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Short Communication

Synthesis of hexagonal NaY(Gd)F₄ ultrafine nanocrystals using sodium acetate as ionic mediator



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ABSTRACT

Hexagonal phase ultrafine nanoparticles of $NaY(Gd)F_4$ were synthesized using chloride precursors and sodium acetate to provide liquid environment for ionic transportand as a source of sodium ions. Prepared ultrafine nanocrystals were analysed by XRD, laser Doppler electrophoresis and TEM measurements. Absence of fluoroacetic acid was confirmed by NMR of wash water obtained by dispersion centrifugation. Synthesized nanocrystals were 8.9 nm in diameter and had a hexagonal crystal structure. The method is appropriate for further experimental development, e.g. the synthesis of luminescent fluorides based on NaY(RE)F4 system, and for possible industrial application because of its ability to prepare large amounts of nanocrystals and due to the fact that the process is affordable and environmental friendly.

1. Introduction

Rare earth fluorides have unique optical properties such as scintillation, down-conversion or up-conversion. These properties determine their considerable potential for both biological and technical applications. Due to the low systemic toxicity and cytotoxicity ionic insoluble rare earth fluorides are very suitable for medical applications. These materials seem to be a possible way to create complex drug delivery systems for anticancer treatment [1]. Also a possibility of use of their luminescent properties in infrared photodynamic therapy of cancer [2] is intensively studied. Similarly, luminescent rare earth nanomaterials are interesting for bioprobe applications [3]. NaYF₄ doped by various rare earth ions, e.g Yb³⁺ and Er³⁺ for up-converting nanocrystals, are commonly used for optical applications. From all available crystallographic modifications of these compounds, hexagonal modification exhibited the best quantum yields [23].

Large range of methods can be utilised for rare earths nanofluorides synthesis. Standard method is synthesis using oleic acid as surfactant and 1-octadecene as a solvent [4,5]. Another methods are based on high-temperature co-precipitation [11], on thermal decomposition of lanthanide organic precursors [12] or on solvothermal synthesis employing ionic liquids (1-butyl-3-methylimidazolium chloride, 1-butyl-3methylimidazolium hexafluorophosphate (bmimPF₆), or 1-butyl-3-methylimidazolium tetrafluoroborate) as a solvent or as a fluorination

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agent [6-10]. Microwave syntheses [13-16] or chemical etching [17] are another methods of choice. Most broadly studied and applied upconverting mixed rare earth fluorides are commonly prepared using hydrothermal synthesis in oleic acid [18], mostly in the form of sodium salt [19–21] or with various other cations such as barium [22].

Sodium acetate is a common affordable and non-toxic chemical substance, which is widely used in industry for example as a food additive or as a base for the reaction mixtures neutralisation. Its trihydrate form has low melting temperature of 58 °C and simultaneously it is the source of sodium ions.

Thus, in the presented work we use sodium acetate trihydrate as a solvent and as a sodium source for affordable and green low temperature synthesis of Na(Gd)F₄ hexagonal nanocrystals in the boundary between solvothermal and solid state reaction.

2. Results and discussion

Synthesized ultrafine NaY(Gd)F4 nanoparticles were characterized by X-Ray powder diffraction analysis to obtain the information about both phase composition and average sizes of nanocrystals from peak broadening. A mixture of cubic and hexagonal modifications was obtained in experiments with only yttrium contribution. Addition of one molar equivalent of gadolinium shifted phase composition to hexagonal as has been previously reported in literature [23]. Therefore, hexagonal



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Fig. 1. XRD patterns of prepared hexagonal NaY(Gd)F₄ nanocrystals: a) sample synthesized at 90 °C, b) sample synthesized at 120 °C. PDF cards from the top down: hexagonal phase, cubical NaF and cubical phase.

phase of NaY(Gd)F₄ was prepared (reference pattern 00-027-0699) only with negligible impurity in the form of cubic phase (Fig. 1). According to the Scherrer formula, average diameters of prepared nanocrystals were estimated to be 8.9 nm.

Temperature and time dependence of the process were investigated in order to figure out whether the lower temperature could be used for successfull preparation of nanocrystals. We found that lower temperature (90 °C) during the synthesis is not suitable, as can be seen in Fig. 1a, where the diffraction pattern of the sample treated 15 h at 90 °C is shown (for the comparison, the sample treated at 120 °C has the reaction time only 1 h). Reaction mechanism involves the formation of both NaF and cubical NaY(Gd)F₄ phase as shown in Fig. 1a. Both of these phases subsequently dissolve in hexagonal NaY(Gd)F₄. Final product prepared at 120 °C contains no NaF and a negligible amount of cubical NaY(Gd)F₄ phase.

TEM measurements of prepared nanocrystals (Fig. 2) showed that these crystals are ultrafine in sizes and tend to aggregate into larger clusters. However, these clusters can be separated by using of ultrasound (as may be seen on bottom panels of Fig. 2) and fabricated as needed, for e.g. stabilized in selected solution.

For the measurements of the dispersion before and after ultrasonic



Fig. 3. Size distribution of the particles in methanol dispersion measured by laser Doppler electrophoresis: a) aggregates before ultrasonic treatment, b) nanocrystals after ultrasonic treatment.

treatment we used laser Doppler electrophoresis (ZetaSizer). As can be seen in Fig. 3, initially prepared dispersion in methanol contained larger particles corresponding by size with those observed by TEM. After ultrasonic treatment we obtained the dispersion containing ultrafine nanocrystals. However, their stability was dependent on subsequent conditions and processing, e.g surface stabilisation.

Sodium acetate proved to be very suitable solvent for ionic transport, serving as a source of sodium ions. Its great advantage is also its solubility in water, thus the purification process can be very effective, affordable and environmental friendly, as well as the synthetic process.

Fluoroacetic acid is dangerous compound, so we decided to analyse their presence in the remaining solution. However we did not expect their occurrence since the reaction process is based on ionic exchange and not on radical reaction. Remaining solution obtained by centrifugation (15 ml) was acidified with aq. HCl to pH = 1, extracted with 3 ml of CDCl₃ and analysed by ¹H NMR and ¹³C NMR. As expected, we found no signs of fluoroacetic acid. NMR spectra (Fig. 4) contain characteristic resonances of acetic acid: ¹H NMR (CDCl₃): 2.10 (s, CH₃) and ¹³C NMR (CDCl₃): 20.88 (CH₃), 177.15 (COOH).

Obtained nanocrystals were quite small in diameter (in ultrafine



Fig. 2. TEM photographs of the material synthesized at 120 °C.



Fig. 4. a) ¹H NMR and b) ¹³C NMR spectra of remaining solution after the nanocrystals synthesis

range) and thus the described synthetic procedure may be adapted for the luminescent nanoparticles preparation by doping of various rare earths ions, based on the requirements. The thermodynamic stability of synthesized material was very good and XRD pattern measured after more than a half of a year yielded the same results as in the case of freshly prepared samples. Also the possibility to obtain entities with larger sizes than is the threshold for nanoparticles (obtained aggregates were larger than 100 nm in diameter), and on the other hand ultrafine nanocrystals below 10 nm, could be very useful. This offers a potential application of prepared nanocrystals in e.g. biomedical or cosmetic research. Our method possesses more than 200 mg of the product in higher than 80% yield and is apparently suitable to gain even much bigger amounts of the final product. Besides, it is cost effective and environmental friendly due to the using of very affordable and water soluble precursor, sodium acetate. Therefore, the method can be adapted also to an industrial use.

3. Conclusions

NaY(Gd)F₄ ultrafine nanoparticles were synthesized using chloride precursors and sodium acetate as both ionic transport medium and basic source of sodium ions. Obtained product was characterized by XRD, laser Doppler electrophoresis and by TEM measurements. The presence of fluoroacetic acid in remaining solution after the centrifugation of dispersion was determined by NMR. Synthesized nanocrystals were 8.9 nm in diameter and possessed hexagonal crystal structure. Presented method is suitable for further development for preparation of luminescent fluorides and for industrial use, since large volumes of nanocrystals can be easily prepared. Moreover, this method is affordable and environmental friendly.

4. Experimental

Gadolinium and yttrium chloride hexahydrates were obtained from Sigma-Aldrich, Ltd. Sodium acetate hexahydrate and ammonium fluoride were bought from LachNer, a.s. In the typical experiment 0.35 g of GdCl₃·6H₂O and 0.20 of YCl₃·6H₂O (equimolar amounts) were mixed with 2.5 g of sodium acetate trihydrate and 0.5 g of NH₄F, placed to Teflon container and homogenized. Reaction mixture was subsequently placed to drying kiln and thermally treated on air at various temperatures and for various times. Next, the solid residue was washed with water, collected by centrifugation and subsequently washed with ethanol, dried and characterized.

X-ray powder diffraction (XRD) data were collected at room temperature with D2 PHASER powder diffractometer CoK α radiation ($\lambda = 1.7902$ Å). XPert HighScore Plus program was used for processing of the data from XRD and calculations of nanoparticle sizes were made

using Scherrer formula.

The samples for transmission electron microscopy were prepared by the deposition of a 6 μ l drop of studied solution onto carbon coated copper grid, excess od 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 analysed by AnalySIS v.3.2 software.

NMR spectra were recorded with an Agilent 400-MR DDR2 (1H: 400 MHz, 13C: 100 MHz). Chemical shifts (δ) are expressed in ppm and are referred to the residual peak of the solvent.

BANDELIN SONOPULS 3200 ultrasonic homogenizer with probe PH163 was used for disintegration of aggregates in order to obtain dispersion of the nanocrystals. Small amount of the material was dispersed in methanol using ultrasonic bath. Subsequently, 0.25 kJ pulses from homogenizer were applied with 10 s active/10 s delay regime. Overall time of ultrasound treatment was 5 min.

Zetasizer Nano series instrument from Malvern Instruments Ltd. was used for the measurements of particle's sizes using laser Doppler electrophoresis and Zetasizer Software 6.32 Malvern Instruments Ltd. was used for the data processing.

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