Electronic Supplementary Information (ESI)

Tysonite type $Gd_{1-y}Ca_yF_{3-y}$ solid solution: hydrothermal synthesis and luminescence properties

Qi Zhao,[ab] Baiqi Shao,[ab] Wei Lü, [a] Yongchao Jia,[ab] Wenzhen Lv,[ab] Mengmeng Jiao[ab], and Hongpeng You*[a]

[a]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China.

[b]University of the Chinese Academy of Sciences, Beijing 100049, P. R. China.

*Corresponding author: E-mail address: hpyou@ciac.ac.cn

	$GdCl_3$ (1 mol·L^{-1}) (mL)	**$CaCl_2$ (1 mol·L^{-1}) (mL)**	**Ethylene glycol (mL)**	**Deionized water (mL)**		**Sodium fluoborate (g)**	**Time/Temperature (℃/h)**
Typical sample							
1	1	1	20	10	8	1.5	160/6
Effect of the ethylene glycol							
2	1	1	0	30	8	0.15	160/6
3	1	1	10	20	8	0.15	160/6
4	1	1	15	15	8	0.15	160/6
5	1	1	25	5	8	0.15	160/6
6	1	1	30	0	8	0.15	160/6
Effect of the calcium amount							
7	1	0	20	11	8	0.15	160/6
8	1	0.2	20	10.8	8	0.15	160/6
9	1	0.4	20	10.6	8	0.15	160/6
10	1	0.8	20	10.2	8	0.15	160/6
11	1	1.5	20	9.5	8	0.15	160/6
12	1	2	20	9	8	0.15	160/6
Effect of the fluorine amount							
13	1	1	20	10	8	0.055	160/6
14	1	1	20	10	8	0.11	160/6
15	1	1	20	10	8	0.22	160/6
Effect of the reagents concentration							
16	0.3	0.3	20	11.4	8	0.05	160/6
17	0.5	0.5	20	11	8	0.075	160/6
18	2	2	20	8	8	0.3	160/6
19	3	3	20	6	8	0.45	160/6
Effect of the time							
20	1	1	20	10	8	1.5	160/0.5
21	1	1	20	10	8	1.5	160/2
22	1	1	20	10	8	1.5	160/8
23	1	1	20	10	8	1.5	160/24
Effect of the temperature							
24	1	1	20	10	8	1.5	120/6
25	1	1	20	10	8	1.5	140/6
26	1	1	20	10	8	1.5	180/6
27	1	1	20	10	8	1.5	200/6
Luminescence properties							
28 2%	Gd 0.98 Tb 0.02	1	20	10	8	1.5	160/6
29 2%	Gd 0.98 Dy 0.02	1	20	10	8	1.5	160/6
30 5%	Gd 0.95 Eu 0.05	1	20	10	8	1.5	160/6

	$GdCl_3$ (1 mol·L^{-1}) (mL)	**$CaCl_2$ (1 mol·L^{-1}) (mL)**	**Ethylene glycol (mL)**	**Deionized water (mL)**		**Sodium fluoborate (g)**	**Time/Temperature (℃/h)**
Luminescence properties							
31 0.1%	Gd 0.999 Eu 0.02 (0.05 mol·L^{-1})	1	20	9.981	8	1.5	160/6
32 0.5%	Gd 0.995 Eu 0.1 (0.05 mol·L^{-1})	1	20	9.905	8	1.5	160/6
33 1%	Gd 0.99 Eu 0.2 (0.05 mol·L^{-1})	1	20	9.81	8	1.5	160/6
34 0.1%	Gd 0.999 Eu 0.02 (0.05 mol·L^{-1})	0	20	10.981	8	1.5	160/6
35 0.5%	Gd 0.995 Eu 0.1 (0.05 mol·L^{-1})	0	20	10.905	8	1.5	160/6
36 1%	Gd 0.99 Eu 0.2 (0.05 mol·L^{-1})	0	20	10.81	8	1.5	160/6
37 5%	Gd 0.95 Eu 0.05	0	20	11	8	1.5	160/6
38 5%	Gd 0.95 Eu 0.05	0.4	20	10.6	8	1.5	160/6
39 5%	Gd 0.95 Eu 0.05	0.8	20	10.2	8	1.5	160/6
40 1%	Gd 0.99 Eu 0.2 (0.05 mol·L^{-1})	0.4	20	10.41	8	1.5	160/6
41 1%	Gd 0.99 Eu 0.2 (0.05 mol·L^{-1})	0.8	20	10.01	8	1.5	160/6

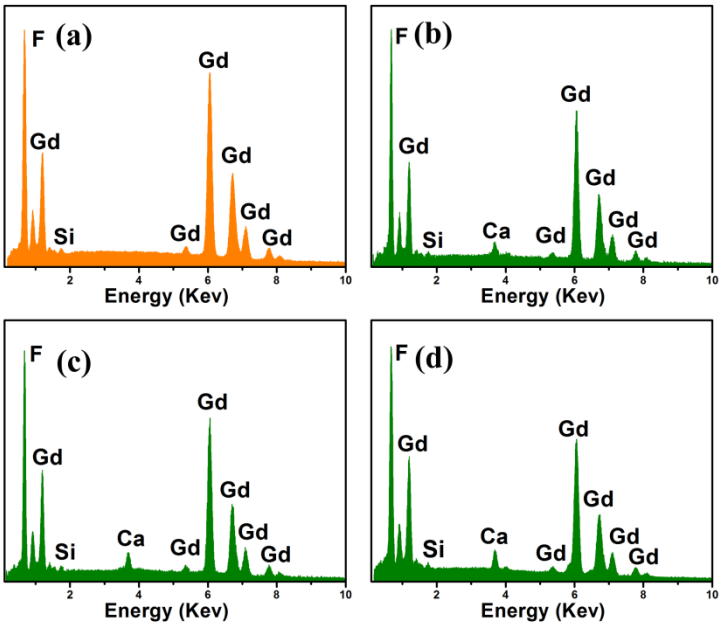

Fig. S1 EDS spectra of samples prepared with different amount of $CaCl_2$: (a) 0.2 mmol, (b) 0.4 mmol, (c) 0.8 mmol, (d) 1 mmol.

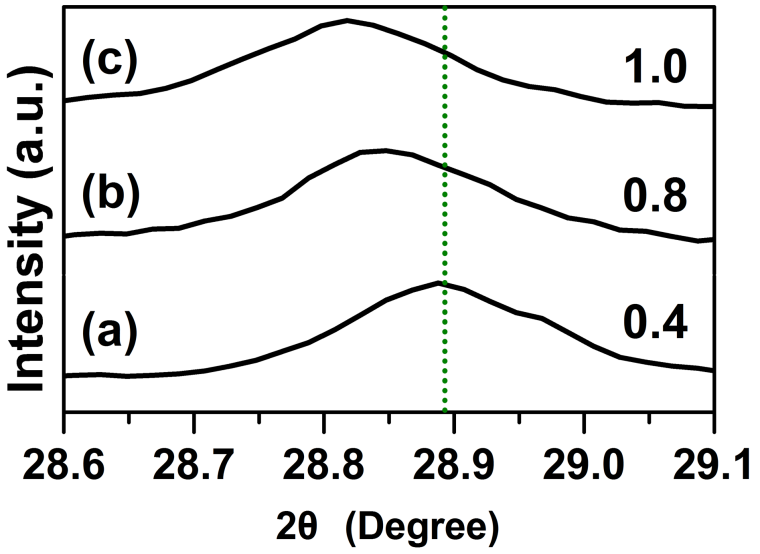

Fig. S2 Partial enlarged detail of XRD patterns of samples obtained with different amount of $CaCl_2$: (a) 0.4 mmol, (b) 0.8 mmol, (c) 1.0 mmol.

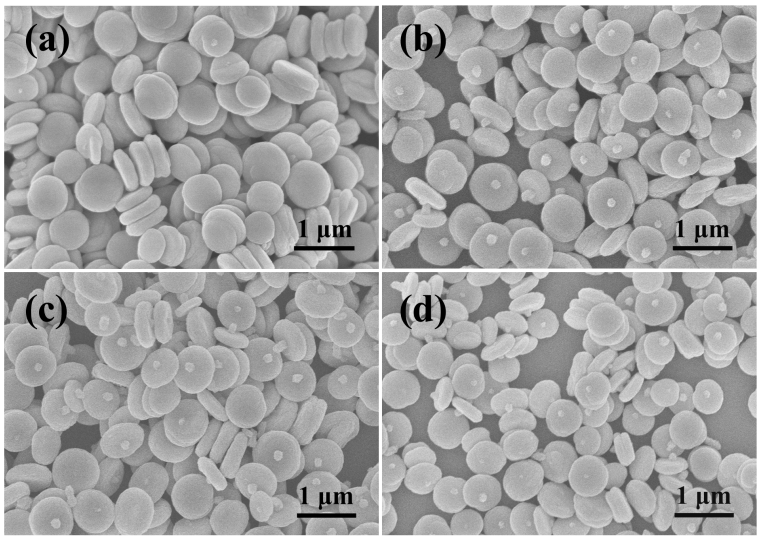

Fig. S3 SEM images of samples prepared with different temperature: (a) 120 ℃, (b) 140 ℃, (c) 180 ℃, (d) 200 ℃.

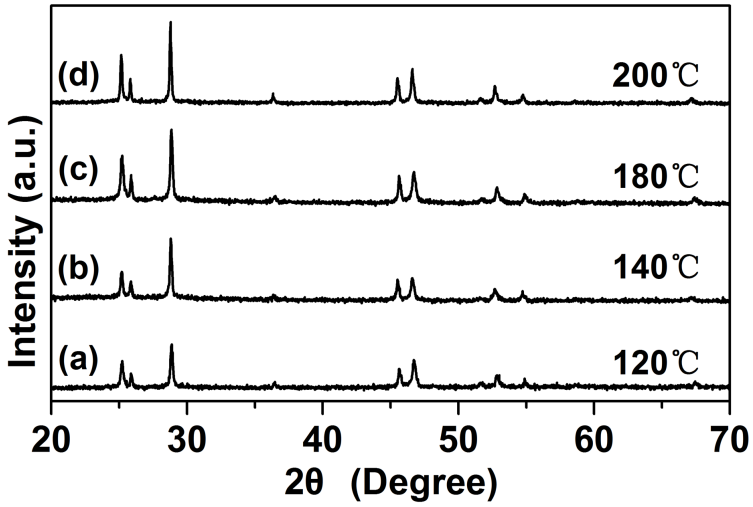

Fig. S4 XRD patterns of samples prepared with different temperature: (a) 120 ℃, (b) 140 ℃, (c) 180 ℃, (d) 200 ℃.

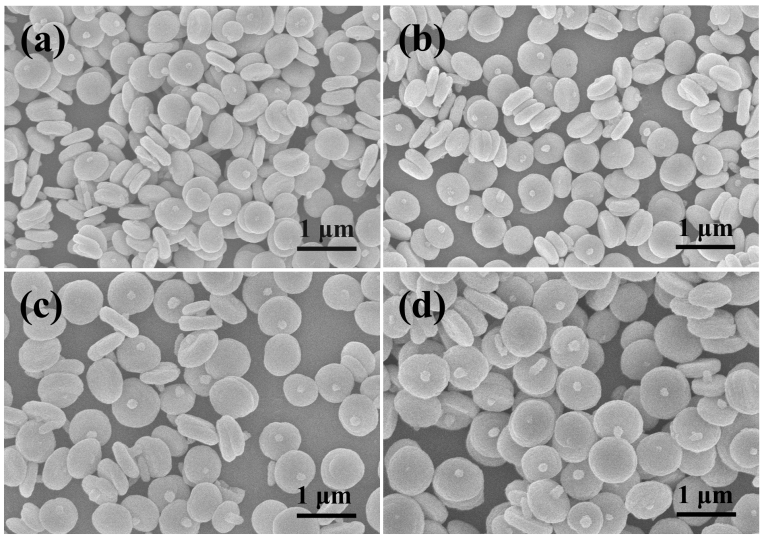

Fig. S5 SEM images of samples prepared with different reaction time: (a) 0.5 h, (b) 2 h, (c) 8 h, (d) 24 h.

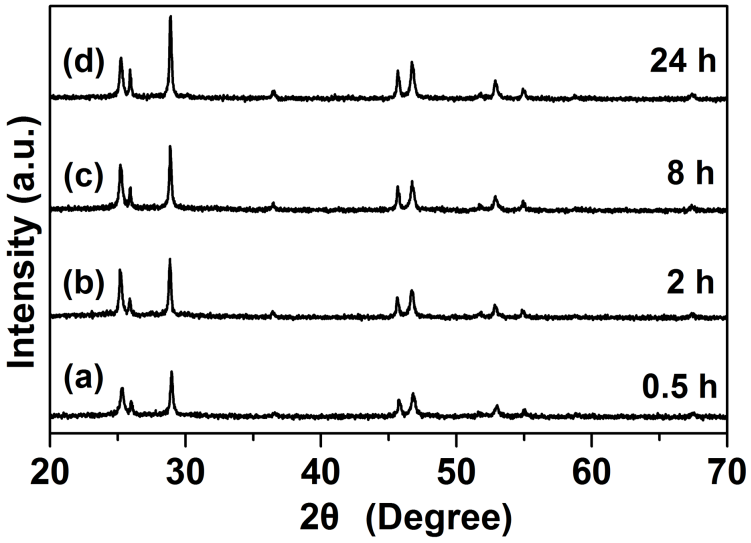

Fig. S6 XRD pattersn of samples prepared with different reaction time: (a) 0.5 h, (b) 2 h, (c) 8 h, (d) 24 h

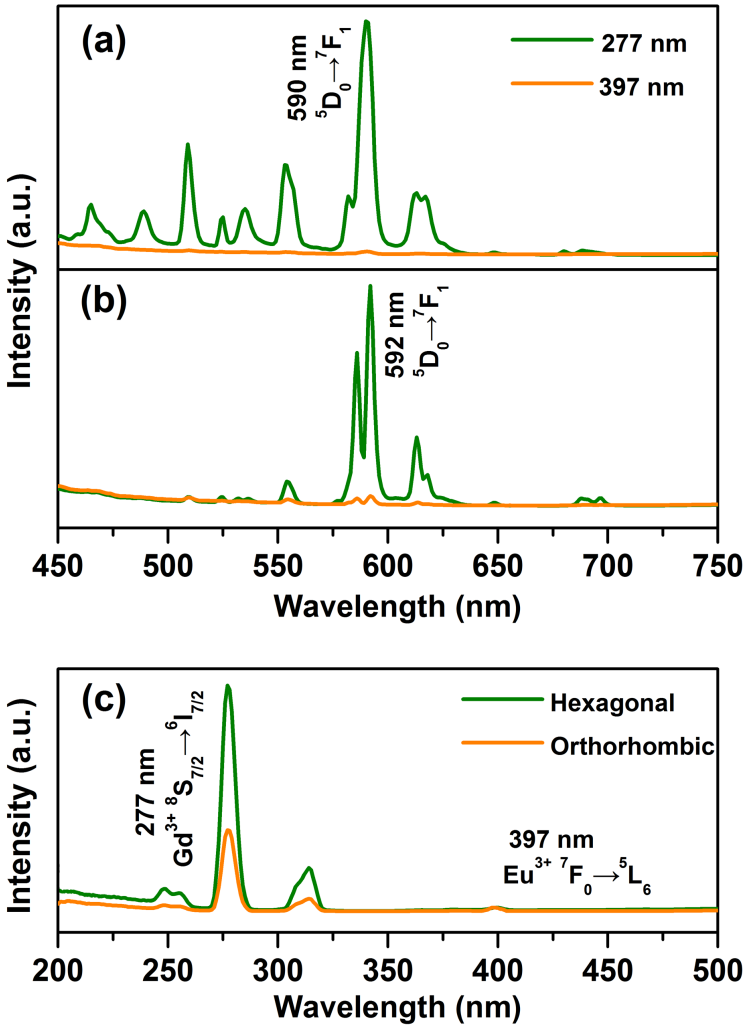

Fig. S7 Emission spectra of (a) hexagonal $Gd_{1-y}Ca_yF_{3-y}$: 0.1 mol% Eu^{3+} and orthorhombic (b) GdF_3:Eu^{3+} excited at 272 nm and 396 nm. (c) Excitation spectra of hexagonal and orthorhombic samples monitored at 590 and 592 nm, respectively.

$I^{H}_{277/397} = 62.10$

$I^{O}_{277/397} = 20.44$

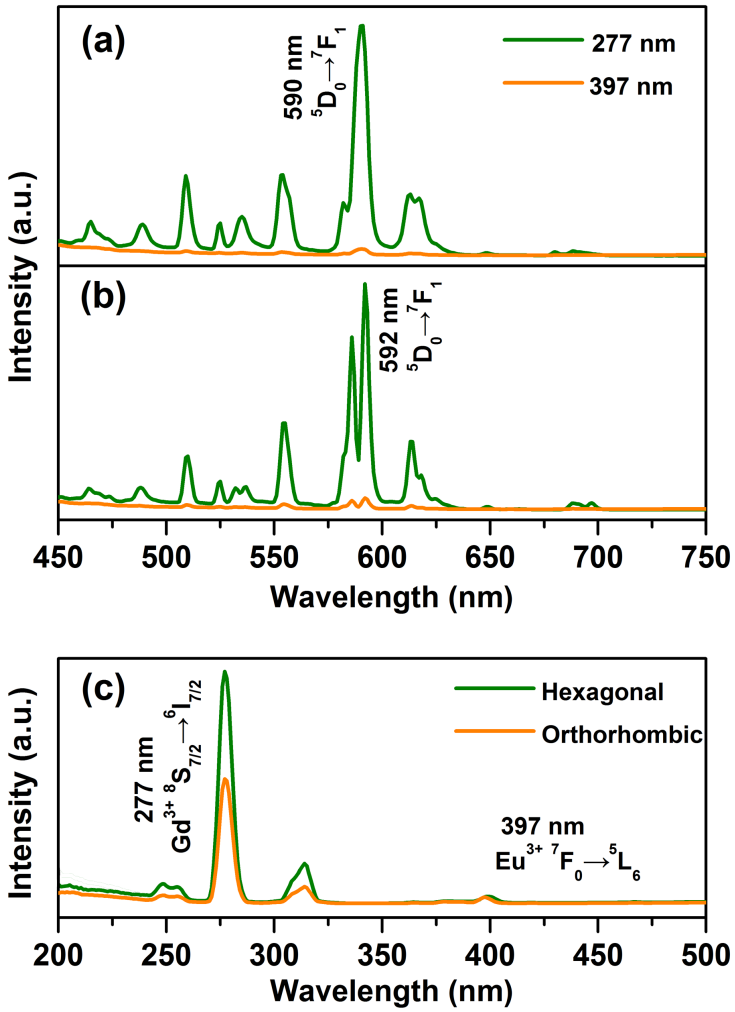

Fig. S8 Emission spectra of (a) hexagonal $Gd_{1-y}Ca_yF_{3-y}$: 0.5 mol% Eu^{3+} and orthorhombic (b) GdF_3:Eu^{3+} excited at 272 nm and 396 nm. (c) Excitation spectra of hexagonal and orthorhombic samples monitored at 590 and 592 nm, respectively.

$I^{H}_{277/397} = 35.51$

$I^{O}_{277/397} = 18.86$

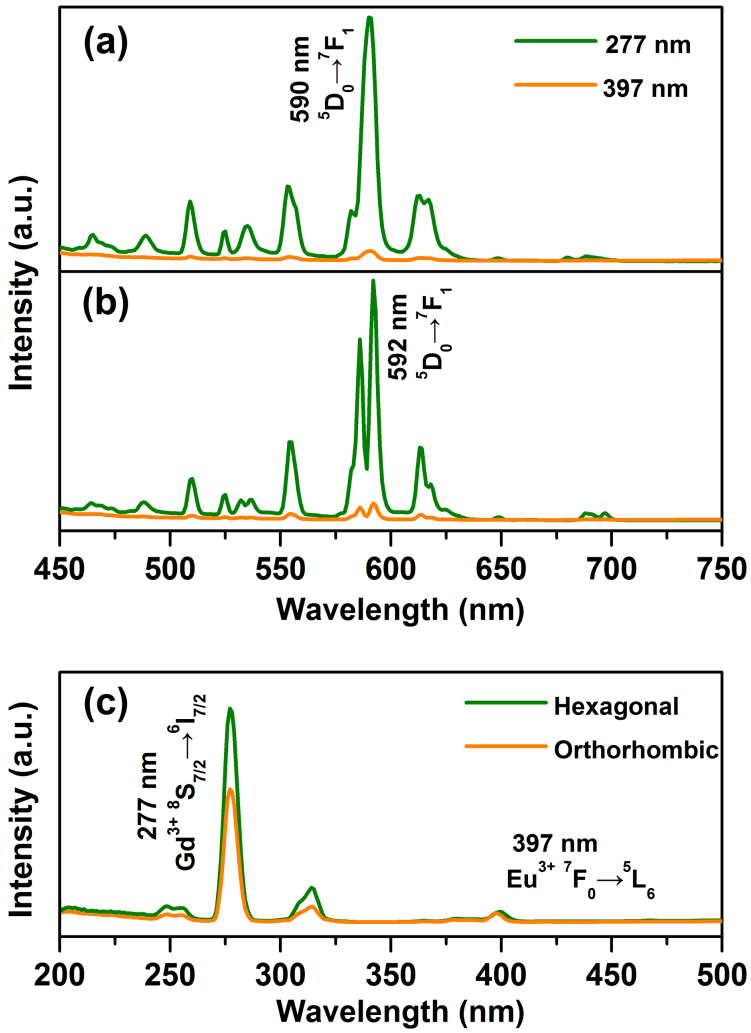

Fig. S9 Emission spectra of (a) hexagonal $Gd_{1-y}Ca_yF_{3-y}$: 1 mol% Eu^{3+} and orthorhombic (b) GdF_3:Eu^{3+} excited at 272 nm and 396 nm. (c) Excitation spectra of hexagonal and orthorhombic samples monitored at 590 and 592 nm, respectively.

$I^{H}_{277/397} = 23.98$

$I^{O}_{277/397} = 13.77$