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**Interacting layered hydroxide nanosheets with KF leading to Y/Eu hydroxyfluoride, oxyfluoride, and complex fluoride nanocrystals and investigation of photoluminescence**

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Treating nanosheets (~4 nm thick) of \( \text{RE}_2(\text{OH})_3\text{NO}_3 - \text{nH}_2\text{O} \) layered hydroxyl nitrate (LREH-NO\(_3^-\)), \( \text{RE} = \text{Y}_{0.95}\text{Eu}_{0.05} \) with KF solution at a low temperature of \(~90^\circ\text{C}\) yielded F\(^-\)-substituted LREH (\( \text{RE}_2(\text{OH})_3\text{F}_n\text{nH}_2\text{O} \)), \( \text{RE} \text{OH}_3\text{F}_x\text{O}_y \) hydroxylfluoride \((x = 1.15-1.51)\), and \( K_9\text{RE}_{32}\text{F}_{126} \) complex fluoride depending on the \( F/\text{RE} \) molar ratio \((R)\) used for phase conversion \((R = \{3:3:200:3\})\). Calcing \( \text{RE} \text{OH}_3\text{F}_x\text{O}_y \) with the higher F content \((x = 1.29-1.51, R = \{40:3:70:3\})\) at 450 °C in air produced \( \text{REO}_3\text{F}_{12}-\text{OF}_x \) oxyfluorides, with the \( F/\text{RE} \) molar ratio close to that of the orthorhombic \( \text{Y}_2\text{O}_2\text{F}_7 \) phase. Oxidation of \( \text{REO}_3\text{F}_{12}-\text{OF}_x \) to form REOF and even \( \text{RE}_2\text{O}_3 \) was observed at temperatures above \(~700^\circ\text{C}\). The materials were characterized in depth by the combined techniques of elemental analysis, XRD, FE-SEM, TEM, FTIR, and TG to reveal the process of composition, phase, and morphology evolution, and the photoluminescent properties of the resultant hydroxyfluoride, oxyfluoride and complex fluoride were also elaborated with respect to the crystal structure of the host lattice, F content, and the temperature of calcination.

**Introduction**

Rare-earth fluorides normally possess a high refractive index (\(~1.56\)), a low phonon energy (\(~350–500\) cm\(^{-1}\)), and adequate thermal and environmental stability, and therefore are regarded as excellent host lattices for down- and up-conversion luminescence of lanthanide (Ln) ions.\(^{1-15}\) Among the investigated fluorides, the \( \text{Y}(\text{OH})_{1-x}\text{F}_x \) hydroxylfluoride and \( \text{YO}_3\text{F}_{1-x} \) oxyfluoride have been drawing great attention due to their significantly broader anion miscibility than their chloride and bromide counterparts of fixed anion substitution phases.\(^{16}\) It was also reported that \( \text{Y}(\text{OH})_{1-x}\text{F}_x \) would decompose to \( \text{YO}_3\text{F}_{1-x} \) and a mixture of \( \text{Y}_2\text{O}_3 \) and \( \text{YO}_3\text{F} \) when \( x < 1\) and \( x > 1\), respectively.\(^{14,16}\) Aside from the benefit that the Y site of \( \text{Y}(\text{OH})_{1-x}\text{F}_x \) and \( \text{YO}_3\text{F}_{1-x} \) can be facilely substituted by an Ln\(^{3+}\) activator without additional charge compensation, the alterable \( \text{OH}^-/\text{F}^- \) and \( \text{O}^2-/\text{F}^- \) ligand molar ratio of these two types of compounds may offer great opportunities for engineering the local symmetry and crystal field strength to achieve tunable luminescence.

The synthesis of \( \text{Y}(\text{OH})_{1-x}\text{F}_x \) with changeable x value was exemplified by hydrothermal reaction under very high temperature and pressure. For example, \( \text{Y}(\text{OH})_{1-x}\text{F}_x \) with the lower F content of \( 0.65 < x < 1.43 \) is obtainable via hydrothermally reacting \( \text{Y}_2\text{O}_3 \) and KF at 400 °C and 25 MPa and that with the higher F content of \( 1.5 < x < 2.0 \) can be synthesized via reacting \( \text{Y}_2\text{O}_3 \) and HF at 450 °C and 4 kb.\(^{16,17}\) Recently, \( \text{RE}(\text{OH})_{3-x}\text{F}_x \) (RE: rare-earth) with some fixed x values (0.86, 0.98, 1.13, 1.43, and 1.90) was obtained via hydrothermal reaction at the lower temperatures of up to \(~220^\circ\text{C}\).\(^{4,6,14,18}\) and the nano-micro-crystals of several types of oxyfluorides (\( \text{RE}_2\text{O}_8\text{F}_9 \), \( \text{RE}_4\text{O}_3\text{F}_{10} \), \( \text{RE}_2\text{O}_3\text{F}_7 \), and \( \text{REOF} \)) were produced via thermolysis of precipitation products and by solid reaction.\(^{8,9,20}\) With these successes, the photoluminescent properties of the hydroxyfluoride and oxyfluoride products were investigated.\(^{8,9,11,12-25}\)

Controlled synthesis of rare-earth compounds has also been achieved by the phase conversion technique,\(^{24-28}\) which generally involves the two different mechanisms of interface chemical transformation\(^{25,26}\) and dissolution-reprecipitation.\(^{24,27,28}\)
The former applies when the precursor and target compound have the same crystal structure. In the course of phase conversion, the precursor serves as both a physical and chemical template and as a result the final product can well preserve the crystalline morphology of the precursor. This is evidenced by the hydrothermal conversion of hexagonal structured \( \text{RE(OH)}_{3} \) nanorods/nanotubes into hexagonal \( \beta \)-NaREF\(_{4} \) crystallites of the same morphology.\(^{25-26} \) The dissolution-recrystallization mechanism takes the role when the precursor and final product differ in crystal structure, as shown by the evolution of LuBO\(_{3} \) microdiscs (hexagonal structured) upon reacting Lu\(_{3} \)O(OH)\(_{5} \)NO\(_{3} \) nanowires (monoclinic structured) with boric acid (H\(_{3} \)BO\(_{3} \)).\(^{24} \) RE\(_{3} \)F\(_{4} \) and Na\(_{2} \)REF\(_{4} \) hollow spheres have also been hydrothermally converted from amorphous RE(\( \text{OH} \))\(_{2} \)CO\(_{3} \) colloidal spheres in the presence of NaBF\(_{4} \) (ref. 27) or NaF.\(^{28} \)

We employed in this work the phase conversion strategy to synthesize Eu\(_{3} \) doped Y(OH)\(_{2} \)-F\(_{2} \) with the nanosheets of \( \text{RE}_{2}(\text{OH})_{5}\text{NO}_{3} \cdot n\text{H}_{2}\text{O} \) layered hydroxyl nitrate (LREH-NO\(_{3} \)) as a new type of sacrificial precursor. The crystal structure of LREH-NO\(_{3} \) is constructed via alternative stacking of the \( \text{RE}_{2}(\text{OH})_{5} \text{NO}_{3} \cdot (\text{H}_{2}\text{O})_{x} \) host layer and anion-exchangeable interlayer NO\(_{3} \) along the c-axis ([001] direction).\(^{29} \) The compound received much research interest owing to the diverse and unique physico-chemical properties of RE, particularly in the areas of nanomaterials exfoliation via anion exchange of the parent crystals, assembly of the delaminated nanosheets into multi-functional films, and derivation of luminescent oxide powders and oriented films.\(^{28-43} \) Different from the traditional LREH-NO\(_{3} \) synthesis via reflux precipitation and hydrothermal reaction, which inevitably yield platelike thick crystals, we developed a “freezing-temperature crystallization” technique that can directly produce LREH-NO\(_{3} \) nanosheets of only ~4 nm thick in an acceptable batch quantity.\(^{27} \) The technique was conceived from the fact that the lateral growth of LREH-NO\(_{3} \) crystallites needs lower activation energy than thickness growth because the hydroxide main layers are close-packed crystal planes. As a result, much thinner platelets (nanosheets) can be directly yielded by restricting the thickness growth through lowering the reaction temperature to ~4 °C. Another distinct advantage of this technique is that it is widely applicable to the RE elements of Pr–Er in the lanthanide family (excluding radioactive Pm).\(^{27} \) To the best of our knowledge, however, sacrificial conversion of LREH-NO\(_{3} \) into fluoride compounds via reacting with KF has hardly been reported prior to us. The phase, morphology, and composition evolution during phase conversion and subsequent calcination and also the photoluminescence properties of the resultant fluoride compounds were investigated in detail.

**Experimental**

**Reactants and materials synthesis**

Eu(NO\(_{3}\))\(_{3} \cdot 6\text{H}_{2}\text{O} \) (99.95% pure) and Y(NO\(_{3}\))\(_{3} \cdot 6\text{H}_{2}\text{O} \) (99.99% pure) were purchased from Kanto Chemical Co. (Tokyo, Japan) while NH\(_{4}\)OH solution (25%) and KF (99% pure) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

For the synthesis of \( \text{RE}_{2}(\text{OH})_{5}\text{NO}_{3} \cdot n\text{H}_{2}\text{O} \) layered hydroxide nanosheets (RE = Y, Eu, Gd, hereafter referred to LREH-NO\(_{3} \)), 250 mL of a 0.2 mol L\(^{-1} \) aqueous solution of RE(NO\(_{3}\))\(_{3} \) was pre-cooled to ~4 °C with a cool circulator, followed by dropwise addition of NH\(_{4}\)OH aqueous solution (1 mol L\(^{-1} \)) till pH ~8.0.\(^{27} \) After aging for 1 h, the resultant suspension was suction filtrated and the precipitate was washed with deionized water two times and ethanol once, followed by drying in air at 70 °C for 24 h.

For phase conversion, a certain amount of KF was dissolved in 50 mL of deionized water at room temperature, to which 3 mmol of the as-prepared LREH-NO\(_{3} \) was added. The F/RE molar ratio (\( \frac{\text{F}}{\text{RE}} \)) was varied in the wide range of 0–200 to investigate its effect on product property. After homogenizing under magnetic stirring for 10 min, the suspension was transferred into a capped glass tube for reaction at 90 °C for 3 h. The resultant precipitate was collected by centrifugation, washed with deionized water three times and ethanol once, followed by drying in air at 70 °C for 12 h.

\[ \text{REO}_{3-x}\text{F}_{x} \text{Oyfluoride was obtained by thermal decomposition of the as-prepared RE(OH)}_{3-x}\text{F}_{x} \text{ in air at a selected temperature for 2 h, with a heating rate of 5 °C min}^{-1} \text{ at the ramp stage.} \]

**Characterization techniques**

Phase identification was performed by powder X-ray diffractionmetry (XRD, Model RINF 2200 V/PC, Rigaku, Tokyo, Japan) under 40 kV/40 mA, using nickel-filtered Cu-k\(_{2} \) radiation and a scanning speed of 1° 2θ per minute. Phase constituent of the product was analysed via Rietveld fitting of the XRD pattern with the TOPAS software. 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, model FEM-3000F, JEOL Ltd., Tokyo) under 300 kV. Topographic images of the LREH-NO\(_{3} \) nanosheets were acquired via atomic force microscopy (AFM, Model NanoScope IIIa, Veeco Instruments Inc., NY) in the tapping mode at the scanning rate of 1 Hz. Fourier transform infrared spectroscopy (FTIR, Model FT/IR-4200, JASCO Co. Ltd., Tokyo) was performed by the standard KBr pellet method. Thermogravimetry (TG, Model Thermo Plus TG8120, Rigaku) of the dried RE(OH)\(_{3} \)-xF, was made in stagnant air with a heating rate of 10 °C min\(^{-1} \). Elemental contents of the products were determined for RE and K via inductively coupled plasma atomic emission spectroscopy (ICP-OES, Model SPS3520UV-DD, SII Nanotechnology, Kyoto, Japan) and for F via the “lanthanum/alizarin complexone (LAC)” absorption technique (Model SPS3520UV-DD, SII Technologies); photoluminescence properties of the products were measured at room temperature using an FP-6500 fluorospectrophotometer, with a 150 W Xe lamp (JASCO) for excitation and with slit width of 5 nm for both excitation and emission.

**Results and discussion**

**Phase/morphology evolution and characterization of the conversion products**

Fig. 1 shows powder XRD patterns of all the products obtained in this work. The precursor precipitated at ~4 °C exhibits a series of 00l and non-00l diffractions that are characteristic of
the orthorhombic structured LREH-NO$_3^-$ compound, whose lattice parameters were analysed to be $a \sim 1.2699(3)$, $b \sim 0.7140(1)$, and $c \sim 1.6870(1)$ nm with the JADE 6.5 software. Reacting the LREH-NO$_3^-$ precursor with KF under the F/RE molar ratio of $R = 3:3$ yielded a product that can be assigned to the F$^-$ substituted LREH of RE$_2$(OH)$_5$F$_n$H$_2$O (LREH-F$^-$).37,46

Owing to the electrostatic attraction arising from strong hydrogen bonding between the interlayer F$^-$ and the hydroxyls/H$_2$O in the adjacent hydroxide main layers, the interlayer distance ($c/2$) of the LREH, calculated from the centre of the 002 peak, contracted from the $\sim$0.844 nm of LREH-NO$_3^-$ to the $\sim$0.740 nm of LREH-F$^-$. Fluorination did not substantially alter the positions of the non-00l diffractions (such as 220), suggesting that the [RE$_2$(OH)$_5$(H$_2$O)$_n$]$^+$ host layers largely remain intact since the non-00l diffractions come from the $ab$ planes (hydroxide layers). The $R = 10:3$ product shows diffractions that can be well indexed with hexagonal structured Y(OH)$_{1.57}$F$_{1.43}$ (JCPDS no. 80-2008), though a trace amount of unreacted LREH-F$^-$ was left behind (indicated with asterisk).37,46 The results thus suggest that, at $R = 10:3$, the F$^-$ anions have replaced the water molecules and also a major portion of the hydroxyls in the hydroxide host layers of LREH-F$^-$. The products obtained with the larger $R$ values of 20:3–70:3 are hexagonal structured RE(OH)$_{3-x}$F$_x$ of high phase purity, which was proposed to form via the reaction of RE$_2$(OH)$_5$F$_n$H$_2$O + (2$x$ – 1)KF → 2RE(OH)$_{3-x}$F$_x$ + (2$x$ – 1)KOH + $n$H$_2$O. The results of elemental analysis for the $R = 20:3$–70:3 products are tabulated in Table 1, where it is clearly seen that the prescribed Eu content (5 at%) was well kept to the reaction product in each case and that the F content (the $x$ value in RE(OH)$_{3-x}$F$_x$) gradually increased from $\sim$1.15 to 1.51 with increasing $R$. It is also notable that the product contains a negligible amount of K$^+$ in each case.

Fig. 2 illustrates the lattice constants as a function of the F content for RE(OH)$_{3-x}$F$_x$. It is seen that the $a$ parameter gradually decreases with increasing F incorporation while the $c$ parameter keeps almost constant at $\sim$3.55 Å. The crystal structure of RE(OH)$_{3-x}$F$_x$ is constructed through linking of each RE(O/F)$_9$ polyhedron with three adjacent ones by edge-sharing along the $a$- and $b$-axis and with the other two by face-sharing along the $c$-axis, leaving a hexagonal tunnel running along the [001] direction (Fig. S1†). As the $a$ constant is related to the
Table 1 The results of elemental analysis and derived chemical formulae for the phase conversion products

| $R$  | Proposed formula | Analysed content (wt%) | Calculated molar ratio |
|------|------------------|------------------------|------------------------|
|      |                  | $Y$ | $Eu$ | $F$  | $K$  | $nY : nEu : nF : nK$ |
| 20 : 3 | RE(OH)$_{1.88}$F$_{1.15}$ | 55.4 | 5   | 14.3 | 0.24 | 0.95 : 0.05 : 1.15 : 0.01 |
| 30 : 3 | RE(OH)$_{1.77}$F$_{1.23}$ | 56.1 | 5   | 15.5 | 0.22 | 0.95 : 0.05 : 1.23 : 0.01 |
| 40 : 3 | RE(OH)$_{1.71}$F$_{1.29}$ | 55.7 | 4.9 | 16.2 | 0.37 | 0.95 : 0.05 : 1.29 : 0.01 |
| 50 : 3 | RE(OH)$_{1.65}$F$_{1.35}$ | 55.5 | 5   | 16.9 | 0.55 | 0.95 : 0.05 : 1.35 : 0.02 |
| 60 : 3 | RE(OH)$_{1.51}$F$_{1.49}$ | 54.7 | 4.9 | 18.3 | 0.75 | 0.95 : 0.05 : 1.49 : 0.03 |
| 70 : 3 | RE(OH)$_{1.49}$F$_{1.51}$ | 54.3 | 4.9 | 18.4 | 0.83 | 0.95 : 0.05 : 1.51 : 0.03 |
| 200 : 3 | K$_2$RE$_3$F$_{12}$ | 43.2 | 3.9 | 32.7 | 11.2 | 8.55 : 0.45 : 30.28 : 5.04 |

![Fig. 2](Image) Correlation of lattice parameters with the F content ($x$ value, Table 1) for the RE(OH)$_{3-x}$F$_x$ products obtained under the $R$ values of 20 : 3 – 70 : 3.

The main reason is that the amount (concentration) of KF needed to completely replace the hydroxyls in RE(OH)$_{3-x}$F$_x$ is so high that either KREF$_4$ or REF$_3$ becomes thermodynamically unstable than the K$_2$RE$_3$F$_{12}$ phase under such conditions. To better understand the process of phase conversion and the characteristics of the conversion products, we performed FTIR analysis and the results are presented in Fig. 3. For the LREH-NO$_3^-$ nanosheets, the sharp absorption band found at $\sim$1384 cm$^{-1}$ is typical of the $\nu_3$ vibration of uncoordinated NO$_3^-$ anions, while those at $\sim$3000–3450 cm$^{-1}$ and 1641 cm$^{-1}$ can be assigned to the OH stretching vibrations ($\nu_1$ and $\nu_3$) and H–O–H bending mode ($\delta_2$) of H$_2$O molecules, respectively. The existence of hydroxyls (OH$^-$) is evidenced by the absorption in the 3500–3750 cm$^{-1}$ region. The results thus well conform to the chemical composition of LREH-NO$_3^-$ (RE$_2$(OH)$_5$NO$_3$·nH$_2$O). Treating LREH-NO$_3^-$ with KF solution under $R = 3 : 3$ led to the vanishing of the NO$_3^-$ absorption but did not appreciably affect the H$_2$O and OH$^-$ vibrations. Such a result suggests that F$^-$ has substituted the interlayer NO$_3^-$ of LREH-NO$_3^-$ to form the LREH-F$^-$ of RE$_2$(OH)$_5$NO$_3$·nH$_2$O. The shallow twin bands in the 1300–1580 cm$^{-1}$ region, which partially overlap with the NO$_3^-$ vibration in the spectrum of LREH-NO$_3^-$, are characteristic of CO$_3^{2-}$ absorptions. The contamination, arising from dissolved atmospheric CO$_2$ and the high affinity of CO$_3^{2-}$ toward RE$^{3+}$, is common to all the samples synthesized in this work and is also widely observed in LREH-NO$_3^-$ studies.
= 10 : 3–70 : 3 products exhibit FTIR absorptions agreeing with the hydroxyfluoride of RE(OH)3–xFx, with the intense and sharp band at ∼3649 cm⁻¹, the one in the ∼743–752 cm⁻¹ region, and the one at ∼500 cm⁻¹ well assignable to the stretching vibrations of virtually free hydroxyls (OH⁻), OH⁻ deformation,³² and ν(F–RE–F), respectively. The occurrence of OH⁻ deformation vibration also implies the existence of intramolecular [O–H···F⁻] hydrogen bonding.¹⁶ The R = 200 : 3 product (K₅RE₉F₃₂) exhibits absorptions arising from ν(F–RE–F) and H₂O at the same time, which may indicate that the sample has some adsorbed water molecules. The results of FTIR, XRD, and elemental analysis are well supporting each other, and confirm the proposed pathway of phase evolution.

Fig. 4 exhibits the results of FE-SEM and TEM analysis for some representative reaction products. The LREH-NO₃⁻ precursor (R = 0) presents flower-like assemblies of nanosheets with the lateral sizes of ∼300 nm and thicknesses of ∼4 nm. AFM analysis of the nanosheets (Fig. S2†) further confirmed the thickness value determined via TEM observation. The R = 3 : 3 sample (the LREH–F of RE₃(OH)xFₙH₂O) generally retained the overall morphology of LREH-NO₃⁻ as agglomerated nanosheets, but TEM observation found tiny holes on the individual nanosheets arising from KF corrosion. A mixture of prismatic particles (dominant) and some thin-platelets were found for the R = 10 : 3 product, which can be assigned to the newly formed RE(OH)₁₋ₓFx and residual LREH–F⁻ phases, respectively, according to the results of XRD analysis (Fig. 1). The R = 20 : 3 product exclusively contains dispersed short hexagonal prisms (lengths and diameters up to ∼300 and 100 nm, respectively), in coincidence with the hexagonal crystal structure of RE(OH)₁₋ₓFx (x ∼ 1.15, Table 1) and the single-phase nature of this product. HR-TEM lattice imaging well resolved the (110) crystal plane (interplanar spacing ∼0.306 nm) and showed that the prisms are elongated along the [001] crystallographic direction. Rice-grain shaped particles of up to ∼300 nm in length were produced by increasing the R value, as shown with the R = 70 sample for example (x ∼ 1.51, Table 1). TEM analysis found that the individual particles are significantly polycrystalline, which is in accordance with the fact that the powder has an average crystallite size of only ∼16 nm as assayed from the XRD pattern with the Scherrer formula. In addition, the interplanar spacing of ∼0.303 nm resolved by HR-TEM is assignable to the (110) plane of RE(OH)₁₋ₓFx. The as-prepared K₅RE₉F₃₂ powder (R = 200 : 3) is composed of nanospheres of up to ∼50 nm in diameter, and the resolved d-spacing of ∼0.326 nm may correspond to the (111) crystal plane. The well-resolved lattice fringes also imply good crystallinity of the products, despite of the low phase-conversion temperature of only ∼90 °C.

RE(OH)₁₋ₓFx, RE(OH)₃, and β-NaREF₄ are all hexagonal structured and present high structure similarities (Fig. S3†).⁵,³³,⁵⁴ As in RE(OH)₃ and β-NaREF₄, the Eu³⁺ activators were proposed to have C₁₅h symmetry in RE(OH)₁₋ₓFx.⁵,⁵² The PL and PLE spectra of RE(OH)₁₋ₓFx are shown in Fig. 5 (R = 20 : 3–70 : 3, x = 1.15–1.51). It is seen that the hydroxyfluorides exhibit emissions at ∼594 nm (F₀ → F₁, medium strong), 618 nm (F₀ → F₂, strong), 652 nm (F₀ → F₃, weak), and 697 nm (F₀ → F₄, medium) under 395 nm excitation (the 7F₀ → 5I₅ excitation transition of Eu³⁺, Fig. 5)⁵,⁵⁴–⁵⁸ The stronger 5D₀ → 7F₂ than 5D₀ → 7F₁ transition conforms to the fact that the Eu³⁺ activators have the relatively low site symmetry of C₁₅h in RE(OH)₁₋ₓFx.⁵⁹ The PLE spectra obtained by monitoring the 618 nm main emission (Fig. 5, the right-hand inset) similarly consist of a series of sharp lines ascribed to the intra-4f transitions of Eu³⁺ as labelled in the figure. It is seen that both the

Fig. 4 FE-SEM and TEM analysis of the products obtained under the different F/RE molar ratios (R) indicated in the figure.
emission and excitation intensities tend to increase with increasing \( R \), which could be due to the gradually lower OH\(^-\) content (higher F\(^-\) content) in RE(OH)\(_3\)\(_x\)\(_{\_\_}\)\(_F\_\_\_) since hydroxyls are known to substantially quench the luminescence of rare-earth activators. The asymmetry factor of luminescence \( \left[I(\Delta \text{Do} \rightarrow \Delta \text{F}_2)/I(\text{Do} \rightarrow \text{F}_1)\right] \) keeps almost constant at 1.8 for all the hydroxyl fluoride samples (Fig. 5, the left-hand inset), which further illustrates that the observed PLE/PL enhancement with increasing F incorporation is due to the decreased content of OH\(^-\) rather than changed coordination environment (site symmetry) of Eu\(^{3+}\). K\(_5\)RE\(_6\)F\(_{32}\) has the fluoride-type cubic structure, which can be deemed as a random replacement of the Ca\(^{2+}\) sites of CaF\(_2\) by K\(^+\) and RE\(^{3+}\) ions, and is similar to that of the cubic-structured \( x\)-NaYF\(_4\) (Fig. S4).\(^{49,60}\) As the Eu\(^{3+}\) ions in K\(_5\)RE\(_6\)F\(_{32}\) would occupy the centrosymmetric \( O_h \) lattice sites,\(^{37,61}\) stronger \( \Delta \text{Do} \rightarrow \Delta \text{F}_2 \) emission (~592 nm, parity allowed magnetic dipole transition) over \( \text{Do} \rightarrow \text{F}_1 \) emission (~617 nm, parity forbidden electric dipole transition) is thus observed from the PL spectrum under 395 nm excitation, and is in compliance with the less than unit (~0.77) asymmetry factor of luminescence (Fig. 5, the left-hand inset). The PLE spectrum obtained by monitoring the \( \Delta \text{Do} \rightarrow \Delta \text{F}_1 \) emission (592 nm) presents excitations essentially identical to those of the RE(OH)\(_3\)\(_x\)\(_{\_\_}\)\(_F\_\_\_) hydroxylfluorides in band position, and the excitation intensity well conforms to the emission intensity.

**Phase/morphology evolution upon heating and characterization of the calcination products**

The thermal behaviour of RE(OH)\(_3\)\(_x\)\(_{\_\_}\)\(_F\_\_\_) was analysed via TG using the composition RE(OH)\(_{1.49}\)\(_{\_\_}\)\(_{F\_1.51}\) (\( R = 70 : 3 \)) as an example (Fig. 6). Three distinct stages of decomposition were observed for the sample, with the initial weight loss of ~2.5 wt% owing to the evaporation of adsorbed species (such as H\(_2\)O molecules, up to ~200 °C) and the second loss of ~9.32% (~200–450 °C) owing to the dehydroxylation of RE(OH)\(_{1.49}\)\(_{\_\_}\)\(_{F\_1.51}\) to form oxyfluoride according to the equation of RE(OH)\(_{1.49}\)\(_{\_\_}\)\(_{F\_1.51}\) = REO\(_{0.74}\)\(_{\_\_}\)\(_{F\_1.51}\) + 0.745H\(_2\)O. The theoretical weight loss calculated from the above equation (~9.18 wt%) is indeed very close to the observed value of ~9.32%. The gradual weight loss occurring at temperatures above ~700 °C (third stage) is due to oxidation of REO\(_{0.74}\)\(_{\_\_}\)\(_{F\_1.51}\) to form the nominal composition of REO\(_{0.745}\)\(_{\_\_}\)\(_{F\_1.51}\). Taking the 1.26% of weight loss at 1028 °C for example, the \( y \) value was assayed to be ~0.088. That is, the product at 1028 °C would have the nominal composition of REO\(_{0.70}\)\(_{\_\_}\)\(_{F\_1.42}\).

Fig. 7 exhibits XRD patterns of the products obtained by thermal decomposition of the as-prepared RE(OH)\(_3\)\(_x\)\(_{\_\_}\)\(_F\_\_\_) (\( x = 1.15–1.51, R = 20 : 3–70 : 3 \)) in air at 450 °C for 2 h. It is seen that the samples from the RE(OH)\(_{1.15}\)\(_{\_\_}\)\(_{F\_1.51}\) (\( R = 40 : 3–70 : 3 \)), RE(OH)\(_{1.25}\)\(_{\_\_}\)\(_{F\_1.51}\) (\( R = 20 : 3 \)) shows peak splitting (Fig. 7a) and are assignable to a mixture of hexagonal REOF (JCPDS no. 71-2100) and RE\(_6\)O\(_4\)F\(_2\) phases. The calcination product of RE(OH)\(_{1.77}\)\(_{\_\_}\)\(_{F\_1.23}\) (\( R = 30 : 3 \)) should also contain a small amount of REOF, as perceived from the existence of a right-hand tail in the amplified diffraction peak in Fig. 7b. Analysis of the phase constituent via Rietveld fitting of the XRD patterns (Fig. S5) indeed found that the products calcined from RE(OH)\(_{1.15}\)\(_{\_\_}\)\(_{F\_1.51}\) and RE(OH)\(_{1.25}\)\(_{\_\_}\)\(_{F\_1.51}\) contain ~44.0 (~0.6) and 11.8 (~0.5)% of the REOF phase, respectively. With the three decomposition products of \( R = 50–70 \) for example, we performed elemental analysis and the results are presented in Table 2. It is seen that the actual F content gradually increases towards a larger \( R \), and the three RE\(_6\)O\(_4\)F\(_2\) phases have the deduced compositions of REO\(_{0.81}\)\(_{\_\_}\)\(_{F\_1.38}\) (RE\(_6\)O\(_{1.05}\)\(_{\_\_}\)\(_{F\_0.90}\)), REO\(_{0.78}\)\(_{\_\_}\)\(_{F\_1.44}\) (RE\(_6\)O\(_{1.90}\)\(_{\_\_}\)\(_{F\_2.20}\)), and REO\(_{0.75}\)\(_{\_\_}\)\(_{F\_1.49}\) (RE\(_6\)O\(_{0.77}\)\(_{\_\_}\)\(_{F\_4.65}\)), if the trace amount of KF contaminant is ignored in each case. The slight (151) peak shifting observed in Fig. 7a could be due to the different F content of the products. In addition, the ass-said RE\(_6\)O\(_4\)F\(_2\) products were assayed from their (151) diffractions with the Scherrer formula to have the average crystallite sizes of ~15 ± 2 nm, not significantly affected by the \( R \) value or the actual content of F.

SEM and TEM analysis (Fig. 8) showed that the products well-retained the overall morphologies and particle sizes of their respective oxyfluoride parents. The particles are
thus PL spectra dominated by the $^5D_0 \rightarrow ^7F_2$ electric dipole transition at $\sim 614$ nm were yielded. The enhanced excitation and emission intensity at a higher $R$ or $F$ content could probably be due to improved crystallinity of the oxyfluoride by the flux effects of F$^-$ anions. With the $^5D_0 \rightarrow ^7F_2$ emission (614 nm) for example, the oxyfluorides have the increasing intensity ratio of 1 : 1.33 : 1.50 : 1.79 with the $R$ increasing from 40 : 3 to 70 : 3 (Fig. 9b).

Structure stability of the oxyfluoride was studied with the most F rich hydroxyfluoride of RE(OH)$_{1.49}$F$_{1.51}$ ($R = 70 : 3$) for sample, and the 450 °C product of which is REO$_{0.755}$F$_{1.49}$ as aforementioned. Fig. 10 shows XRD patterns of the products calcined in air at various temperatures for 2 h. It is seen that those obtained in the range of 450–700 °C can be assigned to the orthorhombic RE$_2$O$_3$F$_7$ phase. Elemental analysis of the 700 °C product found the $nY/nEu:nF:nK$ molar ratio of 0.95 : 0.05 : 1.40 : 0.03, and thus the chemical formula was derived to be $(Y_{0.95}Eu_{0.05})O_{0.80}F_{1.40}$. The sample apparently has less F than the 450 °C product of $(Y_{0.95}Eu_{0.05})O_{0.755}F_{1.49}$ indicating that slight F loss via oxidation has taken place, as also suggested by TG analysis (Fig. 6). Calcining at 900 °C led to the formation of hexagonal REOF, owing to the F loss via oxidation of RE$_2$O$_3$F$_7$. Partial oxidation of REOF took place at 1100 °C, and thus a phase mixture of hexagonal REOF and trace cubic RE$_2$O$_3$ (JCPDS no. 43-1036) was resulted.

Fig. 11 compares excitation and emission properties of the oxyfluorides obtained by calcining RE(OH)$_{1.49}$F$_{1.51}$ ($R = 70 : 3$) in air at the three temperatures of 450, 600, and 700 °C. The PL spectra (Fig. 11a) show the O$^2$––Eu$^{3+}$ charge transfer band (CTB) and the intra-4$^f$ transitions of Eu$^{3+}$ as indicated in the figure. The PL spectra obtained under 255 nm excitation (Fig. 11b) show emission transitions from the $^5D_0$ excited state to the $^7F_j$ ($j = 0–4$) ground states of Eu$^{3+}$ as marked in the figure, with the dominant red emission at $\sim 612$ nm arising from the $^5D_0 \rightarrow ^7F_2$ forced electric dipole transition. The intensity of PL/PLE bands steadily increases with rising temperature of calcination owing to improved crystallinity of the products. The 612 nm emission, for example, has the intensity ratio of $\sim 1 : 1.51 : 2.44$ for the oxyfluorides calcined at 450, 600, and 700 °C. Increasing temperature of calcination led to slight shift of the CTB centre from $\sim 253$ to 259 nm, which could be due to the gradually higher oxygen content (less F) of the product and the smaller electronegativity of oxygen than fluorine. It was also noticed that the intra-4$^f$ transitions gradually gained intensity over CTB with increasing temperature of calcination, as seen from Fig. 11a. That is, CTB dominates the excitation spectrum for the 450 °C product while the $^7F_0 \rightarrow ^5L_6$ intra-4$^f$ transition is the strongest for the 700 °C one. The phenomenon may again suggest that O$^2$– is better coordinated to RE$^{3+}$ than F$^–$ in the 450 °C product, and as a result the PLE spectrum of this sample is similar to that widely observed for the Y$_2$O$_3$:Eu red phosphor. Increasing temperature of calcination promotes crystallization and at the same time better coordination of F$^–$ to RE$^{3+}$. As a result, CTB shows slower intensity increment than the intra-4$^f$ transitions since a significant mixing in of F in the (O, F)–RE bond would reduce the efficiency of charge transfer by the higher

| Analyzed content (wt%) | Derived molar ratio |
|------------------------|---------------------|
| $R$ | Y | Eu | F | K | $nY:nEu:nF:nK$ | $x$ |
| 50 | 62.8 | 5.6 | 19.5 | 0.64 | 0.95 | 0.05 | 1.38 | 0.02 | 1.38 |
| 60 | 62.3 | 5.5 | 20.2 | 0.82 | 0.95 | 0.05 | 1.44 | 0.03 | 1.44 |
| 70 | 61.9 | 5.5 | 20.8 | 0.97 | 0.95 | 0.05 | 1.49 | 0.03 | 1.49 |

| $\chi$ | $\gamma$ | $\delta$ | $\epsilon$ | $\zeta$ | $\iota$ | $\kappa$ | $\lambda$ | $\mu$ | $\nu$ |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 2.3   | 2.6   | 2.9   | 3.2   | 3.5   | 3.8   | 4.1   | 4.4   | 4.7   | 5.0   |

Fig. 7 Powder XRD patterns of the products obtained by calcining RE(OH)$_{1.49}$F$_{1.51}$ ($x = 1.15–1.51$, $R = 20 : 3–70 : 3$) in air at 450 °C for 2 h. (a) and (b) are enlarged views of the 2θ = 27–35° and 45–50° regions, respectively. The standard diffractions of orthorhombic Y$_5$O$_4$F$_7$ (JCPDS no. 80-1124) and hexagonal YOF (JCPDS no. 71-2100) are presented as bars for comparison.

The elemental analysis of the (Y$_{0.95}$Eu$_{0.05}$)O$_{0.755}$F$_{1.49}$ oxyfluorides calcined in air at various temperatures for 2 h.

Table 2 Elemental analysis of the (Y$_{0.95}$Eu$_{0.05}$)O$_{0.755}$F$_{1.49}$ oxyfluorides calcined in air at various temperatures for 2 h.

- Table 2:
- Fig. 9 shows PLE and PL spectra of the REO$_{3(1-\delta)}$F$_x$ products (the said RE$_2$O$_3$F$_7$ phases, $x = 1.38–1.49$; $R = 40 : 3–70 : 3$). The strong excitation bands of O$^2$––Eu$^{3+}$ CTB are located with maxima at $\sim 253$ nm, while the weaker peaks in the longer wavelength region ($\sim 300–500$ nm) can be assigned to the intra-4$^f$ transitions of Eu$^{3+}$. Owing to the much greater energy needed to remove an electron from F$^–$ than from O$^2$–, F$^–$–Eu$^{3+}$ CTB, which generally occurs below 200 nm in the excitation spectrum, is not present in the PLE spectra of this work. Considering that the electronegativity of F (3.98) is higher than that of O (3.44), blue-shifted CTB was initially expected for the oxyfluoride of a higher F content. The almost constant CTB centre actually observed in this work may suggest that the F$^–$ anions have not been as well coordinated to RE$^{3+}$ as O$^2$– in the molecules or the F content has not been sufficiently different to reveal the effects of ligand electronegativity. RE$_2$O$_3$F$_7$ provides the approximate $C_{av}$ site symmetry for the Eu$^{3+}$ activator, and

- Fig. 11 compares excitation and emission properties of the oxyfluorides obtained by calcining RE(OH)$_{1.49}$F$_{1.51}$ ($R = 70 : 3$) in air at the three temperatures of 450, 600, and 700 °C. The PLE spectra (Fig. 11a) show the O$^2$––Eu$^{3+}$ charge transfer band (CTB) and the intra-4$^f$ transitions of Eu$^{3+}$ as indicated in the figure. The PL spectra obtained under 255 nm excitation (Fig. 11b) show emission transitions from the $^5D_0$ excited state to the $^7F_j$ ($j = 0–4$) ground states of Eu$^{3+}$ as marked in the figure, with the dominant red emission at $\sim 612$ nm arising from the $^5D_0 \rightarrow ^7F_2$ forced electric dipole transition. The intensity of PL/PLE bands steadily increases with rising temperature of calcination owing to improved crystallinity of the products. The 612 nm emission, for example, has the intensity ratio of $\sim 1 : 1.51 : 2.44$ for the oxyfluorides calcined at 450, 600, and 700 °C. Increasing temperature of calcination led to slight shift of the CTB centre from $\sim 253$ to 259 nm, which could be due to the gradually higher oxygen content (less F) of the product and the smaller electronegativity of oxygen than fluorine. It was also noticed that the intra-4$^f$ transitions gradually gained intensity over CTB with increasing temperature of calcination, as seen from Fig. 11a. That is, CTB dominates the excitation spectrum for the 450 °C product while the $^7F_0 \rightarrow ^5L_6$ intra-4$^f$ transition is the strongest for the 700 °C one. The phenomenon may again suggest that O$^2$– is better coordinated to RE$^{3+}$ than F$^–$ in the 450 °C product, and as a result the PLE spectrum of this sample is similar to that widely observed for the Y$_2$O$_3$:Eu red phosphor. Increasing temperature of calcination promotes crystallization and at the same time better coordination of F$^–$ to RE$^{3+}$. As a result, CTB shows slower intensity increment than the intra-4$^f$ transitions since a significant mixing in of F in the (O, F)–RE bond would reduce the efficiency of charge transfer by the higher
Fig. 8 FE-SEM and TEM analysis of the products calcined from RE(OH)$_3$$_x$F$_x$ ($x = 1.15\text{--}1.51$, $R = 20:3\text{--}70:3$) in air at 450 $^\circ$C for 2 h.

Fig. 9 PLE (a) and PL (b) spectra of the REO$_{3-x}$.F$_x$ products ($x = 1.38\text{--}1.49$) calcined from RE(OH)$_3$$_x$F$_x$ ($R = 40:3\text{--}70:3$) in air at 450 $^\circ$C for 2 h. The excitation and emission wavelengths used for the measurements are indicated in the figure.
Fluorescence decay curves of the three fluoride phosphors are shown in Fig. S6,† where it was found that the decay kinetics can all be well fitted with the single exponential of \( I = A \exp(-t/\tau_R) + B \), where \( \tau_R \), \( t \) and \( I \) denote the fluorescence lifetime, delay time and relative intensity, respectively, and \( A \) and \( B \) are constants. The phosphors calcined at 450, 600 and 700 °C were analysed to have the increasing lifetime values of 1.39 (±0.01), 2.34 (±0.01) and 2.48 (±0.01) ms and the gradually higher internal/external quantum yields (in percentage) of 33.2/15.9, 45.0/24.2 and 51.0/31.6, respectively. The successively longer fluorescence lifetime and higher quantum yield observed for a higher calcination temperature are primarily owing to the elimination of luminescence quenching defects and improved crystallinity, through crystallite growth, of the phosphor powder.

**Conclusions**

RE(OH)\(_{3-x}\)F\(_x\) hydroxyfluoride (\( x = 1.15-1.51 \)) and K\(_x\)RE\(_x\)F\(_{32}\) crystals have been successfully converted from the nanosheets (~4 nm thick) of RE\(_2\)(OH)\(_5\)NO\(_3\) \( \cdot \) \( n \)H\(_2\)O layered hydroxyl nitrate (LREH-NO\(_3\)), \( RE = Y_{0.95}Eu_{0.05} \) via reacting with KF solution at the low temperature of ~90 °C. Calcining RE(OH)\(_{3-x}\)F\(_x\) of the relatively high F content of \( x = 1.29-1.51 \) at 450 °C in air has also produced REO\(_{3-x}\)F\(_x\) oxyfluorides that are analogous to the orthorhombic structured Y\(_5\)O\(_4\)F\(_7\) phase. It was shown that the actual F content of the product is dependent on the F/RE molar ratio used for phase conversion and the temperature of subsequent calcination. Oxidation of REO\(_{3-x}\)F\(_x\) to form REOF and even RE\(_2\)O\(_3\) was observed at temperatures above ~700 °C. The resultant hydroxyfluorides, oxyfluorides and complex fluoride...
were shown to exhibit photoluminescence dependent on the crystal structure of the host lattice, F content, and temperature of calcination.

Conflicts of interest

There are no conflicts to declare.

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