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Room-temperature fluorination of layered rare-earth hydroxide nanosheets leading to fluoride nanocrystals and elucidation of down-/up-conversion photoluminescence

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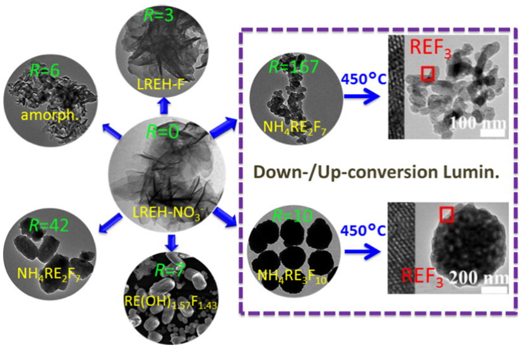
HIGHLIGHTS

- Fluorination of LREH-NO_3^- nanosheets with NH_4F has led to four types of rare-earth fluorides.
- Chemical composition of the product is dependent on the NH_4F/RE molar ratio used for fluorination.
- Calcining ammonium fluorolanthanate at 450 °C produces REF_3 nanocrystals.
- Luminescence of the fluorides has been correlated with crystal structure and chemical bonding.

GRAPHICAL ABSTRACT



Room temperature fluorination with NH_4F of few-layer-thick LREH-NO_3^- nanosheets (~4 nm, RE = Y/Eu or Y/Yb/Er) has led to various fluoride compounds with phase structure and particle/crystallite morphology dependent on RE/R molar ratio. Down-/Up-conversion luminescence of the materials were investigated and deciphered in detail.

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ABSTRACT

In this work, we show that room-temperature fluorination of LREH-NO_3^- nanosheets (~4 nm, RE = Y/Eu or Y/Yb/Er), directly crystallized without exfoliation, can lead to LREH-F^- (anion exchange product), $RE(OH)_{1.57}F_{1.43}$ hydroxyl fluoride, and the fluorolanthanates of $NH_4RE_3F_{10}$ and $NH_4RE_2F_7$ with increasing F/RE molar ratio. Unlike previous studies on nanoconversion which generally need hydrothermal treatment to drive reaction, the significant exposure of the $[RE_2(OH)_5(H_2O)_n]^+$ main layers by the thinness of the nanosheets allows fast reaction kinetics and the products produced at room-temperature are well crystallized. Also, for down-/up-conversion photoluminescence, the REF_3 nanocrystallites were obtained *via* facile calcination of the ammonium fluorolanthanates at 450 °C. The underlying mechanisms of phase conversion, the courses of structure/morphology evolution and the correlation between luminescent properties and crystal structure and chemical bonding have been unveiled.

1. Introduction

Owing to their wide bandgap (~7.34 eV), low phonon energy (~350–500 cm^{-1}), and high refractive index (~1.56), rare-earth (RE) fluorides with the formula of REF_3 are being widely employed as the

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host lattice for down-/up-conversion phosphors and they are widely applied in optics, optoelectronics, biolabels and so on [1–7]. Contrasting to quantum dots and conventional organic fluorophores, rare-earth fluorides show adequate long-term thermal and environmental stability [8]. The MF-REF$_3$ (M = alkali metal or NH_4^+) system comprises a big family of fluoride compounds including many useful materials, such as $MREF_4$, MRE_3F_{10}, and MRE_2F_7 [9–22]. Compared with their alkali counterparts, ammonium fluorolanthanates have received less attention in their synthesis and property exploration, though they are particularly interesting in structural features and may find applications in luminescence and solid-state lasers [11–13].

A number of techniques have been developed to synthesize rare-earth fluorides, typically including thermal decomposition in high boiling-point solvent, coprecipitation, hydro-/solvo-thermal reaction, and ionic-liquid based reaction [5,13,14,22–26], and each methodology has its advantage. For example, the thermal decomposition approach is well known for its precise size/shape control suitable to reach monodispersity of the particles, coprecipitation for its easiness to perform, hydro-/solvo-thermal reaction for better crystallinity of the final product, and reaction in ionic liquid for environmental benignity. Sacrificial conversion has also been introduced for controllable synthesis of rare-earth compounds, in which the target compound is formed *via* reacting a pre-made precursor with an anion source under proper conditions [27–31]. In this strategy, the phase conversion generally proceeds *via* two separate mechanisms: interface chemical transformation [27,28] and dissolution followed by reprecipitation [29–31]. In the former case, the precursor serves as both a physical and chemical template, and the final product may well preserve the particle/crystallite morphology of the precursor when the precursor and the target compound have the same crystal structure. This is exemplified by the hydrothermal synthesis of β-$NaREF_4$ (hexagonal structured) nanorods/nanotubes *via in situ* acid corrosion and anion exchange of hexagonal $RE(OH)_3$ nanorods/nanotubes. The dissolution-reprecipitation mechanism may be applied when the precursor and final product differ in crystal structure, as shown by the evolution of hexagonal $LuBO_3$ microdiscs *via* hydrothermal conversion of monoclinic $Lu_4O(OH)_9NO_3$ nanowires in the presence of boric acid (H_3BO_3) [29]. Hollow structured REF_3 and $Na_xRE_yF_{x+3y}$ microspheres have also been hydrothermally produced *via* conversion of amorphous $RE(OH)CO_3$ colloidal spheres in the presence of $NaBF_4$ [30] or NaF [31].

The anion-exchangeable layered rare-earth hydroxide (LREH) of $RE_2(OH)_5NO_3\cdot nH_2O$ (RE = La-Yb, and Y) drew much research interest during the past several years owing to the diverse physicochemical properties of the rare-earth elements and the rich interlayer chemistry [32–39]. The structure is built up *via* alternative stacking of the hydroxide main layers composed of 8-fold coordinated $[RE(OH)_7H_2O]$ and 9-fold coordinated $[RE(OH)_8H_2O]$ polyhedrons and interlayer NO_3^- anions along the *c*-axis ([001] direction) [33,40]. The studies on this group of relatively new layered inorganic compound have largely been focused on anion substitution of interlayer NO_3^- with inorganic and organic anions [33–37], photoluminescence [32–34,41–43], enhancement of luminescence *via* intercalation of organic sensitizers [44–47], exfoliation of bulk LREH crystals into unilamellar or few-layer-thick nanosheets [48–50], assembly of the pristine and exfoliated nanosheets into multi-functional oriented films [49–54] and composite films [46,47,55], derivation of oxide phosphors *via* calcination [43,56], and fabrication of highly transparent ceramics with LREH nanosheets as a new type of precursor for reactive oxide nanopowders [57–59]. Contrary to the well-established synthetic techniques of reflux and hydrothermal reaction, which usually produce plate-like thick LREH crystals, a “freezing-temperature crystallization” technique that can directly yield LREH nanosheets of only ~4 nm in thickness was very recently developed by us, and the effects of anion exchange on crystal structure and photoluminescence were investigated [34]. To the best of our knowledge, however, the use of LREH nanosheets as a new type of sacrificial precursor to synthesize rare-earth fluorides *via* nanoconversion has not yet been reported prior to us.

Nanocrystalline fluorides have been successfully generated in this work *via* phase conversion of the one-step crystallized $RE_2(OH)_5NO_3\cdot nH_2O$ (RE = $Y_{0.95}Eu_{0.05}$ and $Y_{0.78}Yb_{0.20}Er_{0.02}$) nanosheets under ambient conditions, employing ammonium fluoride (NH_4F) as the fluorine source. Contrary to the aforementioned previous studies, which employed hydrothermal treatment to drive phase conversion, fluorination readily took place at room temperature in this work owing to significant exposure of the $[RE_2(OH)_5(H_2O)_n]^+$ main layers of LREH by the thinness of the nanosheets, which allows fast reaction kinetics. Moreover, it is clear to see that the direct fluorination products of hydroxyl fluoride ($RE(OH)_{1.57}F_{1.43}$) and fluorolanthanates ($NH_4RE_3F_{10}$ and $NH_4RE_2F_7$) have been well crystallized. In addition, calcining the fluorolanthanate compounds at the low temperature of 450 °C has directly yielded REF_3 nanophosphors for down- and up-conversion photoluminescent applications. Detailed characterization was performed for the materials to reveal the process and underlying mechanisms of fluorination, structure/morphology evolution, and also luminescent properties of the products. In the following sections, we report on the material synthesis, characterization, and spectrophotometric properties. We believe that this work may widen the applications of LREH and may have broad implications to the synthesis of other types of optically functional rare-earth compounds *via* nanoconversion of LREH.

2. Experimental details

2.1. Materials synthesis

The starting reagents of $Eu(NO_3)_3\cdot 6H_2O$ (99.95% pure), $Y(NO_3)_3\cdot 6H_2O$ (99.99% pure), $Yb(NO_3)_3\cdot nH_2O$ (99.99% pure), and NH_4F (97%) were purchased from Kanto Chemical Co. Inc. (Tokyo, Japan). Ammonium hydroxide solution (25%) and Er_2O_3 (99.99% pure) were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan) and Rare Metallic Co. Ltd. (Tokyo), respectively. $Er(NO_3)_3$ solution was prepared by dissolving the oxide with slightly excessive nitric acid, followed by evaporation at ~90 °C to dryness to remove the superfluous acid.

The nanosheets of $RE_2(OH)_5NO_3\cdot nH_2O$ (RE = $Y_{0.95}Eu_{0.05}$ and $Y_{0.78}Yb_{0.20}Er_{0.02}$) were produced *via* titration of mixed rare-earth nitrate solution with ammonium water [34]. Briefly, 250 mL of a 0.2 $mol\cdot L^{-1}$ $RE(NO_3)_3$ solution was pre-cooled to ~4 °C, to which a 1 $mol\cdot L^{-1}$ ammonium hydroxide solution was dropwise added till pH ~ 8.0 under magnetic stirring. After aging for 1 h, the solid phase was recovered by suction filtration, followed by washing with deionized water two times and in ethanol, and drying in the air at 70 °C for 24 h.

For fluorination of the LREH nanosheets, a certain amount of NH_4F (according to the predetermined F/RE molar ratio) was dissolved in 50 mL of deionized water, to which 0.6 mmol of the as-prepared LREH was added under magnetic stirring at room temperature. After reaction for 3 h, the white precipitate was collected *via* centrifugation, washed with deionized water and ethanol, and, then, dried at 70 °C in the air. REF_3 was produced *via* annealing the resultant ammonium fluorolanthanate compounds at 450 °C for 2 h in the air.

2.2. Materials characterization

Phase identification was made *via* X-ray diffractometry (XRD, Model RINF 2200 V/PC, Rigaku, Tokyo) operating at 40 kV/40 mA, using nickel-filtered Cu-Kα radiation and the scanning speed of 1° 2θ/min; Fourier transform infrared spectroscopy (FT-IR, Model FT/IR-4200, JASCO Co. Ltd., Tokyo) was performed by the standard KBr method; Thermogravimetry (TG, Model Thermo Plus TG8120, Rigaku) was made in the stagnant air with the heating rate of 10 °C/min; The product morphology was inspected *via* field-emission scanning electron microscopy (FE-SEM, Model S-5000, Hitachi, Tokyo) under an acceleration voltage of 10 kV and transmission electron microscopy (TEM,