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Short communication

Large scale preparation of up- converting YF_3:YbEr nanocrystals with various sizes by solvothermal syntheses using ionic liquid bmimCl

Vilém Bartůněk[a,*], Jakub Rak[b,c], Barbora Pelánková[a,b,d], Jiřina Junková[e], Martina Mezlíková[e], Vladimír Král[b,c], Martin Kuchař[d,j], Hana Engstová[f], Petr Ježek[f], Roman Šmucler[g,h,i]

[a] Department of Inorganic Chemistry, Faculty of Chemical Technology, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic
[b] Department of Analytical Chemistry, Faculty of Chemical Engineering, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic
[c] Clinic of Pediatrics and Adolescent Medicine, First Faculty of Medicine, Charles University in Prague and General University Hospital in Prague, Kateřinská 32, 120 00 Prague 2, Czech Republic
[d] Department of Chemistry of Natural Compounds, Faculty of Food and Biochemical Technology, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic
[e] Department of Food Analysis and Nutrition, Faculty of Food and Biochemical Technology, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic
[f] Institute of Physiology, v. v. i., The Academy of Sciences of the Czech Republic, Vídeňská 1083, 142 20 Prague 4, Czech Republic
[g] Asklepion-Lasercentrum, Londýnská 39, 120 00 Prague 2, Czech Republic
[h] Department of Stomatology, First Faculty of Medicine, Charles University in Prague and General University Hospital in Prague, Kateřinská 32, 120 00 Prague 2, Czech Republic
[i] Department of Stomatology and Maxilofacial Surgery, Faculty of Medicine, Pavol Jozef Šafárik University in Košice, Rastislavova 43, 041 90 Košice, Slovak Republic
[j] Forensic Laboratory of Biologically Active Substances, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic

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ABSTRACT

Simple approach to prepare various sizes of YF_3: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 $NaBF_4$ 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.

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].

* Corresponding author.
E-mail address: vilem.bartunek@vscht.cz (V. Bartůněk).

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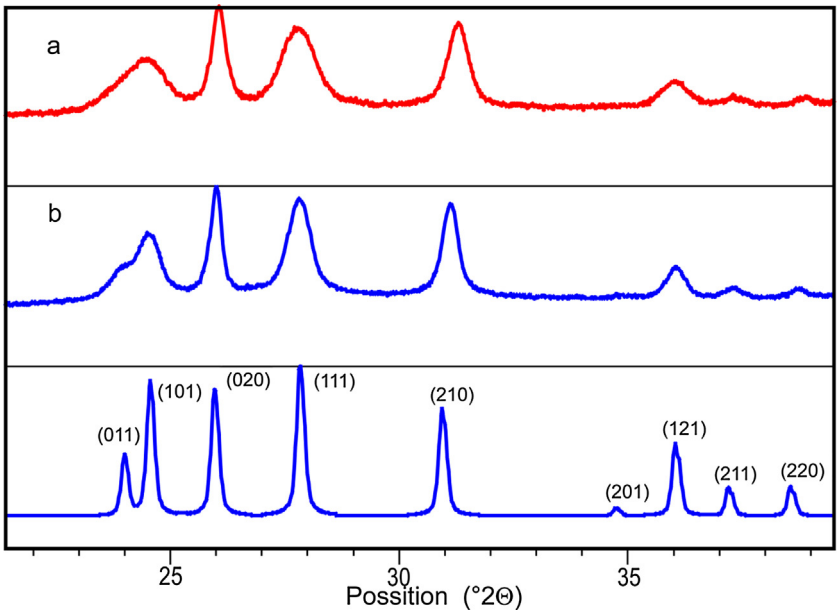

Fig. 1. Apparent difference in peak broadening between a) the smallest nanocrystals and b) the largest nanocrystals. On the bottom is simulated scan orthorhombic phase PDF No. 04-006-0199.

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 ($bmimPF_6$), or 1-butyl-3-methylimidazolium tetrafluoroborate ($bmimBF_4$) 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 nanocrystaline YF_3 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 papered phase is determined to be pure orthorhombic YF_3: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.

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

time [min]	averange 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

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 $NaBF_4$ 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 HNO_3 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 $^2H_{11/2} \rightarrow {}^4I_{15/2}$ (520 nm), $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (545 nm) and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (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 $^4F_{7/2} \rightarrow {}^4I_{13/2}$. 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