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Catalyzing cubic-to-hexagonal phase transition in NaYF₄ via ligand enhanced surface ordering

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Abstract:
The phase-pure hexagonal lanthanide-doped NaYF$_4$ nanocrystals possesses enhanced luminescence properties due to its low phonon energy and chemical stability compared to its cubic phase counterpart. However, the phase-pure hexagonal NaYF$_4$ nanoparticle forms only at high temperature (≥ 180°C) and in the presence of certain ligands (e.g. oleic acid) whereas cubic phase forms at low reaction temperature. To this end, we report low temperature (~48°C) synthesis of phase-pure hexagonal NaYF$_4$ nanoparticle by converting cubic NaYF$_4$ nanoparticle into hexagonal phase through surface oxidation of oleic acid (C-18) ligand to azelaic acid (C-9). The mechanism behind the transformation is investigated using density functional theory (DFT) based studies. DFT studies reveal that the phase transformation from cubic→hexagonal phase involves a disorder→order phase transition since all cationic sites are occupied by either Na or Y in cubic phase while hexagonal phase has more ordered structure with one Y having full occupancy at its cationic site. As carboxyl groups of adsorbents strongly adsorb on Y-terminated surfaces while having no interaction with Na-terminated surfaces of the cubic phase, the surface-ligand interaction promotes surface segregation of Y. This biasing of occupancy towards more ordered arrangement promotes the formation of more ordered phase and correspondingly reduces the energy barrier for transformation to the more ordered hexagonal phase. The surface coverage achieved by oleic acid is low due to its bulky long alkyl chains (C-18) imposing steric restriction that is removed on shortening of alkyl chain length. As a consequence, there is greater surface-ligand interaction leading to further surface segregation of Y and cationic ordering in cubic phase and making the phase transformation to hexagonal phase less energy intensive. In addition, oxidation of oleic acid makes nanoparticles hydrophilic making it suitable for biological applications.
1. Introduction

NaYF₄ is one of the most commonly employed phosphor host matrix for lanthanide doping which has found wide application in variety of the fields such as bioprobes⁵, flat-panel displays⁶, solar-energy harvesting⁵, sensing⁷, photocatalysis⁸-¹¹ and theronaustic¹²,¹³. It is one of the best matrices available for lanthanide doping since it possesses (1) exceptional quantum efficiency¹⁴, (2) high chemical stability with low hygroscopic property with good dispersibility in a wide range of solvents¹⁵,¹⁶, (3) optical transparency over wide wavelength¹⁷,¹⁸ and (4) low phonon energy (350 cm⁻¹)¹⁹. For optical applications, hexagonal phase is preferred over the cubic phase since it gives better photoluminescence properties like upconversion, down-conversion and Stoke’s shift luminescence upon doping with lanthanide ions with lower energy loss during energy transfer process due to presence of lower numbers of non-harmonic phonon modes in hexagonal phase¹⁴, ²⁰-²². However, low temperature synthesis strategies to prepare NaYF₄ yield a mixture of polymorphs with cubic phase predominating over optically efficient hexagonal phase²³, and hence, the phase purification adopted should also necessarily be capable of retaining the nanostructure.

The phase transformation from cubic→hexagonal involves a disorder→order phase transition. The cationic sites of cubic phase are disordered with equal probability of six-fold Na and Y atom for occupation (Fig. 1a). In hexagonal NaYF₄, there are three types of cationic sites: 1) a nine-fold coordinated position occupied by Y³⁺, 2) nine-fold coordinated position occupied randomly by 1/2 Na⁺ and 1/2 Y³⁺ and 3) a six-fold coordinated position occupied by 1/2 Na⁺ (Fig. 1b)⁴. The phase transformation (cubic→hexagonal) involves lowering of randomness in selectivity of cationic positions as all the cationic position of cubic phase can be occupied by either Na⁺ and Y³⁺ whereas in hexagonal phase nine-fold coordinated position comprises only
Y$^{3+}$. Hence the phase transformation from cubic to hexagonal polymorph can be interpreted as disorder $\rightarrow$ order transformation in terms of cationic site arrangement. Decrease of randomness in cationic positions in NaYF$_4$ structure would lead to lowering of energy barrier of cubic $\rightarrow$ hexagonal polymorphic phase transitions. The prevalent strategies for phase transformation are either increasing reaction temperature or reaction duration$^{24-28}$. However, during these processes, the crystals are susceptible to Ostwald ripening to yield larger crystals with broad size distribution and varied morphology. To overcome these issues, alternative synthetic procedures like self-focusing$^{29, 30}$ and doping$^{31-33}$ have been proposed. In self-focusing methodology, cubic phase nanocrystals gets transformed to hexagonal phase over a hexagonal phase seed$^{29, 30}$. Addition of dopants larger than Y atom yields hexagonal phase at lower temperatures$^{31, 32}$. However, addition of dopants may also alter the phonon energy at local sites thereby promoting the multi-phonon relaxation process and inter-dopant energy transfer. Among other methodologies to decrease the activation barrier includes tuning ligand to precursor ratio or varying ligands$^{25, 34-36}$. Increasing ligand concentration has found to yield greater amount of hexagonal phase$^{35, 36}$. However increasing ligand concentration beyond a limit has found to hinder the reaction kinetics thereby lowering the yield of hexagonal phase.

In this context, we demonstrate the manipulation of surface-ligand interaction as an effective way of phase purification strategy to obtain sub-20 nm hexagonal phase nanoparticles. The proposed approach has been extended to phase transformation of pure cubic phase or mixed phase to pure hexagonal phase at low temperature (~48 °C). In the first step, suppression of Ostwald ripening is achieved by using a long-chained ligand (i.e. oleic acid) at the expense of low-ligand coverage. In this step, a mixture of cubic and hexagonal phase of NaYF$_4$ is obtained whereas pure cubic phase is obtained upto 140 °C temperature. In the next step, long-chain
ligand of oleic acid is cleaved by Lemiux-von Rudolf (LVR) reagent at an elevated temperature (>48 °C). The cleaving of ligand has two-fold effect on crystal phase transformation, (1) cleaved oleic ligand yields azelaic acid which imposes less steric hindrance and higher ligand coverage can be achievable and (2) the carboxylic group of azelaic acid imposes higher degree of ordering along the surface thereby reducing the energy barrier for cubic→hexagonal phase transformation. As a result, the phase transformation from cubic→hexagonal can be achieved at lower temperature (>48 °C). DFT studies indicate that carboxylic group favors Y-termination at the surface and does not adsorb at Na-terminated surface. Thus, increased ligand coverage induces less randomness in the cubic phase and transformation to the more ordered hexagonal phase would entail less activation energy. The results give an effective way of lowering the phase transformation energy for disorder→order phase transition by controlling the surface terminations through surface-ligand interactions.

2. Experimental and Computational Details:

2.1. Synthesis

2.1.1. Materials: Y(NO₃)₃, 4H₂O salt [99% pure, (Sigma-Aldrich)], Eu(NO₃)₃, 5H₂O salt [99% pure, Sigma-Aldrich], NaF (Fischer-Scientific) were used as precursors for NaYF₄. As a solvent and ligands, oleic acid, ethanol, t-butyl alcohol, cyclohexane and deionized (DI) water were used. To prepare LVR reagent, NaIO₄ and KMnO₄ were used.

2.1.2. Synthesis of hydrophobic and pure cubic or mixed phase of NaYF₄:Eu³⁺ nanoparticles: NaOH (0.7 g), water (9 mL), ethanol (10 mL), and oleic acid (20 mL) were mixed under agitation to form a homogeneous solution. Subsequently, 1.0 M aqueous solution of NaF (2.5 mL) solution was added dropwise to the above solution (F⁻/Y³⁺=5:1). Then 0.6 mmol of rare-earth nitrate [1.2 mL, 0.5 mol Y (NO₃)₃, 4 H₂O] and 5 mol% Eu(NO₃)₃, 5 H₂O (21 mg)
aqueous solution was added under stirring conditions. The mixture was agitated for about 20
min, and then transferred to a 50 mL autoclave, sealed and treated at different temperature (180
°C, 150 °C and 130 °C) temperature for 8 hrs. After 8 hrs, the system was allowed cool to room
temperature. The product was washed with ethanol thrice and centrifuged in 10,000 rpm for 10
minutes. Pure powder sample was obtained by purifying the samples with ethanol several times
to remove excess oleic acid, sodium oleate, and other remnants and drying the sample under
vacuum for 4 hours.

2.1.3. Conversion of hydrophobic and pure cubic or mixed phase to hydrophilic and phase
pure NaYF₄:Eu³⁺ nanoparticles: A mixture of prepared sample (70mg), cyclohexane (70 mL),
t-butanol (50mL), water (7.5 mL) and 5 wt % K₂CO₃ aqueous solutions (3.5 mL) was stirred at
room temperature for about 20 min and then 15 mL of LVR reagent (5.7 mM KMnO₄ and 0.105
M NaIO₄ aqueous solution) was added dropwise. The pH of the solution was maintained at 8.
The resultant mixture was stirred at about 48 °C for over 48 h. The product was then isolated by
centrifugation and washed with deionized water, acetone, and ethanol. Subsequently, the product
was dispersed in HCl (25 mL) of pH 4-5, and the mixture was stirred for 30 min. At last, the
oxidized product was obtained by centrifugation, washed with deionized water followed by
drying under vacuum.

2.2. Material Characterization: The crystalline structures of the sample were examined by an
X-ray diffraction apparatus (XPERT-PRO) with Cu Kα radiation (λ = 1.54 Å) operating at 45 kV
and 40 mA. The XRD were taken of dried powdered samples. The photoluminescence
measurements were done using a steady-state and time-resolved fluorescence spectrometer
(Edinburgh instruments FLSP 920) attached with a red-sensitive Peltier element cooled
Hamamatsu R928-P PMT detector. Steady-state emission spectra were recorded by exciting the
samples with a steady-state Xe lamp. Decay curves were recorded by exciting the nanocrystals with a Nd: YAG laser, attached with an optical parametric oscillator (OPO) with an optical range of 210–2400 nm. The hydrophobic particles are dispersed in cyclohexane while the hydrophilic particles are dispersed in water while measuring the luminescence property. The effective luminescence lifetime of $^5D_0$ level of Eu$^{3+}$ ions has been estimated by recording the decay curve of 615 nm emission and performing double exponential fitting of the curve$^{39}$. Transmission electron micrographs (TEM) were obtained from an FEI Technai G2 U-Twin (200 KeV) instrument. The hydrophobic particles were dispersed in cyclohexane while hydrophilic particles were dispersed in water, sonicated and then drop-cast in a 200-mesh size Cu-grid to transmission electron micrograph. To examine the surface-ligand interaction, FTIR (Perkin Elmer Spectrum Two Spectrophotometer) was being done.

2.3. Computational Methodology: All Density Functional Theoretical (DFT) simulations were performed using plane-augmented wave as implemented in Vienna Ab initio Simulation Package (VASP) software and the exchange-correlation contributions are treated according to Perdew, Burke and Ernzerhof (PBE)$^{40-42}$. A kinetic energy cutoff of 400 eV was used for all calculations. For bulk calculation of a cubic polymorph, a supercell of 2x2x1 was prepared. Gamma sampling of Brüillion zone with the k-point mesh of 6x6x12 was used. Geometric optimizations of bulk lattice constant of cubic polymorph is found to be 5.44 Å which is close to the experimental lattice constant of 5.45 Å. A vacuum layer of $\sim$15 Å has been used for surface calculation and 4x4x1 k-point mesh was used during calculation. The (001) surface of cubic polymorphs was modelled by a periodic stack of polar slabs, containing three stoichiometric Na/Y-F layers with only bottom slab fixed. During the adsorption energy calculations, considering the length of the long carbon chain of oleic acid or azelaic acid and their sodium salt, acetate adsorbents were
used to reflect the carboxylate containing acids assuming the electronic effect of the long carbon chains could be summed by a single methyl group\textsuperscript{35}. While considering the olefinic bond effect of oleic acid on the surface, an ethylene model molecule was used assuming the electronic effects of long carbon chain does not interact with the surface. The adsorption energy was determined by following equation,

\[ E_{\text{adsorption}} = E_{\text{slab+adsorbate}} - E_{\text{slab}} - E_{\text{adsorbate}} \]

where \( E_{\text{slab+adsorbate}} \) is the energy of the system comprising the crystal surface and adsorbate molecule, \( E_{\text{slab}} \) is the energy of the bare crystal surface and \( E_{\text{adsorbate}} \) is the energy of the isolated adsorbate. The electronic properties of the bare surface influence the adsorption site and ability of bonding with ligands. To understand the influence, Bader charge analysis was being also done\textsuperscript{43}.

3. Results and Discussion

In the present work, hydrophobic NaYF\(_4\) nanoparticles were synthesized using autoclave route in presence of oleic acid at various temperatures (130 °C-180 °C) to prepare pure cubic and mixture of cubic/hexagonal phases at different ratios. After preparation of oleic acid stabilized hydrophobic nanoparticles, the surface ligands were oxidized to azelaic acid by addition of LVR reagent at a temperature of 48 °C. Upon this oxidation, NaYF\(_4\) nanoparticles were converted into hydrophilic nanoparticles which can be easily dispersed in water.

3.1. Phase evolution with change in temperature and surface moiety: Fig. 2a shows the XRD pattern of the hydrophobic NaYF\(_4\) nanoparticles prepared at four different temperatures (130 °C, 150 °C and 180 °C). At a reaction temperature of 130 °C, all the diffraction peaks matches with the cubic phase (Fm-3m) of NaYF\(_4\), while no peaks of hexagonal phase (P-6) of NaYF\(_4\) are observed. This implies that kinetically stabilized disordered cubic phase forms over ordered
hexagonal phase at lower temperature which is also corroborated in literature. XRD pattern shows appearance of hexagonal phase from a temperature of 150 °C. As the reaction temperature increases, hexagonal polymorph becomes a dominant phase. However, presence of small percentage of cubic polymorphs in the samples prepared at reaction temperature of 180 °C suggests that this transformation to hexagonal phase incomplete even at reaction temperature of 180 °C.

Fig. 2b shows the XRD pattern of the hydrophilic particles by oxidizing the surface oleic acid ligand of hydrophobic particles. XRD pattern clearly suggests that all the hydrophilic particles possess pure hexagonal polymorph with complete disappearance of cubic phase of NaYF₄. This suggests that phase transformation in the nanoparticles has occurred with the modification of ligands. The XRD peak width of hydrophilic particles is higher as compared to hydrophobic particles at same peak position, suggesting enhancement of crystallinity during phase transformation process.

3.2. Identification of surface ligands: The ligands on the surface of particles are identified by FTIR spectra as shown in Fig. 3. A small crest at 3007 cm⁻¹ is found in the hydrophobic sample which is attributed to the –HC=CH– stretching vibration. This feature is absent in the spectrum of the hydrophilic sample suggesting cleaving of the –HC=CH– group. Both samples contain peaks a broad band around 3450 cm⁻¹, two sharp peaks around at 2924 cm⁻¹ and other peaks around 2854 cm⁻¹, 1638 cm⁻¹, 1564 cm⁻¹, 1532 cm⁻¹ and 1448 cm⁻¹. The broad band around 3450 cm⁻¹ corresponds to O-H stretching vibration. The sharp peaks around at 2924 and 2854 cm⁻¹ correspond to asymmetric (V_asym) and symmetric (V_sym) stretching vibrations of methylene (-CH₂) in the long alkyl chain respectively. The bands around at 1564 cm⁻¹ and 1448 cm⁻¹ correspond to asymmetric (V_asym) and symmetric (V_sym) stretching vibrations of the -COOH
group respectively. The bands corresponding to the -C=O stretching vibration of -COOH groups are observed at 1638 cm\(^{-1}\) and 1532 cm\(^{-1}\). FTIR spectra clearly suggest formation of azelaic acid from oleic acid.

The oleic acid ligand is attached to the surface of the nanoparticles through unsaturated carboxylic group and olefinic groups. The nanoparticles synthesized from the autoclave route show hydrophobicity since oleic acid has a –CH\(_3\) as terminal group which does not interact with either the surface or water while the other terminal group, –COOH interacts with the nanoparticles surface (see DFT results). During ligand modification oleic acid ligands on the surface of nanoparticles undergoes cleaving of olefinic bonds to convert into azelaic acids which has a two terminal polar –COOH groups. One of the -COOH groups is strongly bounded to surface of the nanoparticles through surface-ligand interaction while the other group renders the particle hydrophilic through its interaction with water.

3.3. Microstructural evolution with change in temperature and surface moiety: To investigate the size and morphological evolution of hydrophobic and hydrophilic nanoparticles at different reaction temperature, TEM has been performed. The hydrophobic nanoparticles prepared at 150 °C and 130 °C, have a spherical morphology with a size range of 10-15 nm (Fig. 4b-c). However with the increase in temperature, smaller nanoparticles begin to disappear with the appearance of long rod hexagonal prism like particles and subsequent increase in sizes of nanoparticles are observed (Fig. 4a). These hexagonal prism nanorods have high aspect ratio (L: D~10:1) with sharp edges and almost no overgrowth at the edge is observed. Hydrophilic particles which are prepared from hydrophobic particles of 130 °C do not show much change in morphology and size (Fig. 4f). Hence, the demonstrated method is a good way to synthesize hexagonal phase at lower temperature. The hydrophilic samples, prepared from 180 °C sample,
consist of long nanorods having a hexagonal base (Fig. 4d). But they do not have sharp edges as observed in hydrophobic samples. Also the small spherical nanoparticles have disappeared during this phase transformation. The spherical particle of cubic phase tends to grow over the rods of hexagonal phase to recrystallize as hexagonal phase which is well reported in literature\textsuperscript{29, 30}. The relative amount of cubic phase decreases with increasing temperature. Hence the loss of sharp edges among the hexagonal nanorods is more pronounced in case of hydrophilic sample of 150 °C as compared to 180 °C.

3.4. Luminescence changes with phase evolution: To further study the phase transformation phenomenon in NaYF\(_4\), Eu\(^{3+}\) is used as an optical probe since (1) it substitutes Y\(^{3+}\) as it has the same charge and ionic radii and (2) upon doping, Eu\(^{3+}\) can be used to investigate the local structures and polymorph-sensitive luminescence properties that follow phase evolution. The magnetic dipole transition intensity is insensitive to its surrounding local structural environment. However the electric dipole transition intensity is hypersensitive to the local field symmetry around the probe atom and the ratio with magnetic to electric dipole transition intensity is significantly influenced by change in local environment around Eu\(^{3+}\) atom\textsuperscript{44, 45}. It is well reported in the literature that 10% doping does not induce any kind of phase transformation in NaYF\(_4\) matrix\textsuperscript{31}. Hence to study the phase transformation phenomena, the dopant concentration has been taken as 5%.

Fig. 5 shows the comparison of the photoluminescence spectra of hydrophobic and hydrophilic particles at different temperatures. The strong emission bands appearing at ~ 592 nm and ~ 615 nm are associated with magnetic dipole induced transition (\(5\,^D_0 \rightarrow 7\,^F_1\)) and electrical dipole induced transition (\(5\,^D_0 \rightarrow 7\,^F_2\)), respectively. From the Table 2, it can be seen that in the pure hydrophobic cubic polymorph, the peak intensity ratio of 615 nm: 592 nm emissions which
is also known asymmetry ratio, is almost unity while it is the maximum in the pure hexagonal polymorph. It is also observed that with increase in the reaction temperature, the asymmetry ratio increases. This may be attributed to increase in asymmetric environment surrounding the Eu\(^{3+}\) atom in hexagonal phase causing electric dipole induced transition to dominate i.e. more cubic nanocrystals are getting phase transformed into hexagonal nanoparticles. The lifetime of hydrophobic particles \(^5D_0\) level increases from 1.92 ms in pure cubic polymorph 3.5.96 ms in pure hexagonal polymorph. The variance of lifetimes in different hydrophilic hexagonal samples are attributed to size of the nanoparticles. For all hydrophobic NaYF\(_4\) samples, the asymmetry ratio has increased from its hydrophobic counterpart indicating the increase of asymmetric environment surrounding the probe atom which can be correlated with an increase of hexagonal polymorph among the nanoparticles. However the lifetime of Eu\(^{3+}\) emission in hydrophilic nanoparticles reduce from their parent hydrophobic particle. The reduced lifetime of hydrophilic particle is ascribed to quenching of photoluminescence by the water molecules\(^{46}\).

3.5. **Role of ligands during phase transformation:** Density Functional Theory (DFT) studies are performed to study the effect of ligands on phase transformation phenomena. In this context, it is to be noted that FTIR studies show that oleic acid get adsorbed onto the surface of nanoparticles as already discussed in previous section. Oleic acid can interact with the surface via carboxylate or olefinic groups. The adsorption energies of acetate adsorbents with different terminations of (001) facet of NaYF\(_4\) are listed in Table 3. Computational studies indicate that both carboxylate and olefinic group of oleate ion can interact with the surface of the nanoparticles. The mode of the interaction of the acetate can be monodentate (single O atom for adsorption) or bidentate (both O atoms binds for adsorption) as shown in Fig. 6(d-g). Though both monodentate and bidentate adsorption is possible, the bidentate adsorption is energetically
more favorable as compared to monodentate as can be observed from Table 3. This might be due to their steric structure of acid during surface interaction. The C–C bonds rather than –C=O bonds of adsorbate align themselves perpendicular to the surface to ensure that the two O atoms of ligand can interact as much as with cations of the surface. The interaction with acetate and surface is also dependent on the surface terminations. The carboxylate group does not interact with surface Na atoms as the interactions with them are energetically unfavorable. However they can easily adsorb with Y-terminated surfaces. It is found from Bader charge analysis that electron deficient regions are centered on Y-atom rather than Na-atom on surfaces. The formal charge over Y-atom on the (001)-surface is 1.5e lower than corresponding surface Na-(001) atom in (001) surface of cubic phase. Hence electron donor ligand like oleate ion tend to adsorpt into Y-terminated surfaces. These results indicate that Y-terminated surfaces are preferred by the ligands containing a –COOH group. The surface segregation of Y³⁺ leads to greater ionic interaction between surface Y-F bonds in absence of ligands as exemplified by decrease of bond-distance of surface Y-F. The surface Y-F bond distance is 2.18 Å in absence of ligands as opposed to 2.20 Å in presence of ligands. It is also observed that surface coverage by acetate cannot exceed 0.75 monolayer due to steric considerations as two adjacent adsorbents in neighboring sites start to interact with each other. It is noted that the steric interaction arising from oleate (C-18) would be far higher than the computed acetate (C-2) leading to lower surface coverage. Similar types of preferential adsorption of ligands on Y-sites over Na-sites are also observed for (110) surfaces (see section S1 of ESI). In addition to hydrogen passivation of the anionic terminations, olefinic bond of oleic acid or oleate tend to interact with F-terminations of polar (001) surfaces of cubic phase. This is observed on adsorbing model ethylene adsorbate with F-terminated (001) surfaces of cubic surfaces (Fig. 7). The strong interaction between C
atom of ethylene molecule and F-termination of (001) surface lowers the surface energies of cubic phase (adsorption energy = -2.5 eV).

During oleate-mediated synthesis of NaYF$_4$ in presence of NaOH, oleic acid generates oleate ion which gets adsorbed on surfaces during the growth stage as evident from FTIR studies. As per computational studies, oleate would favorably adsorb to the places where Y-terminated surfaces are present due to strong interaction between Y-carboxylate while rejecting Na-terminated surface which in turn induce Y-atoms to surface segregate. Hence, to adsorb oleate and lower its surface energy, the surface of cubic polymorph has to undergo cationic re-orientation to form stable surface-adsorbate configurations. To see the effect of neighboring surface cationic position on adsorption of acetate on Y-site, two cases are considered where the neighboring surface position is Na in one case (mixed surface termination) (Fig. 6c) and in another case it is Y-site (single surface termination) (Fig. 6a). It is found that acetate-Y interaction is more stable (by -2.8 eV) in Y-terminated surfaces than mixed surface terminations. This indicates the probability of stabilizing a random cationic terminated surface gets reduced in the adsorbate environment due to preference of ligands for specific surface termination. Thus, oleate ligand promotes cationic rearrangement in cubic phase with surface segregation of Y-atoms while Na-atoms get clustered in the bulk sites. This leads to reduction in the activation energy of cubic to hexagonal phase transformation pathway as lowering of randomness Na/Y atoms reduces the stability of cubic phase (see section S2 of ESI). This is also supported by the experimental observations that excess of oleate favors the formation of hexagonal polymorph$^{25}$. The achievable ligand coverage is less in hydrophobic particles due to the presence of long chain alkyl group present in the oleic acid. The steric interaction of alkyl chain of the adsorbed ligand in the surface prevents particle-particle interaction as well as surface-ligand interaction.
This entails lowering of rate of Ostwald ripening enforced growth kinetics. The olefinic bond of oleic acid stabilizes F-terminated surface through interaction of π-bonds. However on cleaving of olefinic bond to carboxylate reduces the steric interaction of alkyl chains of the ligands. Oxidation of oleic acid to azelaic acid has twin effect on the growth kinetics; (1) stability of F-terminated surface gets reduced exposing it towards other chemical species in the solution and (2) more adsorption of species due to reduced alkyl chain steric interaction. The consequence is two-fold: ripening of these facets of cubic polymorph surface or adsorption of more ligands to induce cation rearrangement by increase surface selectivity thereby lowering the activation energy for cubic to hexagonal phase transformation. The particle-particle interaction/ripening effect is observed from TEM image that sharp-edged hydrophobic particle has gone through irregular growth on edges with the disappearance of smaller particle. However, NaYF₄ did not form in presence of azelaic acid ligand at 48 °C temperature possibly due to the fact that initial transition barrier of formation of NaYF₄ from precursors are much higher than transition barrier of cubic→hexagonal NaYF₄ transformation. The increase in ligand coverage decreases the activation barrier such that phase transformation is achieved at far lower (48 °C) temperature.

4. Conclusion

In summary, we have demonstrated an approach towards reducing activation barrier for phase transformation of disordered cubic phase →ordered hexagonal phase through modification of the ligand adsorbed on surface. The uniqueness of this method is that the phase transformation is carried out at a temperature as low as 48 °C as opposed to more than 180 °C temperature in conventional synthesis procedure. The lowering of activation barrier is due to increase in adsorbent coverage of cation-terminated surfaces where Y-terminated surfaces are favored over Na-terminated surfaces due to adsorbent-surface interaction leading to lowering of randomness.
in occupancy of cationic position by Na and Y atom. The cleavage of bulky oleic acid during ligand oxidation lowers the steric hindrance thereby increasing the adsorbent coverage along the surface. The cubic→hexagonal phase transformation of NaYF₄ nanoparticle has insignificant effects on the size except some overgrowth along the sharp edges of the nanoparticles as observable from TEM images. The enrichment of hexagonal phase is observed in mixture with an increase of luminescence intensity of Eu³⁺ dopant. The particles are also converted into hydrophilic particle making them more suitable for other applications such as bio-labels or photodynamic therapy.

**Supporting Information**

Comparison of bulk energies upon clusterization of Na- and Y-atoms in cubic NaYF₄ phase and adsorption energies of acetate on (110) surface of cubic NaYF₄ phase are provided in the supporting information.

**Acknowledgement**

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**References**


Table 1. Structural data of cubic and hexagonal NaYF$_4$ polymorphs

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<tr>
<th></th>
<th><strong>Cubic (Fm-3m) a=5.45Å$^0$</strong></th>
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<td><strong>Atom</strong></td>
<td><strong>Occupancy</strong></td>
<td><strong>Wycoff position</strong></td>
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<td>Na or Y</td>
<td>0.5 of Na or 0.5 of Y</td>
<td>4a (0,0,0)</td>
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<tr>
<td>F</td>
<td>1.0 of F</td>
<td>8c (0.25, 0.25, 0.25)</td>
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<th></th>
<th><strong>Hexagonal (P-6): a=5.92Å$^0$, c=3.54Å$^0$</strong></th>
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<td><strong>Atom</strong></td>
<td><strong>Occupancy</strong></td>
<td><strong>Wycoff position</strong></td>
</tr>
<tr>
<td>Na (1) or Y (1)</td>
<td>0.5 of Na or 0.5 of Y</td>
<td>1a(0,0,0)</td>
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<td>Na (2) or vacant site</td>
<td>0.5 of Na or 0.5 of vacant site</td>
<td>2h(2/3, 1/3, 0.156)</td>
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<td>Y (2)</td>
<td>1.0 of Y</td>
<td>1f (1/3, 2/3, 0.5)</td>
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<tr>
<td>F (1)</td>
<td>1.0 of F</td>
<td>3j (0.290, 0.257, 0.5)</td>
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<tr>
<td>F (2)</td>
<td>1.0 of F</td>
<td>3k (0.067,0.422,0.00)</td>
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Table 2. The effective luminescence lifetime of $^5\!D_0$ level of Eu$^{3+}$ ions (615 nm) and asymmetry ratio in hydrophobic and hydrophilic NaYF$_4$ nanoparticles.

<table>
<thead>
<tr>
<th>Reaction temperature(°C)</th>
<th>Surface moiety</th>
<th>Lifetime (ms)</th>
<th>Asymmetry ratio</th>
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<tr>
<td>180°C</td>
<td>Hydrophobic</td>
<td>5.96</td>
<td>1.56</td>
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<td></td>
<td>Hydrophilic</td>
<td>3.28</td>
<td>1.69</td>
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<tr>
<td>150°C</td>
<td>Hydrophobic</td>
<td>3.08</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>Hydrophilic</td>
<td>3.26</td>
<td>1.25</td>
</tr>
<tr>
<td>130°C</td>
<td>Hydrophobic</td>
<td>1.92</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>Hydrophilic</td>
<td>1.94</td>
<td>1.46</td>
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Table 3. Adsorption energies of acetate on (001)-facet of cubic phase

<table>
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<tr>
<th>Mode of adsorption</th>
<th>Y site of (Y+Y)-clustered (001) facet</th>
<th>Na-site of Na-clustered (001) facet</th>
<th>Y-site of (Na+Y)-clustered (001) facet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bidentate adsorption</td>
<td>-6.5 eV</td>
<td>Not possible</td>
<td>-3.7 eV</td>
</tr>
<tr>
<td>Monodentate adsorption</td>
<td>-1.6 eV</td>
<td>Not possible</td>
<td>-1.9 eV</td>
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Figure 1: (a) Single cell of cubic polymorph and (2) 2x2x1 supercell of hexagonal polymorph of NaYF₄.
Figure 2. XRD pattern of (a) the hydrophobic NaYF$_4$ nanoparticles that were synthesized at 180 °C, 150 °C and 130 °C temperature respectively, (b) the hydrophilic nanoparticles of NaYF$_4$ after oxidation of hydrophobic NaYF$_4$ nanoparticles that were synthesized at 180 °C, 150 °C and 130 °C temperature.
Figure 3. FTIR of hydrophobic and hydrophilic NaYF₄ nanoparticles before and after ligand modification respectively.
Figure 4. TEM images of the hydrophobic NaYF₄ product with changing reaction temperature. Reaction temperatures were (a) 180 °C, (b) 150 °C and (c) 130 °C respectively. TEM images of the hydrophilic NaYF₄ product after oxidation of hydrophobic NaYF₄ particles that were produced at (d) 180 °C, (e) 150 °C, and (f) 130 °C.
Figure 5. Emission spectra of the hydrophilic and hydrophobic NaYF$_4$ nanoparticles with changing reaction temperature. Reaction temperatures was (a) 180 °C, (b) 150 °C and (c) 130 °C respectively. The emission spectra are normalized with respect to 592 nm emission ($\lambda_{ex} = 395$ nm).
Figure 6. (a–c) Different probable surface slab configurations of (001) facet of cubic NaYF$_4$ are depicted: Top-view of (a) Y-clustered surface termination, (b) Na-clustered surface termination, (c) No clustering of individual atoms at the surface with probability of both atoms at the surface. (d) Top-view of bidentate acetate adsorption on Y-clustered surfaces of (001) facet of cubic phase. The subsurface Na atoms are visible in this figure. (e) Side-view of bidentate acetate adsorption on Y-clustered surfaces of (001) facet of cubic phase. (f) Top-view of monodentate acetate adsorption on Y-clustered surfaces of (001) facet of cubic phase. The subsurface Na atoms are visible in this figure. (g) Side-view of monodentate acetate adsorption on Y-clustered surfaces of (001) facet of cubic phase.
Figure 7. Ethylene adsorption on (001) facet of cubic phase: (a) top view, (b) side view.
For Table of Contents Use Only:
Catalyzing cubic-to-hexagonal phase transition in NaYF₄ via ligand enhanced surface ordering
Sulay Saha, Raj Ganesh S. Pala, Sri Sivakumar

Synopsis: A low temperature phase transformation strategy aimed towards producing phase-pure hexagonal NaYF₄ from mixed phase/phase-pure cubic NaYF₄ is demonstrated. Instead of synthesizing phase-pure hexagonal NaYF₄ at 180°C through solvothermal/hydrothermal synthesis methodology from precursors, a lower phase transformation temperature of 48°C is achieved through increased ligands/adsorbents surface coverage by ligand modification which increases Na/Y clusterization, thus reducing the stability of cubic phase.