# **Electronic Supporting Information**

## **EXPERIMENTAL DETAILS**

#### Chemicals and Materials.

Analytical grade rare earths (RE) oxides (Sc<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub>, Tb<sub>4</sub>O<sub>7</sub>, Yb<sub>2</sub>O<sub>3</sub>, Tm<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub> and Ho<sub>2</sub>O<sub>3</sub>, 99.99%), NaOH ( $\geq$  96.0%), LiOH·H<sub>2</sub>O ( $\geq$  95.0%), NH<sub>4</sub>F ( $\geq$  96.0%), concentrated nitric acid (HNO<sub>3</sub>,  $\geq$  68.0%), ethylene glycol (EG,  $\geq$  99.0%), ethanol ( $\geq$  99.7%), and cyclohexane ( $\geq$  99.5%) were purchased from Sinopharm Chemical Reagent Co., China. Oleic acid (90 wt.%) was supplied by Alfa Aesar Co., China. All of the reagents and solvents were used as received without further purification. Rare earths oxides were separately dissolved in dilute HNO<sub>3</sub> solution and the residual HNO<sub>3</sub> was removed by heating and evaporation, resulting in the formation of aqueous solution of corresponding RE(NO<sub>3</sub>)<sub>3</sub>.

#### **Synthesis**

Na<sub>3</sub>Li<sub>3</sub>Sc<sub>2</sub>F<sub>12</sub> host and lanthanide-doped Na<sub>3</sub>Li<sub>3</sub>Sc<sub>2</sub>F<sub>12</sub> microcrystals were prepared a modified solvo-thermal method. It has been found that the solvo-thermal temperature and the ratio of NH<sub>4</sub>F to Sc(NO<sub>3</sub>)<sub>3</sub> are very crucial for the formation and crystallization of monophasic products with cubooctahedra morphology in this system. Various synthetic parameters for Na<sub>3</sub>Li<sub>3</sub>Sc<sub>2</sub>F<sub>12</sub> microcrystals were summarized in the Tables S1 and S2. Herein took the synthesis of  $Na_3Li_3Sc_2F_{12}$  as an example. 4.0 mL aqueous solution of  $Sc(NO_3)_3$  (0.25) M) was added to a 50 mL flask containing oleic acid (20.0 mL). The mixture was heated at 160 °C for 1 hour to remove the water and to form solution (I). NaOH (12.0 mmol, 0.105 g), LiOH·H<sub>2</sub>O (12.0 mmol, 0.110 g), and NH<sub>4</sub>F (6.0 mmol, 0.232 g) were well mixed with EG (15.0 mL) and H<sub>2</sub>O (3.0 mL; to improve the solubility of the fluorides) in a plastic beaker under stirring at room temperature, to form solution (II). Thereafter, the solution (II) was slowly added into the solution ( I ) under vigorous stirring. The resultant mixing solution was heated to 120 °C for 1 hour (the sample obtained at this step was denoted as precursor) and then transferred into a 50 mL Teflon lined autoclave. The autoclave was then placed in a digital temperature-controlled oven and operated at 180 °C for 18 hours and then was allowed to cool to room temperature naturally. Subsequently, the as-obtained microcrystals were collected by centrifugation, washed sequentially with cyclohexane and ethanol for several times. After drying at 60 °C under dynamic vacuum for 24 hours, Na<sub>3</sub>Li<sub>3</sub>Sc<sub>2</sub>F<sub>12</sub> sample was obtained.

The synthetic procedure of lanthanide-doped  $Na_3Li_3Sc_2F_{12}$  microcrystals was the same as that used to prepare  $Na_3Li_3Sc_2F_{12}$  host, except that stoichiometric amounts of  $Sc(NO_3)_3$  and  $RE(NO_3)_3$  were added to oleic acid.

### Characterization

X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advanced X-Ray Diffractometer with Ni filtered Cu Ka radiation ( $\lambda = 1.5406$  Å) at a voltage of 40 kV and a current of 40 mA. The morphology of the samples was inspected using Field emission scanning electron microscopy (FESEM) (Hitachi S4800). The upconversion and downconversion fluorescence spectra were collected on an Edinburgh Instruments FLS920

phosphorimeter using a 980 nm laser diode Module (K98D08M-30mW, China) and 450 W xenon lamps as excitation source, respectively. The upconversion luminescence spectra have been corrected for the spectral sensitivity of the system. FT-IR spectrum in transmission mode was measured on a Nicolet 5SXC FT-IR spectrophotometer using the KBr pellet technique. All of the measurements were obtained from powder samples and performed at room temperature.

Temp(℃)	Phase information	Shape
Precursor	$Na_3Li_3Sc_2F_{12}+ScF_3$	irregular particles
140	$Na_3Li_3Sc_2F_{12}+ScF_3$	cubooctahedra + irregular particles
160	$Na_3Li_3Sc_2F_{12}+ScF_3$	cubooctahedra + irregular particles
180	$Na_3Li_3Sc_2F_{12}$	cubooctahedra
200	$Na_3Li_3Sc_2F_{12}+ScF_3$	cubooctahedra
220	$Na_3Li_3Sc_2F_{12}+ScF_3$	cubooctahedra + irregular particles



Fig. S1 XRD patterns of as-synthesized precursor and  $Na_3Li_3Sc_2F_{12}$  samples derived at various temperatures [(a) 140, (b)160, (c) 180, (d) 200, and (e) 220 °C] with the fixed amounts of F<sup>-</sup> and Sc<sup>3+</sup> sources.



(a) **Precursor** 

(b) 140 °C



(c) **160** °C

(d) 200 °C



(e) 220 °C

Fig. S2 SEM images of as-synthesized precursor (a) and Na<sub>3</sub>Li<sub>3</sub>Sc<sub>2</sub>F<sub>12</sub> samples after solvo-thermal treatment at various temperatures: [(b) 140, (c) 160, (d) 200, (e) 220 °C].

$F^{-}/Sc^{3+}$ ratio	Phase information
4:1	$Na_3Li_3Sc_2F_{12} + ScF_3$
5:1	$LiF + Na_3Li_3Sc_2F_{12} + unknown phase$
6:1	$Na_3Li_3Sc_2F_{12}$
8:1	$Na_3Li_3Sc_2F_{12} + LiF + unknown phase$
10:1	$LiF + Na_3Li_3Sc_2F_{12} + ScF_3 + unknown phase$

**Table S2** Crystal phase analysis of  $Na_3Li_3Sc_2F_{12}$  microcrystals obtained at different F-/Sc<sup>3+</sup><br/>ratios



**Fig. S3** XRD patterns of Na<sub>3</sub>Li<sub>3</sub>Sc<sub>2</sub>F<sub>12</sub> samples obtained at different  $F^-/Sc^{3+}$  ratios (4:1 ~ 10:1) under solvo-thermal treatment at 180 °C.



Fig. S4 CIE chromaticity diagrams for: (a)  $Na_3Li_3Sc_2F_{12}$  host, (b)  $Na_3Li_3Sc_2F_{12}:Eu^{3+}$  (5 mol%), (c)  $Na_3Li_3Sc_2F_{12}:Tb^{3+}$  (5 mol%).



Fig. S5 FT-IR spectrum of Na<sub>3</sub>Li<sub>3</sub>Sc<sub>2</sub>F<sub>12</sub> host



Fig. S6 CIE chromaticity diagrams for: (a)  $Na_3Li_3Sc_2F_{12}$ :Yb<sup>3+</sup>/Er<sup>3+</sup> (20/2 mol%), (b)  $Na_3Li_3Sc_2F_{12}$ :Yb<sup>3+</sup>/Tm<sup>3+</sup> (20/2 mol%), (c)  $Na_3Li_3Sc_2F_{12}$ :Yb<sup>3+</sup>/Ho<sup>3+</sup> (20/2 mol%).