

Controlled Hydrothermal Growth and Up-Conversion Emission of NaLnF_4 ($\text{Ln} = \text{Y}, \text{Dy–Yb}$)Jianle Zhuang,[†] Lifang Liang,[†] Herman H. Y. Sung,[‡] Xianfeng Yang,[†] Mingmei Wu,^{*,†} Ian D. Williams,[‡] Shouhua Feng,[§] and Qiang Su[†]

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The controlled hydrothermal preparation of NaYF_4 as both cubic and hexagonal phase types with specific associated morphologies, nanospheres and microtubes, respectively, has been achieved in the absence of organic solvents. The hexagonal NaYF_4 compound can be prepared in novel microtubular form and directly co-doped with $\text{Yb}^{3+}/\text{Er}^{3+}$ ions. When excited by infrared light of 980 nm, these hexagonal NaYF_4 microtubes display strong green up-conversion emission, which was much more intense than that of cubic NaYF_4 or hexagonal NaYF_4 nanoparticles. Other related hexagonal-prismatic microtubes of NaLnF_4 ($\text{Ln} = \text{Dy–Yb}$) were also synthesized. A growth mechanism for the microtubes is proposed. In general, the diameter of the hexagonal NaLnF_4 microtubes is strongly dependent on the Ln^{3+} size and increases as the rare-earth ionic radius decreases.

Introduction

Rare-earth ion-doped fluorides based on ALnF_4 ($\text{A} =$ alkaline metal, $\text{Ln} =$ rare-earth element) have been investigated for several decades due to their electrical and optical properties and wide applications as solid electrolytes, solid-state lasers, and up- or down-conversion hosts.^{1–13} Among them, most of the attention has been focused on NaYF_4 because it is a particularly important host material for green and blue up-conversion (UC) phosphors. It is well-established

that hexagonal NaYF_4 is the most efficient UC host material known to date^{4–7} and has great potential applications in solid-state lasers, solar cells, and biolabels.^{3–13} Traditionally, NaYF_4 was prepared via solid-state reaction from stoichiometric mixtures of highly purified NaF and YF_3 with other

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relevant rare-earth fluoride dopants. The reaction was carried out in a sealed tube and/or under argon or even fluoride atmospheres to ensure complete fluorination.¹⁴ Recently, several soft chemistry approaches have been applied to the synthesis of both cubic and hexagonal NaYF₄ with different morphologies with varying degrees of success.^{5,7–13} An early example was the preparation by Haase et al. of colloids of cubic lanthanide-doped NaYF₄ nanocrystals using methanol as the solvent.⁵ Solvothermal conditions were employed to prepare nanorods and nanoparticles of hexagonal NaYF₄.⁷ Hydrothermal synthesis was also carried out by Zeng et al.,^{7c} but it was stated that the size and morphology were not easily controlled with poorly shaped resultant microcrystals. Although hydrothermal syntheses of NaYF₄ have been reported,^{7c,11} detailed and systematic investigations on the controlled growth and related UC emissions have not been carried out. Wang reported the hydrothermal growth of hexagonal NaYF₄ as hard microprisms, but their UC emission has not been reported.^{11a} Well-defined and high-quality hydrothermally synthesized hexagonal NaYF₄ crystals and their comparably enhanced UC emissions need to be explored. The growth of high-quality hexagonal sodium rare-earth fluoride nanocrystals has been achieved by using the thermal decomposition of lanthanide trifluoroacetate precursors over 300 °C in a mixed solvent of oleic acid/oleylamine/1-octadecene; however, this approach has the drawback of the production of toxic byproducts.^{9,10}

The discovery of single-wall carbon nanotubes has stimulated considerable interest in one-dimensional (1-D) structures with hollow interiors due to their unusual mechanical properties, porosity, electronic transfer, optical emission, and wide potential applications in mechanical engineering, chemical catalysis, gas storage and separation, and optoelectronic devices.¹⁵ To date, many materials with hollow tubular structures have been synthesized, with elemental,¹⁶

oxide,¹⁷ nitride,¹⁸ chalcogenide,¹⁹ chloride,²⁰ silicate,²¹ and even organic examples.²² However, there are only limited reports discussing hollow fluoride materials.^{23,24} Previously, we briefly reported the hydrothermal synthesis of rare-earth metal-based NaHoF₄ microtubes and NaSmF₄ nanotubes.²⁴ The comparative aqueous solution growth behavior of the sodium rare-earth tetrafluoride group has yet to be investigated in depth. High-quality and well-defined tubular NaYF₄ crystals with strong UC emission are of great importance in materials science and engineering. Herein, we describe the controlled growth of either cubic or hexagonal NaYF₄ crystallites using mild hydrothermal conditions without any organic cosolvent and have extended our previous work on the syntheses for the related hexagonal NaLnF₄ (Ln = Sm–Yb, Y) crystallites. A new tubular microstructure has been discovered for hexagonal NaYF₄. The optical properties of its Yb³⁺/Er³⁺-co-doped phosphor have been investigated. Syntheses for the related hexagonal NaLnF₄ microtubes are also described for the heavy rare earths (Ln = Dy–Yb), in which the radius of Ln³⁺ is generally smaller than that of Y³⁺.

Experimental Section

Hydrothermal Synthesis. Aqueous solutions of sodium fluoride (NaF, AR grade) and ammonium hydrogen fluoride (NH₄HF₂, AR grade) with a molar ratio of 1.0/2.0 were mixed in a Teflon beaker to form a clear solution A. Another mixed solution B of Ln(NO₃)₃ (Ln = Y, La, Pr, Nd, Sm–Yb) and ethylenediamine tetraacetic acid (EDTA) was prepared in a Teflon cup. A milky suspension C was first formed when the clear solution A was added into solution B under stirring. The molar ratio of the initial reactant mixture for hydrothermal synthesis is 6.0 NH₄HF₂/3.0 NaF/1.0 Ln(NO₃)₃/0.2 EDTA/700 H₂O. The initial pH value was around 3.0. Suspension C was 70% filled in a Teflon-lined stainless steel autoclave (23 mL, Parr type) and sealed for hydrothermal crystallization at different temperatures and time periods. After the autoclave was cooled, the final powder products were washed with distilled water and dried in a desiccator at ambient temperature. Hexagonal NaYF₄ nanoparticles were prepared using ethanol as the solvent with the same mole ratio of initial reactants except with the absence of EDTA.

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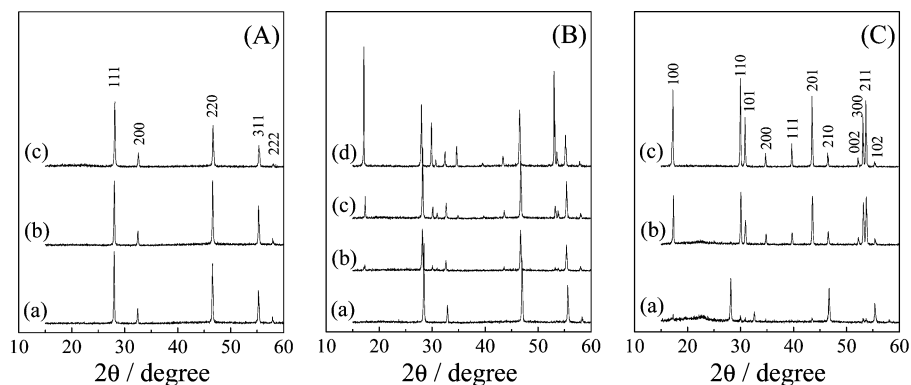


Figure 1. PXRD patterns of NaYF₄ synthesized (A) at 60 °C for (a) 3.0 h, (b) 24 h, and (c) 48 h; (B) at 140 °C for (a) 18 h, (b) 24 h, (c) 36 h, and (d) 48 h; (C) at 220 °C for (a) 1.0 h, (b) 3.0 h, and (c) 48 h.

Characterization. The products were characterized by using powder X-ray diffraction (PXRD) with a Philips Model PW1830 diffractometer using Cu K α radiation ($\lambda = 0.1541$ nm) and a graphite monochromator operating at 40 kV and 30 mA with a 2θ scanning rate of $0.05^\circ \text{ s}^{-1}$. The sizes and shapes of particles were obtained by using a JEOL JSM-6330F field emission gun scanning electron microscope. Dried samples for scanning electron microscopy (SEM) were placed on glass-slide surfaces and then sputter-coated with platinum. Transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) analyses were performed on a JEOL 2010 high-resolution transmission electron microscope equipped with an Oxford Instrument EDS system.

Infrared-to-visible UC spectra of NaYF₄:Yb³⁺/Er³⁺ were recorded by exciting the sample with an unfocused beam from a 980 nm diode laser. The laser power for excitation was fixed at 45 mW for each sample for comparison of their emission intensities. The visible emissions were collected and detected by a fluorescence spectrophotometer F-4500 (Hitachi) equipped with a mechanically ruled concave diffraction grating and a R3788 photomultiplier tube.

Results and Discussion

Phase-Selective Hydrothermal Preparation of NaYF₄

Both cubic and hexagonal forms of NaYF₄ can be readily formed phase-pure under appropriate conditions. The PXRD patterns of NaYF₄ products synthesized at 60, 140, and 220 °C for periods between 1 and 48 h are shown in Figure 1. Subhydrothermally at 60 °C, cubic NaYF₄ with fluorite-related structure (JCPDF No. 77-2042) remains as the phase-pure product for reactions even up to 48 h (Figure 1A). Hydrothermal reaction at 140 °C for shorter time periods also gives cubic NaYF₄, but after 48 h a mixture of cubic and hexagonal phases is observed (Figure 1B). At 220 °C, the cubic form is found after 1 h but is replaced by phase-pure hexagonal NaYF₄ after only 3 h of reaction time. The above results indicate that there is a “phase transformation” from cubic to hexagonal NaYF₄ under hydrothermal conditions and that the cubic phase is a kinetic product. This is consistent with previous data that indicates that the cubic phase is thermally meta-stable up to 691 °C with respect to the hexagonal one.^{14a,25} Hydrothermal synthesis with sufficiently high temperature or aging time is thus a simple, fast, and economic way to synthesize the phase-pure hexagonal form of NaYF₄.

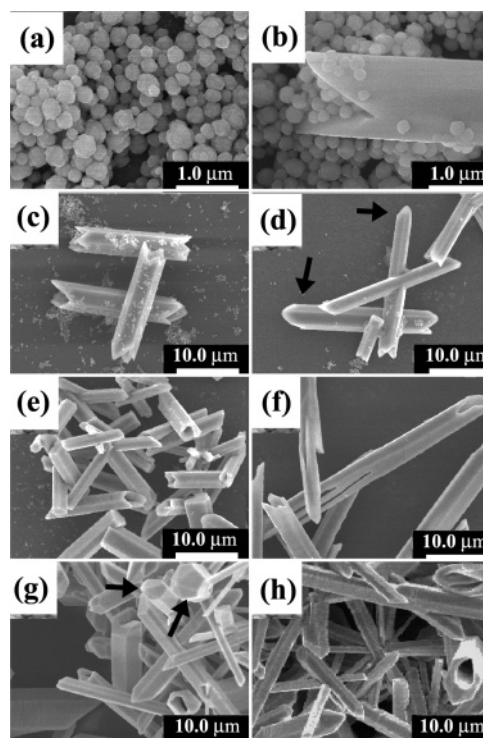


Figure 2. SEM images of NaYF₄ hydrothermally synthesized in the presence of EDTA at 140 °C for (a) 15 h, (b) 24 h, (c) 48 h, (d) 72 h, at 220 °C for (e) 48 h, and (f) in the absence of EDTA at 220 °C for 48 h; and SEM images of (g) NaErF₄ and (h) NaYbF₄ hydrothermally synthesized in the presence of EDTA at 220 °C for 48 h.

Hexagonal-Prismatic Microtubes and Morphological Changes of NaYF₄. Morphological characterization of the hydrothermally prepared NaYF₄ products was carried out by SEM, and selected results are shown in Figure 2. The cubic NaYF₄ form is found as nanospheres with an average size of around 200 nm, and this morphology persists no matter what the aging conditions. An example is shown in Figure 2a. The hexagonal NaYF₄ is found as hollow hexagonal-prismatic microtubes both at 140 and 220 °C (Figure 2b–f). The outer diameters of these tubes on average are around 3.0 μm , and their lengths are in the range of 10–30 μm .

The use of the EDTA additive can lead these microtubes to have better defined hexagonal tubular shape (Figure 2c–e), due to its complexing to rare-earth ions and, consequently, its modulation of the crystal growth. In the absence of EDTA, each tube of these complex fluorides became less defined

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in shape and some crevices appeared along the growth directions as indicated in Figure 2f.

The crystalline structures of both nanospheres and microtubes were further characterized by electron microscopy (Supporting Information, Figure 1). The bright-field TEM images show that the cubic NaYF₄ product consisted of granular particles (Supporting Information, Figure 1a,b). The high-resolution TEM (HRTEM) image with the lattice fringes of 0.19 nm corresponding to (220) lattice planes of cubic NaYF₄ (Supporting Information, Figure 1c) and the SAED patterns taken from different zone axes (Supporting Information, Figure 1d–f) indicate that these nanospheres are attributed to cubic NaYF₄. Whereas the HRTEM image with the lattice fringes of 0.51 nm (Supporting Information, Figure 1h) corresponding to (100) lattice planes of hexagonal NaYF₄ and the related SAED pattern (Supporting Information, Figure 1i) reveals the growth of the hexagonal NaYF₄ tube is along the *c* direction. Thus, it can be confirmed that the spherical crystals belong to cubic NaYF₄ and 1-D tubular microcrystals belong to hexagonal NaYF₄, even in a mixed phase (Supporting Information, Figure 1g,h). The diffraction results indicated that no mixed cubic–hexagonal crystalline zones were ever co-present. This implies that cubic NaYF₄ crystals with spherical shape are formed at the initial stage of the hydrothermal synthesis. Further hydrothermal aging then causes these spherical NaYF₄ crystals to dissolve and then reprecipitate separately as pure hexagonal microtubular NaYF₄.

Infrared-to-Visible UC of Hydrothermally Synthesized NaYF₄:Yb³⁺/Er³⁺ Microtubes. Besides the facile phase-pure preparation of both cubic and hexagonal NaYF₄ mentioned above, the hydrothermal method also allows the ready introduction of other rare-earth dopants to act as activators or sensitizers for luminescent applications. Thus, various co-additions of Yb³⁺ and Er³⁺ into both cubic and hexagonal NaYF₄ have been successfully accomplished, through keeping the whole molar ratio of Ln(NO₃)₃ at 1.00, where Ln = Y + Yb + Er.

The mechanism for frequency up-conversion (UC) of NaYF₄:Yb³⁺/Er³⁺ has been well established.^{4–7} The optimum wavelength of pumping light for UC is 980 nm, which matches the ²F_{7/2} → ²F_{5/2} transition of the Yb³⁺ ion. The excited state ²F_{5/2} of the Yb³⁺ ion may then transfer the energy to an Er³⁺ ion and populate the ⁴I_{11/2} level. Further energy transfer from Yb³⁺ from a second photon absorption can then further excite the Er³⁺ ion from its ⁴I_{11/2} level to ⁴F_{7/2}. Nonradiative decays from Er³⁺ ⁴F_{7/2} to the ²H_{11/2} and ⁴S_{3/2} levels are then believed to occur. Subsequent transitions from ²H_{11/2} and ⁴S_{3/2} to the Er³⁺ ground state ⁴I_{15/2} yield bright-green emissions at 545 and 525 nm, respectively, whereas the red emission around 660 nm is from the Er³⁺ electronic transition ⁴F_{9/2} → ⁴I_{15/2} (Figure 3).

Under the pumping of a 980 nm diode laser at 45 mW, Yb³⁺ and Er³⁺ co-doped hexagonal NaYF₄ exhibits considerably stronger emission than a similarly co-doped cubic NaYF₄ (Figure 3). The UC emission previously reported for the hexagonal phase is 5–10 times that of the corresponding cubic NaYF₄.^{4a} In our work we find a ca. 20 times increase

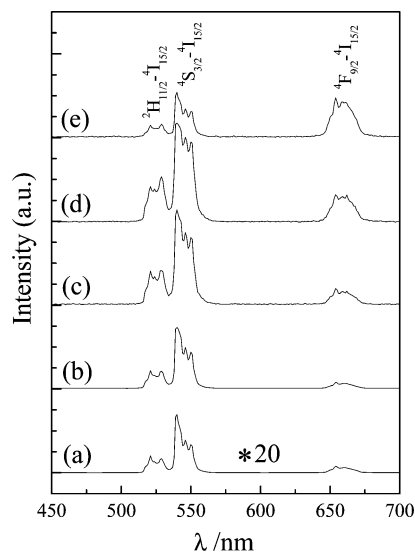


Figure 3. UC emission spectra of NaYF₄:Yb³⁺/Er³⁺ excited by a 980 nm laser: (a) cubic NaY_{0.94}Yb_{0.05}Er_{0.01}F₄, (b) hexagonal NaY_{0.94}Yb_{0.05}Er_{0.01}F₄, (c) hexagonal NaY_{0.79}Yb_{0.20}Er_{0.01}F₄, (d) hexagonal NaY_{0.78}Yb_{0.20}Er_{0.02}F₄, and (e) hexagonal NaY_{0.48}Yb_{0.50}Er_{0.02}F₄.

for the hexagonal form compared with the cubic form measured under conditions of identical laser power density. The variable increase of the UC efficiency of hexagonal as compared with the cubic phase found in various publications may result from the different growth conditions and crystal sizes.

The change of doping concentrations of an activator and/or a sensitizer can modulate the emission intensity of each color. At low concentrations of Er³⁺, we find that the green emission is dominant; however, the red emission becomes increasingly significant as concentrations of Er³⁺ and/or Yb³⁺ go up (Figure 3b–e). Much higher dopant concentrations result in much weaker green emission due to concentration quenching. The optimal composition for green emission from our hydrothermal-synthesized hexagonal-NaYF₄ host is NaY_{0.79–0.78}Yb_{0.20}Er_{0.01–0.02}F₄ (Figure 3). This result is qualitatively similar to those of some other reports.^{5,7c} Importantly, our luminescent results confirm that an efficient co-doping of Yb³⁺ and Er³⁺ into the NaYF₄ host can be carried out by using a facile hydrothermal route.

Recently, hexagonal NaYF₄ nanoparticles were fabricated by Zeng et al. using ethanol as the solvent.^{7c} We similarly prepared the hexagonal NaYF₄:Yb³⁺/Er³⁺ nanoparticles (Supporting Information, Figure 2) to compare their UC emission intensity to our hexagonal microtubes obtained from hydrothermal synthesis. The UC emission of these hexagonal NaYF₄ nanoparticles is shown in Figure 4 and is about 4 times weaker than that of similarly doped microtubes. The result is in contrast with the previous work,^{7c} which indicated the UC emission intensity of the nanoparticles is just a little weaker than that of those synthesized hydrothermally. The marked decrease of the intensity may be due to surface-quenching nanosize effect. Further studies into the differing luminescent properties of these nanoparticulate and microtubular fluorides are under investigation.

Interestingly, although the addition of EDTA in the hydrothermal reaction was found to lead to more regular

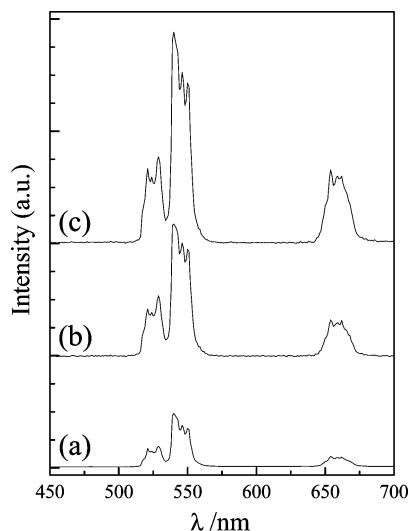


Figure 4. UC emission spectra of $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ excited by a 980 nm laser: (a) hexagonal nanoparticles synthesized using ethanol as the solvent, (b) hexagonal microtubes hydrothermally synthesized in the presence of EDTA, and (c) hexagonal microtubes hydrothermally synthesized in the absence of EDTA.

morphology of the hexagonal microtubes, the effect on UC efficiencies was a substantial decrease in UC emission (Figure 4). The grown crystals might adsorb some organic molecules and/or ions on the surface, and hence, their UC emission intensities are decreased due to faster nonradiative decay. We find that hexagonal NaYF_4 microtubes grown in the absence of EDTA display more intense UC emission than those grown in the presence of EDTA, indicating our synthetic route could make much more efficient hexagonal NaYF_4 -based UC crystals.

Related Sodium Rare-Earth Tetrafluorides. While hexagonal NaLnF_4 ($\text{Ln} = \text{La}–\text{Lu}, \text{Y}$) compounds have been prepared for all lanthanides by solid-state reactions,^{14a,25} with our hydrothermal method, hexagonal NaLnF_4 could not be prepared for the early lanthanide ions in the system of $\text{NaF}–\text{LnF}_3$ ($\text{Ln} = \text{La}–\text{Nd}$), with only hexagonal LnF_3 obtained instead (Figure 5a,b). Hexagonal NaLnF_4 has been synthesized hydrothermally in the present work with $\text{Ln} = \text{Sm}–\text{Yb}$ (Figures 5c–h and 6c,d). The failed hydrothermal synthesis of NaLnF_4 ($\text{Ln} = \text{La}–\text{Nd}$) may be due to the relative thermodynamic stability of the hexagonal LnF_3 ($\text{Ln} = \text{La}–\text{Nd}$), while LnF_3 ($\text{Ln} = \text{Sm}–\text{Yb}$) occurs in the orthorhombic form.²⁵ Some reports of the synthesis of early NaLnF_4 phases have appeared; Mai et al. reported that NaPrF_4 and NaNdF_4 nanocrystals can be prepared in organic solvent at much higher temperatures from toxic precursors.¹⁰ In addition, preparation of NaCeF_4 was previously claimed from “basic” organic solvent, but no detailed reactant receipts and synthesis procedures were described and we have been unsuccessful in duplicating these results.¹³

PXRD patterns of hexagonal NaLnF_4 ($\text{Ln} = \text{Sm}–\text{Yb}$) show almost identical features, indicating that these complex fluorides are isostructural. The general shift of diffraction peaks to high 2θ angle from NaSmF_4 to NaHoF_4 in Figure 5c–h and from NaErF_4 to NaYbF_4 in Figure 6c,d is due to the smaller lanthanide ionic radius as the series is traversed.

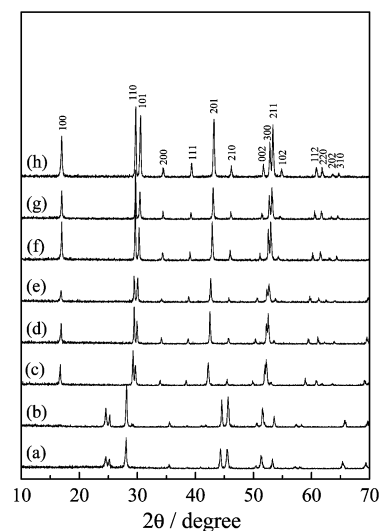


Figure 5. PXRD patterns of hydrothermal products in the system of $\text{NaF}–\text{LnF}_3$ ($\text{Ln} =$ (a) Pr, (b) Nd, (c) Sm, (d) Eu, (e) Gd, (f) Tb, (g) Dy, and (h) Ho) at 140 °C for 14 h.

An advantage of using middle lanthanides in the hydrothermal synthesis is that phase-pure hexagonal NaLnF_4 ($\text{Ln} = \text{Sm}–\text{Ho}$) can be prepared relatively easily under mild conditions (Figure 5c–h), whereas NaYF_4 requires more forcing conditions as described above (Figure 1). This trend is similar to the work by Zhang and Yan¹⁰ but contrasts that of Li.¹³ Phase-pure hexagonal NaYF_4 can be prepared at a higher temperature and/or for a longer time, such as at 220 °C for 3.0 h (Figure 1). However, phase-pure hexagonal NaLnF_4 of smaller lanthanides ($\text{Ln} = \text{Er}, \text{Tm}, \text{Yb}$) cannot be successfully synthesized with similar condition (Figure 6b). From these PXRD patterns in Figures 1, 5, and 6, it can be interpreted that there are common properties among NaHoF_4 , NaYF_4 , and NaErF_4 . Compared with the diffraction peaks of the cubic 111, the peaks of the hexagonal 110 tend to be weaker from NaErF_4 to NaYbF_4 in Figure 6b. This experimental evidence indicates that a higher temperature and/or a longer reaction time is required to prepare phase-pure hexagonal NaLnF_4 with a smaller Ln^{3+} ionic radius. That is, the Arrhenius activation energy (E_a) for the phase-change rate from cubic to hexagonal forms increases.¹⁰ This result is similar to that of ref 10, in which shows that the growth of a hexagonal NaLnF_4 phase is strongly dependent on the Ln^{3+} size. However, hexagonal NaLnF_4 ($\text{Ln} = \text{Dy}–\text{Yb}, \text{Y}$) tends to form tubular crystals in our result but platelike crystals in ref 10.

The diameters of the NaErF_4 and NaYF_4 microtubes cannot be easily distinguished from each other in Figure 2, but they are larger than those of NaHoF_4 illustrated in the Supporting Information, Figure 3a,b. The diameters of NaHoF_4 microtubes (Supporting Information, Figure 3a,b) are generally greater than those of NaDyF_4 (Supporting Information, Figure 4d). Solid nanorods rather than hollow tubules are found for NaLnF_4 ($\text{Ln} = \text{Eu}, \text{Gd}, \text{Tb}$) systems (Supporting Information, Figure 4a–c). The nanorods are often jointed with X-shaped or dendritic nanostructures. We conclude by stating that the diameters of the 1-D crystals are inversely correlated with the Ln^{3+} ionic radii. In general, the microtube diameter

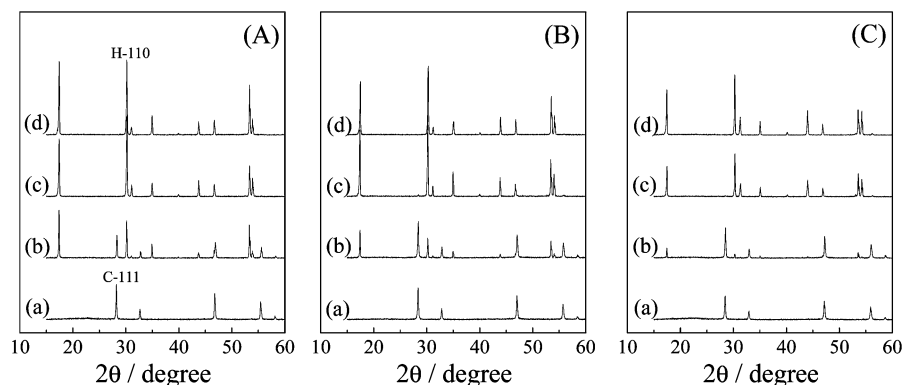


Figure 6. PXRD patterns of (A) NaErF_4 , (B) NaTmF_4 , and (C) NaYbF_4 synthesized at 220 °C for various durations: (a) 1.0 h, (b) 3.0 h, (c) 12 h, and (d) 48 h.

increases as the ionic radii of the rare-earth atoms decrease. These 1-D tubular microstructures and X-shaped nanostructures are destroyed eventually if these hydrothermal reactions are performed at much higher temperatures and/or for much longer times (typical results illustrated in Supporting Information Figure 5). In these SEM images, some grains attributed to hexagonal phases are found. This is due to the known Ostwald ripening process.

Growth Mechanism. HRTEM and SAED techniques do not indicate the presence of NaLnF_4 grains composed of both cubic and hexagonal structures. This suggests that the “phase transformation” is not based on an epitaxial or topotaxial growth from cubic phase to the hexagonal phase. Rather, the hydrothermal phase transformation is based on the dissolution of solid (S) crystals of cubic NaYF_4 , the mass transfer in liquid (L) solution, and the nucleation and growth of solid crystals of hexagonal phase via a SLS (solid–liquid–solid) or a dissolution–recrystallization process; where the crystal’s size of cubic NaYF_4 is smaller than a critical size, the cubic crystal then dissolves quickly. The sudden increase of the growth species concentrations in aqueous solution from the quick dissolution of cubic NaYF_4 promotes hexagonal NaYF_4 to grow quickly at the initial stage (Figure 2). The further redissolution of spherical grains of cubic NaYF_4 still serves as the component source for the maintenance of a high concentration for the further growth of the hexagonal phase with a 1-D tubular microstructure along the *c* axis during hydrothermal aging.

In Supporting Information Figure 3b, a neck is found, as pointed out by a black arrow. The connections from which the nanorods of NaEuF_4 , NdGdF_4 , and NaTbF_4 grew from and yielded X-shaped crystals were clearly observed using TEM (Supporting Information, Figure 4 (black arrows)). A bowtie-like crystal was also observed for NaDyF_4 (Supporting Information, Figure 4d). These findings lead us to propose that the preferential growth at the circumferential edges of these 1-D crystals (Figure 2b–h and Supporting Information Figure 3) facilitates the growth of hollow interiors in a similar way to the elongated growth of tellurium nanotubes along the $+c$ and $-c$ directions.¹⁶ With the disappearance of spherical crystals, the growth species concentration decreases and further growth is restrained. By the maintenance of solution saturation, the further hydro-

thermal aging results in a pyramidal-end-capped microtube (Figure 2d,g, arrows). The further hydrothermal aging, especially performed at higher temperatures, certainly destroys these 1-D and/or hollow structures because of their intrinsic morphological metastability (Supporting Information, Figure 5).

Conclusions

In this paper, we have described a new group of well-defined prismatic microtubes based on multicomponent fluorides, typically, sodium yttrium fluoride (NaYF_4) by a simple hydrothermal processing from NaF , NH_4HF_2 , and lanthanide nitrate. Cubic NaYF_4 with fluorite-related structure, the metastable phase below 691 °C, is formed as the kinetic product but is replaced by thermodynamically stable hexagonal NaYF_4 under hydrothermal conditions. Higher aging temperatures and/or longer aging times can promote this hydrothermal “phase transformation”. Over a wide range of reaction temperatures and times, the hydrothermal route can successfully lead to an easily controlled synthesis of both cubic-phase nanospheres and hexagonal-phase microtubes of NaYF_4 . The crystal morphology of NaYF_4 can be designed through consequent phase control via such wet chemistry.

Rare-earth ions such as Yb^{3+} and Er^{3+} acting as sensitizers and activators can be directly doped into both cubic and hexagonal NaYF_4 hosts through hydrothermal synthesis. These doped materials retain their morphologies related to their respective hosts. The hexagonal $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ microtubes display considerably stronger UC emission than cubic $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ nanospheres and hexagonal $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ nanoparticles. The addition of EDTA decreases the UC emission, though it makes the perfect hexagonal form.

Hydrothermal synthesis of the related sodium rare-earth fluorides is crucially dependent on the ionic radius of the rare-earth ions. In addition to NaYF_4 , tubular NaLnF_4 ($\text{Ln} = \text{Dy}–\text{Yb}$) can be also synthesized with hollow interiors. These prismatic hollow structures are synthesized from safe and simple inorganic reactants. They can be doped with rare-earth ions hydrothermally and might be promising high-efficiency luminescence materials. As these complex fluorides generally also possess excellent fluorine-ionic conductivities, these 1-D microtubes may find wide applications as

microprobes in galvanic chemical sensors in which the hollow interiors can be designed as either anodes or cathodes.

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Supporting Information Available: Additional figures in a PDF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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