Optically active uniform potassium and lithium rare earth fluoride nanocrystals derived from metal trifluroacetate precursors[†]

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This paper reports the first systematical synthesis of near-monodisperse potassium and lithium rare earth (RE) fluoride (K(Li)REF₄) nanocrystals with diverse shapes (cubic KLaF₄ and KCeF₄ wormlike nanowires, nanocubes and nanopolyhedra; cubic LiREF₄ (RE = Pr to Gd, Y) nanopolyhedra; tetragonal LiREF₄ (RE = Tb to Lu, Y) rhombic nanoplates) *via* co-thermolysis of Li(CF₃COO) or K(CF₃COO) and RE(CF₃COO)₃ in a hot oleic acid/oleylamine/1-octadecene solution. The effects of the solvent composition, reaction temperature and time on the crystal phase purity, shape, and size of the as-prepared nanocrystals have been investigated in detail. The formation of monodisperse nanocrystals is found to strongly depend upon the nature of both alkali metals from Li to K, and the rare earth series from La to Lu and Y. Based on the series of experimental results, a controlled-growth mechanism has also been proposed. In addition, the ease of doping of these as-synthesized host nanocrystals for designed luminescence properties is assessed. For example, monodisperse and single-crystalline Eu³⁺ doped KGdF₄, Yb³⁺ and Er³⁺ co-doped LiYF₄ nanocrystals redispersed in cyclohexane exhibit visible room-temperature red and green emissions under ultraviolet (UV) excitation and near infrared (NIR) 980 nm laser excitation, respectively.

Introduction

Studies on monodisperse colloidal inorganic nanocrystals have advanced dramatically in the past few years. The colloidal nanocrystals with controlled shape, size, composition, phase, and surface endow such materials with unique optical, electronic, magnetic, and catalytic properties, which are fundamentally important and technologically useful.¹ Precisely controlled synthesis allows manipulation of the properties of nanocrystals as desired. Therefore, up to present, various wet chemical strategies have been designed and developed for obtaining such nanocrystals, which not only are recognized for their unique material properties, but also have already acted as the building blocks for the advanced nanodevices composed of 2D (two dimensional) and 3D (three dimensional) assemblies.² Amongst these, the relatively successful synthetic methods are based on the nonhydrolytic approach and its alternatives, with which nanocrystalline products can be grown with controlled-size, shape, phase, and composition for a given inorganic compound.1e,g2a-f

Colloidal rare earth (RE) compound nanocrystals such as oxides, phosphates, fluorides, vanadates, sulfides, and oxyhalides have become a new focus of research, due to their extraordinary properties arising from the 4f electron configuration and the potential applications in solid-state lasers, optical amplifies, lighting and displays, and biolabels.³ Among them, the rare earth

doped fluorides based on AREF₄ (A = alkali metal, RE = rare earth) have been investigated for several decades due to their unique luminescent, ferromagnetic, insulating/magnetic, and piezoelectric properties and wide applications in laser devices, three-dimensional flat-panel displays, and low-intensity infrared imaging.⁴ For example, the hexagonal phase of NaYF₄ is considered as the most efficient host material for green and blue upconversion (UC) phosphors until now,^{4e} LiGdF₄ is an outstanding host for downconversion luminescence, for which the quantum efficiency is close to 200%.^{5b} Rare earth doped single crystals of KYF₄ are excellent solid-state laser materials, and laser action has been observed for Yb³⁺, Tm³⁺, Ho³⁺ ions in the KYF₄ lattice.^{5a,c}

As an important category of rare earth fluoride compounds of AREF₄ material, KREF₄ and LiREF₄ are particularly suitable luminescence hosts for doping lanthanide ions due to their low phonon energies, which reduce the thermal disturbance effects under strong pumping conditions.⁵ There have already some reports on the solution phase synthesis and optical characterization of nanosized NaREF₄.⁶ To our knowledge, the systematic study of the synthesis and material properties of monodisperse colloidal KREF₄ and LiREF₄ nanocrystals has never been described until now.⁷ The current synthesis methods available for nanosized KREF₄ and LiREF₄ are mainly based on the liquid coprecipitation reaction between soluble rare earth salts and alkali fluorides.^{7n,df-h}

In this article, we demonstrate a general one-step synthesis of near-monodisperse KREF₄ (RE = La to Gd, Y) and LiREF₄ (RE = Tb to Lu, and Y) colloidal nanocrystals *via* the co-thermolysis of K(CF₃COO) or Li(CF₃COO) and RE(CF₃COO)₃ precursors in oleic acid/oleylamine/1-octadecene. The effects of different experimental conditions on the crystal phase purity, shape and size of the KREF₄ and LiREF₄ nanocrystals have

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been investigated. The formation mechanisms of the nanocrystals have also been proposed. With the developed synthesis method, monodisperse KGdF₄:Eu, LiYF₄:Yb,Er nanocrystals have also been obtained, which show interesting optical properties under ultraviolet (UV) and near infrared (NIR) laser (980 nm) excitations.

Experimental

Materials

The synthesis was carried out using standard oxygen-free procedures and commercially available reagents. Rare earth oxides, oleic acid (OA; 90%, Alpha), oleylamine (OM; >80%, Acros), 1-octadecene (ODE; >90%, Acros), trifluoroacetic acid (99%, Acros), K(CF₃COO) (>97%, Acros), absolute ethanol, cyclohexane were used as received. RE(CF₃COO)₃ and Li(CF₃COO) were prepared with the literature method.⁸ All the chemicals were of analytical grade and used as received without further purification.

Synthesis of $KREF_4$ (RE = La to Gd, Y) nanocrystals

A given amount of K(CF₃COO) and RE(CF₃COO)₃ (1 mmol) were added into 40 mmol of OA/OM/ODE (Table S1, ESI[†]) in a three-necked flask at room temperature. Then the slurry was heated to 120 °C to remove water and oxygen, with vigorous magnetic stirring under vacuum for 30 min in a temperaturecontrolled electromantle, and thus forming a transparent solution. The solution was then heated to a certain temperature in the range of 250-330 °C at a rate of 22 K min⁻¹ and maintained at the given temperature for 15-120 min under an Ar atmosphere. When the reaction was completed, an excessive amount of ethanol was poured into the solution at room temperature. The resultant mixture was centrifugally separated and the products were collected. The as-precipitated nanocrystals were washed several times with ethanol and dried in air at 80 °C overnight. The yields of all the obtained nanocrystals without size-selection were 60-70%. All these as-prepared nanocrystals could be easily dispersed in various nonpolar organic solvents (e.g., cyclohexane).

Synthesis of $LiREF_4$ (RE = Tb to Lu, Y) nanocrystals

The synthetic procedure was the same as that used to synthesize $KREF_4$ nanocrystals, except that a certain amount of as-prepared $Li(CF_3COO)$ and $RE(CF_3COO)_3$ were added into a mixture of 40 mmol of OA/ODE (Table S1, ESI†) in a three-necked flask at room temperature.

Synthesis of KGdF₄:5%Eu and LiYF₄:20%Yb,2%Er nanocrystals

The synthetic procedure was the same as that used to synthesize $KREF_4$ nanocrystals, except that 1 mmol $K(CF_3COO)$ or $Li(CF_3COO)$ and a suitable proportion of $Gd(CF_3COO)_3$, $Eu(CF_3COO)_3$, $Y(CF_3COO)_3$, $Yb(CF_3COO)_3$, and $Er(CF_3COO)_3$ were added into a mixture of OM and/or OA and ODE (total: 40 mmol) in a three-necked flask at room temperature.

Instrumentation

Powder X-ray diffraction (PXRD) patterns of the dried powders were recorded on a Rigaku D/MAX-2000 diffractometer (Japan) with a slit of $1/2^{\circ}$ at a scanning rate of 4° min⁻¹, using Cu-K α radiation ($\lambda = 1.5418$ Å). The lattice parameters were calculated with the least-squares method. Samples for transmission electron microscopy (TEM) analysis were prepared by drying a drop of nanocrystal dispersion in cyclohexane on amorphous carboncoated copper grids. Particle sizes and shapes were examined by a JEOL 200CX-TEM (Japan) operated at 160 kV. High-resolution TEM (HRTEM) characterization was performed with a Philips Tecnai F30 FEG-TEM (USA) operated at 300 kV. FTIR spectra were obtained on a Bruker Vector22 spectrophotometer (German). Room-temperature fluorescence spectrum of KGdF4:Eu nanocrystals were recorded on a Hitachi F-4500 spectrophotometer (Japan) equipped with a 150 W Xe arc lamp at a fixed bandpass of 0.2 nm with the same instrument parameters (10.0 nm for excitation slit, 10.0 nm for emission slit, and 700 V for PMT voltage), with the as-dried nanocrystals redispersed in cyclohexane at a concentration of about 2 wt%. The photoluminescence quantum yields of the KGdF₄:Eu nanocrystals were determined by comparing the integral emission intensity of the dilutions of the concentrated nanocrystal suspension in cyclohexane with that of rhodamine B in absolute ethanol at an excitation of 275 nm with collection between 550 and 700 nm at room temperature.³¹ Upconversion emission spectra of LiYF₄:Yb,Er nanocrystals were obtained on a modified Hitachi F-4500 spectrophotometer with an external tunable 2 W 980 nm laser diode as the excitation source, with the as-dried nanocrystals redispersed in cyclohexane at a concentration of about 2 wt%.

Results and discussion

Characterizations of KREF₄ and LiREF₄ nanocrystals

Cubic KLaF₄ and KCeF₄ wormlike nanowires. The X-ray diffraction (XRD) patterns shown in Fig. 1a reveal that cubic KLaF₄ and KCeF₄ were formed. The peaks are matched with the cubic fluorite type crystal structure (CaF₂ type, space group: *Fm*-3*m*). The calculated lattice constants are as follows: a = 5.928 Å for KLaF₄ (JCPDS: 75–0248) and a = 5.901 Å for KCeF₄ (JCPDS: 75–2021). The broadening of the diffraction peaks distinctly indicates the nanocrystalline nature of the samples. Meanwhile, the atomic ratios of metals in the nanocrystals were determined by energy-dispersive X-ray analysis (EDAX), confirming the formation of stoichiometric KREF₄ (Fig. S1, ESI[†]). The TEM images shown in Fig. 1b and Fig. S2a (see ESI[†]) demonstrate the as-obtained KLaF4 and KCeF4 nanocrystals take on the wormlike wire shape with a uniform diameter of 8.2 ± 0.5 nm and $7.8 \pm$ 0.4 nm, respectively. The inserted HRTEM images indicate that the as-obtained nanowires are single-crystalline, and the preferred 1D (one dimensional) growth direction is along the <111> direction. To our knowledge, such a 1D nanostructure has not been reported for cubic KLaF₄ and KCeF₄ before.^{7a,fg}

Cubic KREF₄ (**RE** = **Pr to Gd, Y**) **nanopolyhedra.** Fig. 2a shows that the peaks for each sample of KREF₄ (**RE** = **Pr to Gd**, **Y**) nanocrystals can be readily indexed to a pure cubic phase (CaF₂ type, space group: *Fm*-3*m*). From Fig. 2a, the calculated lattice constants are as follows: a = 5.891 Å for KPrF₄, a = 5.872 Å for KNdF₄, a = 5.851 Å for KSmF₄, a = 5.829 Å for KEuF₄, a = 5.808 Å for KGdF₄, and a = 5.625 Å for KYF₄. The broadening



Fig. 1 (a) XRD patterns of cubic $KLaF_4$ and $KCeF_4$ wormlike nanowires. (b) TEM and HRTEM (inset) images of $KLaF_4$ wormlike nanowires.

of the diffraction peaks reveals the nanocrystalline nature of the samples. The plots of unit cell volume per $KREF_4$ (RE = La to Gd, Y) molecule along the rare earth series shown in Fig. S3 (see ESI[†]) are in agreement with the lanthanide contraction. The panels b–d of Fig. 2 and Fig. S2 (see ESI[†]) show the TEM images of the as-obtained KREF₄ (RE = Pr to Gd, Y) nanocrystals.



Fig. 2 (a) XRD patterns of as-obtained cubic $KREF_4$ nanopolyhedra. TEM and HRTEM (inset) images of (b) $KPrF_4$, (c) $KEuF_4$, and (d) KYF_4 nanopolyhedra.

The nanocrystals are of polyhedron shape, and have a nearmonodisperse size of 18.2 ± 3.6 nm for KPrF₄, 16.4 ± 4.2 nm for KNdF₄, 18.9 \pm 3.8 nm for KSmF₄, 19.5 \pm 4.1 nm for KEuF₄, 21.2 \pm 6.1nm for KGdF₄, except for KYF₄ in a size of 13.2–25.9 nm. The HRTEM images insets in Fig. 2b–d and Fig. S2b–d (see ESI†) show that all the KREF₄ nanocrystals are of single-crystalline nature, and are mainly enclosed by the (111) and (200) planes.

Tetragonal LiREF₄ (RE = Tb to Lu, Y) nanocrystals. The diffraction peaks shown in Fig. 3a reveal the formation of tetragonal LiREF₄ (RE = Tb to Lu, Y) (scheelite structure, space group: I41/a). From Fig. 3a, the calculated lattice constants are as follows: a = b = 5.180 Å, and c = 10.870 Å for LiTbF₄ (JCPDS: 27–1262), a = b = 5.170 Å, and c = 10.801 Å for LiDvF₄ (JCPDS: 27–1233), a = b = 5.150 Å, and c = 10.751 Å for LiHoF₄ (JCPDS: 27–1243), a = b = 5.151 Å, and c = 10.672 Å for LiErF₄ (JCPDS: 27–1235), a = b = 5.131 Å, and c = 10.602 Å for LiTmF₄ (JCPDS: 27–1265), a = b = 5.128 Å, and c = 10.581 Å for LiYbF₄ (JCPDS: 23–0371), a = b = 5.119 Å, and c = 10.541 Å for LiLuF₄ (JCPDS: 27–1251), and a = b = 5.171 Å, and c = 10.741 Å for LiYF₄ (JCPDS: 81-1940). As expected from the lanthanide contraction, the tetragonal lattice volume has a decreasing tendency from LiTbF₄ to LiLuF₄ (Fig. S3, ESI[†]). TEM characterization has told us that all the as-obtained tetragonal $LiREF_4$ (RE = Tb to Lu, Y) nanocrystals display a rhombic plate-like shape. The panels b-d of Fig. 3 and Fig. S4 (see ESI[†]) depict the rhombic nanoplates of LiREF₄ (RE = Tb to Lu, Y), whose top surfaces are in the size of (27.1 \pm 2.4) nm × (25.8 \pm 4.3) nm for LiTbF₄, (55.1 \pm 3.1) nm × (49.9 ± 3.7) nm for LiDyF₄, (53.1 ± 3.4) nm × (49.8 ± 2.3) nm for LiHoF₄, (51.1 ± 2.3) nm × (50.9 ± 3.0) nm for LiErF₄, $(56.1 \pm 2.3) \text{ nm} \times (54.9 \pm 3.0) \text{ nm}$ for LiTmF₄, $(40.3 \pm 5.9) \text{ nm} \times$ (36.9 ± 4.3) nm for LiYbF₄, (91.5 ± 2.3) nm × (89.3 ± 3.2) nm for LiLuF₄ and (29.2 \pm 3.9) nm × (23.2 \pm 3.0) nm for LiYF₄. From the HRTEM images inserted in Fig. 3b-d and Fig. S4 (see ESI[†]), the (101) and (100) facets are identified on the top surface



Fig. 3 (a) XRD patterns of as-obtained tetragonal LiREF₄ nanoplates. TEM and HRTEM (inset) images of (b) LiTbF₄, (c) LiErF₄, and (d) LiYF₄ nanoplates.

of the nanoplates. From Fig. 3b–d and Fig. S4 (see ESI[†]), it is also noted that most of the LiREF₄ nanocrystals are separated, and exhibit a partially 2D (two dimensional)-ordered arrangement, indicative of the presence of capping ligands on the surfaces of nanocrystals.^{3k,I6d}

The surfactant bound on the nanocrystals surfaces was confirmed by FTIR spectroscopy, the FTIR spectrum of the assynthesized LiYF₄ nanocrystals is shown in Fig. S5 (see ESI†), the presence of strong acyclic C–H stretching at 2931 cm⁻¹ and weak carbonyl peaks at 1712 cm⁻¹ indicated the existence of a large amount of free oleic acid in solution, the broad peaks at 1449 and 1645cm⁻¹ could be assigned to a carboxylate (COO⁻) stretch, implying a chemical bonding of OA molecules on the nanocrystal surfaces.^{9g}

Synthesis of KREF₄ and LiREF₄ nanocrystals

Normally, KREF₄ has two polymorphs at room temperature and ambient pressure: orthorhombic and hexagonal, except that KLaF₄ and KCeF₄ possess a cubic phase. Light and middle $KREF_4$ (RE = Ce to Gd) appear in orthorhombic form, whereas, the heavy one (RE = Tb to Lu, Y) exists in only hexagonal form.^{7a,bd,h} On the other hand, LiREF₄ presents only one tetragonal phase, which is stable in bulk at room temperature.7c,e In addition for most of the $AREF_4$ (A = alkali metal), a hightemperature modification exists, which can be seen as the cubic CaF₂ type structure with statistical distribution of the cations A⁺ and RE³⁺ on the Ca²⁺ sites.^{7d,fg} In our work, however, all the asprepared nanosized KREF₄ from La to Gd including Y only take on a cubic structure, while those from Tb to Lu prefer to form KF and REF₃ instead of producing KREF₄. The stoichiometric LiREF₄ nanocrystals from Dy to Lu including Y only display the tetragonal phase, and LiF and REOF are formed in terms of lighter LiREF₄ ones.

In this work, for a certain compound, the controlled synthesis of monodisperse $KREF_4$ and $LiREF_4$ nanocrystals have been carefully conducted. Experimentally, we found that the crystal phase purity, shape and size of the as-prepared $KREF_4$ and $LiREF_4$ nanocrystals are mainly affected by conditions, such as solvent composition, reaction temperature and time (Table S1, ESI†), the optimal synthetic parameters are screened so as to achieve the appropriate balance between the nucleation and growth stages of the nanocrystals to obtain high-quality products.

Solvent composition effects. When the ratios of precursor concentration K(CF₃COO) or Li(CF₃COO)/RE(CF₃COO)₃, reaction temperature and time were fixed, the solvent composition was found to greatly affect the growth of $KREF_4$ (RE = La to Gd, Y) and LiREF₄ (RE = Tb to Lu, Y) nanocrystals. It seems that the use of a mixed solvent of OA/OM/ODE is essential for the preparation of near-monodisperse KREF4 nanocrystals, while OA/ODE mixture is crucial for phase-pure and monodisperse LiREF₄ ones. For example, for the synthesis of KLaF₄ wormlike nanowires, using 1 mmol K(CF₃COO) and 1 mmol La(CF₃COO)₃ as the precursors, the reaction under OA/ODE = 1:1 at 280 °C for 60 min yielded dispersed but severely-agglomerated nanocrystals (Fig. 4a), implying that the growth of the KLaF₄ nanocrystals became drastic with the addition of more OA, while under OA/OM/ODE = 1:4:5, the dispersible but ill-shaped nanocrystals with poor crystallinity were formed (Fig. 4b). Therefore, near-



Fig. 4 TEM images of $KLaF_4$ nanocrystals synthesized in (a) OA/ODE = 1:1 and (b) OA/OM/ODE = 1:4:5 for 60 min at 280 °C. TEM images of KYF_4 nanocrystals synthesized in (c) OA/ODE = 1:1 and (d) OA/OM/ODE = 1:4:5 for 30 min at 300 °C.

monodisperse $KLaF_4$ wormlike nanowires were obtained at an optimized OA/OM/ODE ratio of 1:1:2 (Fig. 1b), due to a wellmaintained balance between nucleation and growth stages during synthesis under these conditions. The above case was also similar to the synthesis of other $KREF_4$ nanocrystals, such as KYF_4 nanocrystals (Fig. 4c,d).

Different from the KREF₄ (RE = La to Gd, Y) nanocrystals, as for LiREF₄ (RE = Tb to Lu, Y), the presence of a mixed solvent of OA/ODE is a prerequisite to achieve phase-pure and monodisperse LiREF₄ nanocrystals. The presence of OM ligands in the mixed solvent might significantly hinder the growth of LiREF₄ nanocrystals, by producing LiF impurity in the nanocrystal growth. Here, we take LiLuF₄ as an example, using 1 mmol Li(CF₃COO) and 1 mmol Lu(CF₃COO)₃ as the precursors, the reaction under OA/OM/ODE = 4:1:5 at 280 °C for 60 min, produced non-dispersed LiF (space group: *Fm*-3*m*) impurities (Fig. S6, ESI[†]). The synthesis of the other monodisperse LiREF₄ nanocrystals was found to resemble that of LiLuF₄ nanocrystals in OA/ODE (1:1) solvent, such as LiYF₄ nanocrystals (Table S1 and Fig. S6, ESI[†]).

Reaction temperature and time effects. Except for the solvent composition, we found that both the reaction temperature and time also remarkably affected the shapes of the products. For example, under conditions of 1 mmol K(CF₃COO) and 1 mmol La(CF₃COO)₃, OA/OM/ODE = 1:1:2 and a reaction time of 60 min, as reaction temperature was decreased from 280 to 250 °C, hardly any solid matter appeared after the precipitation treatment, indicating deficient energy for the decomposition of the precursor to form KLaF₄. As the reaction temperature was increased to 290 °C, some wormlike nanowires coexisted with a large amount of nanocubes (Fig. 5a). As the reaction temperature was further increased to 300 °C, the as-obtained dispersible KLaF₄ wormlike



Fig. 5 TEM images of $KLaF_4$ nanocrystals synthesized from co-thermolysis of 1 mmol K(CF₃COO) and 1 mmol La(CF₃COO)₃ in OA/OM/ODE (1:1:2) for 60 min at different reaction temperatures: (a) 290 °C, (b) 300 °C and (c) 320 °C.

nanowires vanished to form uniform nanocubes ((9.4 \pm 0.9) nm) (Fig. 5b). Further increase in the reaction temperature to 320 °C resulted in monodisperse KLaF₄ nanopolyhedra ((9.5 ± 0.5) nm) (Fig. 5c). A similar observation was achieved in the case of KCeF₄ wormlike nanowires. Another example was the synthesis of KYF₄ nanocrystals, with 1 mmol K(CF₃COO) and 1 mmol $Y(CF_3COO)_3$ as precursors, under OA/OM/ODE = 1:1:2 at 300 °C for 30 min, poorly crystalline KYF₄ nanocrystals were harvested (Fig. S7a, ESI[†]). As the reaction time was increased to 60 min, highly-crystalline near-monodisperse KYF₄ nanocrystals were obtained (Fig. 2d), suggesting a long reaction time enhanced the crystallinity of the nanocrystals. However, further elevating the temperature to 330 °C resulted in nonuniform aggregated nanocrystals (Fig. S7b, ESI⁺). The influence of the reaction temperature on the other KREF4 nanocrystals was found to resemble that of KYF₄.

As for LiREF₄, the influences of reaction temperature on the composition and shape evolution of as-synthesized nanocrystals were observed. Here, taking LiErF₄ as an example, at reaction temperatures ranging from 280 °C to 300 °C, the co-thermolysis of 1 mmol Li(CF₃COO) and 1 mmol Er(CF₃COO)₃ under OA/ODE = 1:1 for 60 min produced monodisperse ErOF nanocrystals (23.2 \pm 0.4) with few LiF impurities (Fig. S8a,b, ESI^{\dagger}), indicating the relative low temperature (< 300 °C) induced the formation of LiF and monodisperse REOF nanocrystals, instead of stoichiometric LiREF4 ones. As the reaction temperature was increased to 320 °C, the monodisperse LiErF₄ nanoplates were harvested (Fig. 3c), further elevation of the reaction temperature to 330 °C resulted in highly aggregated LiErF₄ nanocrystals (Fig. S8c, ESI[†]). For another example of LiLuF₄, at 280 °C, the co-thermolysis of 1 mmol Li(CF₃COO) and 1 mmol Lu(CF₃COO)₃ under OA/ODE = 1:1 for 60 min produced monodisperse LiLuF4 nanoplates (Fig. S4e, ESI[†]). As

the reaction temperature was increased to 300 °C, the relatively near-monodisperse LiLuF₄ nanoplates with a much broader size distribution (41.6 ± 11.8) nm × (39.8 ± 9.9) nm were formed (Fig. S9a, ESI†). When the reaction temperature was further raised to 320 °C, polygonal aggregated LiLuF₄ nanocrystals in the size range of 16.1–28.2 nm instead of nanoplates were formed (Fig. S9b, ESI†).

Under a fixed reaction temperature of 280 °C, as the reaction time was shortened from 60 min to 30 min, the co-thermolysis of 1 mmol K(CF₃COO) and La(CF₃COO)₃ in OA/OM/ODE (1:1:2) resulted in poorly separated wormlike nanowires (Fig. 6a). When the reaction went on to 120 min, some KLaF₄ wormlike nanowires coexisted with nanocubes (Fig. 6b). The same tendency was observed for the KCeF4 wormlike nanowires. As for KYF_4 , when the reaction time was 15 min, polydisperse KYF_4 nanocrystals (38.5 ± 5.1) nm with relatively low yields were formed (Fig. S10a, ESI[†]). When the reaction time was prolonged to 45 min, the well-crystallized but poorly separated nanocrystals in improved yields were harvested (Fig. S10b, ESI[†]). However, as the reaction time reached 60 min, aggregated KYF₄ nanoparticles were formed (Fig. S10c, ESI[†]). For the LiREF₄ nanocrystals, such as the synthesis of LiErF₄, under a fixed reaction temperature of 330 °C, as the reaction time was shortened from 60 min to 30 min and 15 min, the LiErF₄ products appeared as a mixture of nanoplates and nanowires (Fig. S11a,b, ESI⁺). When the reaction went on to 120 min, the LiErF₄ aggregated polydisperse nanoplates were formed (Fig. S11c, ESI[†]).



Fig. 6 TEM images of KLaF₄ nanocrystals obtained from the thermolysis of 1 mmol K(CF₃COO) and 1 mmol La(CF₃COO)₃ in OA/OM/ODE (1:1:2) at 280 °C for different reaction times: (a) 30 min, (b) 120 min.

To sum up, our pure-phase monodisperse $KREF_4$ (RE = La to Gd, Y) nanocrystals could be obtained in mixed solvents of OA/OM/ODE (1:1:2), and LiREF₄ (RE = Tb to Lu, Y) nanocrystals could be obtained at a high temperature in OA/ODE (1:1) with a relatively long reaction time.

Formation mechansim of KREF4 and LiREF4 nanocrystals

Just like the case of co-thermolysis of Na(CF₃COO) and RE(CF₃COO)₃ in mixed solvents of OA/OM/ODE,⁶⁴ as the reaction solutions containing K(CF₃COO) or Li(CF₃COO) and RE(CF₃COO)₃ were rapidly heated to their thermolysis temperatures under an Ar atmosphere, tiny gas bubbles formed instantly from the reaction system, indicating a decomposition of the precursors and a simultaneous formation of KREF₄ or LiREF₄ nuclei (Scheme 1). As indicated by the experimental results, only LiREF₄ nuclei were generated for the rare earths from Tb to Lu



Scheme 1 Schematic illustration for a controlled growth mechanism of near-monodisperse $KREF_4$ (RE = La to Gd, Y) and $LiREF_4$ (RE = Tb to Lu, Y) nanocrystals with diverse shapes.

and Y, while for La to Gd, the LiF and REOF nuclei coexisted. This result suggests that the tendency for the formation of LiREF₄ nuclei was depressed for the light rare earths. On the contrary for the synthesis of KREF₄ nanocrystals, only KREF₄ nuclei were generated for the rare earths from La to Gd and Y, while KF and REF₃ nuclei coexisted for Tb to Lu, indicating the tendency for the formation of KREF₄ nuclei was easier for the light rare earths, but more difficult for the heavy rare earths. Our research results on the NaREF₄ have demonstrated that the NaREF₄ nuclei were generated for the rare earths from Pr to Lu and Y, while NaF and REF3 nuclei coexisted for La and Ce.6d,gh These results suggest that the lighter the alkali metal and rare earth, the easier AF(A =alkali metal) and REF₃ or REOF nuclei formed, owing to the fact that the basicity of the alkali metal oxide gradually increases along the alkali metal series, while the basicity of the rare earth oxide gradually decreases along the rare earth series.

As is well-known, the crystalline phase of the nuclei, the selective adsorption of the surfactant onto specific crystal planes, and the balance between the kinetic and the thermodynamic growth regimes are the three important factors affecting the shape of nanocrystals.^{1e,9} For the crystalline seeds with an isotropic unit cell structure (*e.g.*, cubic), they often experience an isotropic growth, which results in 0D (zero dimensional) nanostructures. In our synthesis, KREF₄ (RE = La to Gd, Y) have a cubic structure (Fig. 7a); therefore, as expected, we obtained 0D-growth



Fig. 7 Crystal structures of (a) cubic $KREF_4$ and (b) tetragonal LiREF_4 built by CERIUS2 software (ref.: http://www.accelrys.com/cerius2).

shape (nanopolyhedra) of nanocrystals at high temperatures of 300 °C (Scheme 1). The production of wire-like KLaF₄ and KCeF₄ nanocrystals at reduced temperatures (260–280 °C) may be caused by the oriented aggregation of small particles.^{9h} The wire-like shape was considered to be kinetically stable, since it was observed that the metastable wormlike nanowires were transformed to the thermodynamically stable nanocubes and further nanopolyhedra with increasing reaction temperature and reaction time. As for LiREF₄ (RE = Tb to Lu, Y) nanocrystals, the as-observed 2D growth modes for the rhombic nanoplates were probably originated from the crystal structure effect of the anistropic tetrgonal phase (c/a = 2.1) (Fig. 7b).^{1e,7t,9}

Luminescence properties of lanthanide doped KREF₄ and LiREF₄ nanocrystals

In order to study the luminescence properties of lanthanide doped KREF₄ and LiREF₄ nanocrystals, monodisperse and singlecrystalline (27.2 \pm 1.8) nm KGdF₄:5%Eu and (14.9 \pm 1.4) nm LiYF₄:20%Yb,2%Er, nanocrystals were also prepared using the current method (Fig. 8a,b).



Fig. 8 TEM images of lanthanide doped KREF₄ and LiREF₄ nanocrystals: (a) KGdF₄:5%Eu nanopolyhedra (top right is the HRTEM image, bottom right is the eye-visible luminescence photography of its dispersion) and (b) LiYF₄:20%Yb,2%Er nanopolyhedra (top right is the HRTEM image, bottom right inset is the eye-visible upconversion luminescence photography of its dispersion). The luminescent nanocrystal dispersions are excited by the 254 nm hand-held UV lamp at room temperature.

Fig. 9a describes the emission spectrum of KGdF₄:Eu³⁺ nanocrystals. The emission peaks at 589, 613, 649, and 696 nm can be assigned to the typical ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ emissions (J = 0, 1,2, 3, 4) of the Eu³⁺ ions, respectively. The peak located at 589 nm (corresponding to ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ magnetic dipole transition) is weaker than the peak located at 613 nm (corresponding to ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ electric dipole transition), suggesting the presence of a strong surface effect on the red emission of those oleate capped nanocrystals, as compared with the bulk counterpart.^{3k,1,11} The photoluminescence quantum yields (QYs) of KGdF₄:5%Eu nanopolyhedra were determined to be 18%. Fig. 9b exhibits the luminescence decay curves of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ emission at 613 nm for the KGdF₄:5%Eu nanocrystals. These decay curves can be fitted well into a single exponential function: $I = I_0 \exp(-t/\tau)$ (τ is the lifetime of Eu³⁺). The lifetime of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ emission of Eu³⁺ ions (613 nm) is 1.71 ms for the KGdF₄:5%Eu nanopolyhedra, which is close to that (1.72 ms) of 6.3 nm GdOF:5%Eu.^{3k}

Fig. 9c shows the UC fluorescence spectrum of asobtained LiYF₄:20%Yb,2%Er nanopolyhedra dispersed in





Fig. 9 (a) Excitation and emission spectra of KGdF₄:5%Eu nanopolyhedra dispersed in cyclohexane (2 wt%). (b) Luminescence decay curve of the 613 nm emission of Eu³⁺ ions in KGdF₄:5%Eu nanopolyhedra ($\lambda_{ex} = 275$ nm). (c) Upconversion spectra of LiYF₄:20%Yb,2%Er nanocrystal dispersion in cyclohexane (2 wt%). (d) Power density dependence of the upconversion emission intensity for LiYF₄:20%Yb,2%Er nanocrystals under $\lambda_{ex} = 980$ nm.

cyclohexane under 980 nm excitation. The green emissions at 521, 541 and 550 nm are attributable to the transitions from ${}^{2}H_{11/2}$ to ${}^{4}I_{15/2}$ and from ${}^{4}S_{3/2}$ to ${}^{4}I_{15/2}$ of Er³⁺ ions, respectively, and the red emissions at 651 and 667 nm come from the ${}^{4}F_{9/2}$ to ${}^{4}I_{15/2}$ transition of Er³⁺ ions. To determine the number of photons involved in the UC process of the Yb³⁺, Er³⁺ doped LiYF₄ nanocrystals, the relationships between laser diode power density and emission intensities for the green and red emission are depicted in Fig. 9d. The slopes of different curves are found to be approximately 2, suggesting the normal two-photon emission processes are involved in the UC mechanism of the present nanocrystals.¹⁰ Under the 980 nm laser excitation, the activated Yb3+ ion absorbs one photon and transfers it to the Er^{3+} ion, the Er^{3+} ion receives the energy and its ground state ${}^{4}I_{15/2}$ electron is excited to the ${}^{4}I_{11/2}$ level, and the Yb³⁺ promotes Er^{3+} to ${}^{4}\mathrm{F}_{7/2}$ state *via* nonradiative energy transfer process. The excited electron decays nonradiatively to ${}^{2}H_{11/2}$, ${}^{4}S_{3/2}$, ${}^{4}F_{9/2}$ levels, and precedently radiative relaxation to the ground state results in the emission of 525 nm, 541 and 550 nm, 651 and 667 nm, respectively. The as-obtained KGdF₄:Eu³⁺ and LiYF₄:Yb³⁺, Er³⁺ nanocrystals display intense red emission and green emission under UV excitation and 980 nm laser excitation, respectively. (The digital camera images of luminescence from KGdF₄:Eu³⁺ and LiYF₄:Yb³⁺, Er³⁺ nanocrystals are shown in the insets of Fig. 8a and Fig. 8b, respectively).

Conclusions

Near-monodisperse KREF4 and LiREF4 colloidal nanocrystals with various shapes (cubic KLaF4 and KCeF4 wormlike nanowires, nanocubes and nanopolyhedra; cubic $KREF_4$ (RE = Pr to Gd, Y) nanopolyhedra; $LiREF_4$ (RE = Tb to Lu, Y) rhombic nanoplates) have been synthesized via co-thermolysis of Li(CF₃COO) or K(CF₃COO) and RE(CF₃COO)₃ in hot oleic acid/oleylamine/1-octadecene solutions. The crystal phase purity, shape and size of the as-prepared nanocrystals were concluded to be greatly affected by the synthetic parameters such as solvent composition, reaction temperature and time. The controlledgrowth of KREF4 and LiREF4 nanocrystals has suggested that the lighter the alkali metal and rare earth, the easier AF (A = K, Li) and REF₃ or REOF nuclei formed, owing to the fact that the basicity of the alkali metal oxide gradually increases along the alkali metal series, while the basicity of the rare earth oxide gradually decreases along the rare earth series. Contrarily, AREF4 nuclei were more easily formed. With the developed synthetic strategy, the monodisperse and single-crystalline KGdF₄:5%Eu and LiYF₄:20%Yb,2%Er nanocrystals have been prepared. The KGdF₄:5%Eu nanocrystals display intense visible red emission under UV excitation at room temperature. Under a 980 nm near-IR laser excitation, the LiYF4:20%Yb,2%Er nanocrystals can emit UC green light through a two-photon process. We expect the asprepared AREF₄ nanocrystals to be useful in optical nanodevices and bioprobes in the future.

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