

Supporting information

Enhanced upconversion luminescence and tuned red-to-green emission ratio of LiGdF<sub>4</sub> nanocrystals via Ca<sup>2+</sup> doping

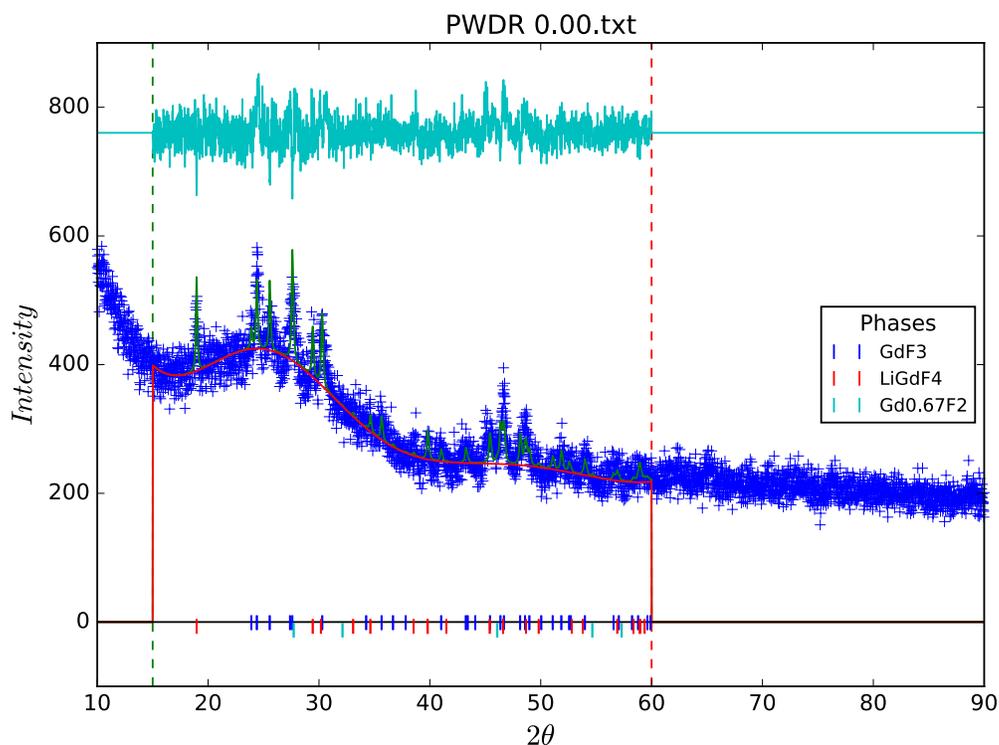


Figure S1. Result of Rietveld refinement of sample S0. The broad peak belonging to the background at ca. 24° could be attributed to the amorphous phase. The background was modeled with a 5-order Chebyshev polynomial and a Gaussian function. The weighted residual was 6.83% and the goodness of fit was 1.22. The phase parameters were listed in Table S1.

Table S1. Phase parameters of sample S0

Name	SG <sup>1</sup>	a	b	c	Atom Position		
LiGdF <sub>4</sub>	I 41/a	5.17	5.17	10.81	Li(0, 1/4, 1/8)	Gd(1/2, 3/4, 1/8)	F(0.31, 0.17, 0.03)
Gd <sub>0.67</sub> F <sub>2</sub>	Fm-3m	5.56	5.56	5.56	Gd(0, 0, 0) <sup>2</sup>	F(1/4, 1/4, 1/4)	
GdF <sub>3</sub>	P n m a	6.50	6.95	4.39	Gd(0.37, 1/4, 0.05)	F1(0.16, 0.06, 0.37)	F2(0.03, 1/4, 0.90)

1. Space Group

2. The fractional occupancy of Gd atom in Gd<sub>0.67</sub>F<sub>2</sub> was 0.67. The fractional occupancy of other atoms were 1.

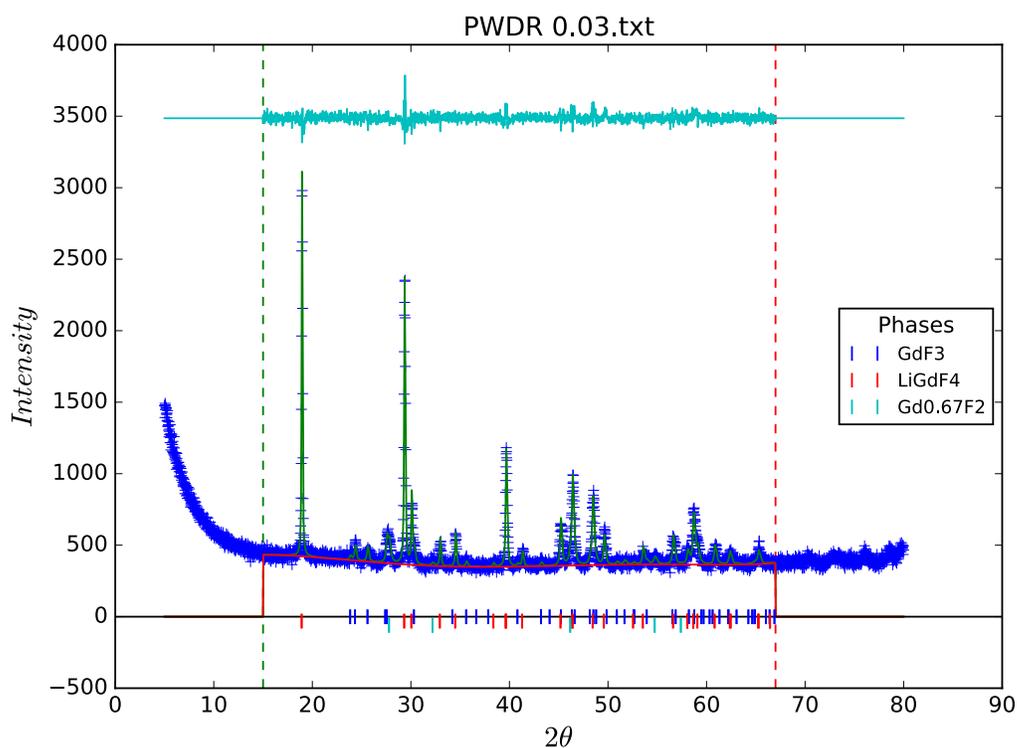


Figure S2. Result of Rietveld refinement of sample S1. The background was modeled with a 6-order Chebyshev polynomial. The weighted residual was 5.64% and the goodness of fit was 1.17. The phase parameters were listed in Table S2.

Table S2. Phase parameters of sample S1

Name	SG <sup>1</sup>	a	b	c	Atom Position		
LiGdF <sub>4</sub>	I 41/a	5.20	5.20	10.87	Li(0, 1/4, 1/8)	Gd(1/2, 3/4, 1/8)	F(0.25, 0.10, 0.05)
Gd <sub>0.67</sub> F <sub>2</sub>	Fm-3m	5.56	5.56	5.56	Gd(0, 0, 0) <sup>2</sup>	F(1/4, 1/4, 1/4)	
GdF <sub>3</sub>	P n m a	6.50	6.95	4.42	Gd(0.37, 1/4, 0.05)	F1(0.16, 0.06, 0.37)	F2(0.03, 1/4, 0.90)

1. Space Group

2. The fractional occupancy of Gd atom in Gd<sub>0.67</sub>F<sub>2</sub> was 0.67. The fractional occupancies of other atoms were 1.

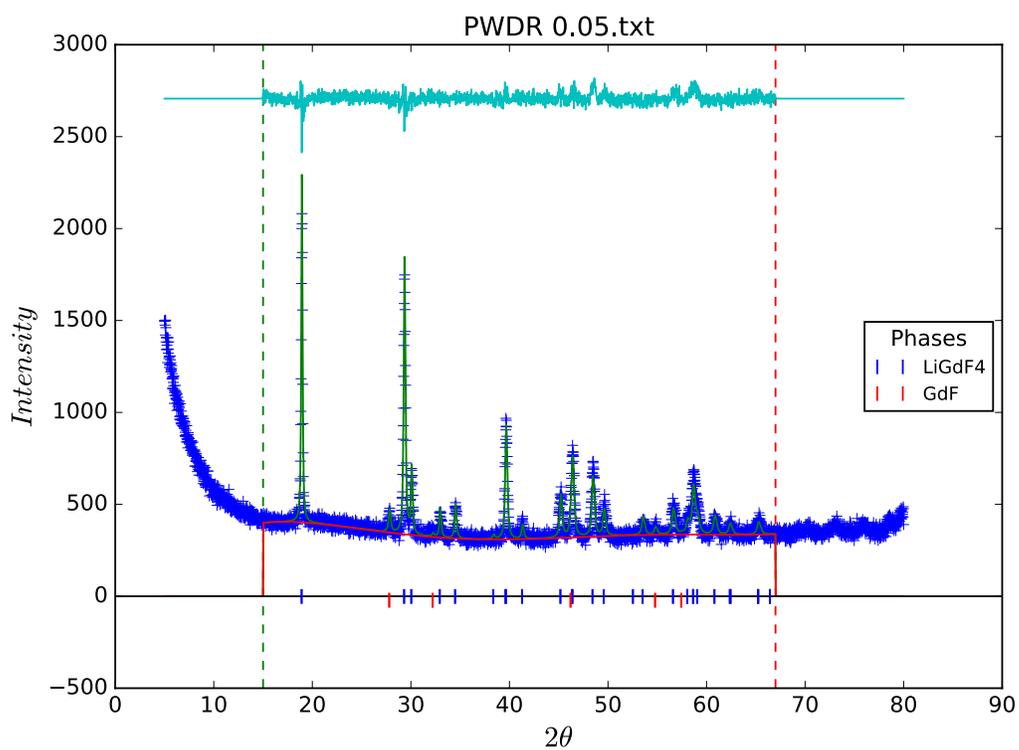


Figure S3. Result of Rietveld refinement of sample S2. The background was modeled with a 6-order Chebyshev polynomial. The weighted residual was 6.23% and the goodness of fit was 1.23. The phase parameters were listed in Table S3.

Table S3. Phase parameters of sample S2

Name	SG <sup>1</sup>	a	b	c	Atom Position		
LiGdF <sub>4</sub>	I 41/a	5.20	5.20	10.87	Li(0, 1/4, 1/8)	Gd(1/2, 3/4, 1/8)	F(0.25, 0.11, 0.05)
Gd <sub>0.67</sub> F <sub>2</sub>	Fm-3m	5.55	5.55	5.55	Gd(0, 0, 0) <sup>2</sup>	F(1/4, 1/4, 1/4)	

1. Space Group

2. The fractional occupancy of Gd atom in Gd<sub>0.67</sub>F<sub>2</sub> was 0.67. The fractional occupancies of other atoms were 1.

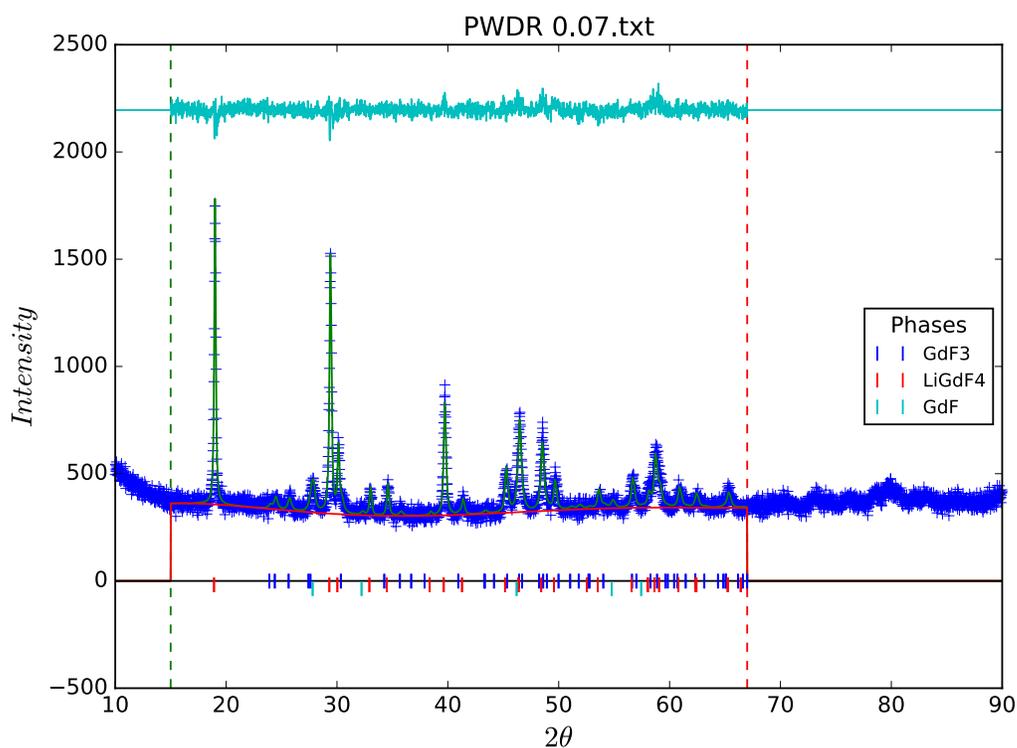


Figure S4. Result of Rietveld refinement of sample S3. The background was modeled with a 6-order Chebyshev polynomial. The weighted residual was 6.00% and the goodness of fit was 1.17. The phase parameters were listed in Table S4.

Table S4. Phase parameters of sample S3

Name	SG <sup>1</sup>	a	b	c	Atom Position		
LiGdF <sub>4</sub>	I 41/a	5.20	5.20	10.87	Li(0, 1/4, 1/8)	Gd(1/2, 3/4, 1/8)	F(0.25, 0.10, 0.05)
Gd <sub>0.67</sub> F <sub>2</sub>	Fm-3m	5.55	5.55	5.55	Gd(0, 0, 0) <sup>2</sup>	F(1/4, 1/4, 1/4)	
GdF <sub>3</sub>	P n m a	6.50	6.94	4.40	Gd(0.37, 1/4, 0.05)	F1(0.16, 0.06, 0.37)	F2(0.03, 1/4, 0.90)

1. Space Group

2. The fractional occupancy of Gd atom in Gd<sub>0.67</sub>F<sub>2</sub> was 0.67. The fractional occupancies of other atoms were 1.

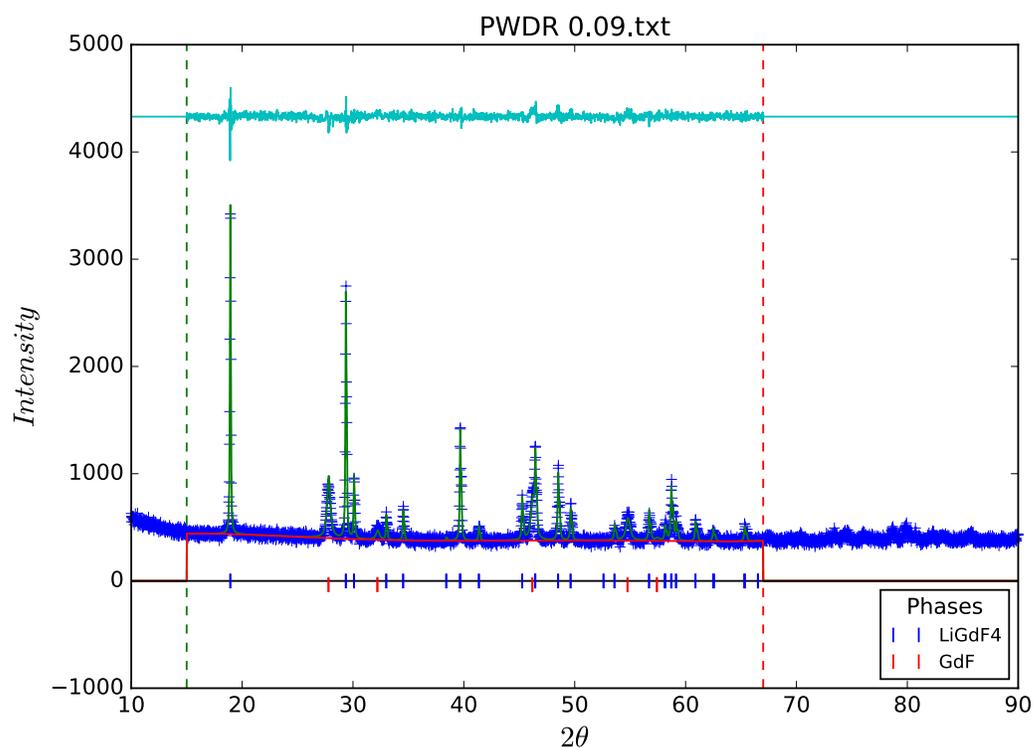


Figure S5. Result of Rietveld refinement of sample S4. The weighted residual was 5.62% and the goodness of fit was 1.19. The phase parameters were listed in Table S5.

Table S5. Phase parameters of sample S4

Name	SG <sup>1</sup>	a	b	c	Atom Position		
LiGdF <sub>4</sub>	I 41/a	5.19	5.19	10.85	Li(0, 1/4, 1/8)	Gd(1/2, 3/4, 1/8)	F(0.26, 0.10, 0.04)
Gd <sub>0.67</sub> F <sub>2</sub>	Fm-3m	5.55	5.55	5.55	Gd(0, 0, 0) <sup>2</sup>	F(1/4, 1/4, 1/4)	

1. Space Group

2. The fractional occupancy of Gd atom in Gd<sub>0.67</sub>F<sub>2</sub> was 0.67. The fractional occupancies of other atoms were 1.

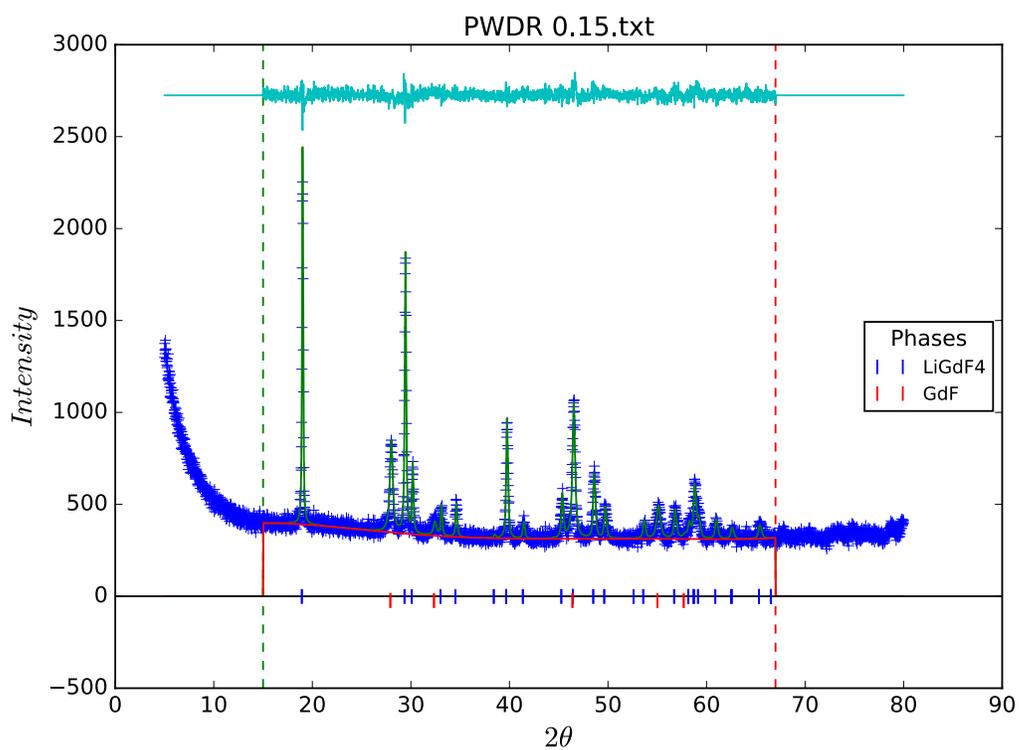


Figure S6. Result of Rietveld refinement of sample S5. The weighted residual was 5.81% and the goodness of fit was 1.14. The phase parameters were listed in Table S6.

Table S6. Phase parameters of sample S5

Name	SG <sup>1</sup>	a	b	c	Atom Position		
LiGdF <sub>4</sub>	I 41/a	5.19	5.19	10.85	Li(0, 1/4, 1/8)	Gd(1/2, 3/4, 1/8)	F(0.25, 0.10, 0.05)
Gd <sub>0.67</sub> F <sub>2</sub>	Fm-3m	5.53	5.53	5.53	Gd(0, 0, 0) <sup>2</sup>	F(1/4, 1/4, 1/4)	

1. Space Group

2. The fractional occupancy of Gd atom in Gd<sub>0.67</sub>F<sub>2</sub> was 0.67. The fractional occupancies of other atoms were 1.

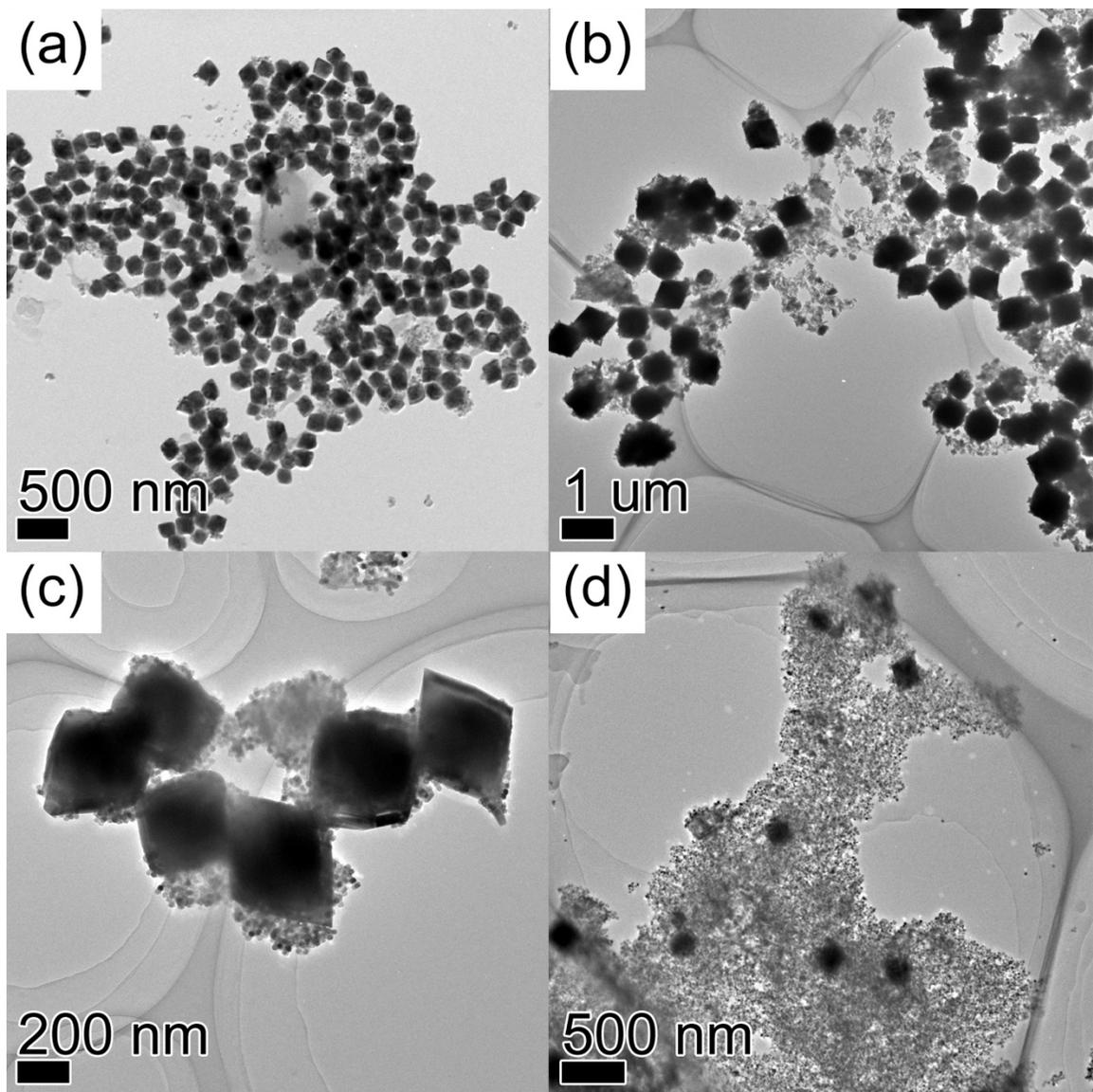


Figure S7. TEM images of sample S1, S3, S4, and S5. The bigger rhombic particles were  $\text{LiGdF}_4$  and the smaller particles were the impurities.

Talbe S7. Fitting parameters and equations for Fig. 4-6.

Figure	Equation	Parameters		
		a	b	c
4	$a \cdot e^{\left[ -\ln 2 \cdot \left( \frac{x-b}{c} \right)^2 \right]}$	4.1784	535.40	20.000
		18.944	557.90	19.511
		203.49	662.60	13.973
		273.54	676.60	12.849
		19.119	691.80	16.177
		8.6477	711.30	14.778
5a	$a \cdot x + b$	a	b	
		37756	-21585	
5b		2004.8	-1035.1	
5c		18.059	0.4595	
6b		1.8274	-1.8491	
		2.1221	-3.8913	