The novel method of synthesis of solid solutions Ln$_x$Ca$_{1-x}$F$_{2+x}$ (Ln=Yb, Nd) using beta-cyclodextrin

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Abstract

In this study we propose the novel method of synthesis of solid solutions Ln$_x$Ca$_{1-x}$F$_{2+x}$ (Ln = Yb, Nd) by decomposition of metal trifluoroacetate hydrates with beta-cyclodextrin. It is important to mention that the decomposition of the similar reaction mixture without beta-cyclodextrin does not induce the formation of such compounds. In this case, the formation of individual fluorides takes place. The metal fluorides were studied by XRD and X-ray fluorescence. The advantages of the method proposed are as follows: relatively low temperature of the synthesis, simplicity of a change in the composition of the prepared compounds, and a homogeneous distribution of the elements in products.

Keywords: Alkaline Earth and Rare-Earth Element Fluorides ; Solid Solution ; Cyclodextrin

1. Introduction

Alkaline earth element fluorides doped by rare earth element fluorides are of great interest due to their physical and chemical properties and promising possibilities of their use in terms of laser materials as well as in medicine and so on$^{1-7}$. Thus, the search for new synthetic methods for obtaining solid solutions of rare earth element fluorides in alkaline-earth element fluorides as well as complex fluorides containing both alkaline earth and rare earth elements is crucial. A uniform distribution of the rare earth component is important for a more effective use because it affects the properties greatly. Therefore, an important task is to find methods of synthesis that allow obtaining fluorides with

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a uniform distribution of components. Solid phase synthesis is the classical method of preparation of these compounds. Significant disadvantages of this method are the necessity of using high temperatures and carrying out the synthesis in the fluorizating atmosphere to prevent pyrohydrolysis process, and also the low homogeneity of complex fluorides obtained. Thus, an important task is to find alternative methods of "soft" chemistry. The most common methods of the synthesis of complex fluorides are co-precipitation of metal fluorides from aqueous solutions, microemulsion precipitation, and hydro- and solvothermal synthesis.

Another interesting method of synthesis is thermal decomposition of the precursors, for instance, metal trifluoroacetates hydrates. This method permits to partially prevent the contamination of products by different impurity phases (oxides, oxifluorides, hydroxosalts) due to the creation of the fluorizating atmosphere directly in the process of the synthesis by the fluoro-organic decomposition products. However, during the decomposition of the mixture of metal trifluoroacetate hydrates in the air, the pyrohydrolysis of samples cannot be completely avoided. To prevent this process and obtain single-phase samples, the synthesis can be carried out in the solution-melt of the mixture of high boiling organic solvents. However, a significant disadvantage of this method is the need to remove an organic solvent. Furthermore, these organic solvents are expensive.

In this work we propose a new method for the preparation of solid solutions of rare earth element fluorides (for example, Yb, Nd) in calcium fluoride by thermal decomposition of a mixture of metal trifluoroacetate hydrates in the presence of beta-cyclodextrin. Previously, we have shown the effectiveness of this approach for production of calcium and magnesium fluorides with high values of specific surface area.

2. Experimental

2.1. Sample preparation

In our synthesis, the following compounds were used as precursors: CaCO₃ (> 99 %), Nd(OH)₃ (> 99 %), Yb (> 99 %), CF₃COOH (99.9 %), beta-cyclodextrin hydrate (> 98 %), and distilled water.

Calcium, ytterbium, and neodymium trifluoroacetates hydrates were obtained by interaction of calcium carbonate, metal ytterbium, and neodymium oxide with excess of aqueous solution of trifluoroacetic acid. Neodimium oxide was prepared by thermal decomposition of neodymium hydroxide at 800°C. The composition of metal trifluoroacetate hydrates was determined by a complexonometric titration with 0.02 M EDTA aqueous solution and xylenol orange as the indicator for Yb and Nd and eriochrome black T as the indicator for Ca determination and also by thermogravimetric analysis. The results showed that the composition of these compounds is as follows: Yb(CF₃COO)₃·3H₂O, Nd(CF₃COO)₃·4H₂O, Ca(CF₃COO)₂·1.5H₂O.

To study the influence of beta-cyclodextrin on the process of decomposition and products composition, we prepared the mixtures of metal trifluoroacetate hydrates with and without beta-cyclodextrin. The weight ratio of the mixture of metal trifluoroacetate hydrates to beta-cyclodextrin was 2:1. The mixtures contained 0.3, 1, 5, 33, and 43 at. % Yb or 0.5, 1, and 5 at. % Nd. The resulting mixtures were put in alumnum crucibles, and distilled water was added into each crucible to obtain homogeneous solutions during heating. Then, the crucibles were placed in a muffle furnace heated from 20 to 150°C for 30 min and were thermally treated for 2 hours at 150°C to remove water. Then, mixtures were heated from 150 to 420 °C for 1 hour and annealed for 2 or 6 hours at 420 °C. The annealing temperature was selected from the thermogravimetric curves study (Fig. 1).

2.2. Sample Characterization

The X-ray diffraction patterns of fluorides were collected on Rigaku D/MAX 2500 X-ray diffractometer with CuKα radiation. The data were processed using the STOE software. The powder data base (PCPDFWIN, Version 2.2, June 2001, JCPDS-ICDD) was used to identify phases in the samples.

Thermal analysis of metal trifluoroacetate hydrates was performed using a NETZSCH STA 409 PC/PG instrument in the temperature range of 20–600 °C at a heating rate of 10 K min⁻¹ in air flow.

The molar content of the rare earth elements in the solid solutions obtained was determined by X-ray fluorescence. X-ray fluorescence was measured with a Spectroscan portable wave dispersion X-ray fluorescence
The measurements were taken at three points of each sample and the calculation was performed using a calibration graph.

3. Results and Discussion

The results of thermogravimetric and differential thermal analyses showed that the decomposition of Ca(CF₃COO)₂·1.5H₂O, Yb(CF₃COO)₃·3H₂O and Nd(CF₃COO)₃·4H₂O has a similar character, and this process takes place in the same temperature range (Fig. 1). Decomposition proceeds in two main stages. The first stage is a loss of water (90-120 °C for M = Ca; 80-140 °C for M = Yb; 80-160 °C for M = Nd) and is observed as several small steps of weight loss on the thermogravimetric curves. The second stage (300-320 °C for M = Ca; 280-300 °C for M = Yb; 210-290 °C for M = Nd) is the decomposition of metal trifluoroacetate to the corresponding metal fluoride. The decomposition of the mixture of Ca(CF₃COO)₂·1.5H₂O and Yb(CF₃COO)₃·3H₂O (molar ratio Ca:Yb = 1:1) has a similar character and also proceeds in two main stages: a loss of water at 70-140 °C and the final decomposition stage at 210-290 °C.

The assumption on the possibility of the synthesis of solid solutions of metal fluorides or complex metal fluorides by decomposition of the mixture of metal trifluoroacetate hydrates was based on the proximity of the decomposition temperatures of metal trifluoroacetate hydrates. However, we found out that the decomposition of the mixture of
calcium trifluoroacetate hydrate and ytterbium trifluoroacetate hydrate leads to formation of the mixture of the respective individual fluorides. At the same time, the introduction of beta-cyclodextrin into the reaction mixture results in the formation of solid solutions of neodymium or ytterbium fluoride in calcium fluoride (Fig. 2). This difference in the reaction of these systems while heated is probably due to the formation of mixed compounds with beta-cyclodextrin in the intermediate stages of decomposition.

Fig. 2. X-ray patterns of the samples CaF$_2$-YbF$_3$ (molar ratio Ca:Yb = 2:1) synthesized without (on the left side) and with (on the right side) beta-cyclodextrin. CaF$_2$ and YbF$_3$ card numbers are [35-816] and [71-1161], respectively, according to the powder data base (PCPDFWIN, Version 2.2, June 2001, JCPDS-ICDD).

Beta-cyclodextrin used as a reaction agent in our study is a macrocyclic oligosaccharide composed of 7 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. The availability of the hydrophobic cavity in conjunction with the solubility in water due to the hydrophilic alcohol groups gives the cyclodextrin molecules the ability to form non-covalent inclusion complexes with other organic molecules in aqueous solutions. In such complexes, the cyclodextrin molecules play the role of the "host molecules".

An important property of cyclodextrins is the ability to form supramolecular structures in aqueous solutions. We assume that beta-cyclodextrin molecules form column structures. The molecules of beta-cyclodextrin are arranged by alternation of the head-to-head and tail-to-tail stacking, thus, forming the system of extended channels.

We suppose that the influence of beta-cyclodextrin on the decomposition process of metal trifluoroacetate can be associated with the formation of the ordered structures of beta-cyclodextrin with trifluoroacetate groups. This leads to the change in the mechanism of the decomposition of the reaction mixture and effects the composition of formed metal fluorides. Likewise, cyclodextrin molecules can form complexes with metal ions due to hydroxyl groups. The formation of such complexes with different metal ions simultaneously can lead to the formation of complex fluorides as a result of mixture decomposition.

However, revealing the cause of this phenomenon requires further research. In addition, it is interesting to note that according to the preliminary research results the increase in the content of ytterbium trifluoroacetate hydrate in the reaction mixture leads to the formation of fluorite-like disordered phases Ca$_2$YbF$_7$ and Ca$_4$Yb$_3$F$_{17}$ (similar phases may be obtained for strontium and barium, according to the preliminary results). Currently, we are carrying out a detailed study of the feasibility of the synthesis of complex fluorides by the decomposition of the mixtures of metal trifluoroacetate hydrates with beta-cyclodextrin.

The samples obtained by the decomposition of the mixture of metal trifluoroacetate hydrates with beta-cyclodextrin are single-phase and have a fluorite-like structure. There is a small shift of the lines of these phases compared to the XRD pattern of pure CaF$_2$ which indicates the formation of solid solutions of YbF$_3$ or NdF$_3$ in CaF$_2$. It is well illustrated by comparing the XRD patterns of samples Nd$_x$Ca$_{1-x}$F$_{2+x}$ with 0.5 at. % and 5 at. % Nd shown in Fig. 3.
The parameters determined by assigning the indices of XRD patterns using reflexes of fluorite are presented in Table 1. Certain changes are observed in the cell parameters after doping CaF$_2$ by Yb or Nd, however, not very significant with small Yb content.

Table 1. Refined cell parameters of the samples Ln$_x$Ca$_{1-x}$F$_{2+x}$ (Ln = Yb, Nd).

| Sample         | Ln content in the sample, at.% | Refined cell parameters | Cell volume | Figure of Merit F | Maximum delta 2Theta |
|----------------|--------------------------------|-------------------------|-------------|-------------------|---------------------|
|                |                                | a, Å                    | V, Å$^3$    |                   |                     |
| Yb$_x$Ca$_{1-x}$F$_{2+x}$ | 0.3                            | 5.465(2)                | 163.2(1)    | 78.0              | 0.032               |
|                | 1                              | 5.4635(6)               | 163.08(3)   | 228.6             | 0.013               |
|                | 5                              | 5.469(2)                | 163.59(8)   | 85.3              | 0.029               |
|                | 33                             | 5.487(1)                | 165.27(7)   | 92.6              | 0.023               |
|                | 43                             | 5.494(2)                | 165.8(1)    | 62.5              | 0.043               |
| Nd$_x$Ca$_{1-x}$F$_{2+x}$ | 0.5                            | 5.465(2)                | 163.2(1)    | 63.8              | 0.055               |
|                | 1                              | 5.466(2)                | 163.3(1)    | 58.6              | 0.035               |
|                | 5                              | 5.481(7)                | 164.7(4)    | 16.2              | 0.1                 |

The molar content of the rare earth elements in the solid solutions obtained was determined by X-ray fluorescence. The results given in Table 2 show that the values of Yb and Nd content in the samples almost coincide with their contents in the reaction mixture. The values of content determined at all three points are very close. This indicates the homogeneity of the samples. Thus, we can state that the rare-earth elements are uniformly distributed in the samples.

Table 2. The results of the X-ray fluorescence analysis of the samples Ln$_x$Ca$_{1-x}$F$_{2+x}$ (Ln = Yb, Nd).

| Sample         | Ln content in the sample, at.% | Ln content, at.%$^*$ |
|----------------|--------------------------------|---------------------|
|                |                                | point 1 | point 2 | point 3 | average value |
|                |                                |         |         |         |               |
| Yb$_x$Ca$_{1-x}$F$_{2+x}$ | 0.3                            | 0.29 (0.27) | 0.28 (0.27) | 0.28 (0.26) | 0.28 (0.27) |
|                | 1                              | 1.13 (1.10) | 1.12 (1.08) | 1.14 (1.09) | 1.13 (1.09) |
|                | 5                              | 5.11 (5.01) | 5.12 (5.01) | 5.09 (5.00) | 5.11 (5.01) |
| Nd$_x$Ca$_{1-x}$F$_{2+x}$ | 0.5                            | 0.42    | 0.40    | 0.41    | 0.41         |
|                | 1                              | 1.10    | 1.10    | 1.11    | 1.10         |
|                | 5                              | 5.02    | 4.64    | 4.66    | 4.77         |

$^*$ – these results are obtained using line L$\beta_1$; ytterbium content given in parentheses is obtained using line L$\alpha$. 

Fig. 3. X-ray patterns of the samples Nd$_x$Ca$_{1-x}$F$_{2+x}$ with 0.5 at. % (blue line) and 5 at. % Nd (violet line).
4. Conclusions

Solid solutions \( \text{Ln}_x\text{Ca}_{1-x}\text{F}_{2+x} \) (\( \text{Ln} = \text{Yb}, \text{Nd} \)) were obtained by the decomposition of metal trifluoroacetate hydrates in the presence of beta-cyclodextrin. It is essential to mention that the decomposition of the reaction mixture without beta-cyclodextrin under similar conditions leads to the formation of individual fluorides \( \text{YbF}_3 \) or \( \text{NdF}_3 \) and \( \text{CaF}_2 \).

The synthetic method presented has several advantages in comparison to other methods used to produce metal fluorides. Thus, it allows a significant reduction of the synthesis temperature compared to the classical method of synthesis by melting metal fluorides. In addition, this method permits to increase the homogeneity of the samples with complex composition. Furthermore, this method permits to carry out the synthesis without using any organic solvents unlike the method of synthesis metal fluorides with the use of high boiling organic solvents. In this synthetic procedure, metal trifluoroacetate hydrates are used as the precursors for metal fluorides. These initial compounds are relatively available chemical reagents.

Thus, we offer a new method for the preparation of solid solutions of the rare earth elements (Yb, Nd) of calcium fluoride. This approach can be used to obtain solid solutions with other rare-earth element fluorides. The method is simple in hardware design, it needs relatively low temperatures and leads to the formation of solid solutions, which are more difficult to obtain by other methods.

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