

Short communication

Large scale preparation of up- converting YF₃:YbEr nanocrystals with various sizes by solvothermal syntheses using ionic liquid bmimCl

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ABSTRACT

Simple approach to prepare various sizes of YF₃:YbEr nanocrystals in large quantities and their up-converting abilities dependent on preparation times and sodium content are described in this paper. Ionic liquid bmimCl was used in the role of a solvent and NaBF₄ as a fluorination agent. Prepared nanocrystals were characterized by XRD, TEM and up-conversion measurements. The method is suitable for preparation of large quantities of nanocrystals and could be easily adapted and used for relevant important pharmaceutical applications.

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1. Introduction

Rare earths (RE) fluorides are well known for their non-linear optical properties as down-conversion or up-conversion [1–3]. Non-linear optical properties determine their huge potential for both technical and biological utilization. Along with the low systemic toxicity and cytotoxicity of almost absolutely insoluble RE fluorides, these materials are very suitable for medical applications. Very promising way is to use these materials for advanced

drug delivery systems in anticancer treatment [4,5]. A specific issue is utilizing its optical properties for advanced photodynamic therapy [6]. Luminescent rare earth nanomaterials are also interesting as bioprobes [7].

RE nanofluorides can be prepared by the broad variety of methods. Classical method is preparation by synthesis using oleic acid as surfactant and 1-octadecene as a solvent [8,9]. Another method lies in solvothermal preparation using ionic liquids [10–14], high-temperature co-precipitation [15] or thermal decomposition lanthanide trifluoroacetates [16]. Microwave syntheses of RE fluorides are also frequently used [17–20]. Another method used is chemical etching [21].

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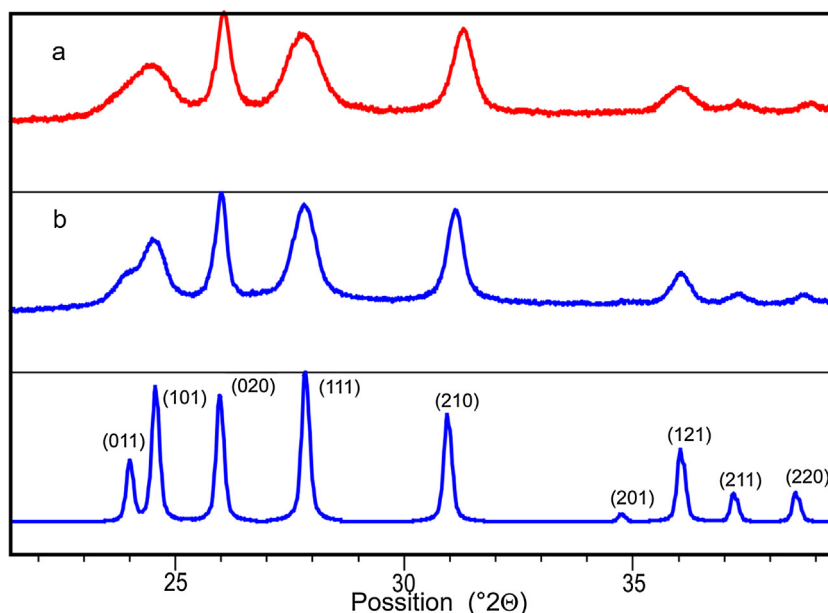


Fig. 1. Apparent difference in peak broadening between a) the smallest nanocrystals and b) the largest nanocrystals. On the bottom is simulated scan orthorhombic phase PDF No. 04-006-0199.

Up-conversion RE fluorides are commonly prepared using hydrothermal synthesis in oleic acid [22] mostly in form of sodium salt [23–25] or with various other cations such as barium [26]. Solvothermal preparation of RE fluorides using ionic liquids is commonly carried out using 1-butyl-3-methylimidazolium chloride (bmimCl), 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆), or 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄) respectively [10–14]. BmimCl is one of the most widely used commercially available ionic liquids; it is a colourless, hygroscopic solid at room temperature. Ionic liquids are commonly described as environmentally friendly “green solvents” because of their negligible vapour pressure; however, they can suffer from environmentally unfriendly degradation processes.

In this study we are presenting a simple preparation of Yb and Er doped nanocrystalline YF₃ with up-converting ability depending on the particle sizes.

2. Results and discussion

Average sizes of prepared nanocrystals depend on reaction times. Based on powder diffraction patterns the prepared phase is determined to be pure orthorhombic YF₃:YbEr phase (compared with card PDF number 04-006-0199). On Fig. 1 comparison of sample with the smallest and the largest diameter and PDF card are shown. Unequal broadening of diffraction patterns indicates irregular shape of nanocrystals. This was confirmed using TEM. For size calculation using XRPD it was selected diffraction pattern at 26.0°2θ. Trends found using XRPD corresponds with sizes

obtained using TEM images (e.g. Fig. 3). For all TEM images see the supplementary.

From control sample annealed for 22 h and from sample annealed for 260 min with Na content 1:1 to stoichiometry the limitation of temperature dependence is apparent. From above we derived that the content of Na⁺ ions originating from NaBF₄ is factor which also influence the crystal sizes (Table 1). With increase of reaction time, the sizes of nanoparticles do not monotonously increase. Also, higher Na content induces smaller size. This can be explained by ionic pressure on forming lattice also by penetration of sodium ions to the crystals. AAS measurements of the samples dissolved in heated HNO₃ confirmed small content of Na⁺ in the samples. Equilibrium between increasing of crystals sizes and dissolving of the surfaces by ionic liquid solvent caused by lower concentrations of rare earths is established, effectively preventing the crystals growth.

As can be seen on Fig. 2 the sample show emission bands which can be attributed to transitions ²H_{11/2} → ⁴I_{15/2} (520 nm), ⁴S_{3/2} → ⁴I_{15/2} (545 nm) and ⁴F_{9/2} → ⁴I_{15/2} (660 nm). It has been found that the preparation time has a significant effect on the emission intensity of up-conversion and distribution of the energy levels (i.e. the wavelength of the emitted light quanta). With increasing time of preparation (40 min, 70 min, 140 min, 180 min, 260 min and 1360 min) increases the overall emission intensity, at shorter times is preferred radiation at approx. 545 nm, while at longer times of preparation starts to be preferred the radiation at approx. 660 nm. Note that the peak at 710 nm is in the most cases not caused by the up-conversion, but it is a measurement artefact presented also in blank sample. Only in case of long-term preparation (1360 min) it appears band which can be attributed to transition ⁴F_{7/2} → ⁴I_{13/2}. Those trends seems to be caused by time of preparation rather than size of prepared nanocrystals. For all up-conversion measurements see the supplementary.

Nanocrystals were prepared in relatively large amounts (up to a gram of the product). Scale is one of the most important advantages of this one-pot syntheses approach using ionic liquids. It is in contrast to other approaches able to prepare ultrafine nanoparticles but extremely diluted such those described in Nature [27]. This approach can be used for the preparation of large

Table 1
Average sizes of nanocrystals as a function of time and sodium content.

time [min]	average diameter [nm]	
	Na	2Na
40	28.0	24.8
70	29.3	28.3
140	29.9	30.7
180	46.9	30.8
260	40.8	32.5
1320	34.4	36.5

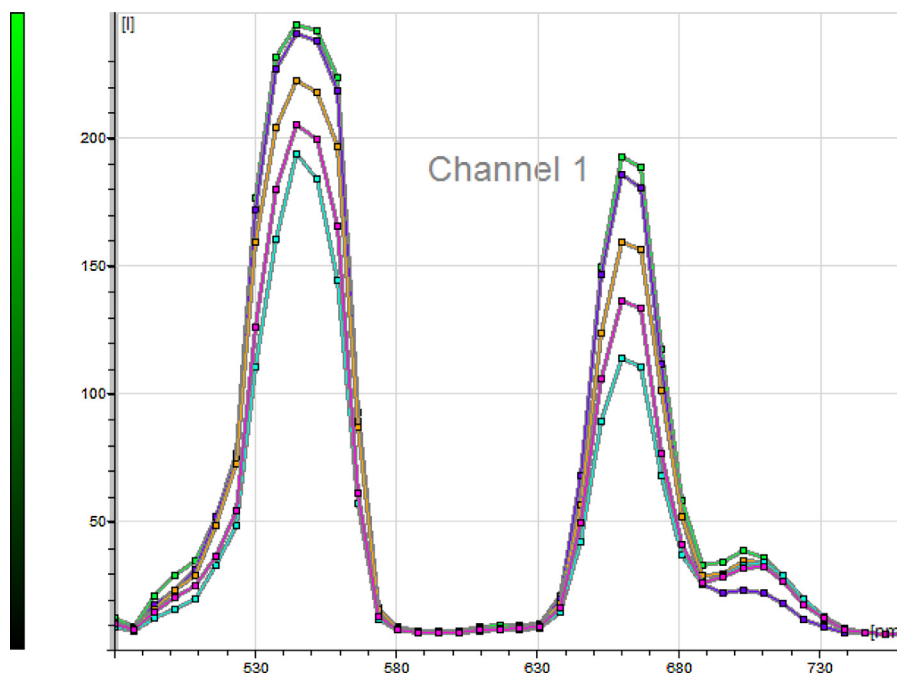


Fig. 2. Typical spectrum of up-conversion of NaYF₄:YbEr nanoparticles.

mass of the up-converting nanocrystals per batch. This is essential for large scale production of this potentially important product.

3. Experimental

The ionic liquid bmimCl, NaBF₄, YCl₃·6H₂O, YbCl₃·6H₂O and ErCl₃·6H₂O were purchased from Sigma-Aldrich Co. LLC. (USA) and stored in desiccator. Ionic liquid bmimCl was melted before experiment approximately at 60 °C.

In typical experiment YCl₃·6H₂O, YbCl₃·6H₂O and ErCl₃·6H₂O were mixed in molar ratio of the elements Y:Yb:Er = 80:18:2. NaBF₄ fluorination agent was added and all mixture was homogenized. Amount of NaBF₄ was calculated to obtain stoichiometry ratio of Na to RE 1:1 and 2:1. Prepared powder was introduced to the melted bmimCl contained in the PFA container and mixed by spatula. Next the mixture was put into drying kiln heated on 240 °C for 40, 70, 140, 180 and 260 min. Control sample was annealed for 22 h.

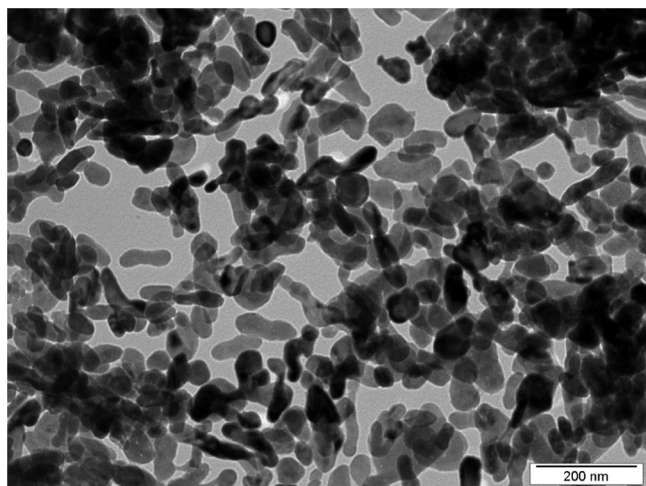


Fig. 3. TEM image of the largest nanocrystals prepared.

X-ray powder diffraction data were collected at room temperature with an X'Pert PRO $\theta - \theta$ powder diffractometer utilising a parafocusing Bragg-Brentano geometry and CuK α radiation ($\lambda = 1.5418 \text{ \AA}$, $U = 40 \text{ kV}$, $I = 30 \text{ mA}$). Samples were characterized by XRD, and the nanocrystal sizes were identified from the full width at half maximum (FWHM) of a selected intense standing peak. The X'Pert HighScore Plus program was used to process the XRD data from and to calculate nanocrystals sizes using the Scherrer formula.

The samples for transmission electron microscopy were prepared by the deposition of a 6 μL drop of studied solution onto carbon coated copper grid, excess of solution was removed and grids were dried by Whatman filtration paper. The samples were observed by transmission electron microscope JEOL JEM-1010 at accelerating voltage of 80 kV. Pictures were taken by SIS MegaView III digital camera (Soft Imaging Systems) and analyzed by AnalySIS v. 2.0 software.

Up-conversion spectra were recorded on a Leica TCS SP2 AOBs confocal inverted fluorescence microscope (Mannheim, Germany) using a PL APO100 \times /1.40–0.70 oil immersion objective (pinhole 1 Airy unit) and a Coherent Chameleon Ultra Ti:sapphire laser (Santa Clara, CA, USA) at 970 nm excitation with correction on a power laser at different wavelengths. All samples for up-conversion measurements were prepared by following procedure. 1 mg of powder were put to the 1 mL of ethanol and treated by ultrasound. 10 μL was dropped to measurement pad and ethanol was subsequently evaporated. By this procedure relatively uniform layer of powder was formed. All measurements are therefore comparable to each other.

4. Conclusions

In our paper simple approach to prepare up-converting YF₃:YbEr nanocrystals is shown. Ionic liquid bmimCl was as a liquid environment and NaBF₄ as a fluorination agent. Nanocrystals were analysed by XRD, TEM and up-conversion was measurements. Crystal sizes and also their up-converting abilities are dependent on preparation times and also on sodium content. Great advantage of this approach is the possibility to prepare various

sizes of up-converting nanocrystals in large quantities which could be essential for commercial applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jfluchem.2016.05.015>.

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