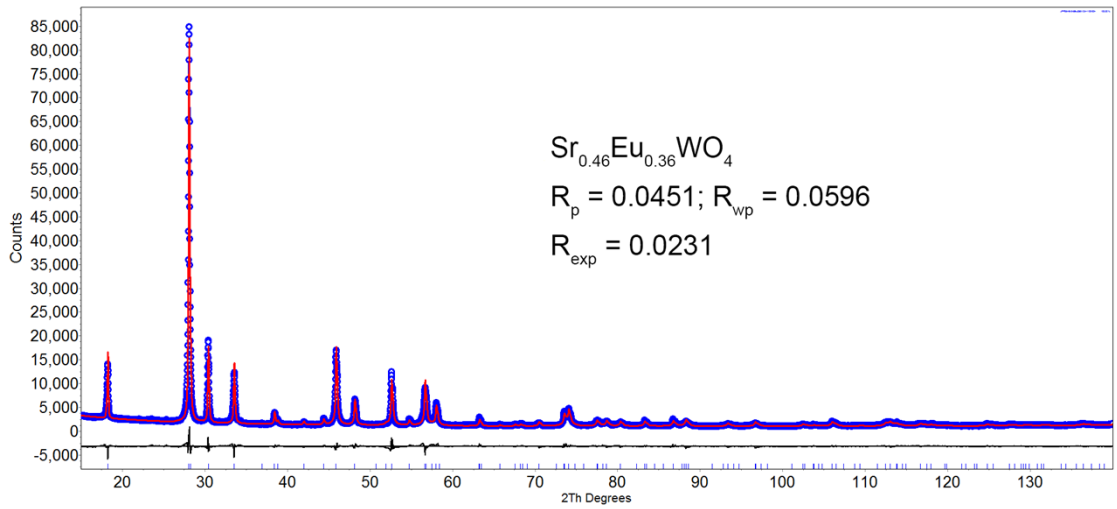
$Sr_{0.58}Eu_{0.28}WO_4$
R_p = 0.0572; R_{wp} = 0.0746
R_{exp} = 0.0416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Rp = 0.0451; Rwp = 0.0596
Rexp = 0.0231
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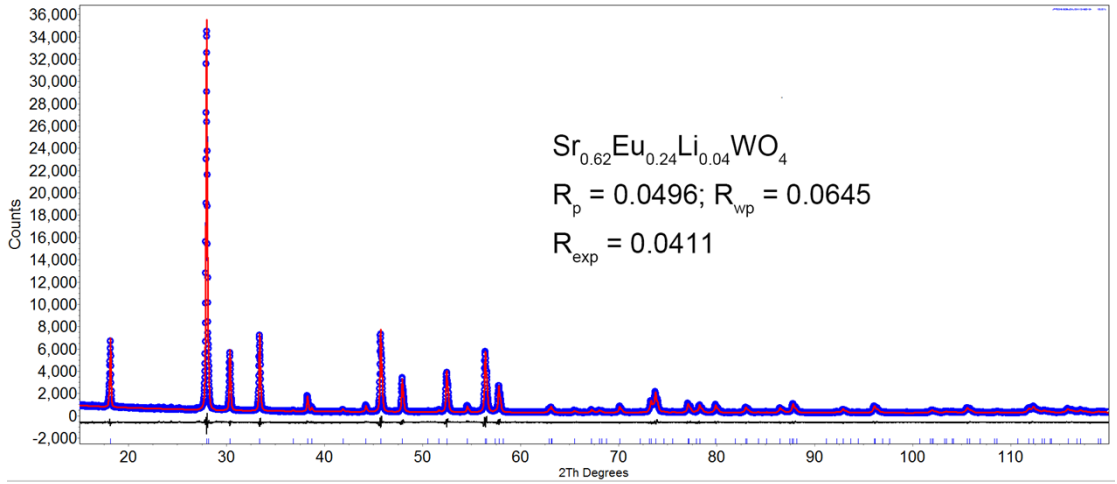
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Rp = 0.0496; Rwp = 0.0645
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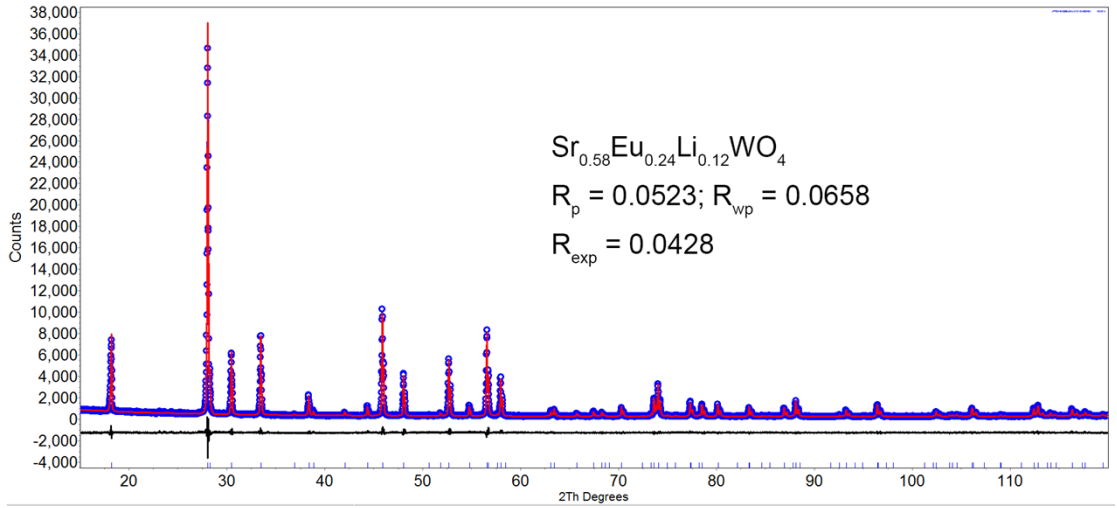
Sr0.58Eu0.24Li0.12WO4
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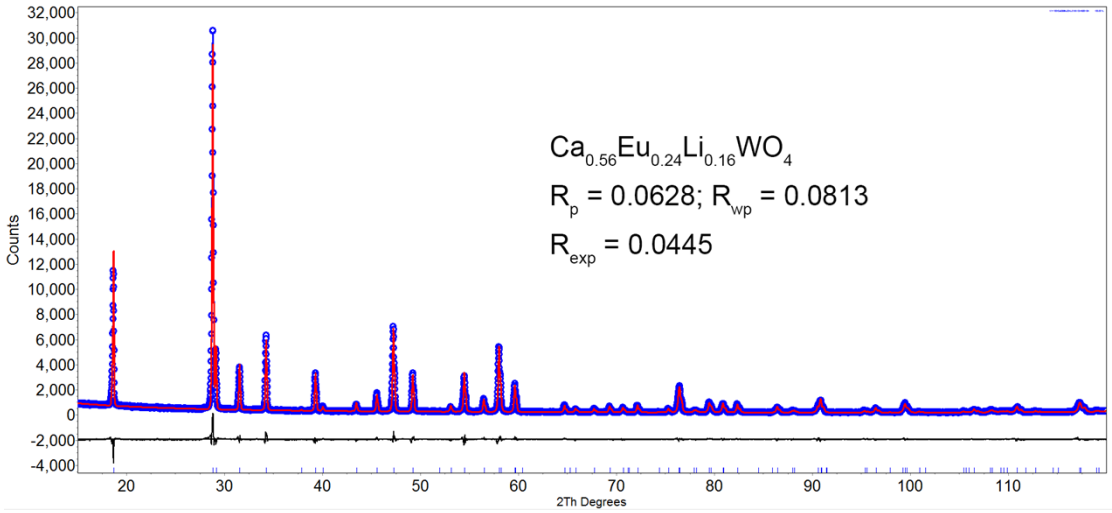
2Th Degrees


Ca0.56Eu0.24Li0.16WO4
Rp = 0.0628; Rwp = 0.0813
Rexp = 0.0445
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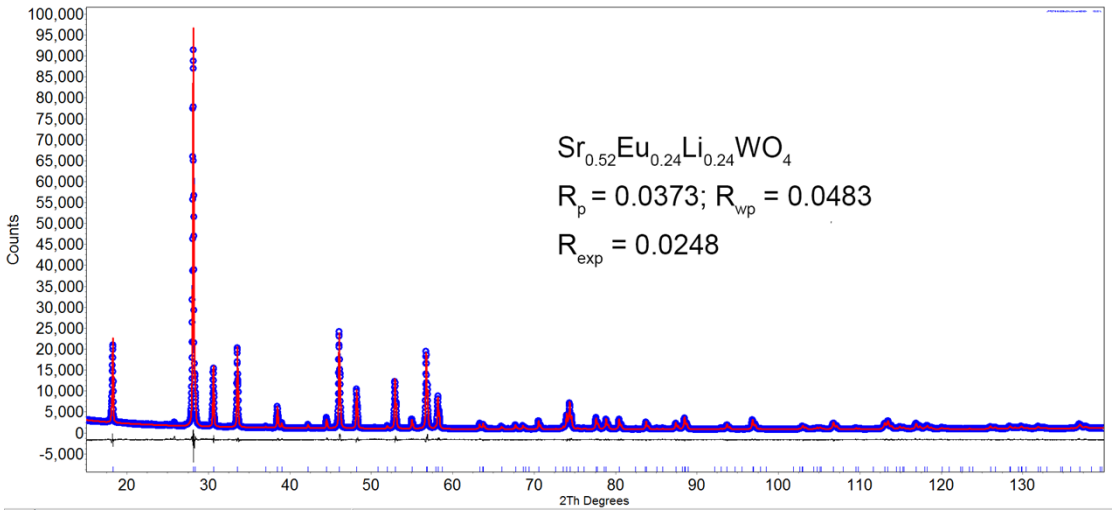
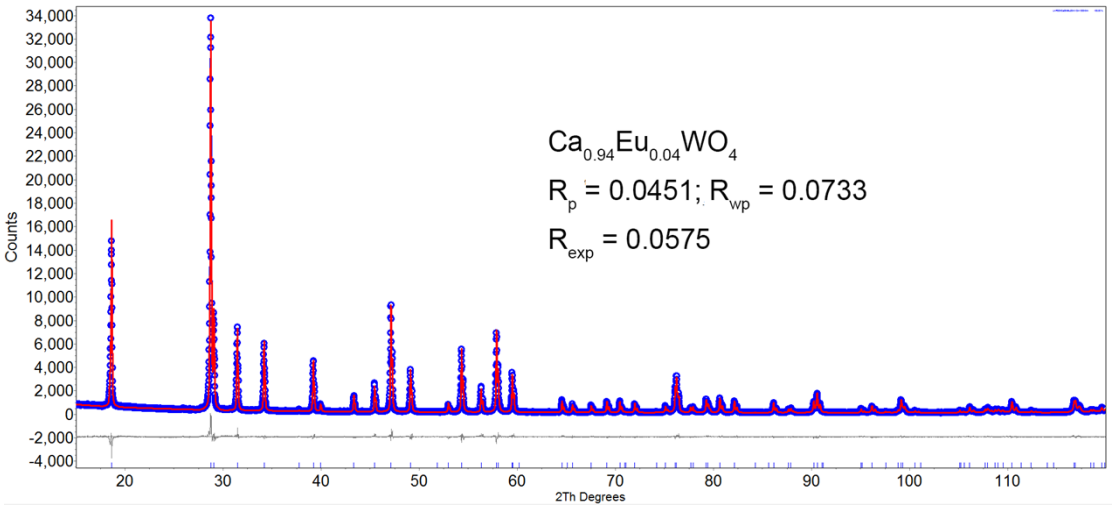
2Th Degrees


Sr0.52Eu0.24Li0.24WO4
Rp = 0.0373; Rwp = 0.0483
Rexp = 0.0248
Counts
2Th Degrees


Ca0.94Eu0.04WO4
Rp = 0.0451; Rwp = 0.0733
Rexp = 0.0575
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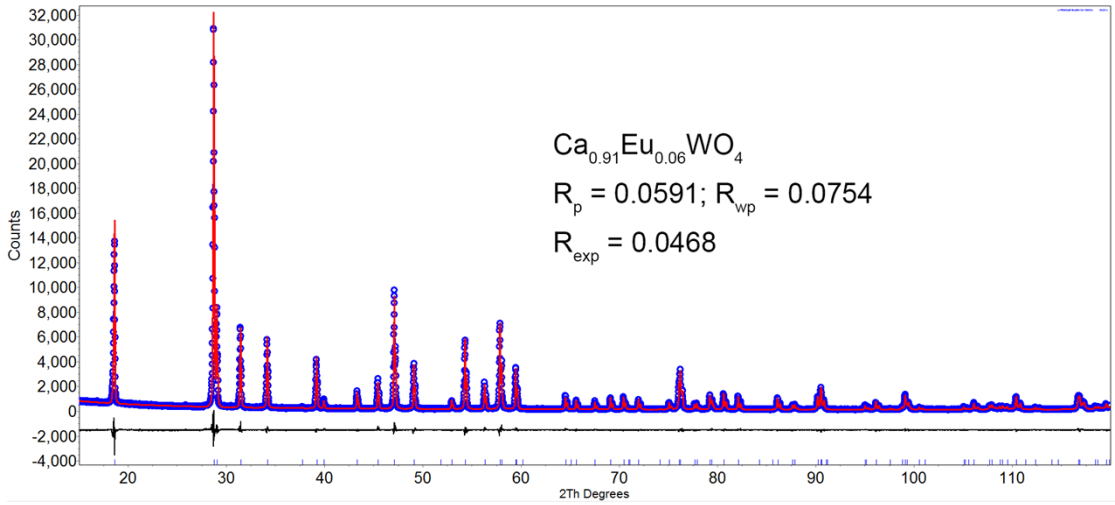
Ca0.91Eu0.06WO4
Rp = 0.0591; Rwp = 0.0754
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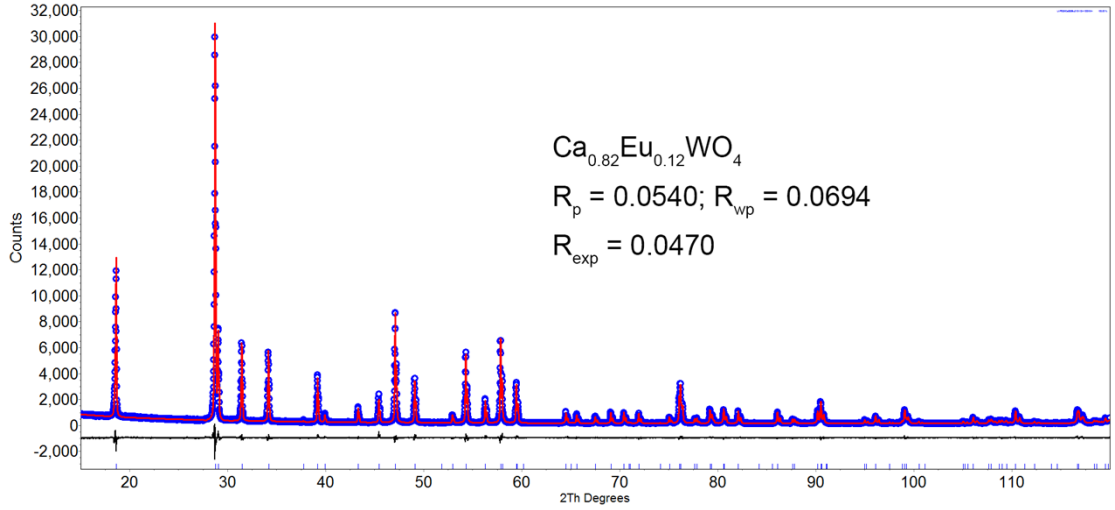
Ca0.82Eu0.12WO4
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Rexp = 0.0470
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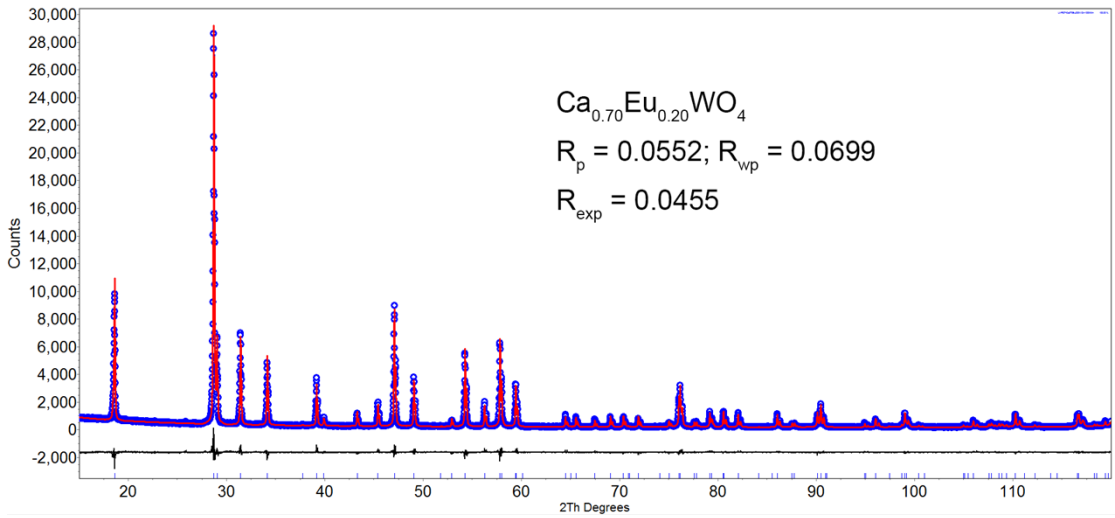
2Th Degrees


Ca0.70Eu0.20WO4
Rp = 0.0552; Rwp = 0.0699
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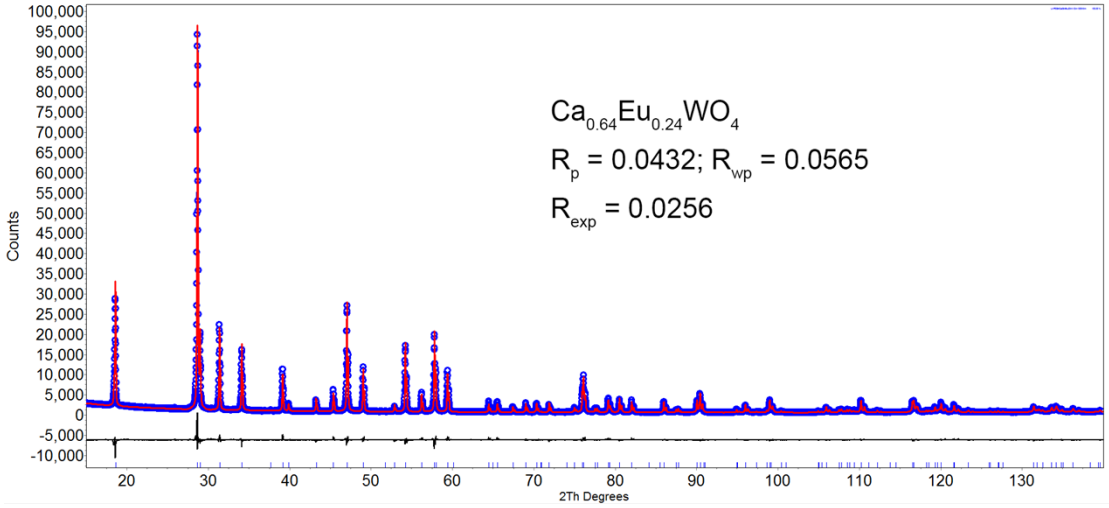
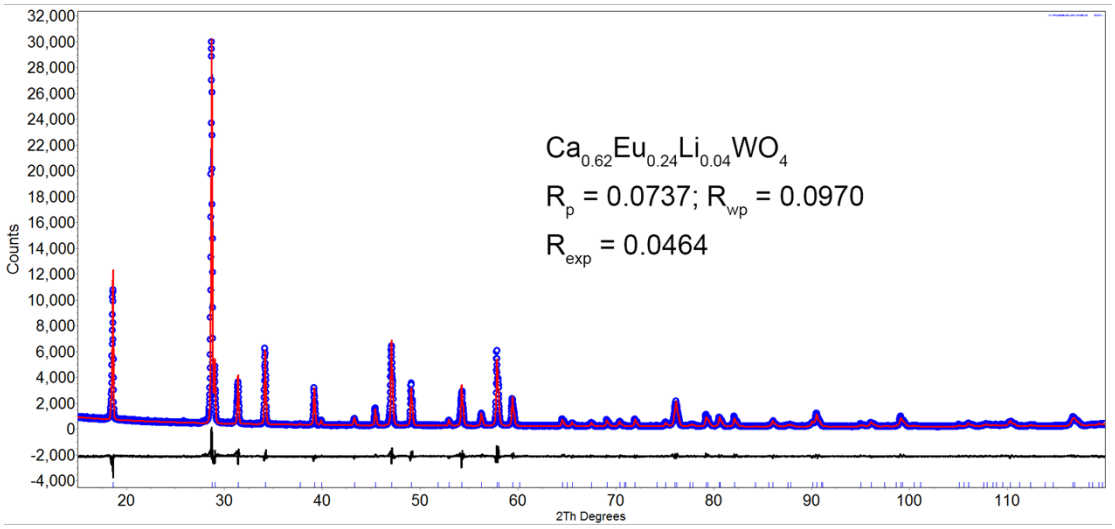
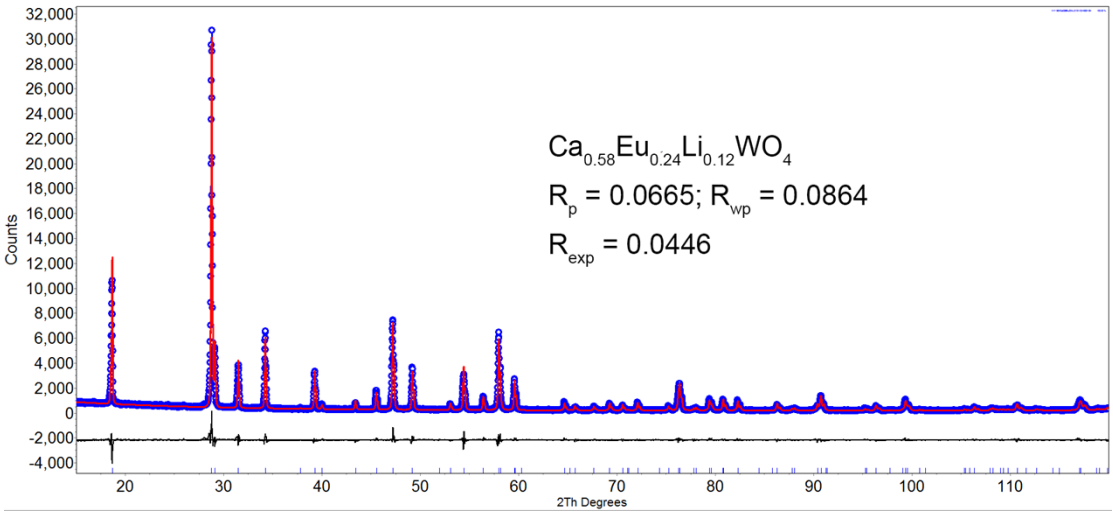
Counts
2Th Degrees


Ca0.64Eu0.24WO4
Rp = 0.0432; Rwp = 0.0565
Rexp = 0.0256
Counts
2Th Degrees


Ca0.62Eu0.24Li0.04WO4
Rp = 0.0737; Rwp = 0.0970
Rexp = 0.0464
Counts
2Th Degrees


Ca0.58Eu0.24Li0.12WO4
Rp = 0.0665; Rwp = 0.0864
Rexp = 0.0446
Counts
2Th Degrees

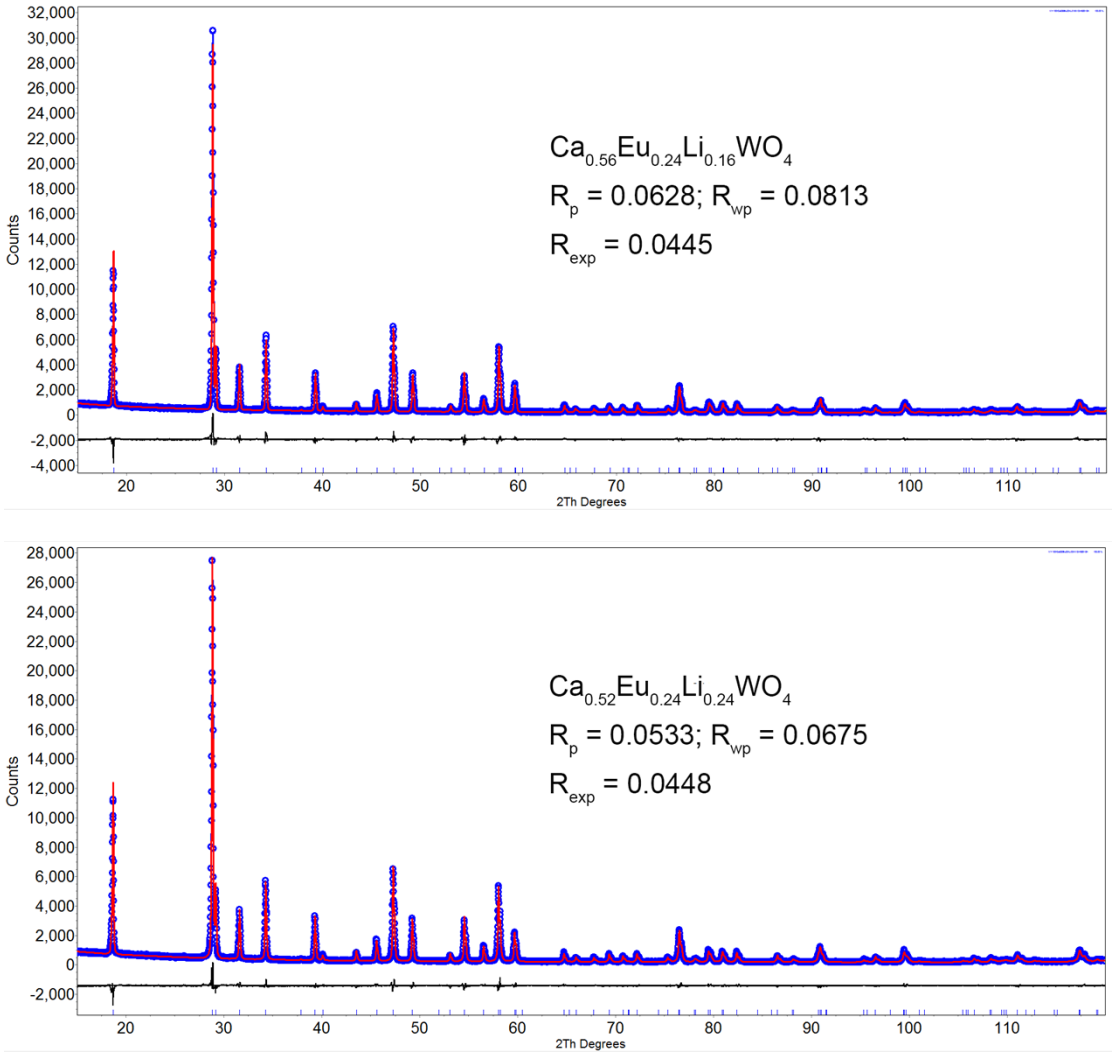


Fig. S4 The final Rietveld refinement patterns of the selected samples for $Sr_{1-1.5x}Eu_x\square_{0.5x}WO_4$ (x = 0.04, 0.12, 0.20, 0.28,0.36), $Sr_{0.64-0.5y}Eu_{0.24}Li_y\square_{0.12-0.5y}WO_4$ (y = 0.04, 0.12, 0.16, 0.24), $Ca_{1-1.5x}Eu_x\square_{0.5x}WO_4$ (x = 0.04, 0.06, 0.12, 0.20,0.24) and $Ca_{0.64-0.5y}Eu_{0.24}Li_y\square_{0.12-0.5y}WO_4$ (y = 0.04, 0.12, 0.16, 0.24). The molecular formula and agreement factors were given in the inserts.

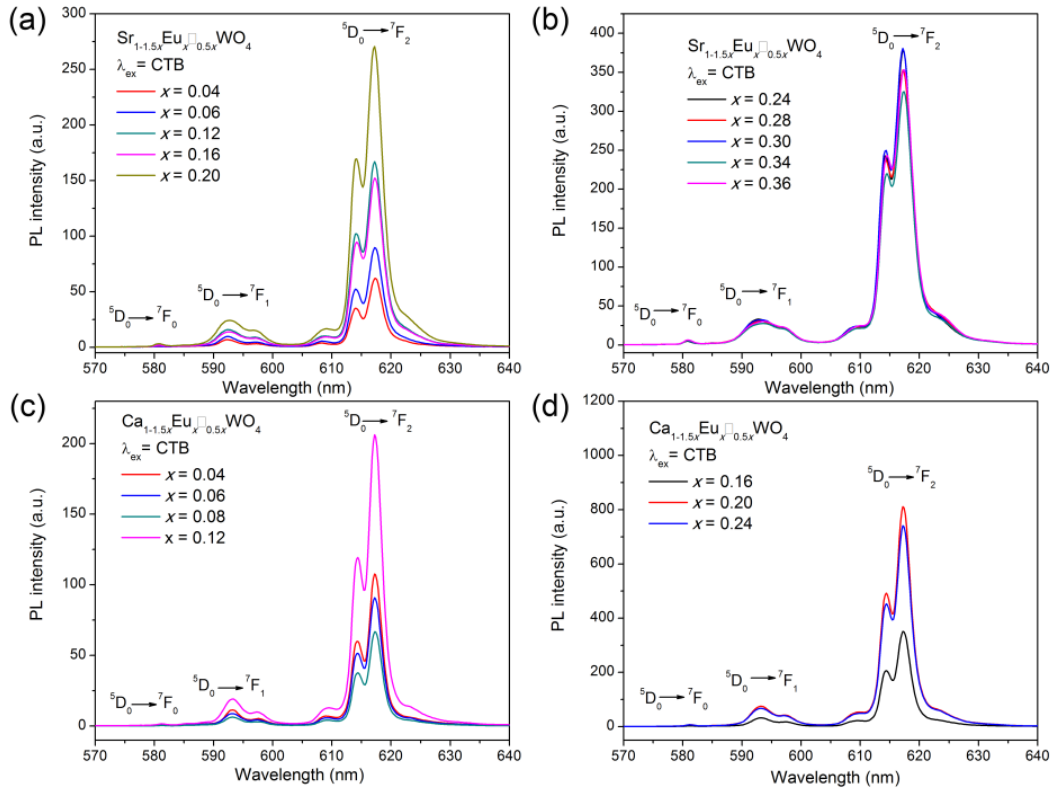


Fig. S5 The emission spectra of **SEW** and **CEW** excited at 274 nm (CT band of $O^{2-} \rightarrow W^{6+}$).

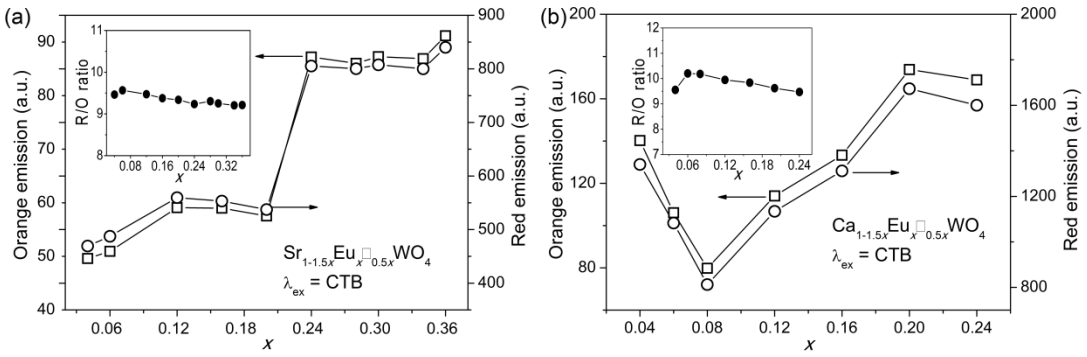


Fig. S6 The emission intensities of (a) **SEW** and (b) **CEW** depend on Eu^{3+} content under 270 nm excitation. The insert of (a) and (b) gives the R/O values.

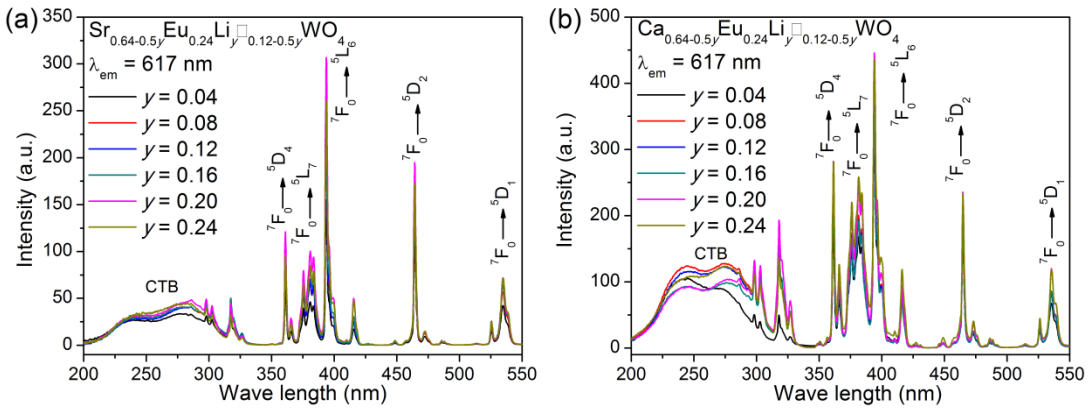


Fig. S7 Excitation spectra of (a) **SELW** and (b) **CELW**, which were measured from 200 to 550 nm by monitoring the strongest emission of Eu^{3+} at 617 nm.

Table S1 The final atomic coordinates, isotropic factors and occupies of the selected samples obtained by Rietveld refinement.

Formula	$Sr_{0.94}Eu_{0.04}WO_4$			$Sr_{0.82}Eu_{0.12}WO_4$		
Atom	Sr/Eu	W	O	Sr/Eu	W	O
x	0	0	0.247(1)	0	0	0.2502(8)
y	0	0	0.1468(8)	0	0	0.1495(7)
z	0.5	0	0.0825(4)	0.5	0	0.0833(4)
Occ.	0.998(3)/0.04	1	1	0.903(3)/0.12	1	1
B_{eq}(Å^2)	0.178(3)	0.010(1)	0.011(3)	0.011(8)	0.006(6)	0.004(1)

Formula	$Sr_{0.70}Eu_{0.20}WO_4$			$Sr_{0.58}Eu_{0.28}WO_4$		
Atom	Sr/Eu	W	O	Sr/Eu	W	O
x	0	0	0.251(1)	0	0	0.256(1)
y	0	0	0.1507(8)	0	0	0.158(2)
z	0.5	0	0.0845(4)	0.5	0	0.0810(6)
Occ.	0.784(4)/0.20	1	1	0.645(5)/0.28	1	1
B_{eq}(Å^2)	0.014(1)	0.007(1)	0.011(3)	0.010(5)	0.003(4)	0.013(6)

Formula	$Sr_{0.46}Eu_{0.36}WO_4$			$Sr_{0.62}Eu_{0.24}Li_{0.04}WO_4$		
Atom	Sr/Eu	W	O	Sr/Eu/Li	W	O
x	0	0	0.248(1)	0	0	0.249(6)
y	0	0	0.153(1)	0	0	0.1459(9)
z	0.5	0	0.0833(4)	0.5	0	0.0844(5)
Occ.	0.575(4)/0.36	1	1	0.672(4)/0.24/0.04	1	1
B_{eq}(Å^2)	0.011(3)	0.005(1)	0.003(3)	0.015(1)	0.0114(8)	0.023(3)

Formula	$Sr_{0.58}Eu_{0.24}Li_{0.12}WO_4$			$Sr_{0.56}Eu_{0.24}Li_{0.16}WO_4$		
Atom	Sr/Eu/Li	W	O	Sr/Eu/Li	W	O
x	0	0	0.2510(9)	0	0	0.2514(9)
y	0	0	0.1450(9)	0	0	0.1490(9)
z	0.5	0	0.0859(4)	0.5	0	0.0859(4)
Occ.	0.586(3)/0.24/0.12	1	1	0.602(3)/0.24/0.16	1	1
B_{eq}(Å^2)	0.0136(9)	0.0140(8)	0.022(2)	0.0147(9)	0.0132(8)	0.019(3)

Formula	$Sr_{0.52}Eu_{0.24}Li_{0.24}WO_4$			$Ca_{0.94}Eu_{0.04}WO_4$		
Atom	Sr/Eu/Li	W	O	Ca/Eu	W	O
x	0	0	0.2549(7)	0	0	0.2557(7)
y	0	0	0.148(1)	0	0	0.1558(7)
z	0.5	0	0.0862(3)	0.5	0	0.0838(3)
Occ.	0.553(2)/0.24/0.24	1	1	1.053(4)/0.04	1	1
B_{eq}(Å^2)	0.0104(6)	0.0121(4)	0.014(1)	0.0175(8)	0.0061(5)	0.009(1)

Formula	$Ca_{0.91}Eu_{0.06}WO_4$			$Ca_{0.82}Eu_{0.12}WO_4$		
Atom	Ca/Eu	W	O	Ca/Eu	W	O
x	0	0	0.2565(7)	0	0	0.2587(8)
y	0	0	0.1570(8)	0	0	0.1561(8)
z	0.5	0	0.0843(3)	0.5	0	0.0846(3
Occ.	0.956(5)/0.06	1	1	0.857(5)/0.12	1	1
B_{eq}(Å^2)	0.0134(8)	0.0055(5)	0.014(1)	0.0132(8)	0.0061(5)	0.013(1)

Formula	$Ca_{0.70}Eu_{0.20}WO_4$			$Ca_{0.64}Eu_{0.24}WO_4$		
Atom	Ca/Eu	W	O	Ca/Eu	W	O
x	0	0	0.2579(8)	0	0	0.2604(7)
y	0	0	0.1615(8)	0	0	0.1639(7)
z	0.5	0	0.0833(4)	0.5	0	0.0828(3)
Occ.	0.753(5)/0.20	1	1	0.720(4)/0.24	1	1
B_{eq}(Å^2)	0.0143(9)	0.0075(8)	0.010(1)	0.0138(5)	0.0056(4)	0.015(1)

Formula	$Ca_{0.62}Eu_{0.24}Li_{0.04}WO_4$			$Ca_{0.58}Eu_{0.24}Li_{0.12}WO_4$		
Atom	Ca/Eu/Li	W	O	Ca/Eu/Li	W	O
x	0	0	0.255(1)	0	0	0.260(1)
y	0	0	0.156(1)	0	0	0.156(1)
z	0.5	0	0.0852(6)	0.5	0	0.0862(5)
Occ.	0.757(7)/0.24/0.04	1	1	0.700(7)/0.24/0.12	1	1
B_{eq}(Å^2)	0.0198(8)	0.0082(5)	0.011(3)	0.0222(9)	0.0119(6)	0.016(3)

Formula	$Ca_{0.56}Eu_{0.24}Li_{0.16}WO_4$			$Ca_{0.52}Eu_{0.24}Li_{0.24}WO_4$		
Atom	Ca/Eu/Li	W	O	Ca/Eu/Li	W	O
x	0	0	0.2572(9)	0	0	0.2555(7)
y	0	0	0.156(1)	0	0	0.1563(8)
z	0.5	0	0.0868(5)	0.5	0	0.0867(4)
Occ.	0.680(6)/0.24/0.16	1	1	0.621(5)/0.24/0.24	1	1
B_{eq}(Å^2)	0.0209(9)	0.0103(5)	0.015(3)	0.0160(9)	0.0055(6)	0.009(1)