New method of beta-NaYF$_4$: Yb^{3+}, Er^{3+} synthesis by using beta-cyclodextrin

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ABSTRACT

The novel method of synthesis of the hexagonal modification beta-NaYF$_4$ doped with Yb^{3+} (17 at.%) and Er^{3+} (3 at.%) using beta-cyclodextrin is proposed. Complex fluorides were prepared by decomposition of the mixture of metal fluoroacetates hydrates with and without addition of beta-cyclodextrin and were investigated by X-ray diffraction, energy dispersive X-ray analysis, scanning and transmission electron microscopy. The samples prepared by adding beta-cyclodextrin in the reaction mixture are single phase and have a hexagonal structure. At the same time, decomposition of the mixture of metal trifluoroacetates hydrates without beta-cyclodextrin is accompanied by pyrohydrolysis, leading to a contamination of the products by impurities of yttrium oxyfluorides and sodium fluoride. So a new synthetic approach proposed in this work allows to obtain pure complex fluorides with homogeneous distribution of elements and with homogeneous pore distribution.

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1. Introduction

Increasing interest to the materials on the base of complex fluoride NaYF$_4$ doped with lanthanide ions is connected with the possibility of their use as perspective up-conversion phosphors. Up-conversion phosphors can be potentially applied in many fields such as solid-state lasers [1,2], fluorescence biolabels [3,4], three-dimensional flat-panel displays [5] and materials for solar cells [6,7].

The compound NaYF$_4$ can exist in two modifications: a high-temperature phase of variable composition Na$_{0.5-x}$R$_{0.5+x}$F$_{2x+2}$ with the structure of fluorite (alpha-NaYF$_4$) and a low-temperature hexagonal modification (beta-NaYF$_4$) [8]. The latter is more suitable as a matrix for up-conversion phosphors [9]. Beta-NaYF$_4$: Yb^{3+}, Er^{3+} has become the object of a special interest as one of the most efficient near-IR-to-visible up-conversion phosphors [10–13]. In this system, beta-NaYF$_4$ acts as a matrix doped with ions of rare earth elements: sensitizer (Yb^{3+}) and activator (Er^{3+}).

The most usual methods of complex fluoride NaYF$_4$ synthesis are co-precipitation of sodium and yttrium fluorides from aqueous solutions [14,15], microemulsion precipitation [16] and hydro-thermal synthesis [17–20].

Another interesting method of its synthesis is the thermal decomposition of the precursors, for instance, metal trifluoroacetates hydrates. This method allows to partially prevent the contamination of the products by different impurity phases (oxides, oxifluorides, hydroxosalts) due to creating a fluoridizing atmosphere directly in the process of the synthesis by the fluoro-organic decomposition products [12].

However, during the decomposition of the mixture of metal trifluoroacetates hydrates in air the pyrohydrolysis of the samples cannot be completely avoided. To prevent this process and to obtain single-phase samples the synthesis can be carried out in the solution-melt of a mixture of high boiling organic solvents OA/OM/ODE (oleic acid/oleylamine/1-octadecene), in TOPO (trioctylphosphine oxide), or in their combination [21–25].

In this work, we propose to use beta-cyclodextrin for suppression of pyrohydrolysis and for obtaining porous metal fluorides beta-NaYF$_4$, beta-NaYF$_4$: Yb^{3+} and beta-NaYF$_4$: Yb^{3+}, Er^{3+}. The use of beta-cyclodextrin has some advantages compare with the use of high boiling organic solvents which are relatively low-cost of beta-cyclodextrin and easiness of its removal from the reaction mixture. Cyclodextrins are macrocyclic oligosaccharides most commonly composed of 6, 7, or 8 glucosidic units (their names are alpha-, beta- and gamma-cyclodextrins, correspondingly) [26]. They consist of D-glucopyranoside units connected by 1,4-glycosidic bonds into the cone-like structure. This structure has a hydrophobic internal cavity and a hydrophilic external surface. Availability of the hydrophobic cavity in conjunction with

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a solubility in water due to the hydrophilic alcohol groups gives the cyclodextrin molecules an ability to form a noncovalent inclusion complexes with other organic molecules in aqueous solutions. In such complexes, the cyclodextrin molecules play a role of the "host molecules".

Important property of cyclodextrins is the ability to form supramolecular structures in aqueous solutions. It is assumed that beta-cyclodextrin molecules form structures in a form of columns [27]. The molecules of beta-cyclodextrin are arranged by alternation of the head-to-head and tail-to-tail stacking, thus forming a system of extended channels.

2. Experimental

2.1. Sample preparation

In our synthesis the following compounds were used as precursors: Na_2CO_3 (>98%), $Y_2(CO_3)_3 \cdot xH_2O$ (>98%), $Er_2(CO_3)_3 \cdot yH_2O$ H_2O (>99%), Yb (>99%), CF_3COOH (99.9%), beta-cyclodextrin hydrate (>98%), distilled water.

Yttrium and erbium trifluoracetates hydrates were obtained from the respective metal carbonates hydrates. The precursors were dissolved in nearly two-fold excess of 50% trifluoracetic acid prepared by diluting the initial acid with distilled water. Sodium trifluoracetate was obtained from sodium carbonate that was dissolved in 50% trifluoracetic acid taken in a 1.5 molar excess. Ytterbium trifluoracetate hydrate was prepared from ytterbium and a two-fold excess of 50% trifluoracetic acid. Composition of trifluoroacetates hydrates of Y, Yb and Er was determined by a complexometric titration with 0.02 M EDTA aqueous solution and xylenol orange as indicator and by thermogravimetric analysis.

To study the influence of beta-cyclodextrin on the decomposition of metal trifluoroacetates hydrates and on the phase composition of fluorides formed, two reaction mixtures for synthesis $NaYF_4$ were prepared. The first mixture contained stoichiometric quantities of CF_3COONa and $Y(CF_3COO)_3 \cdot 4.9H_2O$ and the second one has the same composition but with the addition of beta-cyclodextrin. The weight ratio of the mixture of the metal trifluoroacetates hydrates to beta-cyclodextrin was 2:1. The resulting mixtures were put in alundum crucibles and distilled water was added into each crucible (2 ml of H_2O for 2.5 g of the mixture). Then the crucibles were placed in a muffle furnace and heated from 20 to 150 °C for 30 min. At a temperature close to 100 °C the mixtures were completely dissolved in water forming transparent solutions. Crucibles were then thermally treated for 2 h at 150 °C to remove water. Then mixtures were heated from 150 to 420 °C for 1 h and annealed for 2 h at 420 °C. The annealing temperature was selected from the analysis of thermogravimetric curves (Fig. 1).

Doped samples $NaYF_4$: Yb^{3+} (20 at.% Yb) were obtained from mixtures of the corresponding metal trifluoroacetates hydrates with and without using beta-cyclodextrin. Sample $NaYF_4$: Yb^{3+}, Er^{3+} (17 at.% Yb and 3 at.% Er) was synthesized only from the mixture of the corresponding metal trifluoroacetates hydrates with using beta-cyclodextrin. Heat treatment mode was similar to the described above. For the $NaYF_4$: Yb^{3+} the weight ratio of metal trifluoroacetates hydrates to beta-cyclodextrin was 2:0.66. Data on the sample synthesis and their composition are given in Table 1.

2.2. Sample characterization

The X-ray diffraction (XRD) patterns of metal fluorides were collected on Rigaku D/MAX 2500 X-ray diffractometer with CuK_{alpha} radiation. The data were processed using the STOE software. The powder data base (PCPDFWIN, Version 2.2, June
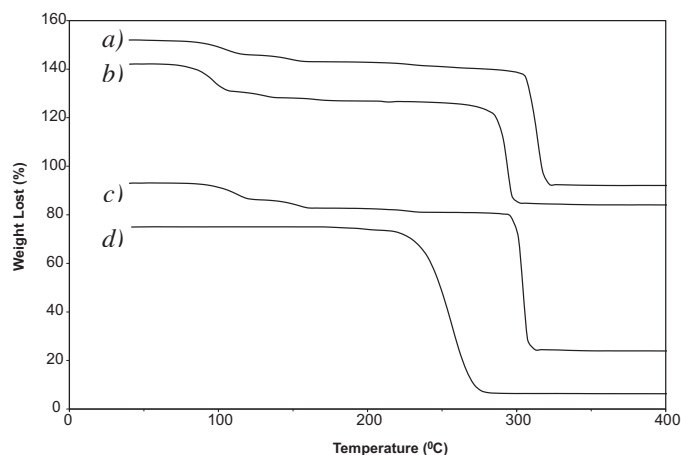

Fig. 1. Thermogravimetric analysis of metal trifluoroacetates hydrates: (a) $Er(CF_3COO)_3 \cdot 4.5H_2O$; (b) $Yb(CF_3COO)_3 \cdot 4.0H_2O$; (c) $Y(CF_3COO)_3 \cdot 4.9H_2O$; (d) CF_3COONa. The graphs are displaced on the ordinate axis relatively to each other.

2001, JCPDS-ICDD) was used to identify phases in the solid materials.

The thermal analysis of metal trifluoroacetates hydrates was performed on a NETZSCH STA 409 PC/PG instrument in the temperature range of 20–500 °C at a heating rate of 10 K min^{-1} in an air flow.

Scanning electron microscopy (SEM) was performed on a Leo Supra 50 VP instrument in a low vacuum mode. Energy dispersive X-ray analysis (EDX) was carried out at the same instrument using spectrometer Inca Energy +.

Transmission electron microscope (TEM) analysis was carried out using a JEM 2100 F transmission electron microscope under a working voltage of 200 kV.

3. Results and discussion

Thermogravimetric analysis of $Y(CF_3COO)_3 \cdot 4.9H_2O$, $Er(CF_3COO)_3 \cdot 4.5H_2O$, $Yb(CF_3COO)_3 \cdot 4.0H_2O$ shows that their decomposition proceeds in two main stages (Fig. 1). The first stage corresponds to a loss of water (100–150 °C) and is observed as several small steps of a weight loss on the thermogravimetric curves. The second stage (280–320 °C) relates to the decomposition of metal trifluoroacetate to the corresponding metal fluoride. The thermal decomposition of sodium trifluoroacetate proceeds in one stage at 225–280 °C. So, we can conclude that the decomposition of trifluoroacetates of Na, Y, Yb and Er occurs in close temperature ranges. It is probably helpful for the formation of complex fluorides by the decomposition of mixtures of these metal trifluoroacetates hydrates.

In our work we propose to use beta-cyclodextrin as a reaction agent which allows to suppress pyrohydrolysis and to obtain porous metal fluorides. The influence of the addition of beta-cyclodextrin on the composition of the resulting product was studied by X-ray diffraction analysis (XRD). The XRD patterns (Fig. 2) show that the presence of beta-cyclodextrin in a reaction mixture of sodium and yttrium trifluoroacetates hydrates prevents pyrohydrolysis and leads to the formation of the single-phase sample (beta-$NaYF_4$). The products obtained by the decomposition of a mixture of metal trifluoroacetates hydrates without beta-cyclodextrin contain impurities of oxifluorides phases, indicating the pyrohydrolysis process.

In the case of a sample $NaYF_4$: Yb^{3+} (CD) (sample names are given in Table 1) smaller content of beta-cyclodextrin was used as compared with the synthesis of a sample $NaYF_4$ (CD) (25 wt.% instead of 33 wt.%). This led to the appearance of weak reflexes

Table 1
Beta-cyclodextrin content in a reaction mixture and sample characteristics.

Sample	ω (beta-CD)[a], wt.%	Molar ratio M/Y		Sample purity[b]	Unit cell parameters[c]		
		In a reaction mixture	In a fluoride product (by EDX)		a, Å	c, Å	V, Å^3
$NaYF_4$	0	–	–	–			
$NaYF_4$ (CD)	33	–	–	+	5.9798(4)	3.5115(2)	108.74(1)
$NaYF_4$: Yb^{3+}	0	Yb/Y 0.25	Yb/Y 0.235(6)	–	5.977(1)	3.5100(8)	108.58(3)
$NaYF_4$: Yb^{3+} (CD)	25	Yb/Y 0.25	Yb/Y 0.241(2)	–	5.993(3)	3.513(2)	109.26(6)
$NaYF_4$: Yb^{3+}, Er^{3+} (CD)	33	Yb/Y 0.21 Er/Y 0.038	Yb/Y 0.205(5) Er/Y 0.034(1)	+	5.9749(3)	3.5031(7)	108.30(5)

[a] This is a weight content of beta-cyclodextrin in a reaction mixture.
[b] Symbol "+" means that sample is single-phase and symbol "−" means that sample is multi-phase.
[c] These parameters were determined by assignment of indices of XRD patterns using reflexes of hexagonal phase beta-$NaYF_4$.

of yttrium and/or ytterbium oxofluoride on the XRD pattern. So in this case the pyrohydrolysis process was not suppressed completely. Thus, there is an optimal content of beta-cyclodextrin in the initial reaction mixture (the value of which lies between 25 and 33 wt.%) at which pyrohydrolysis can be suppressed and synthesis produces a single-phase complex metal fluoride.

It was supposed [28] that the influence of beta-cyclodextrin on the decomposition process of metal trifluoroacetates hydrates can be connected with the formation of ordered structures of beta-cyclodextrin with trifluoroacetate ions. This leads to changing the mechanism of decomposition and affected the properties of formed fluorides.

The sample obtained by the decomposition of a mixture of Na, Y, Yb, Er trifluoroacetates hydrates with beta-cyclodextrin is a single-phase (Fig. 2). There is a small shift of the lines of this phase as compared with the XRD pattern of pure beta-$NaYF_4$, which indicates the introduction of Yb^{3+} and Er^{3+} ions in the hexagonal structure of the beta-$NaYF_4$. The parameters determined by assignment of indices of XRD patterns using reflexes of hexagonal phase are given in Table 1. There are some changes in the cell parameters after doping $NaYF_4$ by cations Yb^{3+} and Er^{3+}, but they are not very significant. This can be attributed to the fact that the radii of all of these three ions are very close. Thus in the case of coordination number 9, which has an Y atom in the structure of beta-$NaYF_4$, the radii of these cations have the following values: 1.075 Å (Y^{3+}), 1.062 Å (Er^{3+}), 1.042 Å (Yb^{3+}) [29].

According to the results of transmission electron microscopy, beta-$NaYF_4$ samples have a porous structure (Fig. 3). A sample of
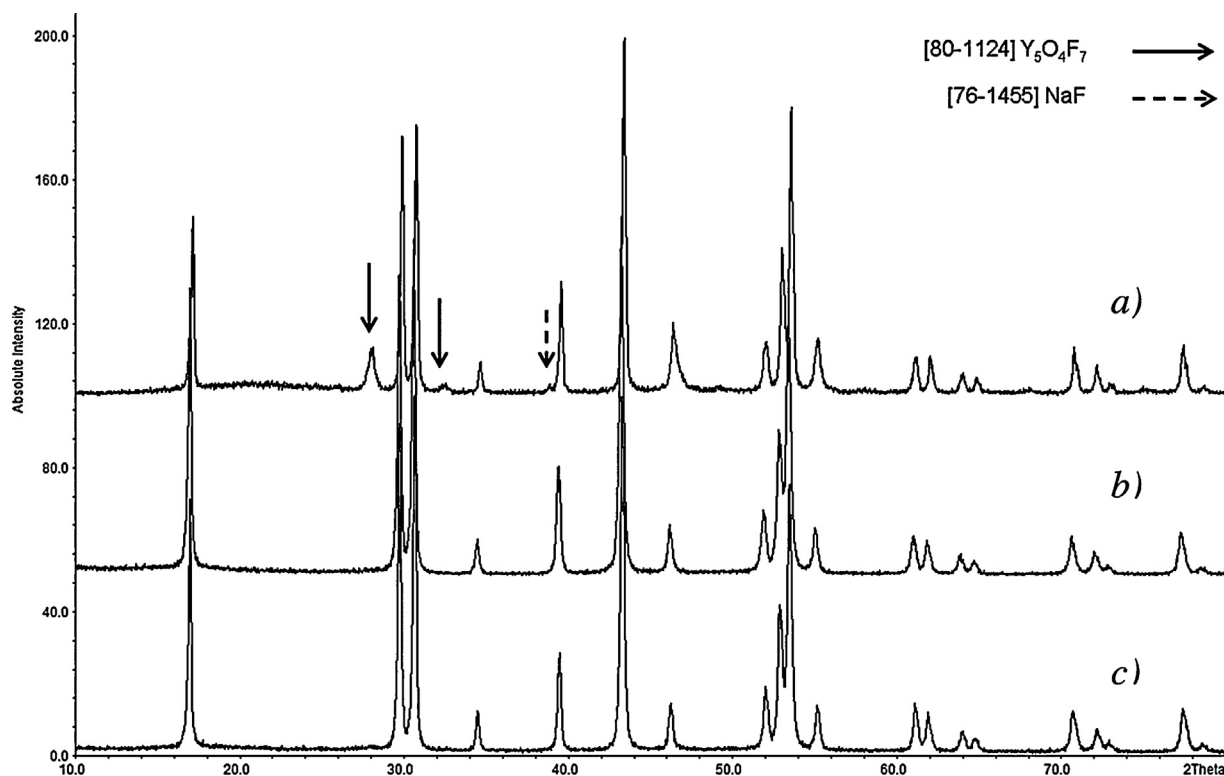

Fig. 2. X-ray patterns of the samples $NaYF_4$ (a), $NaYF_4$ (CD) (b), $NaYF_4$: Yb^{3+}, Er^{3+} (CD) (c). All lines on the patterns correspond to the phase beta-$NaYF_4$ [16–334] except of the lines marked by arrows. All files numbers are given according powder data base (PCPDFWIN, Version 2.2, June 2001, JCPDS-ICDD).
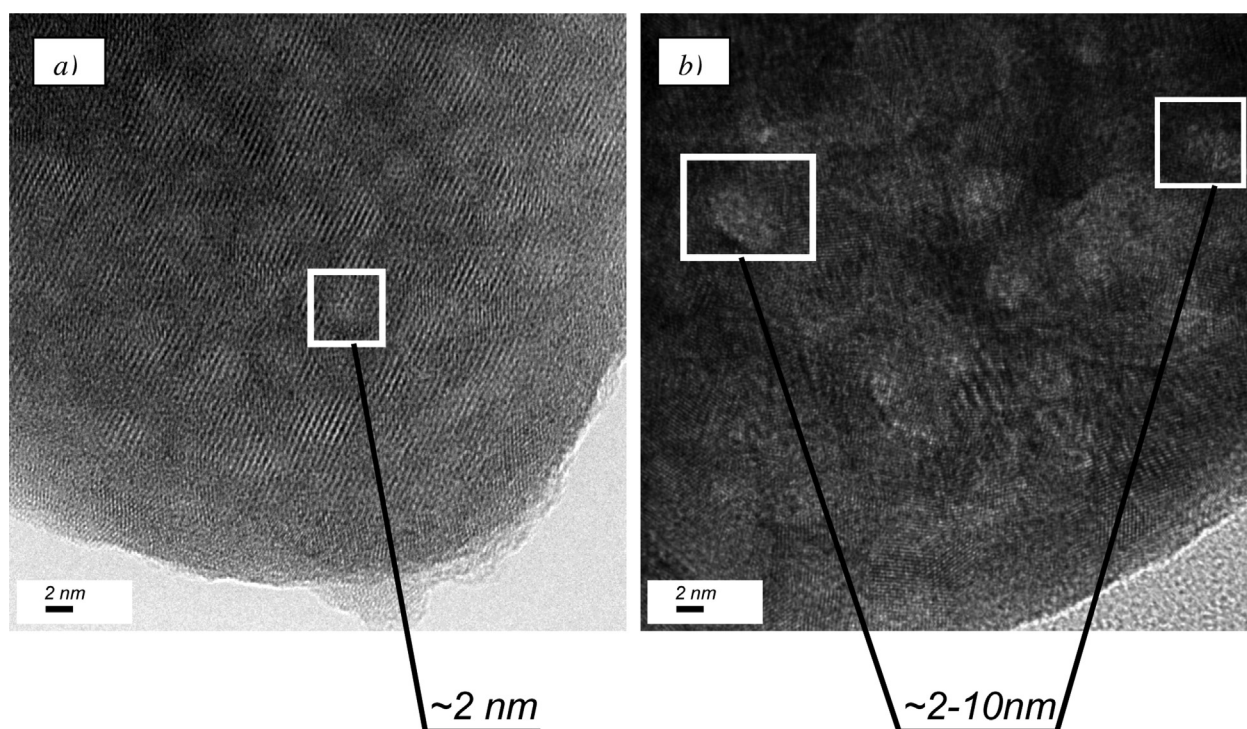
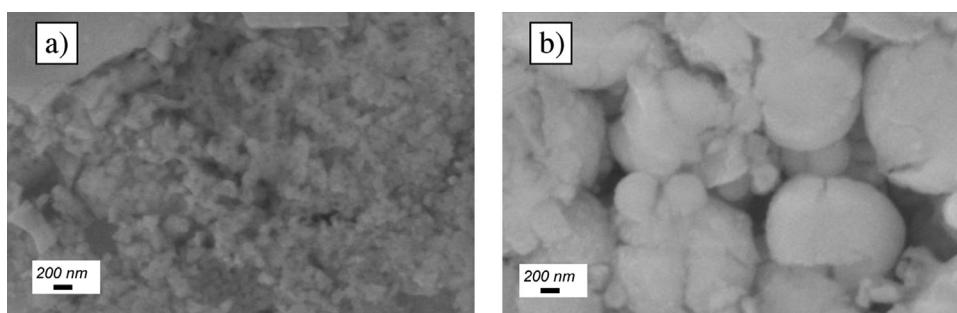**Fig. 3.** TEM microphotographs of NaYF$_4$ synthesized with (a) and without (b) the addition of beta-cyclodextrin.

Fig. 4. SEM microphotographs of NaYF$_4$: Yb^{3+} synthesized with (a) and without (b) the addition of beta-cyclodextrin.

beta-NaYF$_4$ obtained in the presence of beta-cyclodextrin has a more uniform pore size distribution than one obtained without beta-cyclodextrin. The pore size in the sample obtained by the decomposition of a mixture of sodium and yttrium trifluoroacetates hydrates in the presence of beta-cyclodextrin is less (about 2 nm) than in the sample prepared from a mixture without beta-cyclodextrin ($\sim$5 nm). Also according to scanning electron microscopy results the samples prepared with using beta-cyclodextrin consist of smaller particles as compared to the samples prepared without beta-cyclodextrin (Fig. 4).

The distribution of elements on the surface of complex fluorides NaYF$_4$: Yb^{3+} and NaYF$_4$: Yb^{3+}, Er^{3+} was studied by energy dispersive X-ray analysis. It was found that the complex fluorides obtained in the presence of beta-cyclodextrin had more uniform distribution of elements on the surface compared with a sample prepared without beta-cyclodextrin (Table 1). It is important to note that the average molar ratios of Yb/Y and Er/Y observed for all fluorides are very close to these ratios in the initial mixtures of metal trifluoroacetates hydrates. So, we can conclude that using beta-cyclodextrin in the synthesis allows obtaining homogeneous complex fluorides beta-NaYF$_4$: Yb^{3+} and beta-NaYF$_4$: Yb^{3+}, Er^{3+} with the call-off quantity of metals.

4. Conclusions

Complex metal fluorides beta-NaYF$_4$, beta-NaYF$_4$: Yb^{3+} and beta-NaYF$_4$: Yb^{3+}, Er^{3+} were obtained by the decomposition of metal trifluoroacetate hydrates in the presence of beta-cyclodextrin. The decomposition of the mixture without beta-cyclodextrin under similar conditions leads to a contamination of the reaction products by yttrium and/or ytterbium oxofluorides and sodium fluoride. So, the introduction of beta-cyclodextrin to the reaction mixture prevents the pyrohydrolysis process and allows to obtain single-phase samples.

The advantages of the method proposed are relatively low temperature of the synthesis, simple changes in composition of the prepared compounds and the formation of products with a homogeneous distribution of the elements. Also this synthetic approach permits to obtain porous products with homogeneous pore distribution.

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