Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary information

Facile synthesis of ytterbium doped caesium lead halide perovskite powder

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Figure S1B shows the evolution of the fluorescence measured at a few steps of the wet synthesis of $CsPbCl_3$ perovskite: 1 – short grinding of water-dissolved precursor materials, 2 – longer grinding, 3 – annealing, 4 – additional grinding, 5 – additional annealing.

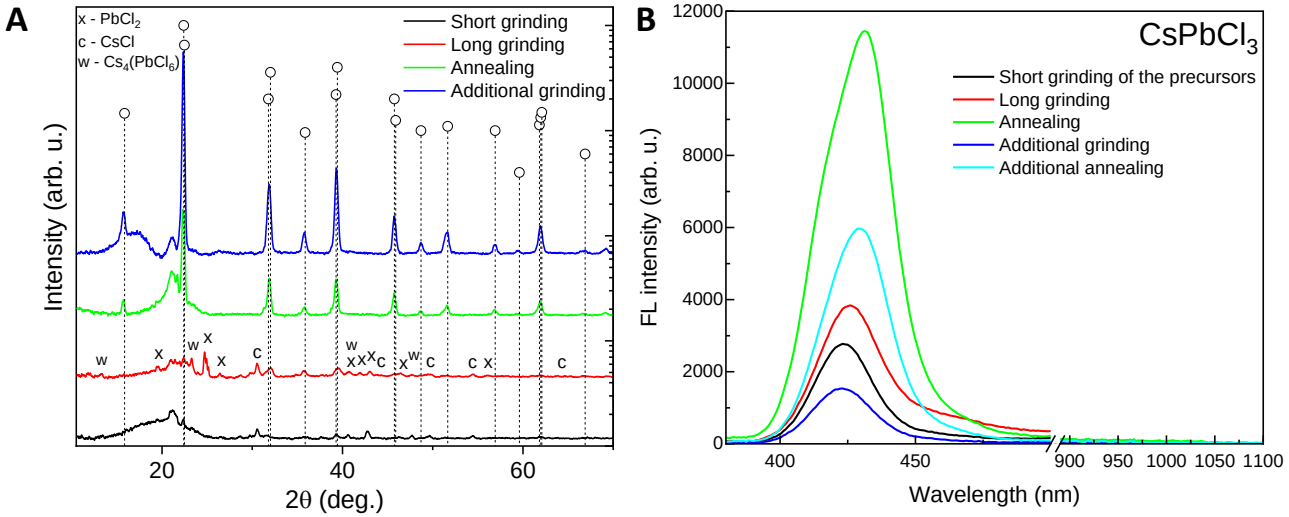


Fig. S1. XRD (A) and VIS-NIR emission spectra (B) at several steps of mechanosynthesis of $CsPbCl_3$ powder prepared by the wet synthesis. In A, dotted lines mark the XRD pattern of the orthorhombic $CsPbCl_3$ standard (ICDD # 04-024-6243). In B, $\lambda_{exc} = 375$ nm.

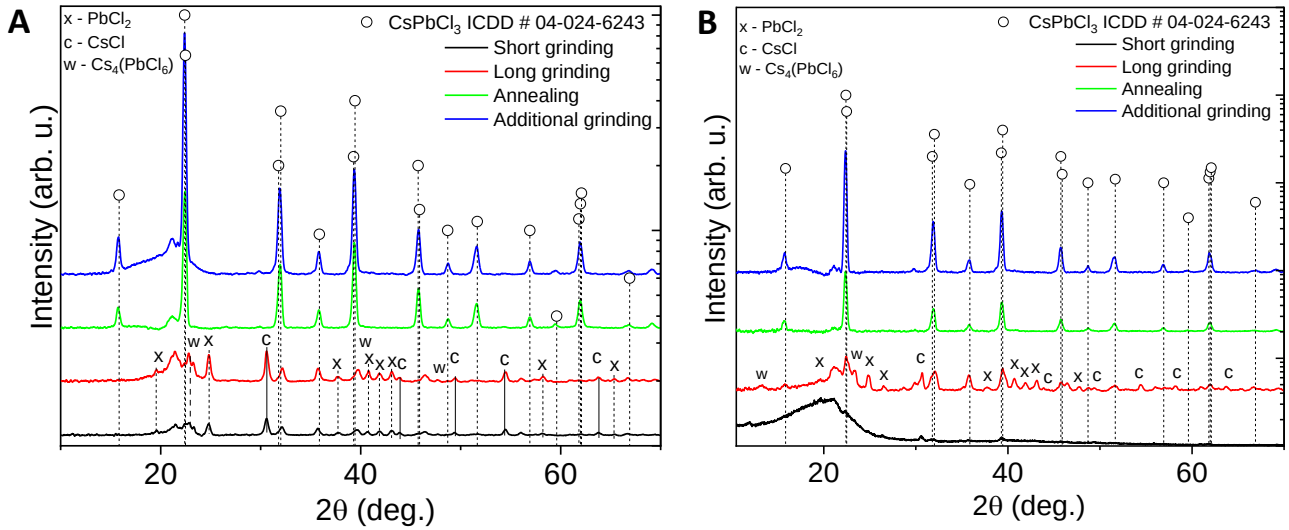


Fig. S2. XRD at several steps of mechanosynthesis of Yb^{3+} doped $CsPbCl_3$ powder prepared by the dry (A) and wet (B) syntheses. Dotted lines mark the XRD pattern of the orthorhombic $CsPbCl_3$ standard (ICDD # 04-024-6243).

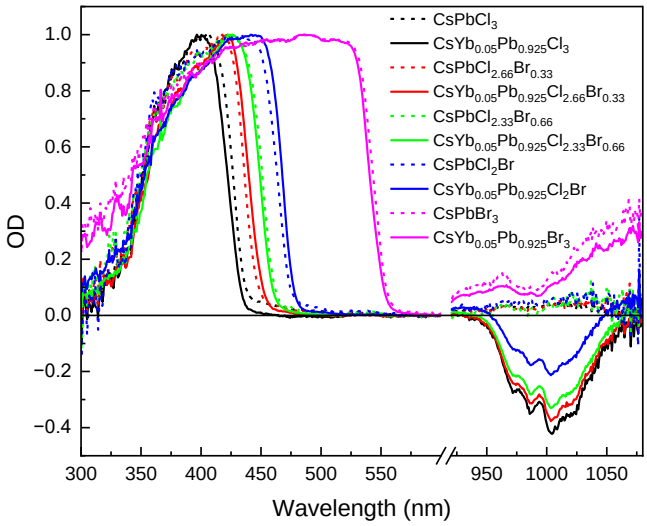


Fig. S3. Absorption spectra of undoped (dotted lines) and Yb^{3+} doped (solid lines) $CsPb(Cl_{1-x}Br_x)_3$ powders in thin quasi-transparent layers prepared by mixing it with a thermoplastic polymer. Powders were prepared by the wet synthesis. Samples were measured by the integrating sphere. These spectra are identical to the raw power spectra.

Table S1. Interatomic distances and crystallite sizes of Yb^{3+} doped $CsPb(Cl_{1-x}Br_x)_3$ powders calculated from the XRD peak shifts.

	a (Ă)	b (Ă)	c (Ă)	Crystallite size (nm)
$CsPbCl_3$	7.902	11.248	7.899	47.4
$CsYb_{0.05}Pb_{0.925}Cl_3$	7.937	11.233	7.908	49.2
$CsPbCl_{2.66}Br_{0.33}$	7.962	11.294	7.953	38.7
$CsYb_{0.05}Pb_{0.925}Cl_{2.66}Br_{0.33}$	7.967	11.333	7.979	35.3
$CsPbCl_2Br$	8.205	11.795	8.255	68.1
$CsYb_{0.05}Pb_{0.925}Cl_2Br$	8.212	11.764	8.260	84.3

Table S2. The amount of each element in different grains of Yb^{3+} doped $CsPbCl_3$ powder sample measured by EDX scans. Also, the elemental composition of undoped sample is shown for comparison.

	Cl (%)	Cs (%)	Pb (%)	Yb (%)
$CsYb_{0.05}Pb_{0.925}Cl_3$				
EDX1	56.98	18.01	21.08	3.91
EDX2	55.88	18.79	21.51	3.80
EDX3	47.42	24.37	22.18	6.00
EDX4	57.28	19.25	19.57	3.89
EDX5	51.32	20.00	21.07	7.59
EDX6	42.99	26.82	26.10	4.08
EDX7	42.85	26.93	23.11	7.09
$CsPbCl_3$				
EDX1	62.38	18.13	19.47	-

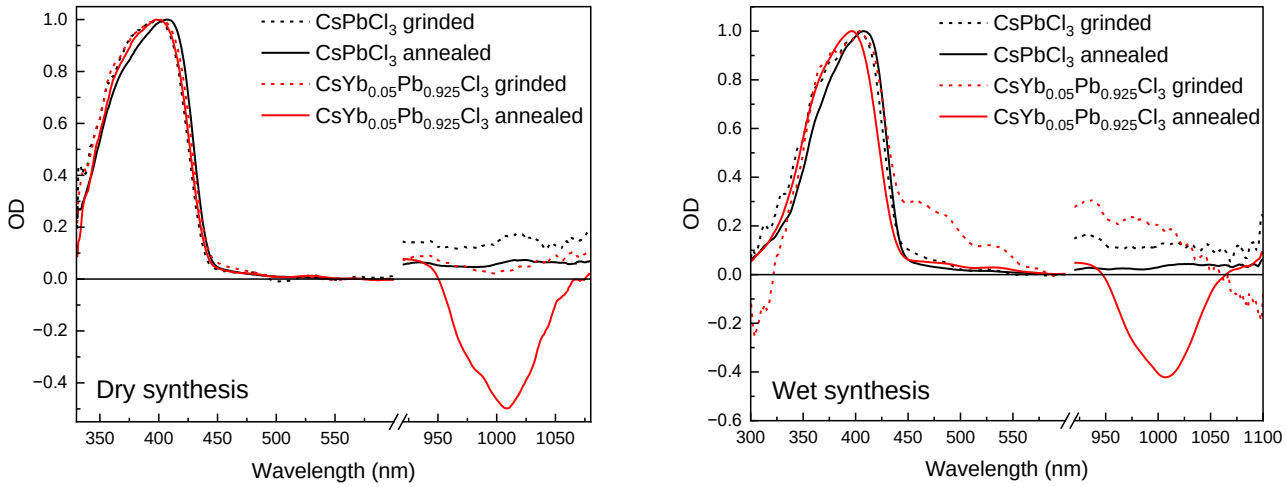


Fig. S4. Absorption spectra of undoped (black lines) and Yb^{3+} doped (red lines) $CsPbCl_3$ powder at two steps of dry (A) and wet (B) synthesis: ground precursor powder and after annealing this powder. Powder was measured in the integrating sphere; therefore, we can observe ytterbium emission in the NIR as the negative signal.

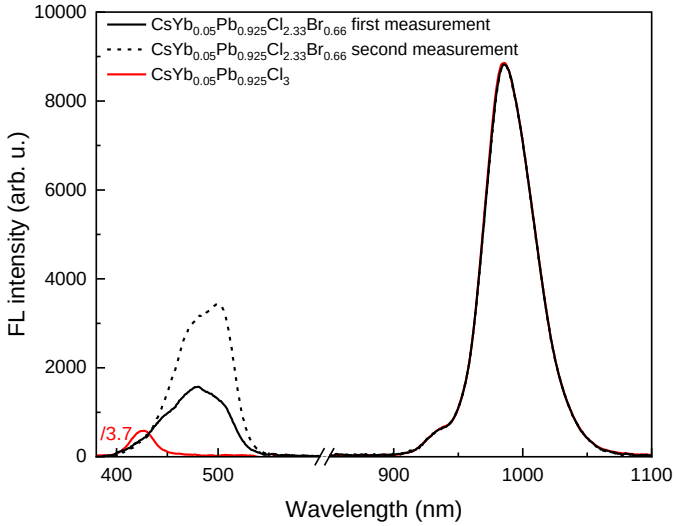


Fig. S5. VIS-NIR emission spectra of Yb^{3+} doped $CsPbCl_{2.33}Br_{0.66}$ powder prepared by the wet synthesis (black lines). Sample was measured two times consequently at the same spot. λ_{exc} = 375 nm. NIR emission is reduced with the 5% light transmission filter. Also, Yb^{3+} doped $CsPbCl_3$ fluorescence spectrum (red line), normalized to the NIR emission intensity, is shown for comparison.

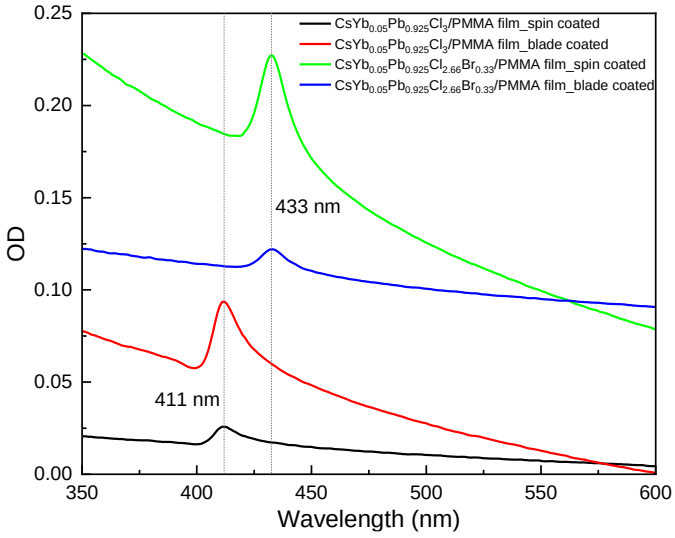


Fig. S6. Absorption spectra of Yb^{3+} doped $CsPb(Cl_{1-x}Br_x)_3$ thin films prepared from the powders, sonicated in PMMA polymer. Films were fabricated in two ways: spin coated and blade coated.

Table S3. Bright field 10x microscopy images of undoped and Yb^{3+} doped $CsPb(Cl_{1-x}Br_x)_3$ powders. Scale bar represents 100 µm.

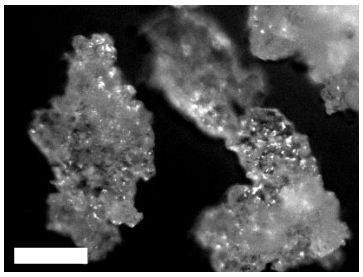
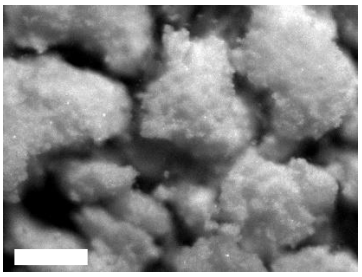
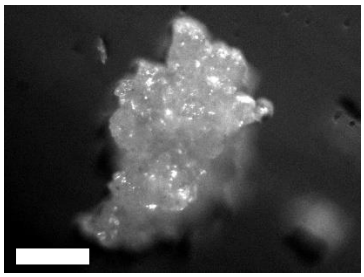
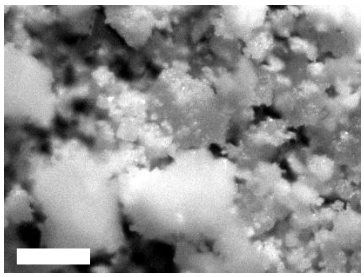
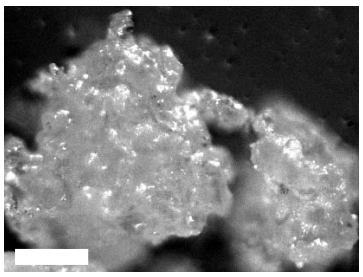
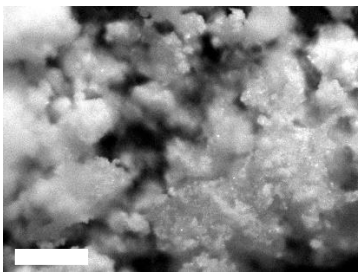
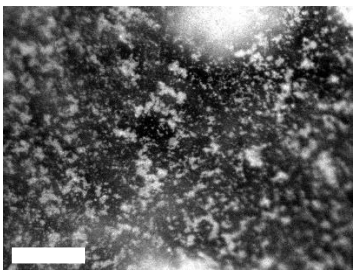
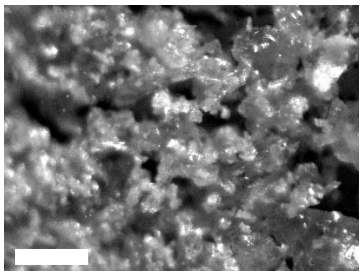
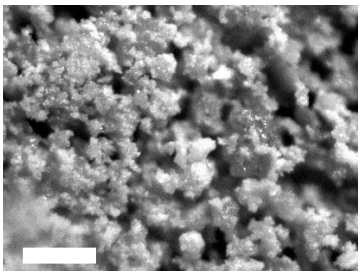
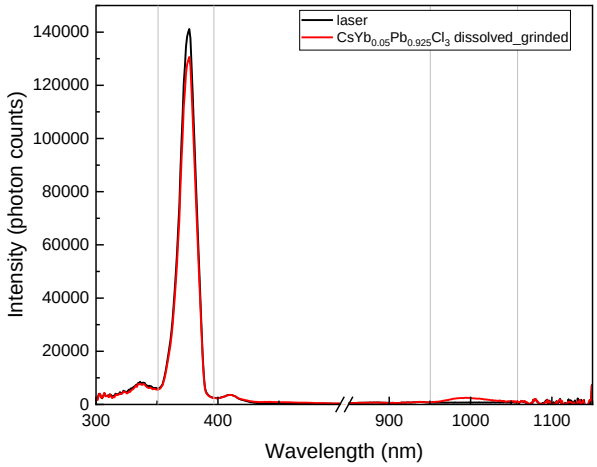
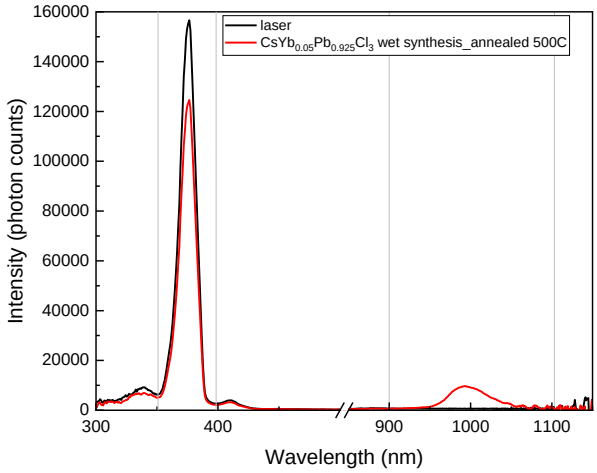
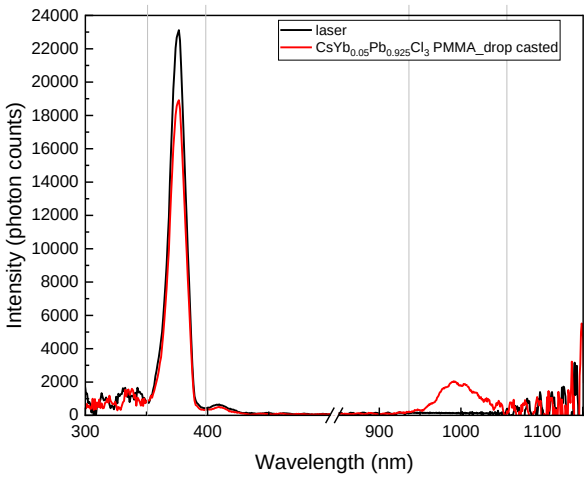
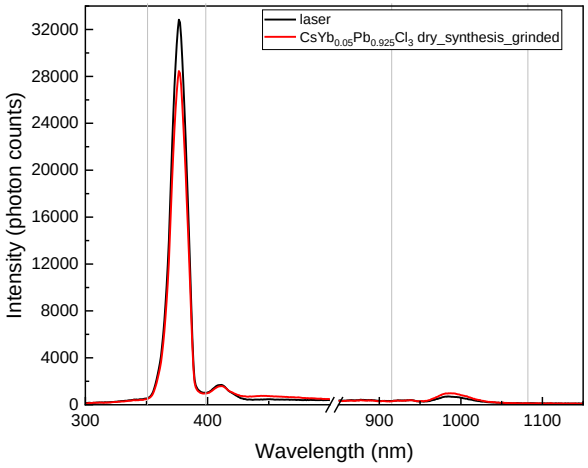
Powder	Undoped	Yb^{3+} Doped
$CsPbCl_3$		
$CsPbCl_{2.33}Br_{0.66}$		
$CsPbCl_{2.66}Br_{0.33}$		
$CsPbCl_{2.66}Br_{0.33}$ sonicated in toluene	-	
$CsPbBr_3$		

Table S4. Data for NIR PLQY calculations obtained from integrating sphere measurements: laser spectra (black lines), sample spectra (red lines) and the values of the integrated areas in the tables below the spectra. For each powder composition multiple samples were prepared, and each sample was measured several times at different spots by slightly changing the sample position in the integrating sphere. Spectra and integrated areas are presented for one of these measurements for one sample. Also, average QY values are shown for each sample. λ_{exc} = 375 nm.

<table>
<tr><th>Synthesis method</th><th>$CsYb_{0.05}Pb_{0.925}Cl_3$</th><th>$QY_{average}$ (%)</th></tr>
<tr><td rowspan="2">Wet synthesis</td><td>1 step: H_2O dissolved+mechanosynthesis
 

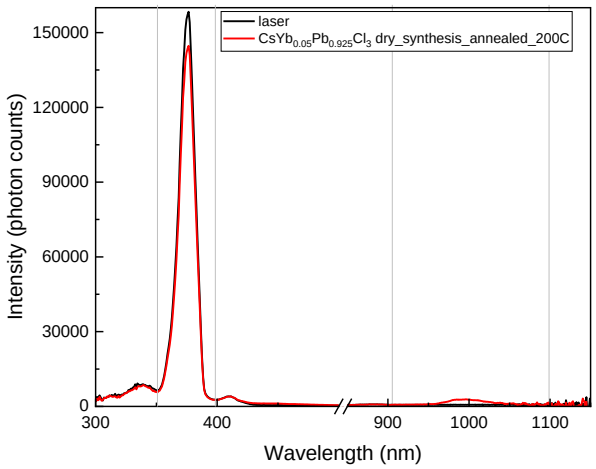
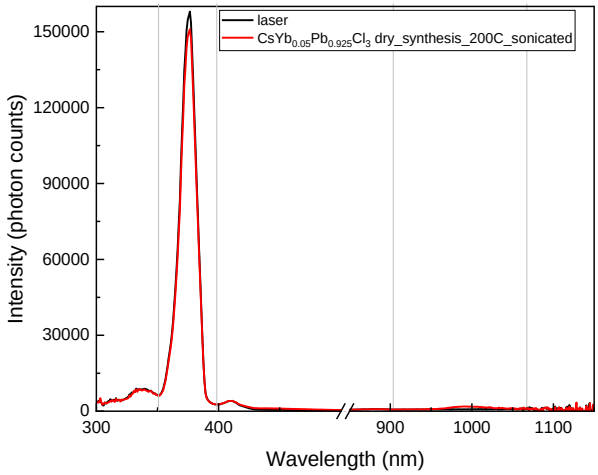
<table>
<tr><th>Sample</th><th>Yb Integral from</th><th>Yb Integral to</th><th>Laser Integral from</th><th>Laser Integral to</th><th>Laser Integral</th><th>Yb Integral</th><th>QY</th></tr>
<tr><td></td><td>nm</td><td>nm</td><td>nm</td><td>nm</td><td>counts*nm</td><td>counts*nm</td><td></td></tr>
<tr><td>laser</td><td>950.5</td><td>1057.78</td><td>350.87</td><td>396.65</td><td>2364071</td><td>0</td><td>--</td></tr>
<tr><td>powder</td><td>950.5</td><td>1057.78</td><td>350.87</td><td>396.65</td><td>2187591</td><td>108811.30</td><td>0.62</td></tr>
</table></td><td>64</td></tr>
<tr><td>2 step: Annealed at 500 ˚C
 

<table>
<tr><th>Sample</th><th>Yb Integral from</th><th>Yb Integral to</th><th>Laser Integral from</th><th>Laser Integral to</th><th>Laser Integral</th><th>Yb Integral</th><th>QY</th></tr>
<tr><td></td><td>nm</td><td>nm</td><td>nm</td><td>nm</td><td>counts*nm</td><td>counts*nm</td><td></td></tr>
<tr><td>laser</td><td>899.99</td><td>1103.14</td><td>350.87</td><td>398.48</td><td>2625441</td><td>0</td><td>--</td></tr>
<tr><td>powder</td><td>899.99</td><td>1103.14</td><td>350.87</td><td>398.48</td><td>2087293</td><td>580985.34</td><td>1.08</td></tr>
</table></td><td>108</td></tr>
</table>

	PMMA film by drop casting  (table below)	162
Dry synthesis	1 step: Mechanosynthesis  (table below)	38

Sample	Yb Integral from	Yb Integral to	Laser Integral from	Laser Integral to	Laser Integral	Yb Integral	QY
	nm	nm	nm	nm	counts*nm	counts*nm	
laser	936.35	1056.04	350.87	398.48	385911.6	0	--
powder	936.35	1056.04	350.87	398.48	317125.5	111434.75	1.62

Sample	Yb Integral from	Yb Integral to	Laser Integral from	Laser Integral to	Laser Integral	Yb Integral	QY
	nm	nm	nm	nm	counts*nm	counts*nm	
laser	915.08	1082.23	350.87	398.48	2663303	0	--
powder	915.08	1082.23	350.87	398.48	2313810	132267.43	0.38

	2 step: Annealed at 200 ˚C  	Sample	Yb Integral from	Yb Integral to	Laser Integral from	Laser Integral to	Laser Integral	Yb Integral	QY
---	---	---	---	---	---	---	---
	nm	nm	nm	nm	counts*nm	counts*nm	
laser	905.32	1098.79	350.87	398.48	2653931	0	--
powder	905.32	1098.79	350.87	398.48	2426310	142624.13	0.63		63
	Additional step: Sonicated  	Sample	Yb Integral from	Yb Integral to	Laser Integral from	Laser Integral to	Laser Integral	Yb Integral	QY
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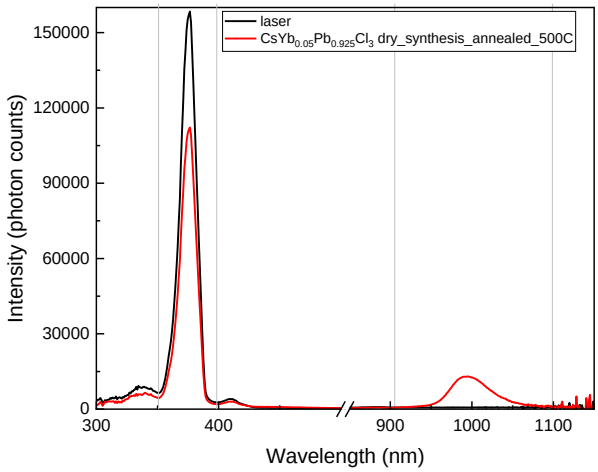
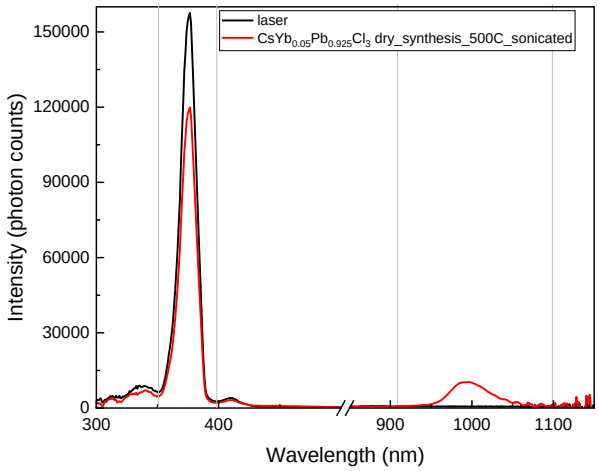
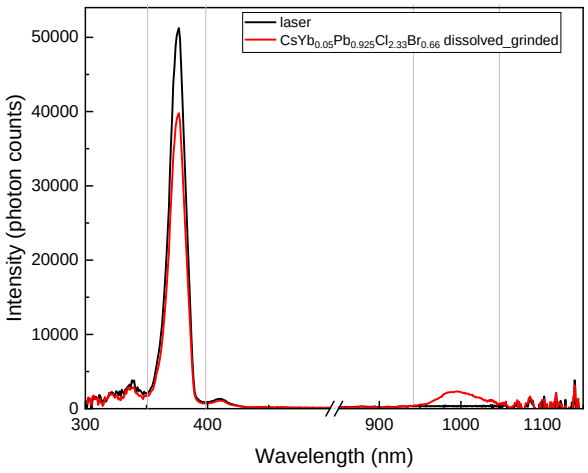
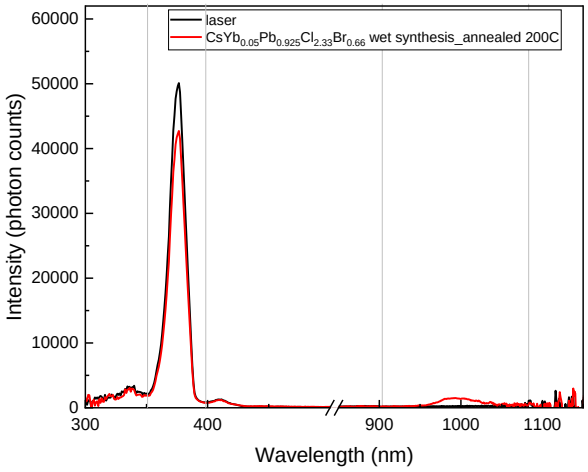
	nm	nm	nm	nm	counts*nm	counts*nm	
laser	903.54	1067.4	350.87	398.48	2644551	0	--
powder	903.54	1067.4	350.87	398.48	2530955	72142.295	0.64		64

	2 step: Annealed at 500 ˚C  Sample / Yb Integral from / Yb Integral to / Laser Integral from / Laser Integral to / Laser Integral / Yb Integral / QY nm / nm / nm / nm / counts*nm / counts*nm laser: 905.32 / 1098.79 / 350.87 / 398.48 / 2653931 / 0 / -- powder: 905.32 / 1098.79 / 350.87 / 398.48 / 1877855 / 802457.28 / 1.03	110
	Additional step: Sonicated  Sample / Yb Integral from / Yb Integral to / Laser Integral from / Laser Integral to / Laser Integral / Yb Integral / QY nm / nm / nm / nm / counts*nm / counts*nm laser: 908.87 / 1098.79 / 350.87 / 398.48 / 2639551 / 0 / -- powder: 908.87 / 1098.79 / 350.87 / 398.48 / 2005784 / 631872.68 / 1.00	103
$CsYb_{0.05}Pb_{0.925}Cl_{2.33}Br_{0.66}$		

Wet synthesis	1 step: H_2O dissolved+mechanosynthesis  	Sample	Yb Integral from	Yb Integral to	Laser Integral from	Laser Integral to	Laser Integral	Yb Integral	QY
---	---	---	---	---	---	---	---
	nm	nm	nm	nm	counts*nm	counts*nm	
laser	941.66	1047.29	350.87	398.48	860135.0	0	--
powder	941.66	1047.29	350.87	398.48	669722.3	116203.12	0.610		59
	2 step: Annealed at 200 ˚C  	Sample	Yb Integral from	Yb Integral to	Laser Integral from	Laser Integral to	Laser Integral	Yb Integral	QY
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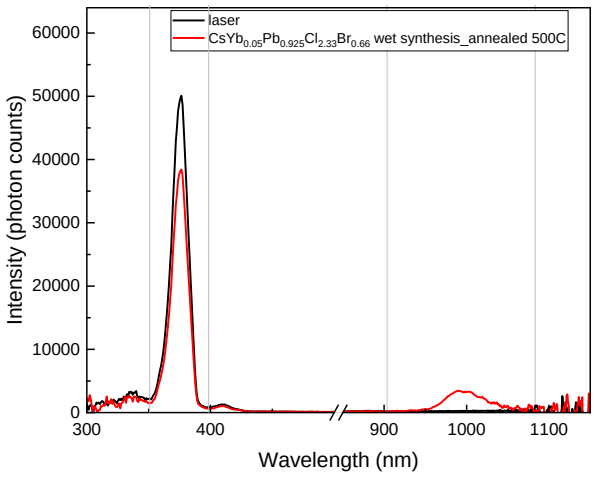
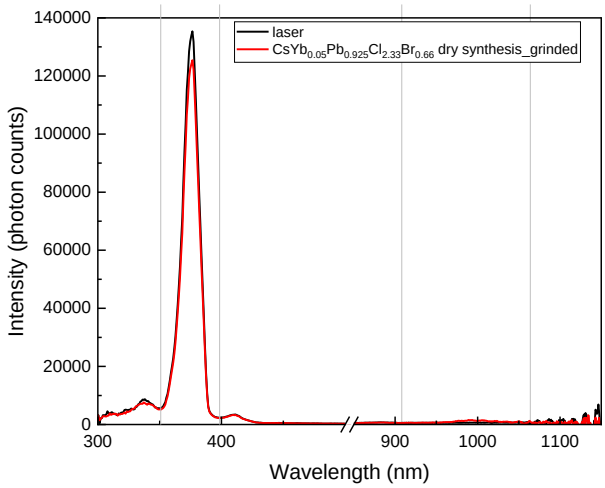
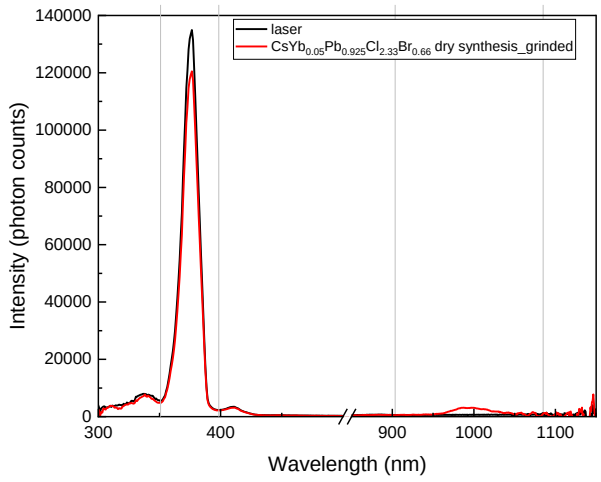
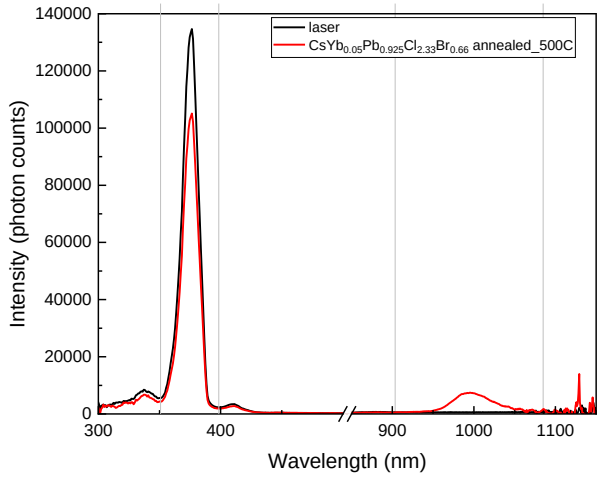
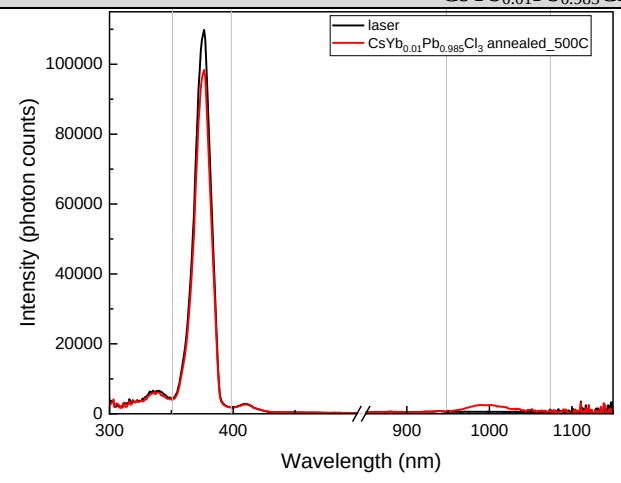
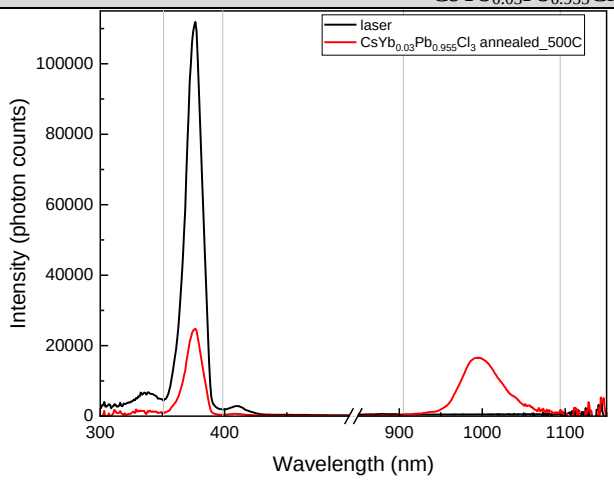
	nm	nm	nm	nm	counts*nm	counts*nm	
laser	903.54	1083.11	350.87	396.65	840970.7	0	--
powder	903.54	1083.11	350.87	396.65	716776.0	79668.014	0.64		66

	2 step: Annealed at 500 ˚C  Sample / Yb Integral from / Yb Integral to / Laser Integral from / Laser Integral to / Laser Integral / Yb Integral / QY nm / nm / nm / nm / counts*nm / counts*nm laser 903.54 1083.11 350.87 398.48 840970.7 0 -- powder 903.54 1083.11 350.87 398.48 645145.8 201230.45 1.03	104
Dry synthesis	1 step: Mechanosynthesis  Sample / Yb Integral from / Yb Integral to / Laser Integral from / Laser Integral to / Laser Integral / Yb Integral / QY nm / nm / nm / nm / counts*nm / counts*nm laser 907.98 1063.9 350.87 398.48 210631.9 0 -- powder 907.98 1063.9 350.87 398.48 195153.2 46269.004 0.28	28

	2 step: Annealed at 200 ˚C  Sample / Yb Integral from / Yb Integral to / Laser Integral from / Laser Integral to / Laser Integral / Yb Integral / QY nm / nm / nm / nm / counts*nm / counts*nm laser: 903.54 / 1084.85 / 350.87 / 398.48 / 2262894.0 / 0 / -- powder: 903.54 / 1084.85 / 350.87 / 398.48 / 2024022.3 / 149457.5 / 0.63	66
	2 step: Annealed at 500 ˚C  Sample / Yb Integral from / Yb Integral to / Laser Integral from / Laser Integral to / Laser Integral / Yb Integral / QY nm / nm / nm / nm / counts*nm / counts*nm laser: 903.54 / 1084.85 / 350.87 / 398.48 / 2260350.2 / 0 / -- powder: 903.54 / 1084.85 / 350.87 / 398.48 / 1763615.4 / 430996.0 / 0.87	89
Wet synthesis, annealed at 500 ˚C	$CsYb_{0.01}Pb_{0.985}Cl_3$  Sample / Yb Integral from / Yb Integral to / Laser Integral from / Laser Integral to / Laser Integral / Yb Integral / QY nm / nm / nm / nm / counts*nm / counts*nm laser: 947.85 / 1074.38 / 350.87 / 398.48 / 177416.793 / 0 / -- powder: 947.85 / 1074.38 / 350.87 / 398.48 / 159482.546 / 122682.42 / 0.66	66

$CsYb_{0.03}Pb_{0.955}Cl_3$



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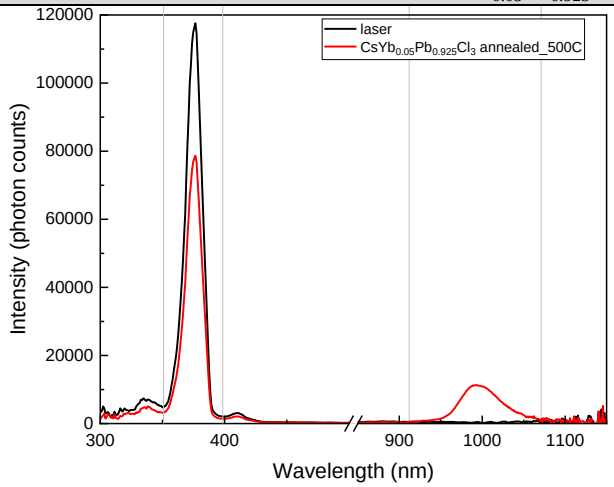
Sample	Yb Integral from	Yb Integral to	Laser Integral from	Laser Integral to	Laser Integral	Yb Integral	QY
	nm	nm	nm	nm	counts*nm	counts*nm	
laser	905.32	1094.43	350.87	398.48	1881385.29	0	--
powder	905.32	1094.43	350.87	398.48	417717.857	1036308	0.71

$CsYb_{0.05}Pb_{0.925}Cl_3$



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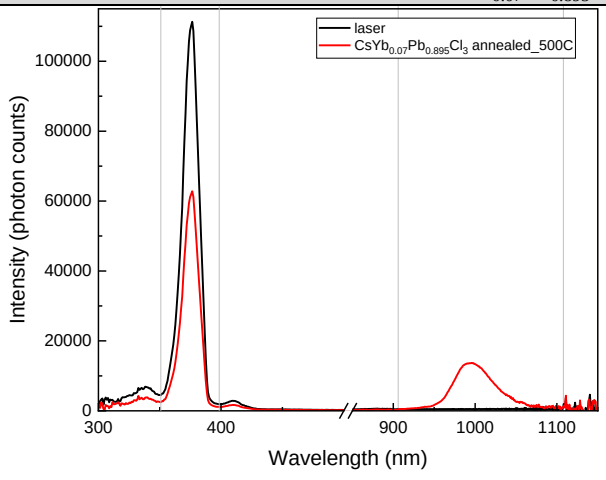
Sample	Yb Integral from	Yb Integral to	Laser Integral from	Laser Integral to	Laser Integral	Yb Integral	QY
	nm	nm	nm	nm	counts*nm	counts*nm	
laser	911.53	1070.89	350.87	398.48	1927575.50	0	--
powder	911.53	1070.89	350.87	398.48	1321039.07	680301.6	1.12

$CsYb_{0.07}Pb_{0.895}Cl_3$



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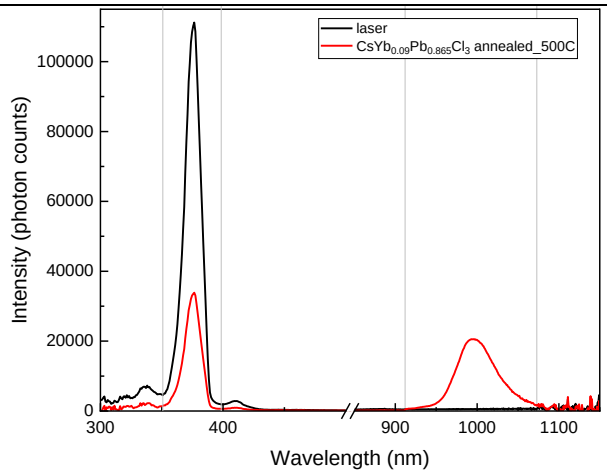
Sample	Yb Integral from	Yb Integral to	Laser Integral from	Laser Integral to	Laser Integral	Yb Integral	QY
	nm	nm	nm	nm	counts*nm	counts*nm	
laser	906.2	1108.36	350.87	398.48	1870616.00	0	--
powder	906.2	1108.36	350.87	398.48	1053979.09	852827.19	1.04

$CsYb_{0.09}Pb_{0.865}Cl_3$



Sample	Yb Integral from	Yb Integral to	Laser Integral from	Laser Integral to	Laser Integral	Yb Integral	QY
	nm	nm	nm	nm	counts*nm	counts*nm	
laser	912.42	1072.64	350.87	398.48	1870239.7	0	--
powder	912.42	1072.64	350.87	398.48	570816.75	1263141	0.97