Electronic Supplementary Material (ESI) for CrystEngComm.

Low temperature route to prepare rare earth fluorides in molten NH_4NO_3system: A systematic study on the effects of NaF/Ln ratio and the reaction temperature and time

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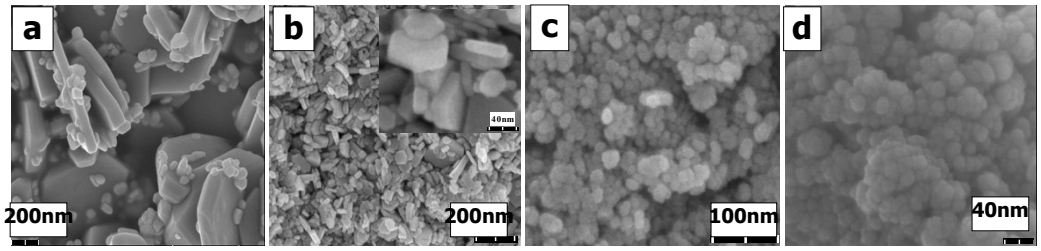

Fig.S1 SEM images of theCe-based products obtained (a) 250°C,24h, NaF/NH_4NO_3/Ce of 3/8/1; (b) 250°C,24h, NaF/NH_4NO_3/Ce of 6/8/1; (c) 100 °C, 40min, NaF/NH_4NO_3/Ce of 3/8/1 (d) 100 °C, 40min, NaF/NH_4NO_3/Ce of 6/8/1

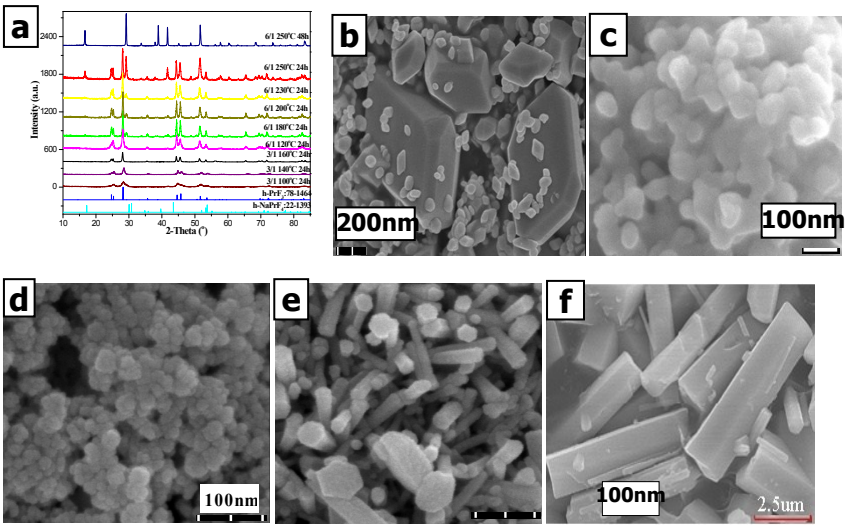

Fig. S2 XRD patterns (a) and SEM images of the Pr-based products obtained at different reaction temperatures of (b)3/1, 250 °C, 24 h; (c)3/1,140 °C, 2 h ; (d)6/1, 100 °C,24 h; (e) 6/1, 200 °C, 24 h; and (f) 6/1, 250 °C, 24 h.

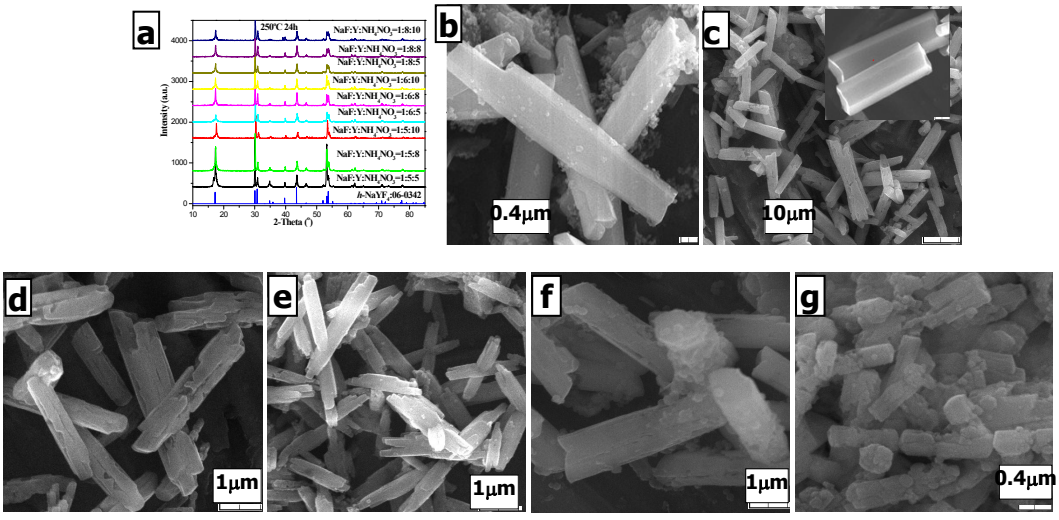

Fig.S3 XRD patterns (a) and SEM images of the Y-based products obtained after 24 h at 250 °C for different NaF/NH_4NO_3/Y molar ratios of (b)5/5/1; (c) 6/5/1; (d) 8/5/1; (e) 5/10/1;(f) 6/10/1 and (g) 8/10/1.

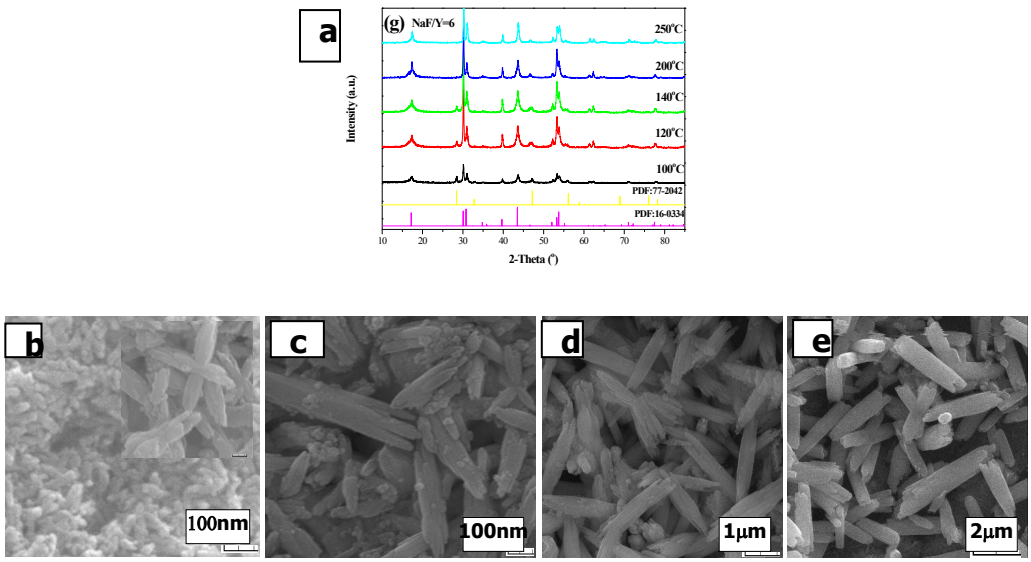

Fig.S4 XRD patterns (a) and SEM images of the Y-based products obtained at 120 °C(b), 140 °C(c), 160 °C(d) and 200 °C (e) for NaF/NH_4NO_3/Y molar ratio of 6/8/1 and for 24h.

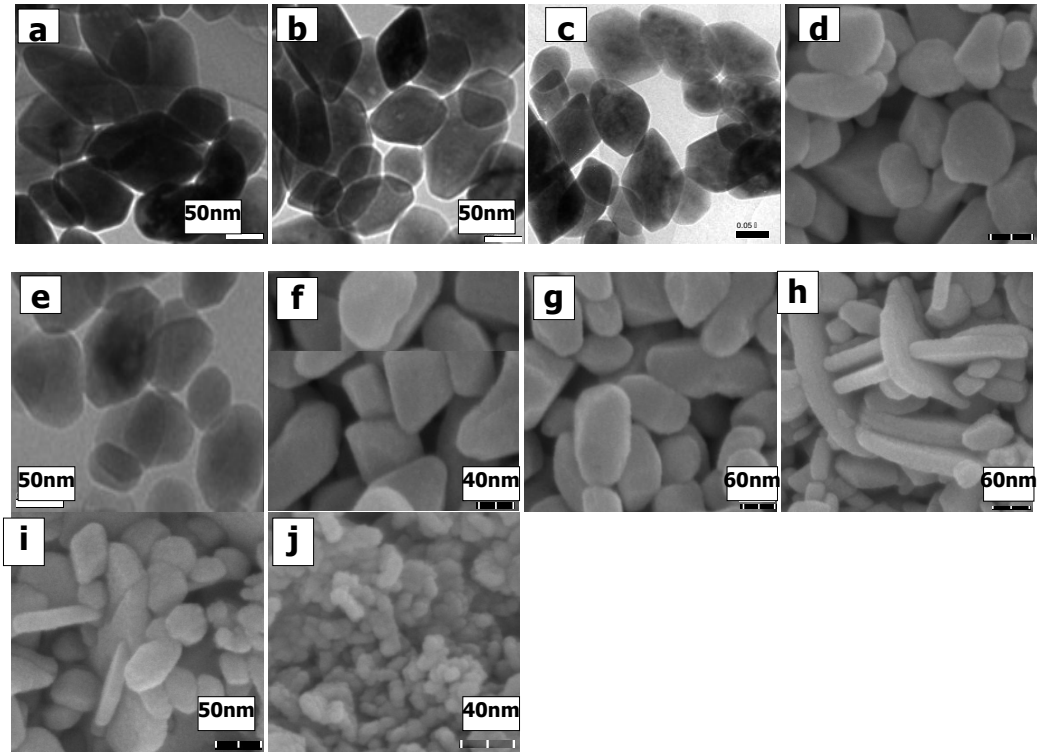

Fig. S5 SEM images of the Group III- and IV-based products obtained after 2 h at 140 °C for NaF/Ln ratio of 3, Sm (a), Eu(b), Ho(c), Tm (d), Er(e), Gd(f), Lu(g), Tb(h), Dy (i) and Yb (j)

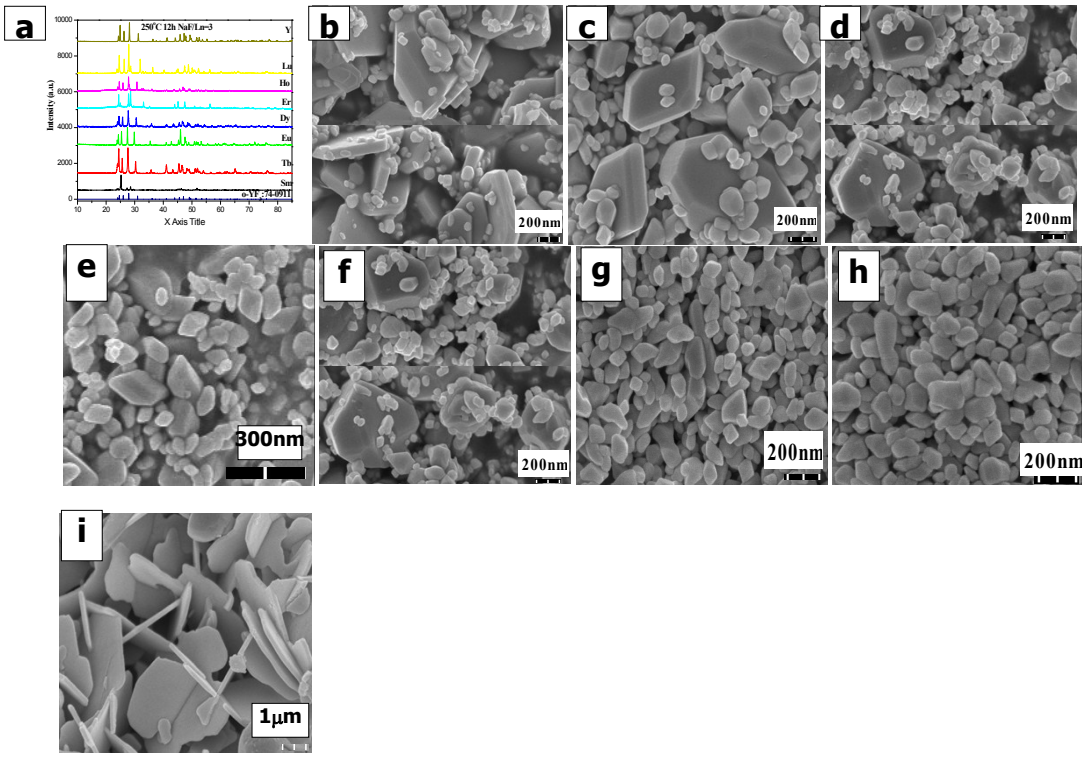

Fig. S6 XRD (a) and SEM images of the Group III-and and IV-based products obtained after 24 h at 250 °Cfor 24h. Sm (b), Eu(c), Ho(d), Tm (e), Er(f), Gd(g), Lu(h) and Yb (i).

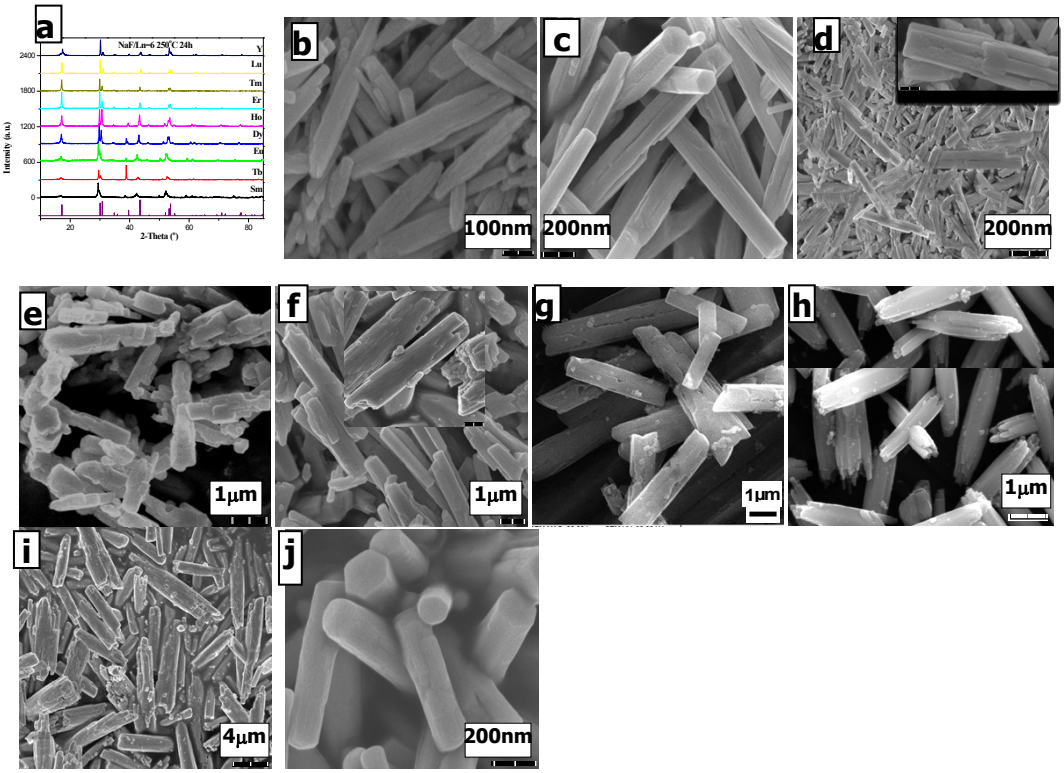

Fig. S7 XRD patterns (a)and SEM images of the Group III- and IV- based products obtained after 24 h at 250 °C for NaF/Ln ratio of 6: Sm (b), Eu(c), Tb(d), Dy(e), Ho(f), Er(g),Tm(h), Lu(i) and Yb (j).

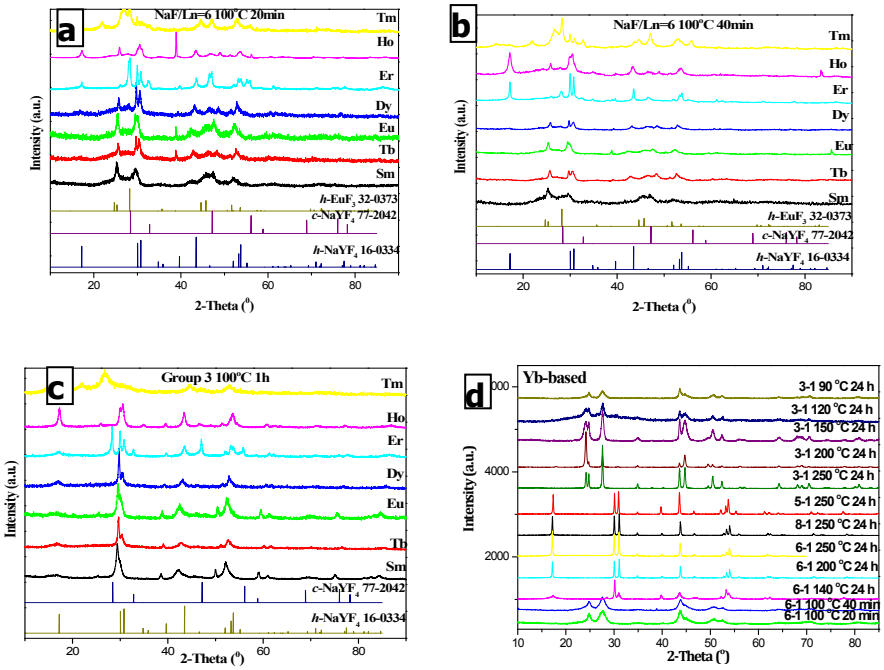

Fig. S8 XRD patterns of the Group III- and IV based products obtained after different times of 20 min (a), 40 min (b) and 1 h (c) at 100 °C for NaF/Ln ratio of 6 and the Yb-based products obtained under different experimental conditions (d).

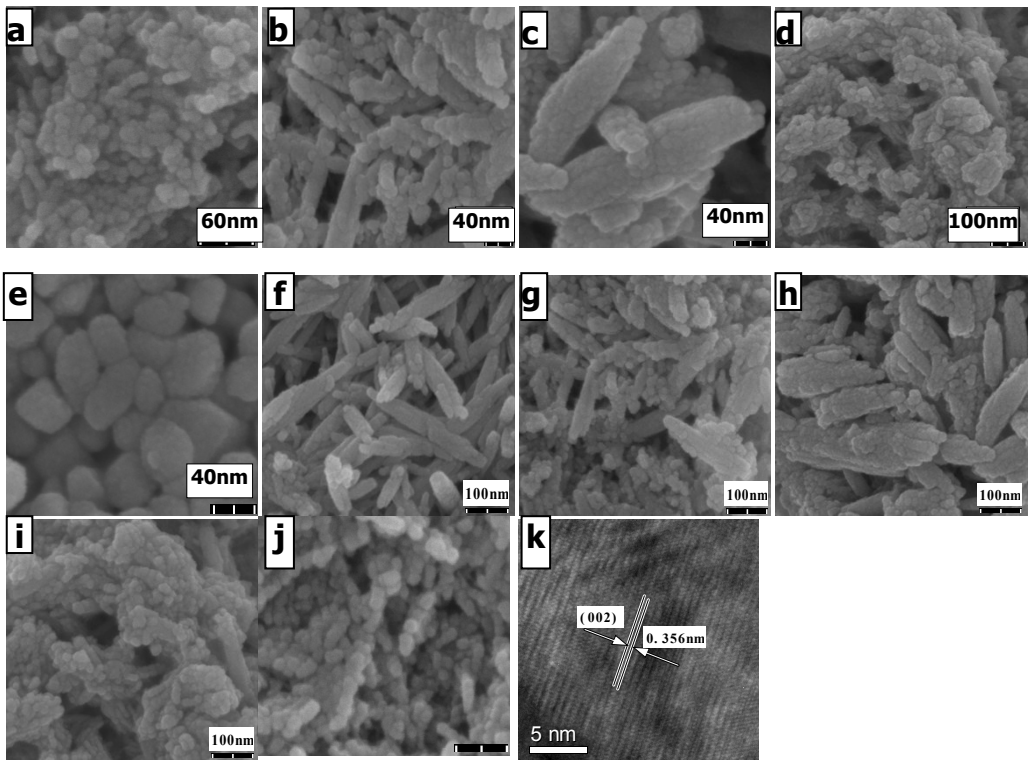

Fig. S9 SEM images of the Group III and IV-based products after 20 min at 100 °C for NaF/Ln ratio of 6: Sm (a), Eu (b), Tb (c), Dy (d), and Ho (e), the products obtained after 40 min at 100 °C for NaF/Ln ratio of 6: Sm (f), Eu (g), Tb (h), Dy (i) and Yb (j), and HRTEM images (k) of the sample obtained after 20 min at 100 °C for $NaF/NH_4NO_3/Eu$ of 6/8/1.

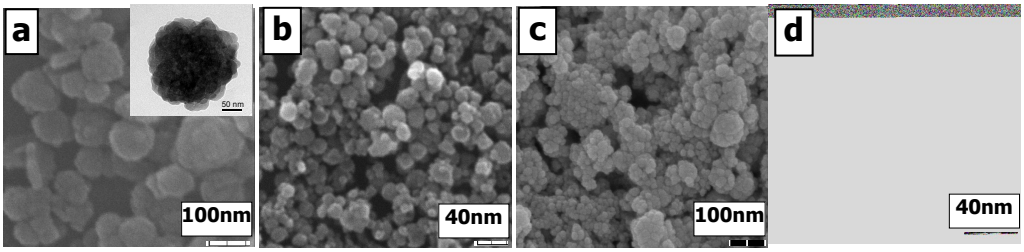

Fig. S10 SEM images of the Group IV-based products obtained after 20 min at 100 °C for NaF/Ln ratio of 6: Er(a), Tm(b), Lu(c) and Yb(d).

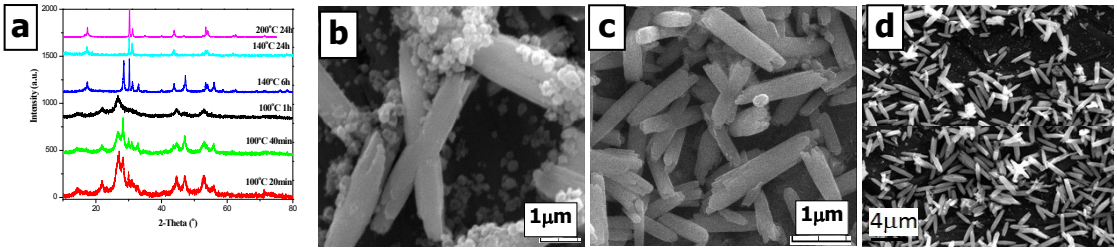

Fig. S11 XRD (a)and SEM images of theTm-based products obtained (b) 140 °C, 6 h; and (c) 140 °C, 24 h (d) 200 °C 24 h for NaF/NH_4NO_3/Tm molar ratio of 6/8/1.

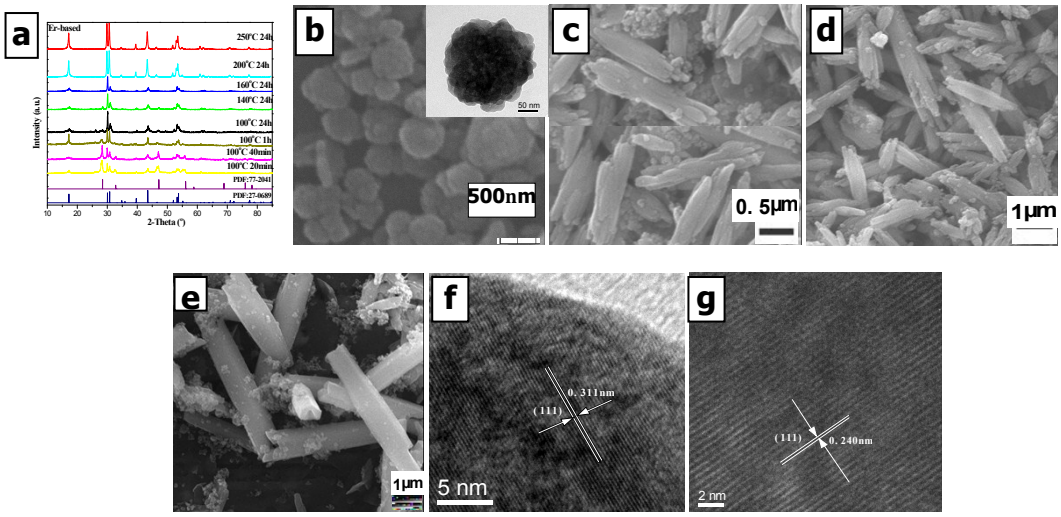

Fig. S12 XRD patterns(a) and SEM images of the Er-based products obtained after 24 h for NaF/NH_4NO_3/Er molar ratio of 6/8/1 at different reaction temperatures of 100 °C (b), 140 °C (c), 160 °C (d) , and 200 °C (e); HRTEM images of quasisphere (f) and the rods (g) of the samples obtained after 24 h at 120 °C.

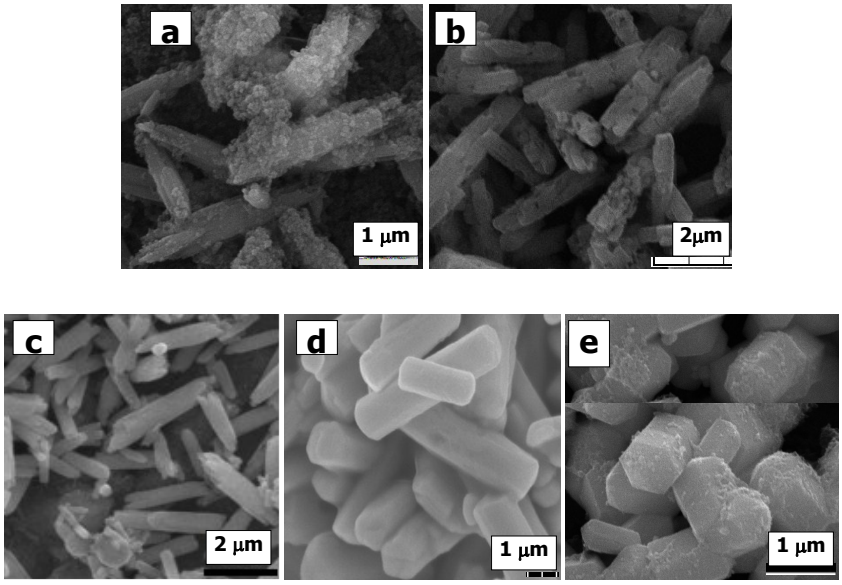

Fig. S13 SEM images of the Yb-based products obtained under the following conditions (a) 6/8/1, 140 °C, 24 h; (b) 6/8/1, 200 °C, 24 h; (c) 6/8/1, 250 °C, 48 h; (d) 5/8/1, 250 °C, 24 h; and (e) 8/8/1, 250 °C, 24 h.

Table S1 The synthetic conditions, crystal phase, shape and sizes of the Group I and II–based products (NH_4NO_3/Ln ratio: 8) (D: diameter, L: length)

Ln	NaF/Ln ratio	T(°C)	T	phase	Shape (size)
La	3	250	24h	*h*-LaF_3	flake (D:5□m,L: 500nm)
	3	250	3h	*h*-LaF_3	flake (D:100-130 nm, L: 30nm)
	3	100	40min	*h*-LaF_3	quasisphere (D:20-40nm)
	6	250	24h	*h*-LaF_3	flake (D:3 □m, L: 130nm)
	6	250	3h	*h*-LaF_3	flake (D:110nm, L: 30-40nm)
	6	100	40min	*h*-LaF_3	quasisphere (D:20-40nm)
Ce	6	250	24h	*h*-CeF_3	flake (D:60-80nm, L: 30nm)
	6	100	20min	*h*-CeF_3	quasisphere (D:20nm)
	3	250	24h	*h*-CeF_3	Plate (D:0.6μm,L: 200nm)
	3	100	24h	*h*-CeF_3	quasisphere (D:20nm)
Pr	3	250	24h	*h*-PrF_3	large: flake, small: Quasisphere
	3	100	40min	*h*-PrF_3	quasisphere (D:50nm)
	6	250	24h	*h*-PrF_3, *h*-$NaPrF_4$	plate (D:2μm,T: 5-7.7μm)
	6	200	24h	*h*-PrF_3	Thin rod/ little Platelet
	6	120	24h	*h*-PrF_3	Quasisphere
	6	100	24h	*h*-PrF_3	Quasisphere (D:400nm)
Nd	3	250	24h	*h*-NdF_3	Large: flake, small: Quasisphere
	3	100	40min	h-NdF_3	quasisphere (D:50nm)
	6	250	24h	*h*-NdF_3, *h*-$NaNdF_4$	rod (large D:150 nm, L: 1.6μm; small:D:50nm L: 1.6μm)
	6	200	24h	h-NdF_3	rod (D:150nm, L: 500-600nm)
	6	160	24h	h-NdF_3	prism(D:100nm, L:150nm)
	6	120	24h	h-NdF_3	mbryonic rod form
	6	100	24h	h-NdF_3	quassphere(D: 20-40 nm)

Table S2 Crystal phase, shape and sizes of the Y-based products under the different NaF/Y molar ratios

NaF/Y ratio	T (°C)	t (h)	product	Shape (size)
3	*100*	*2*	*o*-YF_3	polyhedron (ca. 100nm)
3	*250*	*24*	*o*-YF_3	polyhedron (large: 500nm; small: ca. 100nm)
4	*250*	*24*	*o*-YF_3, *h*-$NaYF_4$	polyhedron (ca. 100nm)+little rod(L:2.5μm,D 0.80μm)
5	*250*	*24*	*h* -$NaYF_4$	rod (L:3.0μm, D 0.80μm)
6	*250*	*24*	*h* -$NaYF_4$	rod (L:2.5μm, D 0.80μm)
8	*250*	*24*	*h* -$NaYF_4$	rod (L:2.5μm, D 0.60μm)

Table S3 Crystal phase, shape and size of the Y-based products for the differentNH_4NO_3/Y molar ratios

T(°C)	t(h)	NaF/Ln ratio	NH_4NO_3/Ln ratio	phase	Shape (size)
250	24	5	5	*h*-$NaYF_4$	rod (D:0.8μm, L:5μm)
250	24	5	8	*h*-$NaYF_4$	rod (L:3.0μm,D 0.80μm)
250	24	5	10	*h*-$NaYF_4$	rod (D: 0.8μm, L:2-4μm)
250	24	6	5	*h*-$NaYF_4$	rod (L:2.5μm, D 0.80μm)
250	24	6	8	*h*-$NaYF_4$	rod(D:1.5μm, L:12μm)
250	24	6	10	*h*-$NaYF_4$	rod (D:1μm, L:5.0μm)
250	24	8	5	*h*-$NaYF_4$	rod (D:0.4μm, L:3.0μm)
250	24	8	8	*h*-$NaYF_4$	rod (L:2.5μm,D 0.60μm)
250	24	8	10	*h*-$NaYF_4$	rod (D:0.4μm, L:1.2μm)

Table S4 Crystal phase and shape and sizes of the Y-based products under different reaction temperatures and reaction times (NH_4NO_3/Ln ratio: 8)

T(°C)	NaF/Y ratio	t(h)	phase	Shape (size)
100	6	0.5	*c*- $NaYF_4$	coarse sphere (D:120 nm)
100	6	1	*c*- $NaYF_4$	quasisphere (D:120 nm), small rod (D:200nm L:500nm)
100	6	2	*c*- $NaYF_4$	quasisphere (D: 120nm) , small rod (D:200nm L:500nm)
100	6	6	*c*- $NaYF_4$	quasisphere (D: 120 nm) , small rod (D:200nm L:500nm)
100	6	12	*c,h*- $NaYF_4$,	quasisphere (D: 120 nm) , small rod (D:200nm L:500nm)
100	6	24	*c,h*- $NaYF_4$,	quasisphere (D: 120nm), small rod (D:200nm L:500nm)
140	6	24	*c,h*- $NaYF_4$,	quasisphere (ca. 100nm), small rod (L:1.2μm,D:0.3μm)
160	6	24	*c,h*- $NaYF_4$,	few quasisphere (ca. 100nm), rod(L:2.0μm, D:0.4μm)
200	6	24	*h*-$NaYF_4$	rod(L:3-5μm,D:1.0μm)
250	6	24	*h*-$NaYF_4$	rod(L:12μm ,D:1.5μm)

Table S5 The synthetic condition, crystal phase, shape and size of the Group III-and IV-based products (NH_4NO_3/Ln ratio: 8)

Ln	NaF/Ln molar ratio	T(°C)	t	phase	Shape (size)
Sm	6	250	24 h	h-$NaSmF_4$	rod (D:0.1μm,L: 0.5μm)
	6	100	20min	h-SmF_3	Short nanorod, quasisphere(D:20nm)
	6	100	40min	h-SmF_3	/
	6	100	1h	h-$NaSmF_4$	nanorod
	3	250	3h	o-SmF_3	polyhedron (60-200nm)
	3	120	2h	o-SmF_3	polyhedron (60-200nm)
Eu	6	250	24h	h-$NaEuF_4$	rod (D:0.2μm,L: 2μm)
	6	100	20min	h-EuF_3	Short rod (D:130nm,L: 250nm), quasisphere(D:20nm)
	6	100	40min	h-EuF_3	/
	6	100	1h	h- $NaEuF_4$	Short rod (D:130nm,L: 250nm), quasisphere(D:20nm)
	3	250	2h	o-EuF_3	polyhedra (large D: 800nm;small: D 100nm)
	3	120	24h	o-EuF_3	polyhedra (100nm)
Gd	6	250	24h	h-$NaGdF_4$	rod (D:0.5μm,L: 2.0μm)
	6	200	24h	h-$NaGdF_4$	rod (D:0.15μm,L: 1.2μm)
	6	160	24h	h-$NaGdF_4$	rod (D:0.1μm,L: 1.0μm)
	6	140	24h	h -$NaGdF_4$	rod (D:50-60nm,L: 300nm)
	6	120	24h	h-$NaGdF_4$	rod (D:50-60nm,L: 300nm)
	6	100	24h	h-$NaGdF_4$	rod (D:50-60nm,L: 150nm)
	3	250	2h	o-GdF_3	polyhedra (100-300nm)
	3	120	2h	o-GdF_3	polyhedra (100 nm)
Tb	6	250	24h	h-$NaTbF_4$	rod (D:0.3μm,L: 0.6μm)
	6	100	1h	h-$NaTbF_4$	short rod (D:80nm,L: 350nm)
	6	100	40min	h-TbF_3	/
	6	100	20min	h-TbF_3	short rod (D:40nm,L: 150nm)
	3	250	24h	o-TbF_3	flake (D:180 nm, L :50nm)
Dy	6	250	24h	h-$NaDyF_4$	rod (D:0.5μm,L: 3μm)
	6	100	1h	h-$NaDyF_4$	rod, quasisphere(D:20nm)
	6	100	40min	h-DyF_3 h-$NaDyF_4$	/
	6	100	20min	h-DyF_3 h-$NaDyF_4$	quasisphere(D:20nm),rod,
	3	250	24h	o-DyF_3	flake (D:100nm,L 20nm),short rod(D:400nm,L 100nm)
Ho	6	250	24h	h-$NaHoF_4$	rod (D:1.0μm,L: 6.0μm)
	6	100	1h	h-$NaHoF_4$	/
	6	100	40min	h-HoF_3 h-$NaHoF_4$	/
	6	100	20min	h-HoF_3 h-$NaHoF_4$	Short rod(D:40nm,L: 80nm)
	6	250	24h	o-HoF_3	polyhedron (60-200nm)
Er	3	250	24h	o-ErF_3	polyhedral (large 800nm, small 100nm)
	3	120	2h	o-ErF_3	polyhedral(100nm)
	6	250	24h	h-$NaErF_4$	rod (D:1μm, L: 4-7μm)
	6	200	24h	h -$NaErF_4$	rod (D:0.5-0.7μm,L: 3.5μm)
	6	160	24h	h -$NaErF_4$	rod (D:0.5-0.7μm,L: 2μm)
	6	140	24h	h,c-$NaErF_4$	rod (D:0.5μm,L: 1.5-2μm)
	6	100	20min	h,c-$NaErF_4$	quasisphere (D:150nm)
Tm	6	250	24h	h-$NaTmF_4$	rod(D:0.5μm,L: 1.5-2.5μm)
	6	140	24h	h-$NaTmF_4$	rod(D:0.5μm,L: 1.5-2μm)
	6	140	6.5h	h,c-$NaTmF_4$	rod(D:0.5μm,L:1.5-2μm), quasisphere(D:200nm)
	6	100	24h	h,c-$NaTmF_4$	quasisphere(D:200nm)
	6	100	1h	c-$NaTmF_4$	quasisphere(D:200nm)
	6	100	40min		/
	6	100	20min		/
	3	250	24h	o-TmF_3	polyhedron (200nm)
	3	100	2h	o-TmF_3	polyhedron (80nm)
Yb	6	250	48h	h-$NaYbF_4$	rods (D: 3μm,L: 0.5μm)
	6	250	24h	h-$NaYbF_4$	rod (D: 0.8μm,L: 0.1μm)
	6	200	24h	h-$NaYbF_4$	rod (D:3μm,L: 0.8μm)
	6	140	24h	h,c-$NaYbF_4$	rod(D:2μm,L: 0.5μm), quasisphere
	6	100	40min	h-YbF_3	quasisphere (D:20-nm)
	6	100	20min	h-YbF_3	quasisphere (D:20-nm)
	5	250	24 h	h-$NaYbF_4$	rod (D: 2-3μm,L: 1μm)
	8	250	24h	h-$NaYbF_4$	prism (D: 1μm,L: 0.8μm)
	3	250	24h	h-YbF_3	flake (D:150-200nm,L: 50-60nm)
	3	250	3h	h-YbF_3	flake (D: 200nm,L: 50-60nm)
	3	100	40min	h-YbF_3	quasisphere (D:20nm)
Lu	6	250	24h	h-$NaLuF_4$	rod (D:4μm,L: 8-12μm)
	6	100	20min	h,c-$NaLuF_4$	quansphere (D:50nm)
	3	250	24h	o-LuF_3	short rod (D:100nm, L:200nm)
	3	120	2hs	o-LuF_3	short rod (D:80nm, L:160nm)

Table captions:

Table 1 The synthetic conditions, crystal phase, shape and sizes of the Group I and II–based products (NH_4NO_3/Ln ratio: 8) (D: diameter, L: length)

Table 2 Crystal phase, shape and sizes of the Y-basd products under the different NaF/Y molar ratios

Table 3 Crystal phase, shape and size of the Y-basd products for the differentNH_4NO_3/Y molar ratios

Table S4 Crystal phase and shape and sizes of the Y-based products under different reaction temperatures and reaction times (NH_4NO_3/Ln ratio: 8)

Table S5 The synthetic condition, crystal phase, shape and size of the Group III-and IV-based products (NH_4NO_3/Ln ratio: 8)