Excitation Wavelength Dependent Photoluminescence and Photochromic Studies of Yb\(^{3+}/Er^{3+}\) Doped \(\beta\)-KYF\(_4\) and \(\beta\)-NaYF\(_4\) Nanoparticles

Pratik S. Solanki\(^{a,b}\), Sangeetha Balabhadra\(^{a,b}\), Lara D. Browne\(^{b,c,d}\), Michael F. Reid\(^{a,b}\), Nathaniel J. L. K. Davis\(^{b,c,d}\), Jon-Paul R. Wells\(^{a,b}\) *

\(^{a}\)School of Physical and Chemical Sciences, University of Canterbury, Christchurch 8140, New Zealand

\(^{b}\)The Dodd-Walls Centre for Photonic and Quantum Technologies, New Zealand

\(^{c}\)School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington 6140, New Zealand

\(^{d}\)The MacDiarmid Institute for Advanced Materials and Nanotechnology, New Zealand

* Corresponding author email: jon-paul.wells@canterbury.ac.nz

KEYWORDS

KYF\(_4\), NaYF\(_4\), nanoparticles, upconversion fluorescence, color purity, quantum efficiency, color-coordinate temperature

ABSTRACT

We report both resonant and off-resonant laser excitation of Er\(^{3+}\) upconversion fluorescence and colour tunability in Er\(^{3+}/Yb^{3+}\) co-doped KYF\(_4\) and NaYF\(_4\) nanoparticles. The nanoparticles were prepared using a hydrothermal method with particle sizes of 74 ± 20 nm and 345 ± 91 nm for \(\beta\)–KYF\(_4\) and \(\beta\)–NaYF\(_4\), respectively. The Yb\(^{3+}\) \(2F_{7/2} \rightarrow 2F_{5/2}\) absorption spectra exhibit absorption maxima at 10237 cm\(^{-1}\) (977 nm) for \(\beta\)–NaYF\(_4\) and 10267 cm\(^{-1}\) (974 nm) for \(\beta\)–KYF\(_4\) nanoparticles. The Er\(^{3+}\) upconversion fluorescence spectra consist of the \(^2H_{11/2}, ^4S_{3/2},\) and \(^4F_{9/2} \rightarrow ^4I_{15/2}\) transitions for either 974, 977 or 980 nm laser excitation in both materials. We
observed an enhancement in the upconversion intensity by a factor of up to 20 for $\beta$–KYF$_4$ and 1.5 fold for $\beta$–NaYF$_4$ under resonant excitation compared with off-resonant excitation at 980 nm. Tuneable upconversion fluorescence wavelength was achieved in $\beta$–KYF$_4$:Yb/Er nanoparticles by adjusting the excitation wavelength. The CIE chromaticity coordinates are (0.6836, 0.3151) with a highest red colour purity of 99.70% for $\beta$–KYF$_4$ (4700 K) and (0.3953, 0.5915) with a colour purity of 96.84% for $\beta$–NaYF$_4$ (4533 K) nanoparticles. The respective absolute upconversion quantum yields are 1.18% and 2.34% under low power density (1.65 W.cm$^2$).

1. Introduction

Lanthanide ion doped near-infrared to visible upconverting nanomaterials have been the subject of many investigations over the last two decades due to their attractive optical properties, making them favourable materials in sensing and imaging, lighting, display technologies, and drug delivery [1-4]. Their spectroscopic properties derive from the lanthanide contraction whereby the 4f valence shell is shielded from its environment by closed outer shells resulting in sharp absorption and fluorescence lines, long fluorescent lifetimes (up to tens of ms) as well as high photo-stability and colour purity [5-7]. However, increasing the output fluorescent intensity is necessary for many applications. To address this challenge, several strategies have been implemented to enhance the fluorescence (intensity, quantum efficiency) and photometric (chromaticity, colour purity) properties of the upconverting nanomaterials. The most promising strategies reported to enhance the fluorescence properties are the host matrix, size, shape, laser excitation density, excitation wavelength, crystal structure, and other dopant ions. However, the effect of such parameters on photometric behaviour is less often reported. So far, only the lanthanide ion concentration [8], laser excitation density [9, 10], and irradiation time [11] dependent colour tuning have been reported. We are not aware of investigations into the effect of excitation wavelength on the colour tuning of Yb$^{3+}$/Er$^{3+}$ doped upconverting nanoparticles.

Fluoride-based nanomaterials containing trivalent yttrium cations are an excellent choice as a host material because they provide a convenient site for substituting lanthanide ions with the same valence. Moreover, fluoride materials have relatively low phonon energies (~350 cm$^{-1}$), thereby minimising non-radiative relaxation, ensuring good fluorescence quantum efficiencies for the principal emitting levels [12, 13]. In this study, we have chosen sodium yttrium fluoride
(NaYF₄) and potassium yttrium tetrafluoride (KYF₄) since it has an isomorphic structure of NaYF₄. As with NaYF₄, KYF₄ exists in two phases: cubic (α) and hexagonal (β), depending on the synthesis temperature [14]. The hexagonal phase of KYF₄ and NaYF₄ matrices have a multi-site structure in which lanthanide dopant ions are randomly distributed into different sites. Typically, lanthanide ions occupy two different cationic sites in NaYF₄, while KYF₄ contains three layers of cation sites stacked in an 'abc' sequence perpendicular to the c axis. [14-17]. Unlike NaYF₄, only a few studies are reported in the literature on α-KYF₄ nanoparticles [13, 18, 19] and almost none related to β-KYF₄ [20].

In the present work, we have synthesized Yb³⁺/Er³⁺ co-doped NaYF₄ and KYF₄ upconverting nanoparticles. Both nanoparticle systems were prepared via a hydrothermal synthesis method followed by calcination. The as-synthesized nanoparticles were characterized using powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM) techniques. High-resolution absorption spectra were measured using Fourier transform infra-red (FTIR) spectroscopy. We have investigated the Er³⁺ upconversion luminescence properties of both KYF₄:Yb/Er and NaYF₄:Yb/Er using in and off-resonant excitation. In addition, we present measurements of the chromaticity, colour purity, colour coordinate temperature (CCT) for these two phosphors. Finally, we have also performed quantum efficiency measurements at the low laser power density of both nanoparticles.

2. Experiment

2.1 Materials

As the starting reagents, ytterbium nitrate pentahydrate (Yb(NO₃)₃·5H₂O, 99.90%, Sigma-Aldrich), yttrium nitrate (Y(NO₃)₃, 99.90%, Sigma-Aldrich), and erbium nitrate pentahydrate (Er(NO₃)₃·5H₂O, 99.90%, Sigma-Aldrich) were utilized. Anhydrous potassium fluoride (KF, BDH laboratory, 98.00%) and sodium fluoride (NaF, Riedel-de-Haën Research Chemicals, 99.00%) were used as the alkali ion and fluoride source. To wash the samples, Milli-Q water, ethanol (Analytical grade, 99.50%), nitric acid (Merck, 65.00%), and acetone (Analytical grade, 99.98%) were used, and these were also employed for preparing the samples for characterization measurements.
2.2 Synthesis of (α and β phase) MYF₄ (M = K, Na):Yb³⁺/Er³⁺ upconverting nanoparticles

β-MYF₄ (M = K⁺, Na⁺) nanoparticles embedded with 20 mol% Yb³⁺ and 2 mol% Er³⁺ were prepared via a hydrothermal method. Two different autoclaves were used to prepare the KYF₄ and NaYF₄ nanoparticles. 0.090 g Yb(NO₃)₃·5H₂O (0.2 mmol), 0.009 g Er(NO₃)₃·5H₂O (0.02 mmol) and 0.215 g Y(NO₃)₃ (0.78 mmol) were dissolved in a solution of Milli-Q water and ethanol (2:3) and vigorously stirred to form a homogenous rare-earth metal complex solution. Then, KF (10 mmol, 0.580 g) or NaF (10 mmol, 0.420 g) was added to the above rare-earth metal complex solution to obtain Yb³⁺/Er³⁺ doped KYF₄ and NaYF₄. After stirring for 30 min, the as-obtained milky solution was transferred into a 200 mL Teflon-lined stainless-steel autoclave and then heated at 200 °C for 3 h. The autoclave was quickly brought to room temperature to limit the reaction time and, consequently, the growth of the nanoparticles. The precipitate was collected through centrifugation (7000 rpm, 10 min) and thoroughly washed with ethanol and Milli-Q water three times, and then kept for drying at 80 °C for 12 h. The nanopowders obtained are α-KYF₄:Yb/Er and α-NaYF₄:Yb/Er. The as-synthesised α-phase nanoparticles are then calcined at 500 °C for 3 h in a furnace to obtain β-KYF₄:Yb/Er and β-NaYF₄:Yb/Er nanoparticles. The upconverting nanoparticles were prepared using the nominal molar concentrations of Yb³⁺/Er³⁺ (20:2 mol %) to optimise energy transfer rates whilst avoiding concentration quenching processes [21, 22].

2.3. Characterisation

Powder X-ray diffraction patterns were collected on a RIGAKU 3 kW SmartLab X-ray diffractometer with CuKα₁ radiation source, λ=1.5406 Å, operating at 40 kV and 30 mA, in the 2θ range 10° to 60° with a 0.5°·min⁻¹ scanning rate and 0.01° step size in the reflection scanning mode. The reference data was taken from the JCPDS database. High-resolution transmission electron microscope (TEM) images were obtained using a PHILIPS CM200 transmission electron microscope operating at 200 kV. The concentration of lanthanide ions was investigated using an Agilent 4210 Microwave Plasma Atomic Emission Spectrophotometer (MP-AES). The samples were prepared using 0.10-gram powder digested by 2 wt% HNO₃ acid and diluted to 10 ppm in MiliQ-water. The absorption measurements were performed using a Bruker Vertex 80 FTIR having better than 0.1 cm⁻¹ resolution with an optical path purged by N₂ gas. For the absorption measurements, the air-dried powders of nanoparticles were pressed using a pellet maker to form a thin pellet (~1 mm), which was then placed into a sample holder. Upconversion fluorescence spectra were measured using an Intense 3120 model laser diode.
controlled with a Newport 560B laser diode driver and Newport 350B temperature controller. The laser wavelength is tuned from 972 to 982 nm by changing the laser diode temperature. The laser has a linewidth of around 1 nm. Fluorescence spectra in the visible region were recorded on a modular double grating iHR550 spectrophotometer (Horiba) coupled to an R3896 Hamamatsu photomultiplier. An external UV-VIS mini-spectrometer (Ocean Optics USB2000) was used to monitor the laser diode wavelength. The absolute photoluminescence quantum yield (PLQY) were calculated as described by de Mello et al. [23]. PLQEs were taken with an 8-inch Labsphere integrating sphere coupled to an Andor Solis Kymera 328i spectrograph and DU490A-1.7 iDus InGaAs detector array. The samples were formed into pellets for measurement by taking 100 mg of sample and pressing them under 9 tonnes of pressure in a hydraulic press. The samples were then excited via a high stability 975 nm Infrared Diode Laser (MDL-III-975-1W) powered by a DPSSL Driver laser power supply. Incident power was measured on a ThorLabs - PM130D - Digital Power & Energy Console and S130C- Slim Si Sensor, Power meter. The spot size was measured using a Thorlabs - BC106N-VIS/M - CCD Camera Beam Profiler.

3. Results and Discussion

3.1. Phase and morphology

Powder XRD patterns of the prepared α and β-phase of KYF₄:Yb/Er and NaYF₄:Yb/Er nanoparticles are shown in Fig. 1 (a-d), respectively. The diffractograms of the α-KYF₄:Yb/Er and β-KYF₄:Yb/Er nanoparticles indicate the cubic (space group: Fm̅3m) and hexagonal (space group: P31) phase, well-matched with their standard XRD patterns (ICDD No. 00–065–0575 and (JCPDS No. 79–1688), respectively, (Fig. 1(a) and (b)) [24, 25]. The cubic KYF₄:Yb/Er diffraction pattern is compared with the standard XRD pattern of cubic KErF₄ due to the unavailability of the standard XRD pattern of cubic KYF₄ in the database. We assume that there would not be a significant shift in the diffraction pattern of cubic KErF₄ because the ionic radius of the Er³⁺ (0.1004 nm) and Y³⁺ (0.1040 nm) ion is comparable [26]. A similar comparison was made in previous work [25]. The diffractograms of the α-NaYF₄:Yb/Er and β-NaYF₄:Yb/Er nanoparticles demonstrate the cubic (space group: Fm̅3m) and hexagonal (space group: P63/m) phase, compared with standard XRD patterns (JCPDS No. 77–2042 and JCPDS No. 28–1192), respectively, (Fig. 1(c) and (d)) [27]. There are no other peaks detected in the XRD patterns, which indicates that pure α– and β–phases of the KYF₄:Yb/Er and...
NaYF₄:Yb/Er nanoparticles have formed. However, a few extra peaks for α–NaYF₄:Yb/Er show modest quantities of impurities, which are eliminated during the calcination process. The diffraction peaks are slightly shifted towards a higher angle in all cases, showing crystal strain produced by the high concentration of Yb³⁺ (20 mol%) and Er³⁺ (2 mol%) ions.

![Image of X-ray diffraction patterns](image)

**Fig. 1.** Powder X-ray diffraction patterns of (a and b) α−KYF₄:Yb/Er, (c and d) α− and β−NaYF₄:Yb/Er nanoparticles. The standard cards of α−KErF₄ (PDF Card No.: 00−065−0575), β−KYF₄ PDF (JCPDS No. 79−1688), α−NaYF₄ (JCPDS No. 77−2042), β−NaYF₄ (JCPDS No. 28−1192) are also provided in the figure. (*) indicates the impurities in α−NaYF₄:Yb/Er.

The morphology and the particle size distribution of the nanoparticles have been examined by transmission electron microscopy. Fig. 2 (a-d) shows the TEM images of the α− and β−phase of KYF₄:Yb/Er and NaYF₄:Yb/Er nanoparticles, respectively, which indicates that nanoparticles have an irregular shape with a broad size distribution. The nanoparticle sizes were measured (from Fig. 2 (a-d) for over 100 nanoparticles), and the size distributions were fitted to a log-normal distribution (Fig. 2 (e-h)), which resulted in an average diameter value of 24 ± 4 nm, 74 ± 20 nm for α− and β−KYF₄:Yb/Er, and 69 ± 16 nm, 345 ± 91 nm for α− and β−NaYF₄:Yb/Er nanoparticles, respectively. The size difference between cubic phase KYF₄:Yb/Er and NaYF₄:Yb/Er nanoparticles is approximately a factor of three, indicating that the growth rates are affected by the different cation (Na⁺/K⁺) sources [28]. After calcination,
the hexagonal phase of KYF₄ has three times, and NaYF₄ has five times higher nanoparticle size than in their corresponding cubic phase. A significant particle size increase was found due to the change of the crystal phase and the continuous agglomeration of fine particles [29, 30]. Furthermore, the molar concentration of lanthanides ions in the nanoparticles were determined by Microwave Plasma Atomic Emission Spectrophotometer (MP-AES). MP-AES shows a good agreement with the stoichiometric concentrations used as the precursors during the synthesis. The molar concentration of Y, Yb and Er were 71.7%, 25.6%, 2.4% and 72.4%, 24.4%, 2.1% for β-KYF₄:Yb/Er and β-NaYF₄:Yb/Er, respectively. The NaREF₄ type nanoparticle system has been well investigated and the hexagonal phase is found to be the most efficient and brighter than the cubic phase. The hexagonal phase has a multi-site structure compared to the cubic phase [26, 31-34]. Therefore, we performed and compared all the photoluminescence and photochromic measurements only on the β-KYF₄:Yb/Er and β-NaYF₄:Yb/Er nanoparticles.

![Fig. 2. TEM images of (a) α–KYF₄:Yb/Er, (b) β–KYF₄:Yb/Er, (c) α–NaYF₄:Yb/Er, and (d) β–NaYF₄:Yb/Er nanoparticles. (e) to (h) Corresponding size distribution histograms (over 100 nanoparticles were measured) of the nanoparticles. The solid lines are the best fit of the experimental data to a log-normal distribution.](image)

3.2. Yb³⁺ near-infrared absorption and Er³⁺ visible upconversion fluorescence

The normalised absorption spectra at 10 K and 297 K for β-KYF₄:Yb/Er and β-NaYF₄:Yb/Er nanoparticles are shown in Fig. 3 (a) and (b), respectively. Both samples exhibit characteristic absorption peaks associated with the 2F₇/₂→2F₅/₂ inter-multiplet transitions of the Yb³⁺ ion measured in the near-infrared spectral region (10000–11000 cm⁻¹). These absorption spectra are well-matched with the literature data reported for the KYF₄:10% Yb³⁺ crystal and
NaYF$_4$:Yb$^{3+}$/Er$^{3+}$ nanoparticles [26, 35]. At 10 K, the measured Yb$^{3+}$ absorption spectra have sharp peaks at 10268 cm$^{-1}$ (974 nm) for $\beta$-KYF$_4$:Yb/Er and 10236 cm$^{-1}$ (977 nm) for $\beta$-NaYF$_4$:Yb/Er. The shift in the absorption peaks is due to the different crystal structures of the host materials, which provide different crystal field potentials to the lanthanide ions. At 297 K, the absorption spectra are similar, albeit having broader spectral linewidths because of phonon-induced dephasing and multiphonon relaxation at higher temperatures. The $^4I_{15/2} \rightarrow ^4I_{11/2}$ absorption transition of Er$^{3+}$ is centred near 10305 cm$^{-1}$ and overlaps with the Yb$^{3+}$ spectral features [36].

The absorption spectra demonstrate that 10268 cm$^{-1}$ (974 nm) and 10236 cm$^{-1}$ (977 nm) are the optimum laser excitation frequencies for the $\beta$-KYF$_4$:Yb/Er and $\beta$-NaYF$_4$:Yb/Er nanoparticles in order to achieve the maximum fluorescence intensity. These wavelengths are away from the most commonly used 980 nm laser diode excitation source for upconverting nanoparticles. To compare the effect of resonant and off-resonant excitation on the photoluminescence and photochromic behaviour of $\beta$-KYF$_4$:Yb/Er and $\beta$-NaYF$_4$:Yb/Er nanoparticles, both nanoparticles were excited at 974 nm, 977 nm and the commonly used 980 nm laser excitation wavelength.

Fig. 3. Normalised FTIR absorption spectra for $^2F_{7/2} \rightarrow ^2F_{5/2}$ Yb$^{3+}$ inter-multiplet measured at 10 K (black line) and 297 K (red line) for (a) $\beta$-KYF$_4$:Yb/Er and (b) $\beta$-NaYF$_4$:Yb/Er nanoparticles.

Fig. 4. shows the room temperature upconversion fluorescence spectra measured using 974 nm, 977 nm and 980 nm laser excitation wavelength at a laser excitation density of 15 W·cm$^{-2}$. Both nanoparticles show the characteristic Er$^{3+}$ transitions: $^2H_{11/2} \rightarrow ^4I_{15/2}$ (517 – 527 nm) and $^4S_{3/2} \rightarrow ^4I_{15/2}$ (535 – 560 nm) green fluorescence bands, as well as the $^4F_{9/2} \rightarrow ^4I_{15/2}$ (640 – 680 nm) red fluorescence band.
For β-NaYF₄:Yb/Er, we observe an enhancement in the integrated area of the green ($^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) and red ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$) upconversion fluorescence by a factor of approximately 1.5 for resonant 977 nm laser excitation when compared with either 974 nm or 980 nm excitation, using a fixed laser power density (15 W·cm⁻²) and identical measurement conditions. Therefore, the red to green (R/G) intensity ratio is the same (~2.3) under 974 nm, 977 nm or 980 nm laser excitation, as shown in table 1. Thus the upconversion intensity for β-NaYF₄:Yb/Er nanoparticles follow the absorption spectral profile (and thus is dominated by ground-state absorption transitions); changing the excitation wavelength does not affect the upconversion energy transfer aside from the fluorescence intensity. This behaviour is also seen in KY₃F₁₀:Yb/Er nanoparticles reported by our group [37]. By contrast, the β-KYF₄:Yb/Er nanoparticles exhibit a decrease in the upconversion fluorescence, relative to that of resonant excitation, by a factor of 2 for the green band and 6 for the red band when exciting at 977 nm, and a decrease of a factor of 7 for the green band and 20 for the red band when exciting at 980 nm. The non-uniform variation in the intensity of the green and red fluorescence bands indicates that they originate from fundamentally different excitation pathways. The R/G ratios are around 50:1, 15:1 and 17:1 for 974 nm, 977 nm and 980 nm laser excitation. The drastic change in the value of the R/G ratio strongly suggests that the red upconversion fluorescence has its origins in resonant ground state absorption, whilst the green band is probably due to non-resonant excited state absorption. This observed behaviour of β-KYF₄:Yb/Er also indicates a possibility for tuning the upconversion fluorescence ‘colour’ by adjusting the excitation wavelength similar to that observed in β-KYF₄:Yb/Er nanoparticles by varying the concentration of Yb/Er [20]. We speculate that strong energy back transfer between Yb³⁺ and Er³⁺ ion is the reason for the intense red colour of the β-KYF₄:Yb/Er upconversion fluorescence as singly doped β-KYF₄:Er (2 mol%) fluoresces primarily in the green for 974 nm excitation [38, 39].
Fig. 4. Room temperature Er$^{3+}$ upconversion fluorescence spectra measured for (a) β−KYF$_4$:Yb/Er and (b) β−NaYF$_4$:Yb/Er nanoparticles for 974 nm (black line), 977 nm (red line) and 980 nm (blue line) laser excitation. All the spectra were recorded with 15 W·cm$^{-2}$ laser power excitation density.

Table 1. Red to green ratio (R/G) in β−NaYF$_4$:Yb/Er and β−KYF$_4$:Yb/Er nanoparticles under 974 nm, 977 nm and 980 nm laser excitation with 15 W·cm$^{-2}$ laser power excitation density.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\lambda_{\text{ex}}$ (nm)</th>
<th>Red/Green</th>
</tr>
</thead>
<tbody>
<tr>
<td>β−NaYF$_4$:Yb/Er</td>
<td>974</td>
<td>2.29:1</td>
</tr>
<tr>
<td></td>
<td>977</td>
<td>2.31:1</td>
</tr>
<tr>
<td></td>
<td>980</td>
<td>2.36:1</td>
</tr>
<tr>
<td>β−KYF$_4$:Yb/Er</td>
<td>974</td>
<td>49.92:1</td>
</tr>
<tr>
<td></td>
<td>977</td>
<td>15.36:1</td>
</tr>
<tr>
<td></td>
<td>980</td>
<td>17.13:1</td>
</tr>
</tbody>
</table>

To understand the UC mechanism, power-dependent upconversion fluorescence intensities of the nanoparticles were measured. In general, the UC emission intensity ($I_{\text{UC}}$) is directly proportional to the $n^{th}$ power of the excitation laser power ($I_{\text{LP}}$): $I_{\text{UC}} \propto I_{\text{LP}}^n$, where $n$ is the absorbed photon number per visible photon emitted, obtainable from the slope of a plot of $\ln(I_{\text{UC}})$ versus $\ln(I_{\text{LP}})$. The slopes of the log-log curves for the two green, (2H$_{11/2} \rightarrow$ 4I$_{15/2}$ and 4S$_{3/2} \rightarrow$ 4I$_{15/2}$), and red (4F$_{9/2} \rightarrow$ 4I$_{15/2}$) fluorescence bands in the β−KYF$_4$:Yb/Er nanoparticles are 2.60, 1.95, 2.04 (Fig. 5 (a)) for 974 nm excitation and 2.56, 1.95, 1.66 (Fig. 5 (b)) at 977 nm excitation and 2.44, 2.01, 1.82 (Fig. 5 (c)) for 980 nm excitation. And the slope values for β−NaYF$_4$:Yb/Er nanoparticles are 2.28, 2.10, 2.11 (Fig. 5 (d)) for 974 nm excitation and 2.24, 2.05, 2.05 (Fig. 5 (e)) for 977 nm excitation and 2.15, 1.97, 1.93 (Fig. 5 (f)) for 980 nm excitation. Thus, the exact excitation wavelength does not seem to influence the order of the
upconversion process. Moreover, the $n$ value for both the combined green upconversion ($^2H_{11/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$) and red upconversion ($^4F_{9/2} \rightarrow ^4I_{15/2}$) is nearly 2, in β-NaYF$_4$:Yb/Er, confirming the findings reported in the literature [40, 41]. Interestingly, for β-KYF$_4$:Yb/Er, the $n$ value for the combined green upconversion is much larger than 2, suggesting that the process is, at a minimum, a three-photon process, while for the red upconversion, the $n$ value is very close to 2, suggesting a minimum of a two-photon process [20]. The combination of predominantly red fluorescence and a three-photon excitation process involved in green upconversion is rarely reported. Yanping Li et al. observed the same phenomena in Lu$_2$O$_3$:Yb$^{3+}$, Er$^{3+}$ nanocrystals and suggested that the three-photon process for the green upconversion is related to the red-emitting level as follows: $^2F_{5/2}$ (Yb$^{3+}$) + $^4F_{9/2}$ (Er$^{3+}$) $\rightarrow$ $^2F_{7/2}$ (Yb$^{3+}$) + $^4G_{11/2}$ (Er$^{3+}$), which relaxes quickly to the $^2H_{11/2}$/$^4S_{3/2}$ (Er$^{3+}$) states by non-radiative relaxation (Fig. 6) [42].

Fig. 5. Log-log plots of the upconversion fluorescence intensity versus laser excitation power for the $^2H_{11/2}$ $\rightarrow$ $^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions of the Er$^{3+}$ ion in (a, b and c) β-KYF$_4$:Yb/Er and (d, e and f) β-NaYF$_4$:Yb/Er nanoparticles for 974 nm, 977 nm and 980 nm laser excitation, respectively.
Fig. 6. Energy level diagram for (a) β−NaYF₄:Yb/Er and (b) β−KYF₄:Yb/Er nanoparticles shows possible excitation and de-excitation mechanisms under IR excitation. ET – Energy Transfer; CR – Cross Relaxation; BET-Back Energy Transfer; MPR- Multiple Photons Relaxation.

3.3. Photochromic studies

The upconversion fluorescence spectra of both samples (shown in Fig. 4 (a and b)) for different NIR excitation wavelengths (974 nm, 977 nm and 980 nm) have been converted into chromaticity coordinates (Commission Internationale de l’éclairage CIE 1931) and shown in Fig. 7 as measured at a fixed laser power density of 15 W·cm⁻². The CIE chromaticity coordinates are given in Table 2. The coordinates of the β−NaYF₄:Yb/Er nanoparticles are (0.3949, 0.5918), (0.3953, 0.5915) (0.3981, 0.5896) for 974 nm, 977 nm and 980 nm laser excitation, respectively. The coordinates are similar for all excitation wavelengths, lying within the yellowish-green zone in the CIE diagram (shown in Fig. 7) with a dominant 563 nm fluorescence wavelength. For the β−KYF₄:Yb/Er nanoparticles, the coordinates are (0.6836, 0.3151), (0.6101, 0.3865) and (0.6212, 0.3758) for 974 nm, 977 nm and 980 nm laser excitation, respectively. Thus for non-resonant excitation, the fluorescence is reddish-orange (centred at 597 nm and 599 nm for excitation at 977 nm and 980 nm, respectively). By contrast, for resonant excitation at 974 nm, the fluorescence is bright red (centred at 617 nm), which is in good agreement with the National Television System Committee (NTSC) primary system.
[NTSC ideal red =0.67,0.33] and also superior to commercial Y₂O₂S:Eu³⁺ red-emitting phosphors [(0.622, 0.351)] [43] [44].

Table 2. Comparison of various colorimetric properties, i.e., colour coordinates (x, y), dominant wavelength, color purity (%), and CCT (K) of β−KYF₄:Yb/Er and β−NaYF₄:Yb/Er nanoparticles.

<table>
<thead>
<tr>
<th>Material</th>
<th>λₑₓ (nm)</th>
<th>CIE chromaticity coordinates (x, y)</th>
<th>Dominant wavelength</th>
<th>Colour purity (%)</th>
<th>CCT (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>β−KYF₄:Yb/Er</td>
<td>974</td>
<td>D (0.6836, 0.3151)</td>
<td>617</td>
<td>99.70</td>
<td>4700</td>
</tr>
<tr>
<td></td>
<td>977</td>
<td>E (0.6101, 0.3865)</td>
<td>597</td>
<td>99.05</td>
<td>1761</td>
</tr>
<tr>
<td></td>
<td>980</td>
<td>F (0.6212, 0.3758)</td>
<td>599</td>
<td>99.30</td>
<td>1875</td>
</tr>
<tr>
<td>β−NaYF₄:Yb/Er</td>
<td>974</td>
<td>A (0.3949, 0.5918)</td>
<td>563</td>
<td>96.83</td>
<td>4538</td>
</tr>
<tr>
<td></td>
<td>977</td>
<td>B (0.3953, 0.5915)</td>
<td>563</td>
<td>96.84</td>
<td>4533</td>
</tr>
<tr>
<td></td>
<td>980</td>
<td>C (0.3981, 0.5896)</td>
<td>564</td>
<td>97.02</td>
<td>4489</td>
</tr>
</tbody>
</table>

The colour purity of the samples was calculated using the following equation:[45] [46]

\[
\text{Color purity} = \frac{\sqrt{(x - x_i)^2 - (y - y_i)^2}}{\sqrt{(x_d - x_i)^2 - (y_d - y_i)^2}} \times 100\%
\]

where (x, y) represents the colour coordinates of the sample point, (xᵢ, yᵢ) is the illuminant point of the 1931 CIE Standard Source with coordinates of (0.3101, 0.3162), and (xᵩ, yᵩ) refers to the colour coordinates of the dominant wavelength. The calculated colour purities of the β−KYF₄:Yb/Er nanoparticles are 99.70%, 99.05% and 99.30% under 974 nm, 977 nm, and 980 nm laser excitation, respectively (as listed in Table 2). This is the highest red colour purity among different red phosphors reported in the literature such as CaWO₄:Eu³⁺ (91.3%) [[44]] Ca₂GdTaO₆:0.4Eu³⁺ (96%) [[47]] Ba₆Gd₂Ti₄O₁₇:Eu³⁺ (94.41%) [[48]] Cs₁EuGe₃O₉:Eu³⁺ (95%) [[49]], Sr₉Al₆O₁₈:Sm³⁺ (90%) [[50]]. For β−NaYF₄:Yb/Er nanoparticles, the calculated colour purity is ~97% for the three laser excitation wavelengths employed here. This is amongst the highest yellowish-green colour purity achieved for Yb³⁺/Er³⁺ based upconverting green phosphors, such as KY(WO₄)₂:Yb/Er (95%) [[51]], VO₂:Yb/Er (88%) [[11]], LaAlGe₂O₇:Er (92%) [[43]], Ca₂Gd₈Si₆O₂₆:Er (96%) [[52]].

The colour coordinate temperature (CCT) was calculated using Mc.Camy’s approximation [53]

\[
\text{CCT} = 449n^3 + 352n^2 + 6823n + 5520.33
\]
where \( n = (x−0.3230)/(0.1859−y) \), in which \( x \) and \( y \) are the CIE chromaticity coordinates of the nanomaterials (Fig. 7). The CCT value rating below 3200 K is considered as a “warm” source (lamp), while the above value is regarded as a “cold” source \([54, 55]\). The calculated CCT values for the \( \beta \)-KYF\(_4\):Yb/Er nanoparticles are 4700 K, 1761 K and 1875 K, whilst the \( \beta \)-NaYF\(_4\):Yb/Er nanoparticles, they are 4538 K, 4533 K and 4589 K for 974 nm, 977 nm and 980 nm laser excitation respectively. These CCT values demonstrate that \( \beta \)-KYF\(_4\):Yb/Er nanoparticles can be considered for use as a \textit{switchable light source} because it serves as either a warm or cold light source for off-resonant and resonant excitation, respectively. Whereas the CCT values of \( \beta \)-NaYF\(_4\):Yb/Er nanoparticles are similar for all laser excitation wavelengths, which comes under the cold source range.

![Fig. 7. CIE chromaticity diagram showing the colour coordinates calculated from the fluorescence spectra for (A, B, and C) \( \beta \)-NaYF\(_4\):Yb/Er and (D, E, and F) \( \beta \)-KYF\(_4\):Yb/Er nanoparticles for 974 nm, 977 nm and 980 nm laser excitation, respectively. Inset shows efficient visible yellowish-green and red UC luminescence for (i) \( \beta \)-NaYF\(_4\):Yb/Er for 977 nm and (ii) \( \beta \)-KYF\(_4\):Yb/Er for 974 nm excitation, with a 15 W·cm\(^{-2}\) laser power density.](image)

### 3.4. Absolute photoluminescence quantum yield

The absolute photoluminescence quantum yield (PLQY) of our samples were calculated using the method reported by de Mello \textit{et al.} \([23, 56]\).

\[
\text{PLQY} = \frac{\text{number of emitted photons}}{\text{number of absorbed photons}}
\]
The observed absolute PLQY was 1.18% and 2.34% for $\beta$-KYF$_4$:Yb/Er and $\beta$-NaYF$_4$:Yb/Er, respectively, under 1.65 W cm$^{-2}$ laser power density. However, it is evident that the nanoparticle size strongly affects the quantum efficiency of nanoparticles, and as such, these two values are not entirely comparable [56, 57]. Nevertheless, compared with the previously reported literature (listed in Table 3), both $\beta$-KYF$_4$ and $\beta$-NaYF$_4$ amongst the highest absolute quantum yield values for the Yb-Er system under very low excitation power density. Additionally, having a small size (<100 nm) and a high value of absolute PLQY under low power density, which is close to the biological window (0.7 W cm$^{-2}$), of $\beta$-KYF$_4$:Yb/Er makes it a perfect candidate for bio-imaging application [58].

Table 3. Absolute PLQY (%) of various fluoride nanoparticles based on particle size and laser power-density (W cm$^{-2}$). All the PLQY values were integrated into a 500-700 nm spectral range under NIR laser excitation.

<table>
<thead>
<tr>
<th>Material</th>
<th>Size</th>
<th>Absolute QY (%) (Sum of green and red QY)</th>
<th>Power (W cm$^{-2}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$–NaYF$_4$:20%Yb/2%Er</td>
<td>Bulk</td>
<td>3.0 ± 0.3</td>
<td>20</td>
<td>[56]</td>
</tr>
<tr>
<td></td>
<td>100 nm</td>
<td>0.3 ± 0.1</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 ± 1 $\mu$m</td>
<td>4.16 ± 0.6</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>9%Yb,1%Er:La$_2$O$_3$S</td>
<td>5 ± 2 $\mu$m</td>
<td>4.71 ± 0.7</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>3%Yb,7%Er:Gd$_2$O$_3$S</td>
<td>5 ± 2 $\mu$m</td>
<td>2.28 ± 0.34</td>
<td>09</td>
<td>[59]</td>
</tr>
<tr>
<td>1%Yb,1%Er:Y$_2$O$_3$S</td>
<td>5 ± 2 $\mu$m</td>
<td>3.05 ± 0.44</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>$\beta$–NaYF$_4$:18%Yb/2%Er</td>
<td>250 nm</td>
<td>2.5 ± 0.5</td>
<td>50</td>
<td>[57]</td>
</tr>
<tr>
<td></td>
<td>0.5–1.0 $\mu$m</td>
<td>4.8 ± 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiLuF$_4$:20%Yb/1%Er</td>
<td>28 nm</td>
<td>0.11</td>
<td>127</td>
<td>[12]</td>
</tr>
<tr>
<td>LiLuF$_4$:20%Yb/1%Er @LiLuF$_4$ (8-ML)</td>
<td>40 nm</td>
<td>3.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiLuF$_4$:20%Yb/1%Er @LiLuF$_4$ (16-ML)</td>
<td>50 nm</td>
<td>5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KYb$_2$F$_7$:2%Er</td>
<td>100 nm</td>
<td>0.37</td>
<td>-</td>
<td>[60]</td>
</tr>
<tr>
<td>$\beta$–NaYbF$_4$:2%Er</td>
<td>250 nm</td>
<td>0.056</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4. CONCLUSIONS

We have used a hydrothermal method to prepare the cubic and hexagonal phases of Yb\(^{3+}/Er^{3+}\) doped MYF\(_4\) (M=Na\(^+\), K\(^-\)) nanoparticles. The samples were characterized by powder XRD and TEM for phase and morphological analyses. The Yb\(^{3+}\) absorption spectra of the two nanoparticles exhibit different absorption maxima at 10268 cm\(^{-1}\) (974 nm) and 10236 cm\(^{-1}\) (977 nm). The Er\(^{3+}\) upconversion fluorescence spectra consist of \(2\text{H}_{11/2}, 4\text{S}_{3/2}, \text{and } 4\text{F}_{9/2} \rightarrow 4\text{I}_{15/2}\) transitions for resonant and non-resonant laser excitation in both materials. For resonant excitation, \(\beta-KYF_4\) shows a 20 fold increase in overall fluorescence intensity, whereas \(\beta-NaYF_4\) shows a 1.5 fold enhancement for resonant excitation compared with excitation at 980 nm. The highest colour purity was observed for KYF\(_4\) of 99.70%, whilst a value of 96.84% was obtained for NaYF\(_4\). The corresponding CCT is warm light at 4700 K for KYF\(_4\) and cold light at 4533 K for NaYF\(_4\). The measured quantum efficiencies are 1.18% and 2.34% for KYF\(_4\) and NaYF\(_4\), respectively.

DECLARATION OF COMPETING INTERESTS
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

ACKNOWLEDGMENTS

PSS would like to thank the Dodd-Walls Centre for Photonic and Quantum Technologies for the award of a Ph.D. studentship. The authors acknowledge the expert technical assistance of Mr. Shaun Mucalo and Mr. Robert Stainthorpe. In addition, the technical assistance of Mr. Stephen Hemmingson, Mr. Robert Thirkettle, Mr. Graeme MacDonald, is acknowledged.

5. REFERENCES
