

**Electronic Supplementary Information (ESI)**

# Doping alkaline-earth: a strategy of stabilizing hexagonal $\text{GdF}_3$ at room temperature

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**Table S1**

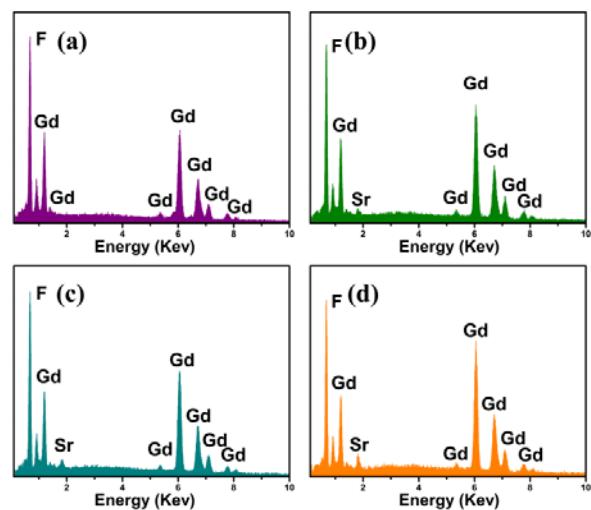
| Amount of $\text{LnCl}_3$<br>(1 mol/L) (mL) | Amount of $\text{MCl}_2$ (mL)<br>(1 mol/L) (mL) | Nominal composition<br>(mol %) | Content by EDS<br>(mol %) |
|---|---|--------------------------------|---------------------------|
| Gd 0.9                                      | Sr 0.1  | Sr 10                          | Sr 0                      |
| Gd 0.8                                      | Sr 0.2  | Sr 20                          | Sr 8.2                    |
| Gd 0.7                                      | Sr 0.3  | Sr 30                          | Sr 9.3                    |
| Gd 0.6                                      | Sr 0.4  | Sr 40                          | Sr 10.6                   |
| Gd 0.5                                      | Sr 0.5  | Sr 50                          | Sr 11.9                   |
| Gd 0.4                                      | Sr 0.6  | Sr 60                          | — —                       |
| Gd 0.3                                      | Sr 0.7  | Sr 70                          | — —                       |
| Gd 0.9                                      | Ca 0.1  | Ca 10                          | Ca 0                      |
| Gd 0.8                                      | Ca 0.2  | Ca 20                          | Ca 5.0                    |
| Gd 0.7                                      | Ca 0.3  | Ca 30                          | Ca 7.3                    |
| Gd 0.6                                      | Ca 0.4  | Ca 40                          | Ca 8.7                    |
| Gd 0.5                                      | Ca 0.5  | Ca 50                          | Ca 9.6                    |
| Gd 0.4                                      | Ca 0.6  | Ca 60                          | — —                       |
| Gd 0.3                                      | Ca 0.7  | Ca 70                          | — —                       |
| Gd 0.95<br>Eu 0.05                          | 0   | — —                            | Eu 6.2                    |
| Gd 0.76<br>Eu 0.04                          | Sr 0.2  | Sr 20                          | Sr 7.1<br>Eu 5.8          |
| Gd 0.8<br>Yb 0.18<br>Er 0.02                | 0   | — —                            | — —                       |
| Gd 0.64<br>Yb 0.144<br>Er 0.016             | Sr 0.2  | Sr 20                          | — —                       |

**Table S2**

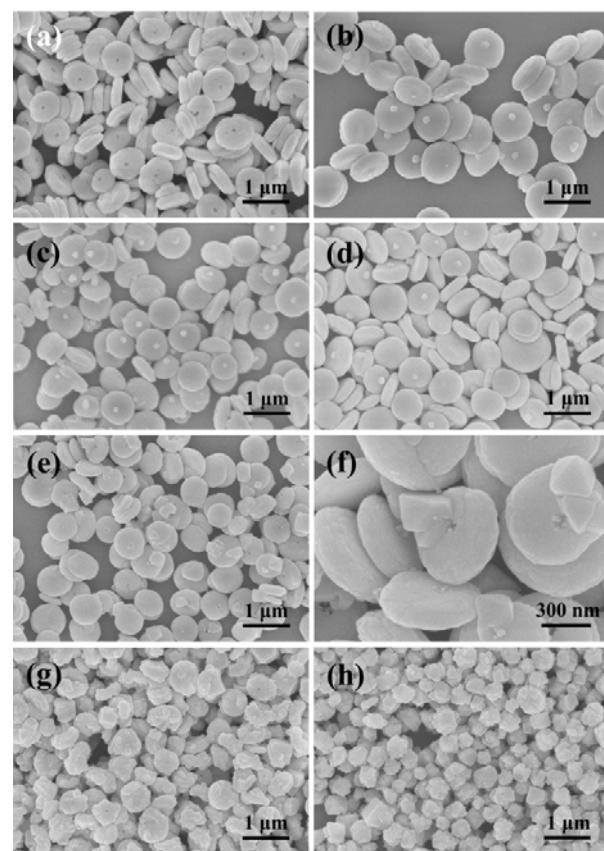
| Nominal content of La (mol %)                              | 10  | 20  | 30  | 40  | 50  | 60  | 20                 |
|--|-----|-----|-----|-----|-----|-----|--------------------|
| Amount of $\text{Gd}(\text{Eu})\text{Cl}_3$ (1 mol/L) (mL) | 0.9 | 0.8 | 0.7 | 0.6 | 0.5 | 0.4 | Gd 0.76<br>Eu 0.04 |
| Amount of $\text{LaCl}_3$ (1 mol/L) (mL)                   | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.2                |

**Table S3**

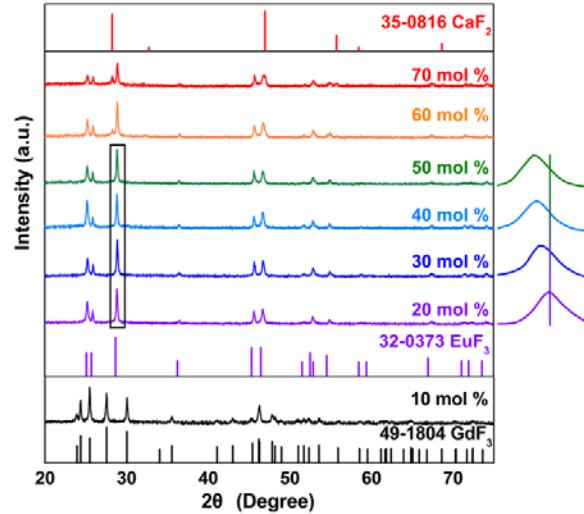
| Nominal content of Sr (mol %)    | 20                             | 30                             | 40                             | 50                             |
|----------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| Cell parameters ( $\text{\AA}$ ) | $a = b = 6.889$<br>$c = 7.065$ | $a = b = 6.896$<br>$c = 7.075$ | $a = b = 6.899$<br>$c = 7.079$ | $a = b = 6.905$<br>$c = 7.086$ |



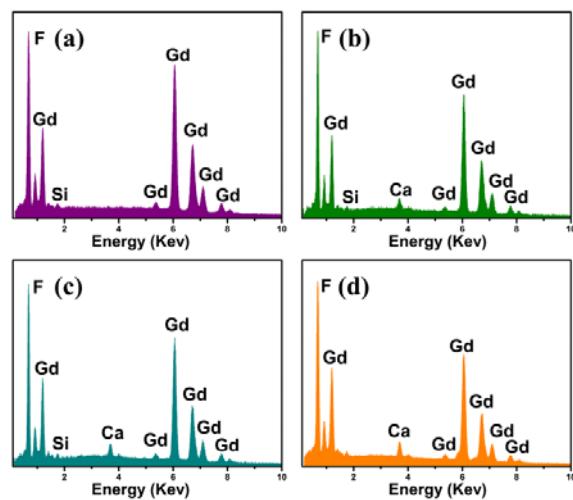
**Fig. S1** The EDS spectra of the Sr-doped  $\text{GdF}_3$  with different nominal compositions: (a) 10 mol%, (b) 20 mol%, (c) 30 mol%, (d) 50 mol%



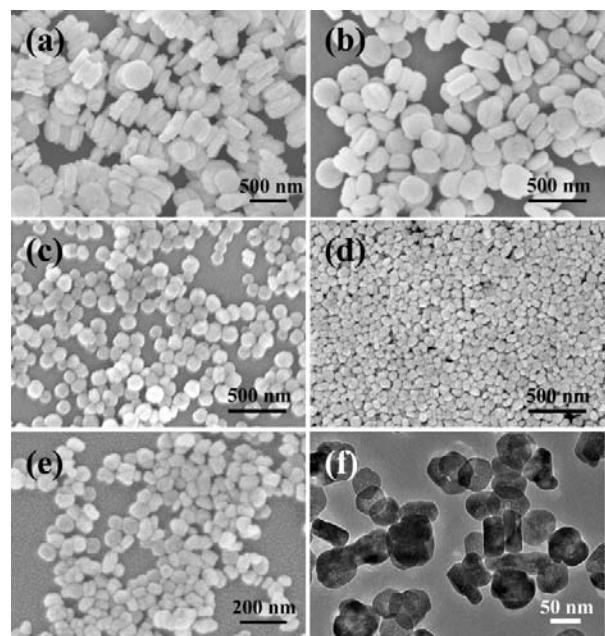
**Fig. S2** The SEM images of the Ca-doped  $\text{GdF}_3$  with different nominal compositions: (a) 10 mol%, (b) 20 mol%, (c) 30 mol%, (d) 40 mol%, (e,f) 50 mol%, (g) 60 mol%, and (h) 70 mol%.



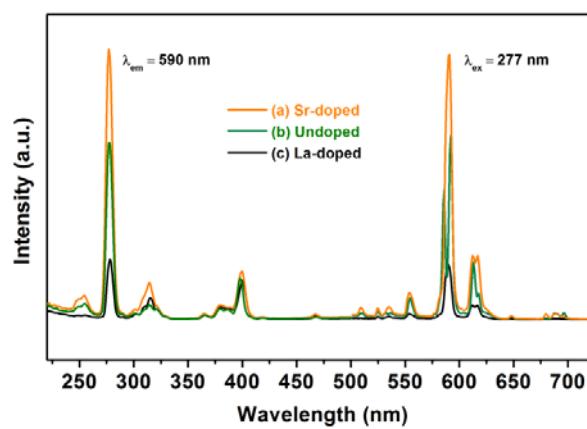
**Fig. S3** The XRD patterns of the Ca-doped GdF<sub>3</sub> with different nominal compositions. The right is partial enlarged detail from 28.6 to 29.1 degree.



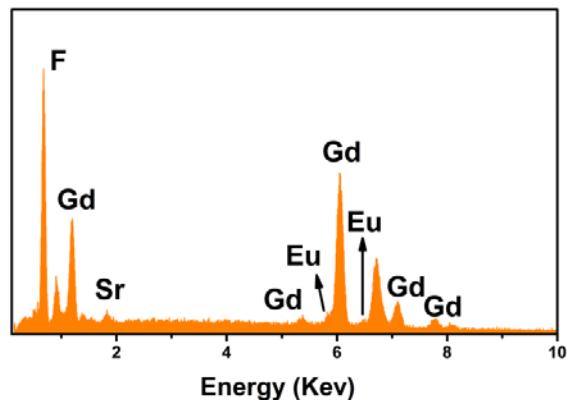
**Fig. S4** The EDS spectra of of the Ca-doped GdF<sub>3</sub> with different nominal composition: (a) 10 mol%, (b) 20 mol%, (c) 30 mol%, (d) 50 mol%.



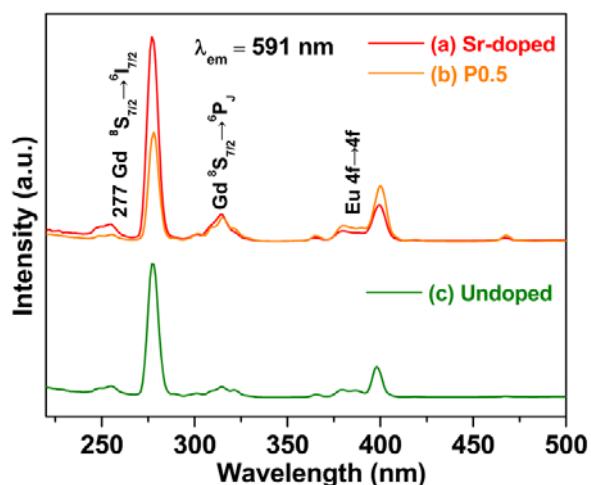
**Fig. S5** The SEM images of the La-doped  $\text{GdF}_3$  with different nominal compositions: (a) 10 mol%, (b) 20 mol%, (c) 30 mol%, (d) 40 mol%, (e) 50 mol%, and (f) 60 mol%.



**Fig. S6** The excitation (left) and emission (right) spectra of (a) 20 mol% Sr-doped  $\text{GdF}_3:\text{Eu}$ , (b) undoped  $\text{GdF}_3:\text{Eu}$ , and (c) 30 mol% La-doped  $\text{GdF}_3:\text{Eu}$ .



**Fig. S7** The EDS spectrum of Sr-doped  $\text{GdF}_3:\text{Eu}$ .



**Fig. S8** The excitation spectra of (a) the hexagonal Sr-doped  $\text{GdF}_3:\text{Eu}$ , (b) the hexagonal  $\text{GdF}_3:\text{Eu}$  obtained after reacting for 0.5 h (**P0.5**), and (c) the orthorhombic  $\text{GdF}_3:\text{Eu}$ .