

## Supporting Information

### Phase and morphology evolution of luminescent NaLnF<sub>4</sub> (Ln= La to Yb) microcrystals: Understanding the Ionic radii and surface energy dependent solution growth mechanism

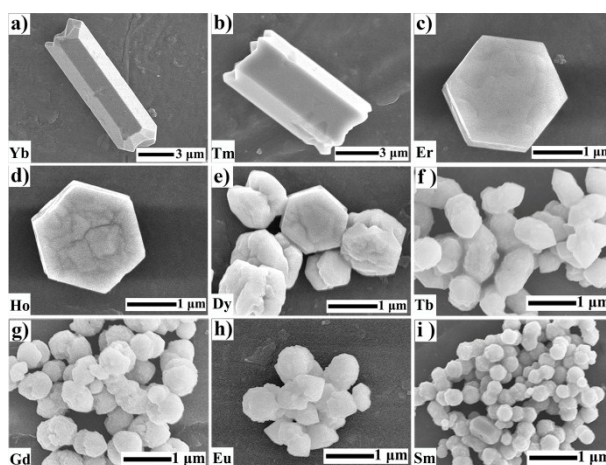
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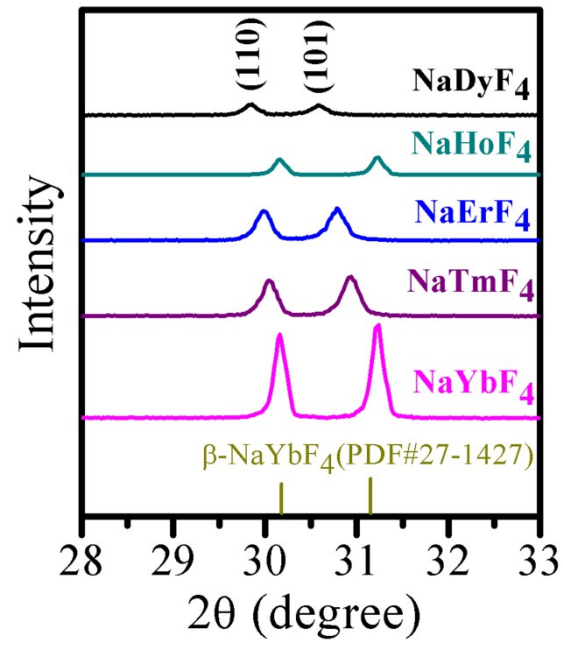
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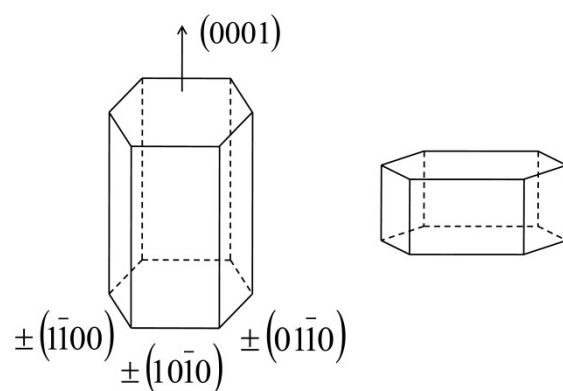
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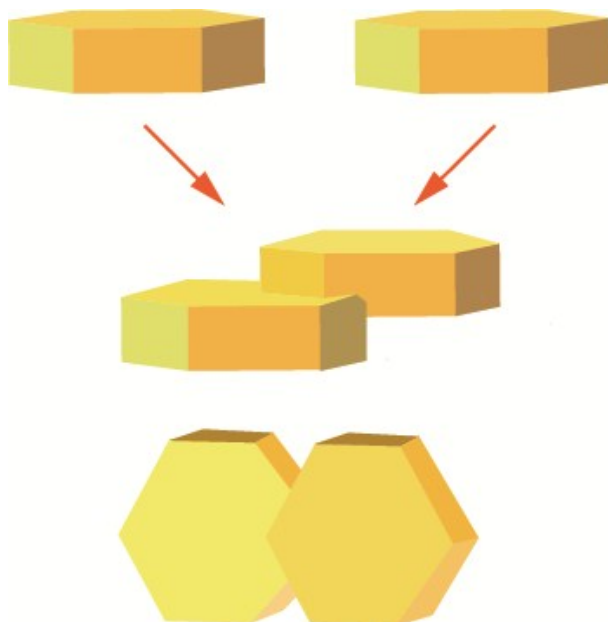
**Figure S1.** SEM images of lanthanide fluoride MCs NaLnF<sub>4</sub> (Ln: Yb- Sm).



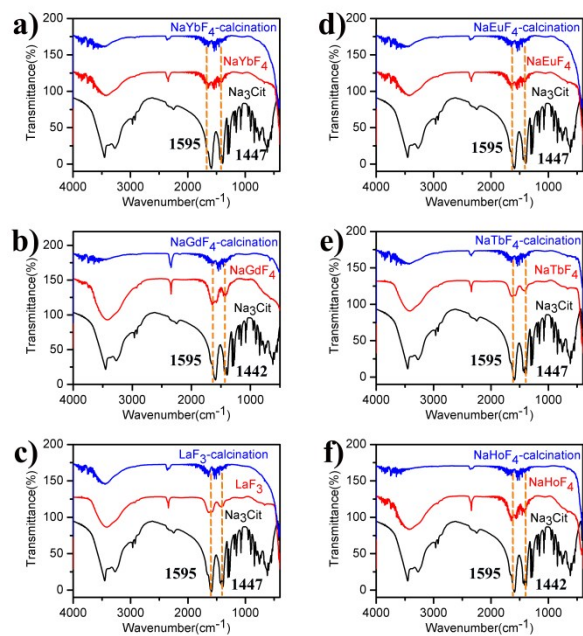
**Figure S2.** The amplification peak of (110) and (101) of NaLnF<sub>4</sub> (Ln: Yb-Dy).



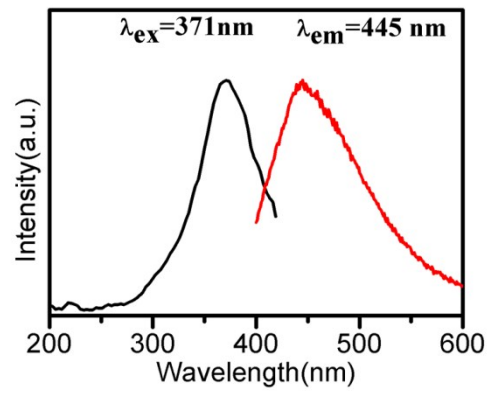
**Figure S3.** Schematic diagram showing the anisotropy of the  $\text{NaLnF}_4$  (Ln= La to Yb) Structures.



**Figure S4.** The formation of double hexagonal microdisks like  $\text{NaLnF}_4$  (Ln:Tb-Sm)



**Figure S5.** FT-IR spectra for Na<sub>3</sub>Cit and before and after (a) NaYbF<sub>4</sub>, (b) NaGdF<sub>4</sub>, (c) LaF<sub>3</sub>, (d) NaEuF<sub>4</sub>, (e) NaTbF<sub>4</sub> and (f) NaHoF<sub>4</sub> samples



**Figure S6.** PL excitation and emission spectra of Na<sub>3</sub>Cit

**Table S1.** The surface energy and the formation energy of NaSmF<sub>4</sub> and NaYbF<sub>4</sub>.

	$E_{s-(001)}$ (eV/Å <sup>2</sup> )	$E_{s-(100)}$ (eV/Å <sup>2</sup> )	$E_s$ (eV)	$E_f$ (eV)
NaSmF <sub>4</sub> - 2F	0.007	0.041	6.112	33.00
NaYbF <sub>4</sub> - 2F	0.054	0.036	9.764	26.11

**Table S2** Ionic radii (Å) of Ln<sup>3+</sup> and Na<sup>+</sup>

Ln <sup>3+</sup>	<sup>1*</sup> R <sub>ionic</sub> (CN6)	<sup>2*</sup> R <sub>ionic</sub> (CN8)	<sup>3*</sup> R <sub>ionic</sub> (CN9)	<sup>4*</sup> R <sub>ionic</sub> (CN11)
La <sup>3+</sup>	1.032	1.160	1.126	1.360
Ce <sup>3+</sup>	1.01	1.143	1.196	1.340
Pr <sup>3+</sup>	0.99	1.126	1.179	
Nd <sup>3+</sup>	0.983	1.109	1.163	1.27
Pm <sup>3+</sup>	0.97	1.093	1.144	
Sm <sup>3+</sup>	0.958	1.079	1.132	1.24
Eu <sup>3+</sup>	0.947	1.066	1.120	
Gd <sup>3+</sup>	0.938	1.053	1.107	
Tb <sup>3+</sup>	0.923	1.040	1.095	
Dy <sup>3+</sup>	0.912	1.027	1.083	
Ho <sup>3+</sup>	0.901	1.015	1.072	
Er <sup>3+</sup>	0.890	1.004	1.062	
Tm <sup>3+</sup>	0.880	0.994	1.052	
Yb <sup>3+</sup>	0.868	0.985	1.042	
Lu <sup>3+</sup>	0.861	0.977	1.032	
Na <sup>+</sup>	1.02	1.118	1.24	

1\*. ionic radius of lanthanide at 6 coordination (Shannon)

2\*. ionic radius of lanthanide at 8 coordination (Shannon)

3\*. ionic radius of lanthanide at 9 coordination (Shannon)

4\*. ionic radius of lanthanide at 11 coordination (Shannon)

**Table S3** (110) FWHM (°) of XRD peaks assigned to NaLnF<sub>4</sub> (110) plane

Ln-based fluoride	(110)FWHM(°)
LaF <sub>3</sub>	0.34
CeF <sub>3</sub>	0.34
PrF <sub>3</sub>	0.35
NdF <sub>3</sub>	0.36
NaSmF <sub>4</sub>	0.37
NaEuF <sub>4</sub>	0.36
NaGdF <sub>4</sub>	0.36
NaTbF <sub>4</sub>	0.34
NaDyF <sub>4</sub>	0.23
NaHoF <sub>4</sub>	0.25
NaErF <sub>4</sub>	0.24
NaTmF <sub>4</sub>	0.21
NaYbF <sub>4</sub>	0.18



## Supplementary Note-surface and absorption models

All the first-principles calculations have been carried out based on density functional theory (DFT) using the Vienna *ab initio* simulation package (VASP) [1,2] within the Perdew-Burke-Ernzerh of generalized gradient approximation (PBE-GGA) exchange-correlation potential [3]. Ionic potentials were treated by the projector-augmented wave (PAW) pseudo potential method [4,5]. The kinetic energy cutoff was set to 400 eV. The convergence criteria for the electronic energy and the geometry relaxation were set to  $10^{-4}$  eV and 0.02 eV/Å, respectively. In the case of slabs, the vacuum space of at least 15 Å was set to avoid spurious interactions between two neighboring sheets. Monkhorst-Pack k-point sampling [6] was used with  $5 \times 5 \times 3$  grid meshes for bulk structures, and  $5 \times 5 \times 1$  grid meshes for slabs. The Grimme's method (DFT-D3) [7] was employed to incorporate the effects of van der Waals interactions. Atoms with purple, green, blue and brown colors represent sodium, fluorine, samarium and ytterbium atoms, respectively.

The surface energy ( $E_s$ ) is defined as:

$$E_s = (E_{\text{slab}} - N \times E_{\text{bulk}} - 2 \times \frac{1}{2} \times E_{\text{F}_2}) \times \frac{1}{2S}$$

where  $E_{\text{bulk}}$  is the energy per unit of NaREF<sub>4</sub>,  $E_{\text{slab}}$  and  $E_{\text{F}_2}$  represent the total energy of the slab structure and the isolated F<sub>2</sub>, respectively.  $N$  is the number of unit NaREF<sub>4</sub> contained in the slab model.

The formation energy ( $E_f$ ) is calculated by:

$$E_f = E_{\text{bulk}} - E_{\text{Na}} - E_{\text{RE}} - 4 \times E_{\text{F}}$$

where  $E_{\text{bulk}}$ ,  $E_{\text{Na}}$ ,  $E_{\text{RE}}$  and  $E_{\text{F}}$  represent the total energy of the bulk NaLnF<sub>4</sub> (Ln=Yb,Sm), the isolated Na, Ln and F atom, respectively.

## Supplementary References

- 1 G. Kresse and J. Furthmüller, *Computational Materials Science*, 1996, **6**, 15-50
- 2 G. Kresse and J. Furthmüller, *Physical Review B*, 1996, **54**, 11169-11186.
- 3 J.P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1996, **77**, 3865-3868.
- 4 P. E. Blochl, *Physical Review B*, 1994, **50**, 7953-17979.

- 5 G. Kresse and D Joubert, *Physical Review B*, 1999, **59**, 1758-1775.
- 6 H.J. Monkhorst and J. D. Pack, *Physical Review B*, 1977, **16**, 1746-1747.
- 7 S. Grimme, S. Ehrlich, L. Goerigk, *J Comput Chem*, 2011, 32, 1456-1465.