Chapter 4

Investigation into the Phase Controlled Synthesis of Hexagonally Ordered KLaF$_4$ and its Properties as a Luminescence Host
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Selection of appropriate host materials is essential for favourable optical properties such as high upconversion (UC) efficiency and controllable emission profile. Ideal host materials should also have low lattice phonon energies, which are a requirement to minimize non-radiative loss and to maximize the radiative emission. To date, NaYF₄ system has attracted the attention of researchers as an efficient host matrix for the green, red and blue emission UC process through appropriate doping [4.1-4.4]. The choice of fluorides as the host matrix for the UC studies has been justified due to its low phonon energy (~ 350 cm⁻¹, preventing non-radiative relaxation), multisite character of the host crystal lattice, i.e. occupation of the rare earth active centre in two or more non-equivalent crystallographic sites. However, heavier halides like chlorides, bromides and iodides generally exhibit even lower phonon energies (less than 300 cm⁻¹) but they are hygroscopic and are of limited use. Whereas oxides exhibit high chemical stability, but their phonon energies are relatively high and generally larger than 500 cm⁻¹ due to the stretching vibration of the host lattice [4.5].

The critical role played by the size of the alkali metal ions and the rare earth ions in determining the structure type, lattice symmetry and stoichiometry was exemplified by the research of Tyagi et al [4.6] in which Li₃ScF₆ was obtained at atmospheric pressure readily and scheelite structure type LiScF₄ was realized only at
high pressures. Generally, KREF\textsubscript{4} has two polymorphs at room temperature and ambient pressure; orthorhombic and hexagonal except in the case of KLaF\textsubscript{4} and KCeF\textsubscript{4} which possess a cubic phase [4.7]. Liu et al [4.8] has recently reported the controlled synthesis and the optical properties of mono-dispersed nanocrystals of rare earth ion doped cubic KLaF\textsubscript{4}. As it is known that the variation of the crystal structure of the host materials can significantly influence the optical properties of nanocrystals. For example, hexagonal-phase NaYF\textsubscript{4}:Yb\textsuperscript{3+}/Er\textsuperscript{3+} bulk materials exhibit about an order of magnitude enhancement of UC efficiency relative to their cubic phase counterparts [4.9, 4.10]. The phase-dependent optical property can be ascribed directly to the different crystal-fields around trivalent lanthanide ions in matrices of various symmetries [4.11]. For this reason, a possible investigation on the hexagonal counterpart of cubic KLaF\textsubscript{4} is sought. Except for the identification of hexagonal KLaF\textsubscript{4} from the phase diagram of KF-LaF\textsubscript{3} system by Zachariasen [4.12], there are no further literature reports on the possible synthesis of this ordered lattice and remained a challenge.

In case of NaYF\textsubscript{4}, it is observed that hexagonal ordering is thermodynamically more stable than its cubic form; even though the crystals in cubic symmetry are more easily produced by the solution based synthetic method. Generally, the hexagonal phase of the alkali metal ternary fluorides has been stabilized by wet chemical methods, with the hydrothermal method being the most investigated. The stabilization of the hexagonal phase of NaYF\textsubscript{4} has been achieved by the addition of excessive amounts of fluoride source, conducting the reactions at high temperatures as well as by ageing process [4.13-4.16]. Usually, a chelating ligand (e.g. EDTA, CTAB, citrate, etc) is reported to act as a phase controller, facilitating the slow and directed growth
of the hexagonal phase. Optimization of various reaction parameters such as pH of the medium of growth and annealing temperature have been required for the preferential synthesis of the hexagonal form without the presence of cubic phase [4.17, 4.18]. Recently, Chen et al [4.19] developed a new strategy of synthesizing hexagonal NaYF$_4$ by doping-induced phase transition via solvothermal method using Ti$^{4+}$, Zr$^{4+}$ and Ca$^{2+}$ ions as dopants. Grzechnik et al [4.20] studied the effect of high pressures (up to 11 GPa) at ambient temperature as well as at higher temperatures (up to 1100°C) on the cubic to hexagonal phase transformation of NaYF$_4$. In addition to these possible strategies, size induced phase transformations have also been reported for many materials existing in various polymorphs [4.21-4.26]. Farvid et al [4.21] have studied the kinetics of phase transformation of rh-In$_2$O$_3$ to bcc-In$_2$O$_3$ nanocrystals during its colloidal synthesis. Correlation of the kinetic results with TEM images of the product at different points of time during the reaction suggested that the phase transformation occurs by nucleation of bcc-In$_2$O$_3$ at the interfaces between contacting rh-In$_2$O$_3$ nanocrystals. The rate of phase transformation was found to critically depend on both nanocrystals size and concentration; it increased with increasing concentration and decreasing size, owing to a higher probability of nanocrystals contact formation. Recently Sabyrov el al [4.22] observed anatase-to-rutile phase transformation in TiO$_2$ nanocrystals that likely involves aggregation. The compactness of the aggregates affected the processes significantly. That is, densely aggregated particles show higher transformation and growth rates as compared to loosely aggregated ones. A similar size dependent phase transformation is also reported for ZrO$_2$, ZnS systems existing in cubic-tetragonal, hexagonal-cubic polymorphs. Among the available synthetic strategies for solids, simple, robust,
effective and convenient, energy efficient solution based techniques are being investigated for the fabrication of technologically important materials including the nanophosphors [4.27-4.29].

In this chapter, detailed investigations into the synthesis of hexagonally ordered KLaF$_4$ in pure form by the fluorination reaction of three different precursors of lanthanum and KF in non-aqueous medium and at atmospheric pressures are described. Doping this host lattice with the optically active Er$^{3+}$ and Tb$^{3+}$ ions, were carried out to functionalize it to be a robust fluorescence host system.

For the experiments, LaCl$_3$ [Sigma Aldrich 99.9%, 0.2452 g, 1 mol], La(acac)$_3$·xH$_2$O [Sigma Aldrich, 0.4362 g, 1 mol] and La(O$i$Pr)$_3$ [Sigma Aldrich, 0.3162 g, 1 mol] and KF [Merck, GR 0.2324 g, 4 moles] were used. Methanol was employed as the solvent medium for the reactions involving LaCl$_3$ and La(acac)$_3$. Mixed solvent system of isopropanol and methanol was used for the reaction of La(O$i$Pr)$_3$ and KF. Typically, the reactants were dissolved in 20 mL of the solvent.

In order to establish the optimal conditions for the synthesis of pure hexagonal KLaF$_4$, a series of reactions in non-aqueous medium were carried out by systematically varying the lanthanum precursor, utilizing KF as the fluorinating as well as structure directing agent. The solution containing the lanthanum ion was added drop-wise under constant stirring to KF solution. The addition of lanthanum precursor solution (in methanol or isopropanol) to the KF (in methanol) at room temperature resulted in a white colour suspension. Two different approaches were followed after this step. In one set, the reaction was continued at room temperature under constant stirring for ~12 h. In the other, the suspension was aged at 65°C for ~12 h.
The reaction between LaCl$_3$ and KF, driven by the salt elimination, was very fast at room temperature and the PXRD pattern of the product contained reflections pertaining to KCl, cubic KLaF$_4$ and LaF$_3$. After repeated washing with methanol, complete removal of KCl occurred resulting in cubic KLaF$_4$ (as the major phase) and LaF$_3$ (as the minor phase). From the aging reaction performed at 65°C for 12 h, formation of only LaF$_3$ was observed (Figure 4.1).

![Figure 4.1: The PXRD patterns of the product obtained from LaCl$_3$ at (a) 25°C and (b) 65°C. # denotes reflections due to LaF$_3$.](image)

Taking the lead from the fact those ligands capable of expanding the coordination number of the metal ions (such as EDTA) favour the formation of hexagonally ordered NaYF$_4$, two different lanthanum precursors viz., La(acac)$_3$ and La(O’Pr)$_3$ were reacted with KF at room temperature as well as at 65°C. The reactions
were not as rapid as in the case of LaCl\(_3\). The high chelate constants and the polymeric nature of these precursors might have influenced the slow formation kinetics of the final products. While the products from the room temperature reactions of La(acac)\(_3\) and La(O\(\text{Pr}\))\(_3\) has been identified to be cubic KLaF\(_4\) phase from their PXRD patterns, the ageing reactions performed at 65°C using these two lanthanum precursors yielded product whose PXRD patterns matched very well with the hexagonal form of KLaF\(_4\) (JCPDS File no. 75-1927 and Figure 4.2). The reflections in the PXRD pattern of hexagonal KLaF\(_4\) were sharp and intense, implying good crystallinity. It is noteworthy that highly crystalline hosts are quite advantageous for higher emission efficiency due to fewer defect traps [4.30]. No other crystalline by-products were observed in these sets of reactions. The reproducibility as well as the

![Figure 4.2: PXRD patterns of hexagonal KLaF\(_4\) prepared from (a) La(acac)\(_3\) and (b) La(O\(\text{Pr}\))\(_3\). JCPDS reference pattern of hexagonal KLaF\(_4\) is also provided.](image_url)
yield of hexagonal KLaF₄ from the reaction involving La(O\textsuperscript{i}Pr\textsubscript{3}} was quite high as compared to La(acac)\textsubscript{3} indicating the subtle difference in their behaviour as precursors in the fluorination reaction. This might again be related to the different chelate constants of the ligands as well as the difference in the vapour pressure of the La(acac)\textsubscript{3} and La(O\textsuperscript{i}Pr)\textsubscript{3} when subjected to ageing at 65°C.

It is interesting to analyze these results to find the key factors responsible for this phase transformation from cubic to hexagonal in KLaF₄. Firstly, the observation of LaF\textsubscript{3} being the only crystalline product from the reaction between LaCl\textsubscript{3} and KF conducted at 65°C suggested that the cubic KLaF\textsubscript{4} phase was a kinetically stable one, undergoing dissociation to the thermodynamically more stable LaF\textsubscript{3}. Additionally, the formation of cubic KLaF\textsubscript{4} at room temperature and hexagonal KLaF\textsubscript{4} at 65°C from the other precursors indicated that temperature of the reaction might be one of the factors inducing the transformation. To verify this, solid cubic KLaF\textsubscript{4} obtained using La(acac)\textsubscript{3} was subjected to TG-DTA analysis in which no exothermic signal (usually observed for the cubic-hexagonal phase transition in NaYF\textsubscript{4} [4.18]) was observed till 500°C, signifying the absence of a solid-solid phase transition (Figure 4.3).

To ascertain whether size of the crystallites, initially formed, induced the phase transition from cubic to hexagonal on ageing, the average crystallite size (estimated by using the Scherrer analysis of their PXRD patterns) of the cubic KLaF\textsubscript{4} from the reactions of LaCl\textsubscript{3}, La(acac)\textsubscript{3} and La(O\textsuperscript{i}Pr)\textsubscript{3} with KF at room temperature (Figure 4.1 and 4.4) and the hexagonal KLaF\textsubscript{4} from the reactions of La(acac)\textsubscript{3} and La(O\textsuperscript{i}Pr)\textsubscript{3} with KF at 65°C (Figure 4.2) were compared. The average crystallite size of cubic KLaF\textsubscript{4} using LaCl\textsubscript{3}, La(acac)\textsubscript{3} and La(O\textsuperscript{i}Pr)\textsubscript{3} were 16.7, 6.3 and 2.1 nm respectively. Thus, it is evident that the products using the lanthanum precursors with
Figure 4.3: Simultaneous TG-DTA trace of cubic KLaF$_4$ sample and the DDTA plot is shown in the inset.

Figure 4.4: PXRD patterns of the cubic KLaF$_4$ obtained from the reaction of KF with (a) La(acac)$_3$ and (b) La(O'Pr)$_3$ at room temperature (25°C).
chelating groups produced relatively lower crystallite size of cubic KLaF$_4$ as compared to the lanthanum salt. The average crystallite size of the hexagonal KLaF$_4$ samples from the reactions of La(OiPr)$_3$ and La(acac)$_3$ with KF were 9 nm and 21 nm respectively. As the higher crystallite size of cubic KLaF$_4$ obtained from LaCl$_3$ (16.7 nm) did not yield hexagonal KLaF$_4$ and the smaller crystallites of cubic KLaF$_4$ [obtained from La(acac)$_3$ and La(OiPr)$_3$] transformed to hexagonal KLaF$_4$ (on ageing at 65°C), it is proposed that the average crystallite size of the cubic KLaF$_4$ produced from the reactions of these three lanthanum precursors is the major factor for effecting its phase transformation to hexagonal. Also, the higher average crystallite size of hexagonal KLaF$_4$ [9 nm and 21 nm from La(OiPr)$_3$ and La(acac)$_3$ respectively] as compared to the lower average crystallite size of cubic KLaF$_4$ [2.1 nm and 6.3 nm from La(OiPr)$_3$ and La(acac)$_3$ respectively] clearly indicated that the larger crystallites have been obtained at the expense of smaller ones along with the phase transformation. Such a process has been explained with the help of interface nucleation mechanism for the phase transformation of colloidal In$_2$O$_3$, ZrO$_2$ and TiO$_2$ nano crystals [4.21-4.26]. Also, the densely aggregated nanocrystals showed higher transformation and growth rates as compared to the loosely aggregated crystals in those systems. A comparison of TEM images of cubic and hexagonal KLaF$_4$ obtained from La(acac)$_3$ revealed the presence of agglomeration in both the samples suggesting that a similar mechanism might be effecting the phase transformation of the cubic KLaF$_4$ nano crystals to the hexagonal form (Figure 4.5). It can further be argued that the smaller nano crystallites have higher packing density relative to the larger ones, might result in higher probability of particle-particle contact formation and thereby accelerated the phase transformation rate in KLaF$_4$. Also, the temperature of the
reaction (65°C) would have contributed further to the increased probability of nanocrystallites having such interaction and rapid hexagonal phase nucleation. It is possible that the larger crystallites of the cubic KLaF$_4$ obtained from LaCl$_3$ (16.7 nm) might have low particle-particle contact density hindering interface nucleation to transform to hexagonal polymorph, instead dissociated to LaF$_3$. Thus, temperature, fluorination reaction time, nature of the lanthanum precursor and the size of the crystallites (formed initially) influenced the formation of hexagonal KLaF$_4$. Summary of the results from all these reactions is shown pictorially in Figure 4.6.

A Diamond drawing of the hexagonally ordered KLaF$_4$ lattice is shown in Figure 4.7 and the structure consists of an ordered array of F$^-$ ions with two types of relatively low-symmetry cation sites that are selectively occupied by K$^+$ and La$^{3+}$ ions. This arrangement results in significant electron cloud distortion of the cations differing from its cubic polymorph in which the high-symmetry cationic sites are

\[ \text{Figure 4.5: TEM images of (a) cubic and (b) hexagonal KLaF}_4 \text{ sample obtained using La(acac)}_3. \]
Figure 4.6: Summary of the results of the reaction between La\textsuperscript{3+} precursor and KF in non-aqueous medium at room temperature and at 65°C.

Figure 4.7: Structural diagram of hexagonal KLaF\textsubscript{4}.
randomly occupied by K$^+$ and La$^{3+}$ ions [4.31]. It has been well documented that the transformation from cubic into hexagonal form in these fluoride systems is of a disorder-to-order character with respect to cations. Hexagonal KLaF$_4$, has been considered to be isomorphous to the $\beta_1$-K$_2$UF$_6$ structure with the formula given as (KLaF$_4$)$_{1.5}$ [4.32]. In the structural model employed for the Rietveld refinement, the site 2$d$ was considered to be shared by 1.5 K$^+$ and 0.5 La$^{3+}$ ions while the site 1$a$ was exclusively occupied by La$^{3+}$ ions. Six F$^-$ ions were equally distributed in sites 3$f$ and 3$g$. Assuming spherical particles without strain, the diffractogram was well fit in the hexagonal space group $\overline{p}6_2m$ (#189), with lattice constants of $a = 6.5842$ (3) Å and $c = 3.8165$ (3) Å (Figure 4.8). The crystal data and structure refinement parameters of the hexagonal KLaF$_4$ are summarized in Table 4.1. The refined unit cell and position parameters, after the final cycle of refinement, are provided in Table 4.2.

**Figure 4.8**: Final Rietveld fit (red line) of the observed PXRD pattern of hexagonal KLaF$_4$ nanocrystals (blue line) and residuum.
Table 4.1: Crystallographic data of hexagonal KLaF$_4$

<p>| | |</p>
<table>
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<tr>
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<td>Hexagonal</td>
</tr>
<tr>
<td>Space Group</td>
<td>$P6_2m$ (# 189)</td>
</tr>
<tr>
<td>$a$ [Å]</td>
<td>6.5842(3)</td>
</tr>
<tr>
<td>$c$ [Å]</td>
<td>3.8165(3)</td>
</tr>
<tr>
<td>$V$ [Å$^3$]</td>
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</tr>
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<td>$Z$</td>
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<tr>
<td>$\rho$ calc [g/cm$^3$]</td>
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</tr>
<tr>
<td>$R_{exp}$ (%)</td>
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<tr>
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<tr>
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</tr>
<tr>
<td>Number of restraints</td>
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<tr>
<td>Temperature</td>
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</tbody>
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Table 4.2: Refined Atomic parameters after the Final cycle of Refinement.

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<th>x</th>
<th>y</th>
<th>z</th>
<th>B$_{eq}$</th>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>K1/La2</td>
<td>2d</td>
<td>0.75/0.25</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.5</td>
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</tr>
<tr>
<td>F1</td>
<td>3g</td>
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<td>0.6288(2)</td>
<td>0.0</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>F2</td>
<td>3f</td>
<td>1.0</td>
<td>0.2152(3)</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
</tr>
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Hexagonal KLaF$_4$ obtained from the reaction of La(O\textsuperscript{3}Pr)$_3$ and KF also showed agglomeration of crystallites in its TEM image (Figure 4.9 (a)). Lattice fringes of the individual crystallites were seen in the HRTEM image indicative of their good crystallinity (Figure 4.9 (b)). The distances between the lattice fringes were measured to be 0.33 nm corresponding to the $d$-spacing for the (110) lattice plane of the hexagonal KLaF$_4$ structure. The selected area electron diffraction (SAED) pattern of the crystallites (inset of Figure 4.9 (b)) could be indexed to the (100), (101), (200),

**Figure 4.9:** (a) TEM and (b) HR-TEM images (A SAED pattern of the nanocrystal is shown in the inset.), (c) FE-SEM image and (d) DLS of hexagonal KLaF$_4$ prepared from La(acac)$_3$. 
(302) and (311) planes of the hexagonal KLaF$_4$ structure. The low-magnification SEM image (Figure 4.9 (c)) revealed a uniform and densely distributed hexagonal shaped crystals. The histogram of the particle diameter (Figure 4.9 (d)) obtained experimentally using a particle size analyzer revealed that most of the particles were having diameter in 70-120 nm range, with an average value of about 88 nm.

Room temperature Raman spectrum of hexagonal KLaF$_4$ (prepared from the La(O'Pr)$_3$ as the precursor) showed four phonon bands centered at 161, 231, 292 and 383 cm$^{-1}$ (Figure 4.10). The effective phonon energy was calculated to be 262 cm$^{-1}$ by the Lorentzian fitting procedure [4.33], which is lower than the one reported for the widely studied NaYF$_4$ system (360 cm$^{-1}$) [4.34-4.36]. Other Lorentzian fitted parameters are provided in Table 4.4. As lower phonon energies are an important aspect for minimizing non-radiative (multi-phonon) losses as well as to increase the

![Raman spectrum of hexagonal KLaF$_4$ obtained by exciting with $\lambda = 785$ nm.](image)

**Figure 4.10:** Raman spectrum of hexagonal KLaF$_4$ obtained by exciting with $\lambda = 785$ nm.
overall metastable energy lifetime of the UC processes, our estimation reinforced the superiority of KLaF₄ over NaYF₄ as the host lattice.

Table 4.3: Energy, Intensity and Full Width at Half Maximum (FWHM) of the Lorentzian peaks fitted to the Raman Spectrum of hexagonal KLaF₄.

<table>
<thead>
<tr>
<th></th>
<th>1st Peak</th>
<th>2nd Peak</th>
<th>3rd Peak</th>
<th>4th Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position (cm⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intensity (arb. units)</td>
<td>552313</td>
<td>454757</td>
<td>1748840</td>
<td>206988</td>
</tr>
<tr>
<td>FWHM (cm⁻¹)</td>
<td>77</td>
<td>60</td>
<td>82</td>
<td>35</td>
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</table>

Doping the hexagonal KLaF₄ with the optically active Er³⁺-ions was examined to study its solubility and the associated optical properties including the UC. The choice of Er³⁺ ion (as a dopant) could be justified by the fact that its electronic energy levels allow for many radiative transitions and longer life times of its excited state ^4I_{11/2}, which can easily be populated by the low-cost and high power near-infrared (NIR) diode lasers. Er³⁺-doped samples were prepared under experimental conditions identical to those that were employed for the undoped samples. For this Er(acac)₃ were prepared from ErCl₃·6H₂O (Sigma-Aldrich, 99.9%) [4.37] The hexagonal KLaF₄ were doped with 3, 5 and 10 mol% of Er³⁺ using La(acac)₃ as a precursor while 3 mol% of Er³⁺ using La(OiPr)₃ as a precursor. The close size match between La³⁺ (LaⅨ: 1.30 Å) and Er³⁺ (ErⅨ: 1.14 Å) ions certainly facilitated its accommodation in hexagonally ordered fashion [4.38]. However, because of poor reproducibility of hexagonal KLaF₄ on using La(acac)₃ as a precursor, a small
shoulder on the side of the $hkl$ reflection of the hexagonal \( \text{KLaF}_4 \), corresponding to the cubic \( \text{KLaF}_4 \) phase was noted in the PXRD patterns of doped samples. The Le-bail fitting procedure (Figure 4.11) was used to determine lattice constants of the cubic and the hexagonal phases of the doped samples. It is evident that no clear systematic trend is observed from the extracted lattice constants, except the general decrease in the lattice constants suggesting the doping of the smaller \( \text{Er}^{3+} \) ion for the bigger \( \text{La}^{3+} \) ion in the corresponding crystallographic sites. While the hexagonal \( \text{KLaF}_4:\text{Er}^{3+}(3\%) \) sample prepared by using \( \text{La(OiPr)}_3 \) as a precursor is highly pure. Rietveld refinement of the PXRD pattern of the sample is provided in Figure 4.12.

![Figure 4.11](image)

**Figure 4.11:** Final Le-bail fit (red line) of the observed PXRD patterns of hexagonal \( \text{KLaF}_4:\text{Er}^{3+} \) nanocrystals prepared from \( \text{La(acac)}_3 \) (blue line) and residuum.
Figure 4.12: Final Rietveld fit (red line) of the observed PXRD pattern of hexagonal KLaF₄:Er³⁺(3%) nanocrystals prepared from La(O′Pr)₃ (blue line) and residuum.

The energy level diagram showing the intra-configurational $f$−$f$ transitions of Er³⁺ shown in Figure 4.13. The measured UV-Visible diffuse reflectance spectrum in the visible and NIR regions of the KLaF₄:Er³⁺ samples prepared from La(acac)₃ as a precursor are reproduced in Figure 4.14 (a). The reflectance spectra of the more dilutely doped nanocrystalline samples are usually characterized by weaker $f$−$f$ transitions, whose intensity scales with the Er³⁺ concentration. This portion of the spectrum consisted of eight reflectance manifold series of relatively sharp features in the UV and visible region. The sharp bands were assigned to the intra-configurational $f$−$f$ transitions from the $^4$I₁₅/₂ ground state to the $^4$I₁₁/₂, $^4$I₉/₂, $^4$F₉/₂, $^2$H₁₁/₂, $^4$F₇/₂ and $^4$F₅/₂ excited states [4.39]. A similar reflectance behavior was also observed for the hexagonal KLaF₄:Er³⁺(3%) sample prepared by using La(O′Pr)₃ (Figure 4.14 (b)).
**Figure 4.13:** Energy level schemes for intra-configurational $f$-$f$ transitions of Er$^{3+}$ ions.

**Figure 4.14:** UV-Visible diffuse reflectance spectra of (a) undoped and Er$^{3+}$ doped hexagonal KLaF$_4$ prepared from La(acac)$_3$ and (b) monophasic hexagonal KLaF$_4$:Er$^{3+}$(3%) prepared from La(O’Pr)$_3$.  

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Three predominant emission bands at 522, 544 and 662 nm, attributed to the transition from the $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ states to the $^4\text{I}_{15/2}$ ground state, respectively, were observed in the Er$^{3+}$ doped hexagonal KLaF$_4$ samples prepared from La(acac)$_3$ under 980 nm excitation (Figure 4.15). The blue emission could not be observed efficiently in the absence of sensitizer due to the low efficiency of three- or four-photon UC and strong scattering of host lattices [4.40]. On comparison of the emission spectra of cubic KLaF$_4$:Er$^{3+}$ were compared with that of the hexagonal KLaF$_4$:Er$^{3+}$ samples, it was evident that there were no changes in the location of the green and the red bands. However, the integral luminescence intensity of the hexagonal KLaF$_4$ enhanced by manifolds as that of cubic KLaF$_4$. A similar behaviour was reported earlier in hexagonal-phase of NaYF$_4$:Yb$^{3+}$/Er$^{3+}$ bulk materials which exhibit about an order of magnitude enhancement of UC efficiency relative to their

![UC spectra of hexagonal KLaF$_4$:Er$^{3+}$ nanocrystals prepared from La(acac)$_3$ under 980 nm laser excitation.](image)

**Figure 4.15:** UC spectra of hexagonal KLaF$_4$:Er$^{3+}$ nanocrystals prepared from La(acac)$_3$ under 980 nm laser excitation.
cubic phase counterparts \[4.8, 4.10\]. The phase-dependent optical property can be ascribed directly to the different crystal-fields around trivalent lanthanide ions in matrices of various symmetries. Low symmetry hosts typically exert a crystal-field containing more uneven components around the dopant ions compared to high symmetry counterparts. The uneven components enhance the electronic coupling between \(4f\) energy levels and higher electronic configuration and subsequently increase \(f-f\) transition probabilities of the dopant ions \[4.11\].

The green to red ratio (GRR) in the upconversion emission was 21.8, 37.8 and 1.6 for the 3, 5 and 10\% Er\(^{3+}\) doped hexagonal KLaF\(_4\) samples respectively. Mai et al \[4.41\] obtained a very high GRR of 30 for hexagonal NaYF\(_4\):Yb\(^{3+}\)/Er\(^{3+}\) nanocrystals, the highest GRR ever reported to best of our knowledge. As suggested in many reports \[4.42\], a very low or a very high GRR is preferred in bio-labeling applications since a narrow spectral emission of the light is emitted. Materials with a high GRR can be effectively used to replace filters to capture only the green emission \[4.42\]. Thus, 5\% Er\(^{3+}\) doped hexagonal KLaF\(_4\) nanosized crystals having the highest ever recorded GRR could be a potential system that could be investigated for various bio-labeling studies \[4.43\]. Several factors, such as doping concentration, excitation density, synthesis temperature, crystallinity, impurities and defects are known to influence GRR of a system. A smaller GRR value could be expected for very small crystallites of Er\(^{3+}\) doped KLaF\(_4\) as they might be located on the surface and hence in proximity to the surface defects as well as impurities, paving way for quenching of the excited states \[4.44\]. Since, all the syntheses and UC measurements were performed under identical conditions, therefore surface defects and impurities may not be playing a major role in affecting variable GRR observed in the Er\(^{3+}\) doped hexagonal KLaF\(_4\) samples.
Due to the low phonon energy of hexagonal KLaF$_4$ lattice, it can be argued that at least ten lattice phonons would be required for the non-radiative decay from the green to the red emission state. One cannot rule out the possibility of quenching by the adsorbed impurities such as OH$^-$ and CO$_3^{2-}$ ions [4.45]. In the FTIR spectra of Er$^{3+}$ doped hexagonal KLaF$_4$, presence of bands at 3400 cm$^{-1}$ and 1615 cm$^{-1}$ suggested the presence of adsorbed OH$^-$ ions in the samples (Figure 4.16). Thus, it is convenient to assume that the presence of OH$^-$ ions possibly favoured the multi-phonon relaxation of $^3$H$_{11/2}$ state which in turn enhanced the intensity of the red luminescence by populating the $^4$F$_{9/2}$ state. It is interesting to note that the energy difference between the $^4$F$_{9/2}$ level and the next lower $^4$I$_{9/2}$ level is also the same as the energy difference between $^2$H$_{11/2}$ and $^4$F$_{9/2}$ levels i.e. 3000 cm$^{-1}$. Therefore, the probability for the multi-phonon relaxation of $^4$F$_{9/2}$ state should be comparable to that of $^2$H$_{11/2}$ state. However,

![FTIR spectrum of hexagonal KLaF$_4$ nanocrystals prepared from La(acac)$_3$.](image-url)
the green emission was the most intense in 5% doped (GRR = 37.8) and red emission was much stronger in 10% Er\(^{3+}\) doped hexagonal KLaF\(_4\) nanocrystals (GRR = 1.6). Thus, this ruled out the possibility that the multi-phonon relaxation processes affected the observed GRR to a greater extent.

The trend of the variation of GRR value in the Er\(^{3+}\) doped KLaF\(_4\) samples could possibly be explained by a cross relaxation (CR) mechanism suggested by Capobianco and co-workers [4.46]. A possible mechanism for the process as depicted in Figure 4.17. The CR process involved the higher excited \(^4F_{7/2}\) level of Er\(^{3+}\) ions which on relaxation to the \(^4F_{9/2}\) level emitting red bypassing the green emitting levels. It could occur via two resonant transitions \(^4F_{7/2} \rightarrow ^4F_{9/2}\) state and \(^4I_{11/2} \rightarrow ^4F_{9/2}\) states taking place at the same time. This proposal would also favour the energy match

![Figure 4.17: Proposed energy level schemes for the UC and normal emission processes in KLaF\(_4\):Er\(^{3+}\) system under 980 nm and 532 nm laser excitation respectively.](image)
between these levels (~5000 cm\(^{-1}\)). The efficiency of the CR process would increase as the average distance between the dopant ions decrease and therefore with increasing the Er\(^{3+}\) concentration, enhancement of the red emission would result. This was evident by the presence of a very strong red emission in 10 mol\% Er\(^{3+}\) doped sample with a very small GRR. Moreover, Vetrone et al [4.47] suggested that the ratio of \(^{2}\)H\(_{11/2}\) emission to \(^{4}\)S\(_{3/2}\) emission increased with recording temperature. Thus, the low intensity of \(^{4}\)S\(_{3/2}\) emission could be attributed to its small energy gap with respect to \(^{2}\)H\(_{11/2}\) state favouring the thermal population of the latter at room temperature.

The UC of monophasic hexagonal KLaF\(_{4}:\text{Er}^{3+}(3\%)\) prepared from La(O\(^{i}\)Pr\(_{3}\) at 980 nm laser operating at 150 mW power level, gave predominant emission at 545 nm along with low intense peaks at 522 and 662 nm were observed (Figure 4.18). The digital photograph of the intense green UC emission observed from the sample is also shown in Figure 4.18 as inset. In order to determine the number of photons as well as to understand the mechanism involved in the UC process in this system, pumping power (P) dependence of the intensities of the UC emissions was carried out (Figure 4.19 (a)). The logarithmic plots of emission intensity as a function of excitation power of 980 nm laser for the emissions \(^{2}\)H\(_{11/2}\) \(\rightarrow\) \(^{4}\)I\(_{15/2}\), \(^{4}\)S\(_{3/2}\) \(\rightarrow\) \(^{4}\)I\(_{15/2}\) and \(^{4}\)F\(_{9/2}\) \(\rightarrow\) \(^{4}\)I\(_{15/2}\) is shown in Figure 4.19 (b). It is very well known that for the UC process, the emission intensity (I) is proportional \(P^n\) (where \(n > 1\)) for one emitted photon [4.48]. The plot of log I versus log P yields a straight line for the \(^{2}\)H\(_{11/2}\) \(\rightarrow\) \(^{4}\)I\(_{15/2}\), \(^{4}\)S\(_{3/2}\) \(\rightarrow\) \(^{4}\)I\(_{15/2}\) transitions with slope values of \(n\) to be 1.85, 1.52 respectively. This implies a two-photon green (545 and 522 nm) emission process initiated at relatively low excitation powers. The slope for the red (662 nm) emission, \(^{4}\)F\(_{9/2}\) \(\rightarrow\) \(^{4}\)I\(_{15/2}\), is 1.01 indicating the energy transfer is the dominant mechanism for the UC process [4.49, 4.50]. Power
Figure 4.18: UC spectrum of monophasic hexagonal KLaF$_4$:Er$^{3+}$ (3 mol %) sample excited with 980 nm laser at 150 mW power and the digital photograph of the green glow UC are shown in the inset.

Figure 4.19: (a) UC spectra and (b) Log-log power dependence of the UC emissions of monophasic hexagonal KLaF$_4$:Er$^{3+}$ (3 mol %) sample excited with 980 nm laser at various powers.
dependencies of the UC emissions became non-linear above 300 mW suggesting the saturation of the UC processes [4.48]. The observed GRR value varies from 6-12 in range of 50-350 mW laser power.

The room temperature normal emission spectra of hexagonal KLaF$_4$:Er$^{3+}$ samples prepared from La(acac)$_3$ excited at 532 nm is shown in Figure 4.20. The observed trends of GRR in the normal emission were similar to that of the UC emission. Unlike UC process, in normal emission, $^2$H$_{11/2}$ state could directly be populated by at 532 nm laser diode. By a non-radiative relaxation, $^2$H$_{11/2}$ state could easily come to lower $^4$S$_{3/2}$ state. A sharp green emission observed in the normal emission process in the present study was attributed to phonon relaxation from $^4$S$_{3/2}$ state to $^4$I$_{15/2}$ ground state. Similar to the UC process, higher GRR was observed in the Er$^{3+}$ doped KLaF$_4$ samples. The GRR in the normal emission was 6.8, 20.8 and 3.9

![Figure 4.20: Normal emission spectra of hexagonal KLaF$_4$:Er$^{3+}$ samples prepared from La(acac)$_3$ under 532 nm laser excitation.](image-url)
for the 3%, 5% and 10% Er\textsuperscript{3+} doped hexagonal KLaF\textsubscript{4} samples respectively. A slight decrease in green emission followed by the enhancement in the red emission on the Er\textsuperscript{3+} concentrations in the KLaF\textsubscript{4} host lattice could possibly arise from the quenching of ions leading to multi-phonon relaxation of green emission. The normal emission and corresponding excitation spectra for the 3 mol% Er\textsuperscript{3+} doped hexagonal KLaF\textsubscript{4} sample [prepared from the La(O\textsuperscript{3}Pr\textsubscript{3}) dispersed in water (~1 wt%) are shown in Figure 4.21. The excitation spectrum monitored at an emission wavelength of 545 nm consisted of two broad excitation lines centred at 366 and 460 nm corresponding to \textsuperscript{4}I\textsubscript{15/2} \rightarrow \textsuperscript{4}G\textsubscript{9/2} and \textsuperscript{4}I\textsubscript{15/2} \rightarrow \textsuperscript{4}F\textsubscript{5/2} transition, respectively [4.51]. The normal emission spectrum excited at 460 nm followed a similar intense green emission as its upconverted emission. Two predominant peaks centred at 522 nm and 545 nm were observed arising out of the transition from \textsuperscript{2}H\textsubscript{11/2} and \textsuperscript{4}S\textsubscript{3/2} states to the \textsuperscript{4}I\textsubscript{15/2} ground.

![Graph](image)

**Figure 4.21:** Normal excitation (dotted line) and emission spectra (solid line) of 3 mol % Er\textsuperscript{3+} doped monophasic hexagonal KLaF\textsubscript{4} sample.
state, respectively. To measure the colour of the visible emissions a naked eye can perceive, the chromaticity coordinates are calculated from the luminescence spectra using the 1931 CIE method and the CIE1931 XY diagram of the hexagonal KLaF₄:Er³⁺ samples are presented in Figure 4.22. When the Er³⁺ content changes from 3 to 10%, the calculated CIE colour coordinates shift only slightly and fall well within the green region for UC and normal emission. The corresponding CIE coordinates are listed in Table 4.4.

The UC decay curves of ²H₇/₂ energy level of Er³⁺ doped hexagonal KLaF₄ samples prepared from the La(acac)₃ (Figure 4.23 (a)) could not be fitted into the single exponential function, but could very well be fitted into a double exponential function as I(t) = I₁ e⁻ᵗ/τ₁ + I₂ e⁻ᵗ/τ₂, with I₁ + I₂ = 1 [4.52]. The double-exponential character of the decay process suggested strongly the presence of a significant non-
Table 4.4: Chromaticity coordinates (x, y) of the KLaF$_4$:Er$^{3+}$ nanocrystals calculated for the 522 nm green emission under $\lambda_{ex} = 980$ nm (a-d) and 532 nm (e-h).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Chromaticity Coordinate (x)</th>
<th>Chromaticity Coordinate (y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. KLaF$_4$:Er$^{3+}$ (3%)</td>
<td>0.081</td>
<td>0.911</td>
</tr>
<tr>
<td>b. KLaF$_4$:Er$^{3+}$ (5%)</td>
<td>0.181</td>
<td>0.775</td>
</tr>
<tr>
<td>c. KLaF$_4$:Er$^{3+}$ (10%)</td>
<td>0.306</td>
<td>0.591</td>
</tr>
<tr>
<td>d. Monophasic KLaF$_4$:Er$^{3+}$ (3%)</td>
<td>0.355</td>
<td>0.623</td>
</tr>
<tr>
<td>e. KLaF$_4$:Er$^{3+}$ (3%)</td>
<td>0.352</td>
<td>0.621</td>
</tr>
<tr>
<td>f. KLaF$_4$:Er$^{3+}$ (5%)</td>
<td>0.323</td>
<td>0.662</td>
</tr>
<tr>
<td>g. KLaF$_4$:Er$^{3+}$ (10%)</td>
<td>0.372</td>
<td>0.599</td>
</tr>
<tr>
<td>h. Monophasic KLaF$_4$:Er$^{3+}$ (3%)</td>
<td>0.384</td>
<td>0.564</td>
</tr>
</tbody>
</table>

Figure 4.23: UC luminescence decay curves of (a) KLaF$_4$:Er$^{3+}$ samples prepared from La(acac)$_3$ (b) monophasic KLaF$_4$:Er$^{3+}$ (3%) sample prepared from La(O'Pr)$_3$ recorded at an emission of 522 and 545 nm, respectively.
radiative process and/or the presence of more than one site in which the dopant ions could be accommodated in the KLaF$_4$ crystal lattice. As the non-radiative decay process is known to depend heavily on the absorbed surface impurities and defects leading the dopant ions, located close to the surface, to decay faster than the ones located inside the nanocrystals [4.53]. However, the decay time (1$^{\text{st}}$ and 2$^{\text{nd}}$ order) observed in our system was comparable suggesting that the double exponential decays could not be solely due to non-radiative process. The presence of a minor amount of cubic KLaF$_4$ observed in the PXRD patterns of the doped samples along with the hexagonal KLaF$_4$ indicated the different local environments around the lanthanide ion and could result in different emission features. Thus, the double-exponential character of the decay curves attributed due to presence of cubic KLaF$_4$ in hexagonal KLaF$_4$ samples. The average lifetime, defined as $\tau_{av} = (I_1\tau_1^2 + I_2\tau_2^2) / (I_1\tau_1 + I_2\tau_2)$, of the $^2\text{H}_{11/2}$ levels of Er$^{3+}$ are presented in Table 4.5 [4.54]. It was observed that the emission intensity and the lifetimes of $^2\text{H}_{11/2}$ green emission increased initially with the increase of Er$^{3+}$ concentration, reaching a maximum at 5% of the dopant and then

**Table 4.5:** UC luminescence lifetimes of 3, 5 and 10 % Er$^{3+}$ doped KLaF$_4$ calculated for the emission wavelength of 522 nm.

<table>
<thead>
<tr>
<th>Er$^{3+}$ ions</th>
<th>GRR</th>
<th>$^2\text{H}<em>{11/2} \rightarrow ^4\text{I}</em>{15/2}$ ($\lambda_{ex} = 980$ nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\tau_1$(ms)</td>
</tr>
<tr>
<td>3%</td>
<td>21.8</td>
<td>9.30 (17.0%)</td>
</tr>
<tr>
<td>5%</td>
<td>37.8</td>
<td>13.60 (39.9%)</td>
</tr>
<tr>
<td>10%</td>
<td>1.6</td>
<td>6.98 (28.5%)</td>
</tr>
</tbody>
</table>
decreased with further increment, probably, due to the concentration quenching effects [4.55]. The average decay times of the $^2\text{H}_{11/2}$ levels of Er$^{3+}$ are depicted in Table 4.5. The UC decay time of $^4\text{S}_{3/2}$ state of monophasic hexagonal KLaF$_4$:Er$^{3+}$(3%) sample prepared from the La(OiPr)$_3$ (Figure 4.23 (b)) was calculated from single exponential fitting to be 2.55 ms, suggesting the minimal clustering effects.

Owing to the smaller crystallite size of the hexagonal KLaF$_4$:Er$^{3+}$ sample, it was realized that if they are dispersed in a polymer matrix, preferably, a transparent one, it will find potential applications in 3-D displays, optoelectronic and radiation detectors [4.56-4.59]. For this purpose, 1 wt % of the KLaF$_4$:Er$^{3+}$(3%) was dispersed in acetone and added to the monomer solution of methyl metha acrylate (MMA) in acetone and subjected to polymerization using benzoyl peroxide initiator [4.60]. The resultant composite PMMA (Poly Methyl Metha Acrylate) films showed intense greenish color on shining with white light radiation (digital picture shown in Figure 4.24). These preliminary results are quite promising and need to be explored further.

The hexagonal KLaF$_4$ has also been doped with another efficient green emitter Tb$^{3+}$ ion and the associated optical properties were also studied. Tb$^{3+}$ ions are also known to possess high magnetic moment with high relaxation time due to which it is being used in Magnetic resonance imaging (MRI) system [4.61]. Tb$^{3+}$-doped KLaF$_4$ sample was prepared under experimental conditions identical to those that were employed for the undoped sample using TbCl$_3$. 3% Tb$^{3+}$ doped KLaF$_4$ sample retained the hexagonal symmetry of KLaF$_4$. Rietveld refinement of the PXRD pattern of the 3% Tb$^{3+}$ doped hexagonal KLaF$_4$ sample prepared from La(acac)$_3$, TbCl$_3$ and KF is provided in Figure 4.25. The refinement parameters obtained were $a = 6.6068$ (9) and $c = 3.8351$ (7) Å with the reliability factors $R_{\text{exp}} = 3.26 \%$, $R_p = 4.76 \%$, $R_{wp} = 3.85 \%$ and Goodness of fit of 1.01.
Figure 4.24: Transparent PMMA film containing and 1 wt. % monophasic hexagonal KLaF₄:Er³⁺ (3 mol %) film. Intense green emission on shining with white light is shown as in inset.

Figure 4.25: Final Rietveld fit (red line) of the observed PXRD pattern of 3% Tb³⁺ doped hexagonal KLaF₄ nanocrystals (blue line) and residuum.
The room temperature excitation and emission spectra of hexagonal KLaF₄:Tb³⁺ (3%) sample under 337 nm radiation are shown in Figure 4.26. For comparison studies, 3 mol% Tb³⁺ doped cubic KLaF₄ sample was also prepared as per the synthetic procedure elaborated in chapter 3 and its luminescence features are compared in Figure 4.27. The several sharp excitation bands in Figure 4.26 (a) could be assigned to the intra 4f⁸ transitions from the 7F₆ to the 5H₆ (303 nm), 5D₀ (318 nm), 5L₇, 5L₈ (340 nm), 5L₉ (351 nm), 5L₁₀ (368 nm), 5G₆ (377 nm) and 5D₄ (486 nm) wave function into 4f wave function producing a small amount of opposite parity wave functions which led to some partially allowed intra-configurational transitions [4.62]. Additionally, the peak observed at 486 nm indicated the contribution of the direct excitation of the Tb³⁺ process to the luminescence of Tb³⁺ ions. The emission spectra consisted of emission peaks centred at 490, 545, 598 and 627 nm corresponding to the transitions 5D₄ → 7F₆, 5D₄ → 7F₅, 5D₄ → 7F₄, 5D₄ → 7F₃ of the Tb³⁺ ions, respectively (Figure 4.26 (b)). A simple schematic energy level diagram illustrating the energy

**Figure 4.26:** Normal (a) excitation and (b) emission spectra of 3 mol % Tb³⁺ doped monophasic cubic and hexagonal KLaF₄ samples.
levels of Tb\textsuperscript{3+} ions is shown in Figure 4.27. Among all the transitions, green \( ^{5}\text{D}_{4} \rightarrow ^{7}\text{F}_{5} \) emission at about 545 nm has the highest probability for both the electric-dipole and magnetic-dipole induced transitions and therefore observed as the strongest one [4.63]. The integral luminescence intensities of Tb\textsuperscript{3+} doped sample dramatically enhanced by 2-3 times as along with the crystal phase change from cubic to hexagonal as in the case of Er\textsuperscript{3+} doped KLaF\textsubscript{4} samples.

![Energy Level Scheme for Tb\textsuperscript{3+}](image)

**Figure 4.27:** Proposed energy level schemes for normal emission processes in KLaF\textsubscript{4}:Tb\textsuperscript{3+} system under 337 nm excitation.

Magnetic responses of cubic and hexagonal KLaF\textsubscript{4}:Tb\textsuperscript{3+}(3\%) samples at room temperature (300 K) are plotted as M vs H curves in Figure 4.28. Both showed paramagnetic behaviour with the observed magnetic susceptibility \( (\chi_{g}) \) of 4.741×10\textsuperscript{-6} and 1.627×10\textsuperscript{-6} emu/g for the cubic and hexagonal sample respectively. The lower
Figure 4.28: Room temperature M-H curves of Tb$^{3+}$ doped monophasic cubic and hexagonal KLaF$_4$ samples.

magnetic susceptibility of hexagonal phase could be arising from the different synthetic approach employed. The coercivity field ($H_c$) and the remnant magnetization ($M_r$) were almost zero at room temperature in which no hysteresis was observed. Also, the magnetization of the Tb$^{3+}$-doped KLaF$_4$ samples showed no saturation in the applied magnetic field investigated ($\pm$20 kOe).

We have further investigated the possibility to increases the UC efficiency of hexagonal KLaF$_4$ system by co-doping process. For this purpose, Yb$^{3+}$ (20%) and Er$^{3+}$ (2%) co-doped KLaF$_4$ was prepared, using Yb(acac)$_3$ and Er(acac)$_3$ following the procedure described earlier. The PXRD pattern of the Yb$^{3+}$ and Er$^{3+}$ co-doped KLaF$_4$ is presented in Figure 4.29, confirming the cubic symmetry of the product. This
observation suggested the instability of hexagonal ordering of La\(^{3+}\), Yb\(^{3+}\) and Er\(^{3+}\) ions under the present synthesis conditions. Cubic KLaF\(_4\):Yb\(^{3+}\)(20%)/Er\(^{3+}\)(2%) was also prepared at room temperature following the procedure described in chapter 3. PXRD patterns of cubic KLaF\(_4\):Yb\(^{3+}\)(20%)/Er\(^{3+}\)(2%) is also shown in Figure 4.29.

**Figure 4.29:** PXRD patterns of the cubic KLaF\(_4\):Yb\(^{3+}\)(20%)/Er\(^{3+}\)(2%) samples prepared from La(acac)$_3$.

In the UC spectra of cubic KLaF\(_4\):Yb\(^{3+}\)(20%)/Er\(^{3+}\)(2%) nanocrystals, excitation of the Yb\(^{3+}\) ions from ground state \(^2\)F\(_{7/2}\) to \(^2\)F\(_{5/2}\) state was observed (Figure 4.30). From this excited state, energy transfer (ET) from the \(^2\)F\(_{5/2}\) state of the Yb\(^{3+}\) ion to the adjacent \(^4\)I\(_{15/2}\) state of Er\(^{3+}\) ion would be the most viable option. Second ET from an Yb\(^{3+}\) ion could result in the further excitation of \(^4\)I\(_{11/2}\) state to \(^4\)F\(_{7/2}\) state of the Er\(^{3+}\) ion. The non-radiative decay of the \(^4\)F\(_{7/2}\) state to \(^2\)H\(_{11/2}\) and \(^4\)S\(_{3/2}\) states led to the green
Figure 4.30: Proposed energy level schemes of UC luminescence processes in cubic KLaF$_4$:Yb$^{3+}$(20%)/Er$^{3+}$(2%) nanocrystals.

Emission ($^2$H$_{11/2} \rightarrow ^4$I$_{15/2}$ and $^4$S$_{3/2} \rightarrow ^4$I$_{15/2}$). Also, the non-radiative decay of $^4$I$_{11/2}$ to $^4$I$_{13/2}$ state can also populate the $^4$I$_{13/2}$ state. The Er$^{3+}$ ion from the $^4$I$_{13/2}$ state can further populate the $^4$F$_{9/2}$ state by absorption of another photon, or ET from an Yb$^{3+}$ ion, which can possibly lead to the red $^4$F$_{9/2} \rightarrow ^4$I$_{15/2}$ emission. The lower luminescence intensity of cubic KLaF$_4$:Yb$^{3+}$(20%)/Er$^{3+}$(2%) (prepared at RT and at 65°C) samples over the hexagonal KLaF$_4$:5% Er$^{3+}$ nanocrystals demonstrated the dominant role of the symmetry over the presence of sensitizer in this KLaF$_4$ host lattice (Figure 4.31). Because of the very strong red emission observed in cubic KLaF$_4$:Yb$^{3+}$(20%)/Er$^{3+}$(2%) nanocrystals, its GRR value was in the range 2.1-3.5, quite low as compared to the hexagonal KLaF$_4$:5% Er$^{3+}$ nanocrystals (GRR = 37.8). As in
Figure 4.31: UC spectra of hexagonal KLaF₄:Er³⁺(5%) and cubic KLaF₄:Yb³⁺(20%)/Er³⁺(2%) (prepared at RT and at 65°C) nanocrystals under 980 nm laser excitation.

Figure 4.32: Normal emission spectra cubic KLaF₄:Yb³⁺(20%)/Er³⁺(2%) samples (prepared at RT and at 65°C) are compared with the hexagonal KLaF₄:5% Er³⁺ nanocrystals under 532 nm laser excitation.
the case of UC, the normal emission also suggested its dependence on the symmetry of the host lattice over the presence of sensitizer by showing lower luminescence intensity (cubic KLaF$_4$:Yb$^{3+}$(20%)/Er$^{3+}$(2%) prepared at RT and at 65°C) as compared to the hexagonal KLaF$_4$:5% Er$^{3+}$ samples (Figure 4.32).

**Conclusions**

This work demonstrated that phase transformation of KLaF$_4$ nanocrystals in solution is a kinetically controlled process, and provided improved understanding of the growth and phase transformation mechanism of fluorides nanocrystals. The results of this study allowed for a rational manipulation of the nanocrystals surfaces and their interactions by controlling the reaction conditions, such as time and temperature, enabling the synthesis of colloidal nanocrystals building blocks with a desired crystal structure and properties. Studies on the hexagonally ordered KLaF$_4$ by solution based method revealed that both the temperature and the ligands attached to the lanthanum precursor influenced its formation. While the simple lanthanum salt (LaCl$_3$) did not yield the hexagonal KLaF$_4$, La(acac)$_3$ and La(O$i$Pr)$_3$ yielded hexagonally ordered KLaF$_4$ after aging at 65°C for 12 h. It is reasoned out that the cubic to hexagonal phase transformation in KLaF$_4$, from the reactions involving La(acac)$_3$ and La(O$i$Pr)$_3$ as the reactants, could possibly be induced by the nano sized crystallites produced in these sets of reactions via interface nucleation mechanism. The first time synthesis of this phase facilitated its structural refinement by the rietveld refinement procedure of its PXRD pattern. The total conservation of atoms between the reactants and the products as well as the non-generation of hazardous HF during the synthesis are some
of the aspects that need to be highlighted from the green chemistry point of view. Also, this method does not require a calcination step or post-annealing process. Phonon energy of this hexagonal KLaF$_4$ lattice has been determined for the first time which is lower than the widely investigated NaYF$_4$ system. Doping the hexagonal polymorph with optically active Er$^{3+}$ ions, illustrated its suitability as a host lattice for the energy upconversion process. A two-photon emission process has been demonstrated to result in the strong green UC in this system, opening a window of additional host matrix for various applications. An optically transparent thick film of PMMA containing the upconverting hexagonal KLaF$_4$:Er$^{3+}$ phosphor was prepared, suggesting its additional futuristic applications. The room-temperature magnetization measurements with varying field of the 3% Tb$^{3+}$ doped monophasic cubic and hexagonal KLaF$_4$ samples showed paramagnetic behavior, adding magnetic function to this material. The higher luminescence intensity of hexagonal KLaF$_4$:Er$^{3+}$(5%) over the cubic KLaF$_4$:Yb$^{3+}$(20%)/Er$^{3+}$(2%) samples demonstrated the dominant role of the symmetry over the presence of sensitizer in this host lattice.
References:


