SUPPORTING INFORMATION

Selective Synthesis of LaF_3 and $NaLaF_4$ Nanocrystals via Lanthanide Ion Doping†

Li Nie,[+a] Yuxing Shen,[+a] Xi Zhang,[a] Xiuwen Wang,[a] Botong Liu,[a] Yangbo Wang,[a] Yue Pan,[b] Xiaoji Xie,*[a] Ling Huang*[a] and Wei Huang[a]

[a]*Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211816, P. R. China. E-mail: iamxjxie@njtech.edu.cn, iamlhuang@njtech.edu.cn, iamwhuang@njtech.edu.cn*

[b]*School of Chemistry and Chemical Engineering, Inner Mongolia University, 235 West Daxue Road, Hohhot 010021, P. R. China*

Experimental section

Materials

$La(NO_3)_3 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, $Pr(NO_3)_3 \cdot 6H_2O$, $Nd(NO_3)_3 \cdot 6H_2O$, $Ho(NO_3)_3 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$, $Gd(NO_3)_3 \cdot 6H_2O$, $Tb(NO_3)_3 \cdot 6H_2O$, $Dy(NO_3)_3 \cdot 6H_2O$, $Yb(NO_3)_3 \cdot 5H_2O$, $Er(NO_3)_3 \cdot 6H_2O$, $Tm(NO_3)_3 \cdot 5H_2O$, $Sm(NO_3)_3 \cdot 6H_2O$, and $Lu(NO_3)_3 \cdot 6H_2O$ with purity >99.99% were purchased from Jinan HH. Ethylene glycol (EG), $NaNO_3$ and NH_4F were all analytical grade reagents, respectively purchased from Shanghai Shisihewei Chemical CO., Sinopharm Chemical Reagent Limited Corporation, and Shanghai Shenbo Chemical CO..

Characterization

All samples were measured by powder X-ray diffraction (XRD) on a Rigaku D/max 2550, which under the monochromatized Cu Kα radiation (λ = 0.15418 nm), Transmission electron microscopy (TEM) images were recorded on a Hitachi 7700 transmission electron microscope at an acceleration voltage of 100 kV. The inductively coupled plasma mass spectroscopy (ICP-MS) analysis was performed on a PE Optima 5300DV spectrometer. Both DC and UP luminescence spectrum were recorded on a Hitachi F-4600 spectrometer equipped with a Xe lamp and an external continuous diode 980 nm laser.

Synthesis of hexagonal LaF_3 and hexagonal $NaLaF_4$ nanocrystals

Lanthanide-doped hexagonal LaF_3 and hexagonal $NaLaF_4$ nanocrystals were synthesized by a solvothermal method. Briefly, 0.65 mmol $RE(NO_3)_3$ was dissolved in 15 mL ethylene glycol (EG). After vigorous stirring for 30 minutes, $NaNO_3$ and NH_4F were introduced into the solution with the mole ratio of RE^{3+}:Na^+:F^- at 1:3:30. After 30 mins further stirring, the resulting solution was transferred into a 25 mL sealed Teflon autoclave and maintained at 180 °C for 12 h. The precipitates were collected by centrifugation and washed several times with ethanol and deionized water after the autoclave was cooled down to room temperature. The products were dried in at 70 °C for 24 h and stored for further use. Controllable synthesis of hexagonal $NaLaF_4$ and hexagonal LaF_3 under different doping conditions. Similarly, other lanthanides also are used as dopants in the same synthesis procedures.

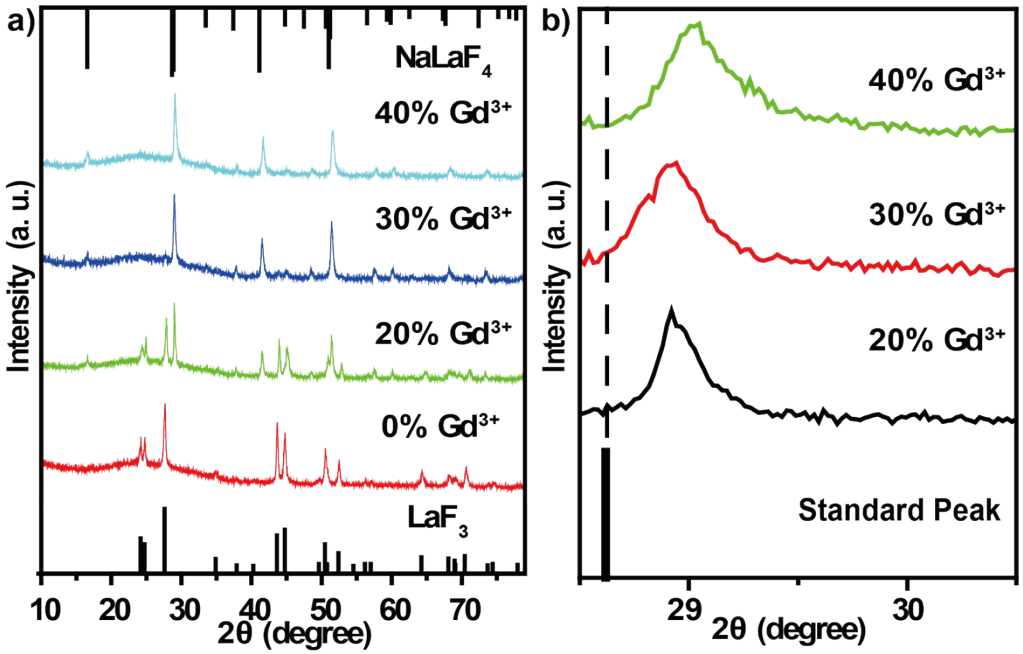

Fig. S1 (a) XRD patterns of the final products at 0, 20, 30, and 40 mol% Gd^{3+} doping. (b) Details of the right shift of the characteristic XRD peak of $NaLaF_4$ nanocrystals at 28.7° when Gd^{3+} worked as dopant ions.

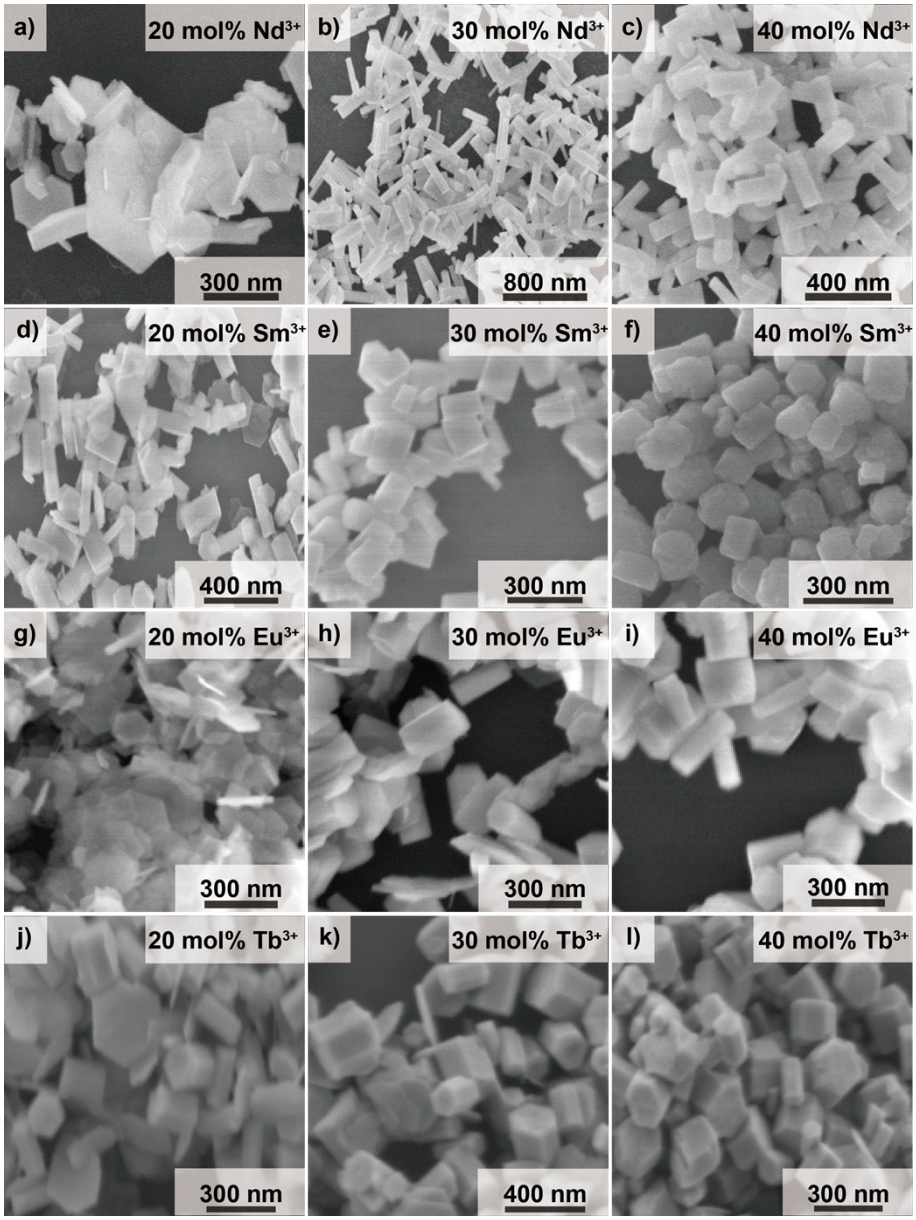

Fig. S2 SEM images of β-$NaLaF_4$ nanocrystals doped with (a-c) Nd^{3+}, (d-f) Sm^{3+}, (g-i) Eu^{3+}, and (j-l) Tb^{3+} at varying concentrations.

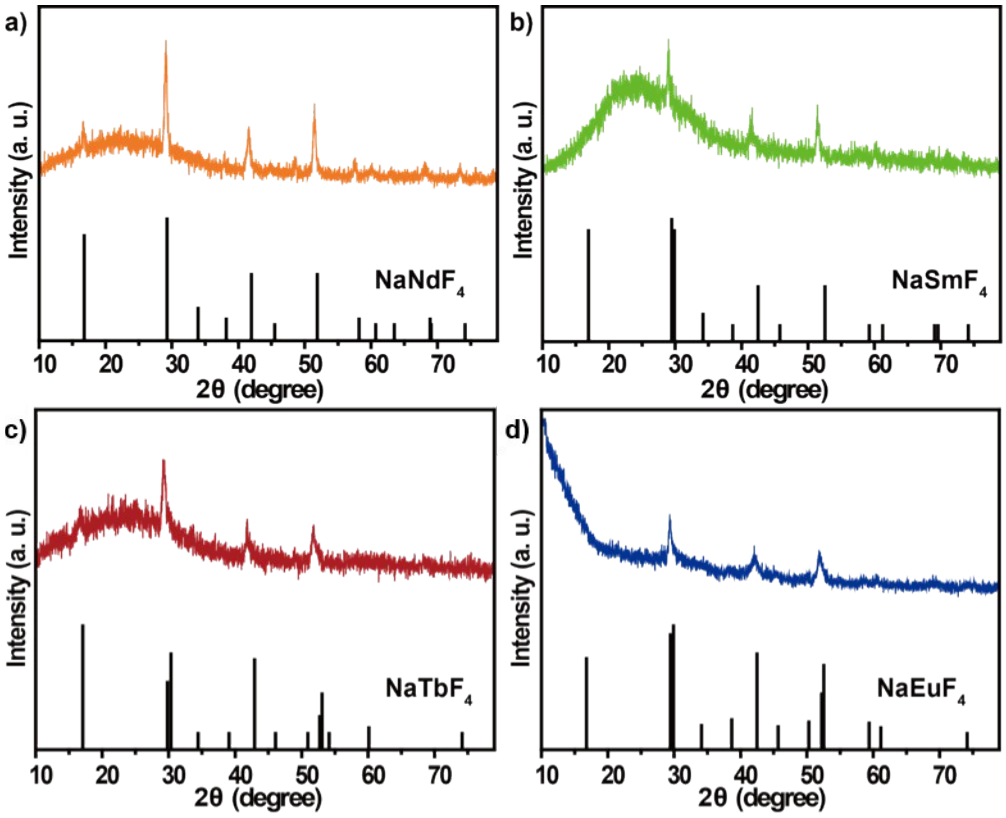

Fig. S3 XRD patterns of β-$NaMF_4$ (M = Nd, Sm, Eu, and Tb) nanocrystals doped with 60 mol% (a) Nd^{3+}, (b) Sm^{3+}, (c) Tb^{3+}, and (d) Eu^{3+}.

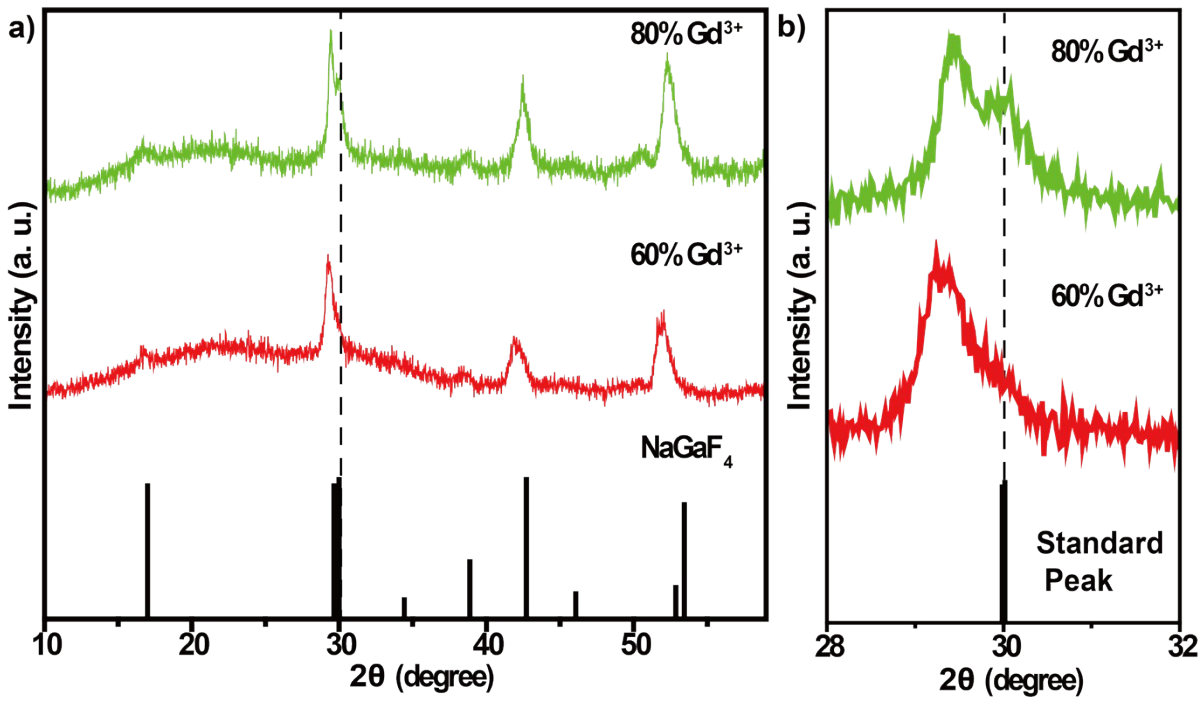

Fig. S4 (a) XRD patterns of the final products at 60 and 80 mol% Gd^{3+} doping. (b) Details of the left shift of the characteristic XRD peak of $NaGdF_4$ nanocrystals at 30° when La^{3+} worked as dopant ions.

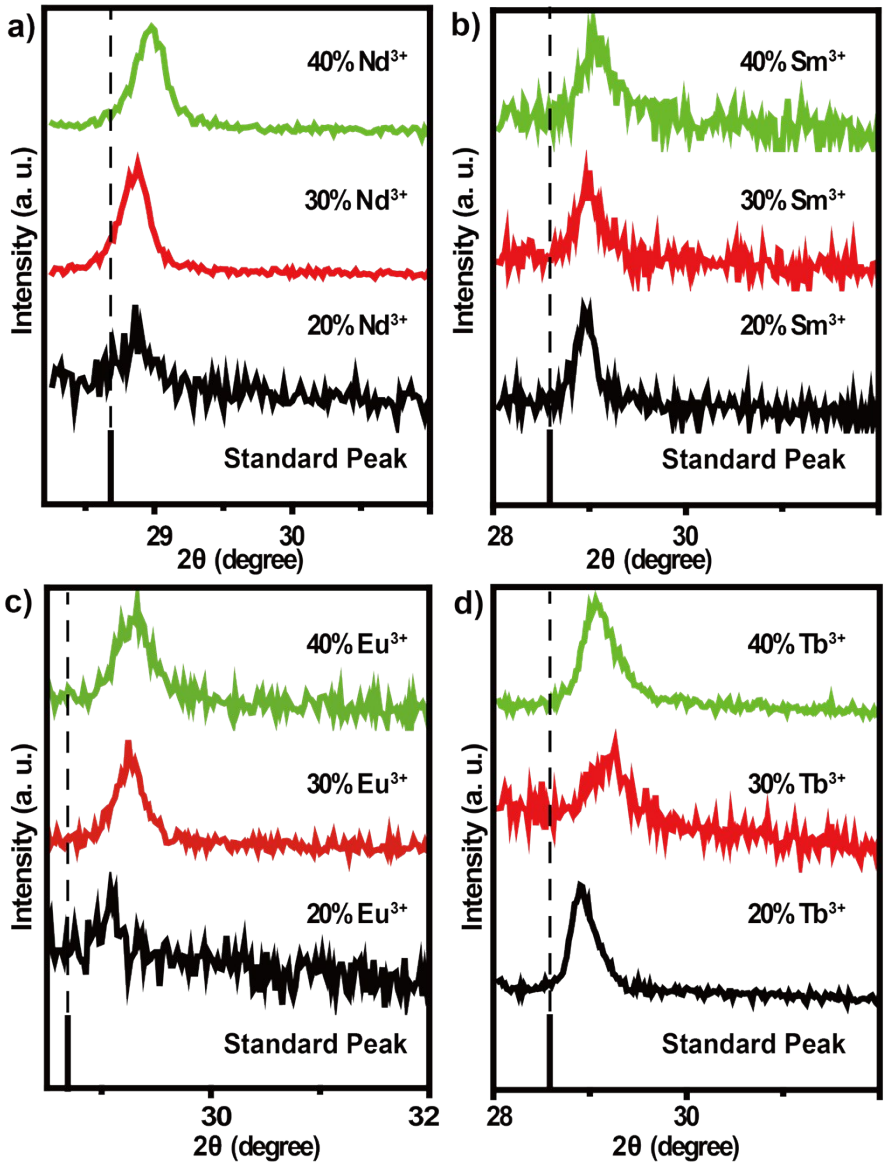

Fig. S5 Details of the right shift of the characteristic XRD peaks of β-$NaLaF_4$ nanocrystals doped with (a) Nd^{3+}, (b) Sm^{3+}, (c) Eu^{3+}, and (d) Tb^{3+} at varying concentrations.

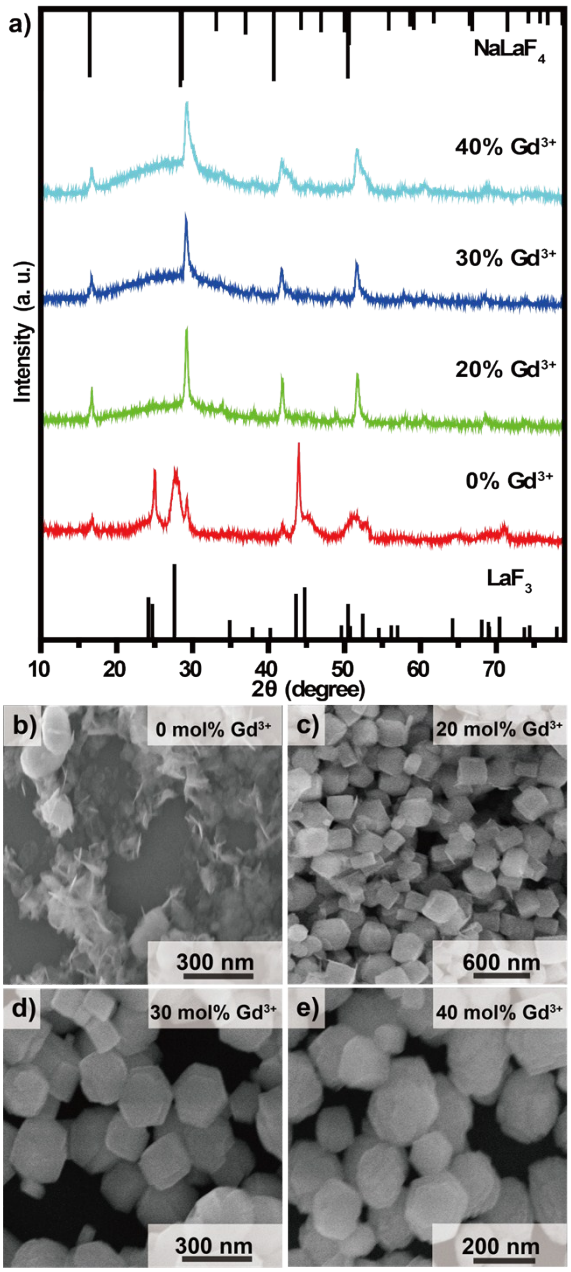

Fig. S6 (a) XRD patterns and (b-e) SEM images of nanocrystals at varying Gd^{3+} doping concentrations. Co-doping of Yb^{3+} (18 mol%) and Er^{3+} (2 mol%) is for the studies of both the doping effect on the nanocrystal growth mechanism and upconversion luminescence.

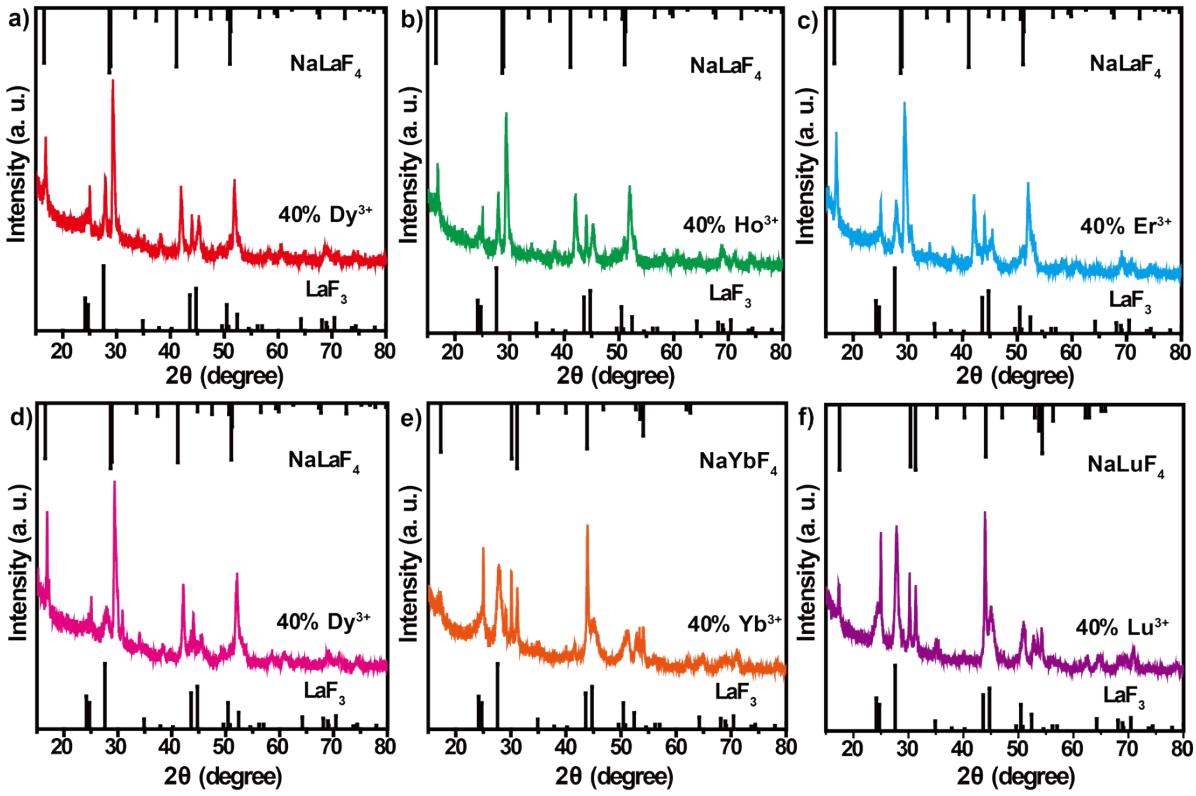

Fig. S7 XRD patterns of products doped with (a) Dy^{3+}, (b) Ho^{3+}, (c) Er^{3+}, (d) Tm^{3+}, (e) Yb^{3+}, and (f) Lu^{3+} at 40 mol% doping concentrations, which are the mixture of LaF_3:Ln and $NaLaF_4$:Ln (Ln = Dy, Ho, Er, Tm, Yb, and Lu) nanocrystals.

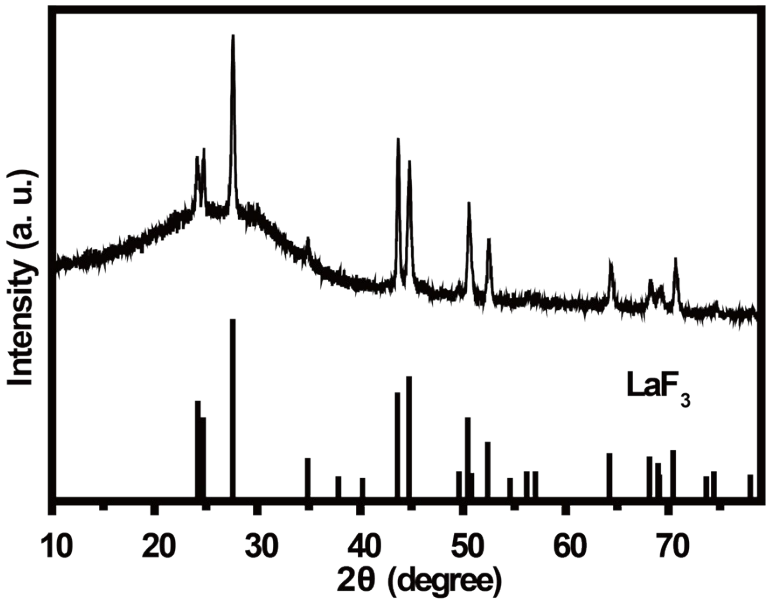

Fig. S8 XRD patents of the nanocrystals obtained after post-doping of Gd^{3+} into the reaction system with pre-synthesized LaF_3 nanocrystals.