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# Does BaYF<sub>5</sub> nanocrystals exist? – The BaF<sub>2</sub>-YF<sub>3</sub> solid solution revisited using photoluminescence spectroscopy

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#### A R T I C L E I N F O

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#### ABSTRACT

During thermolysis of metal trifluoroacetates in high boiling organic solvents the two  $Ba_{1-x}RE_xF_{2+x}$  phases with cubic fluorite-type structure are formed in  $BaF_2$ -YF<sub>3</sub> system. In contrast to previous reports formation of so-called 'BaYF<sub>5</sub>' nanocrystals was not observed. Besides the X-ray diffraction analysis the samples doped with optically active  $Eu^{3+}$  and  $Er^{3+}$  ions were characterized with photoluminescence spectroscopy and results provided by both methods corroborates each other. Upconversion emission observed under excitation at 980 nm for the  $Ba_{1-x}Y_xF_{2+x}$  phase co-doped with Yb<sup>3+</sup> and  $Er^{3+}$  ions is strongly composition dependent. Its intensity increases with increasing of REF<sub>3</sub> content for 0.2 < x < 0.45, whereas the opposite trend is evident for x > 0.45 and upconversion emission is totally quenched for x > 0.6. The important outcome of the present study is that compositions other than that with x = 0.5 should be probed to fully benefit from photoluminescence potential of  $Ba_{1-x}RE_xF_{2+x}$  nanofluoride phases activated with lanthanide ions.

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#### 1. Introduction

Fluorides are known as excellent hosts for optically active lanthanide ions. Early studies on lanthanide doped fluorides were mostly focused on their application as solid state gain media [1]. In recent years lanthanide doped fluoride nanocrystals (NCs) have emerged as an important class of materials for use in modern bioassays [2] due to their unique property of converting near-infrared light to visible light (up-conversion process, UC). So far hexagonal NaYF<sub>4</sub> NCs co-doped with Yb<sup>3+</sup> and Er<sup>3+</sup> ions appear as the most efficient UC material [3]. The Er<sup>3+</sup> and Yb<sup>3+</sup> co-doped hexagonal  $\beta$ -NaGdF<sub>4</sub> NCs that additionally exhibit magnetic properties due to the presence of gadolinium ions, present as an example of single-phase bifunctional material [4].

At the same time attempts have been undertaken to develop other fluoride hosts for the incorporation of luminescent lanthanide ions with hope to obtain nanocrystals exhibiting properties superior to those of lanthanide doped NaYF<sub>4</sub>. As result of these efforts a number of papers have been published in recent years reporting on the synthesis and luminescence properties of nanocrystals of 'BaYF<sub>5</sub>' and 'BaGdF<sub>5</sub>' composition doped with rare-earth

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report [15] amine-functionalized BaYF<sub>5</sub>:Yb<sup>3+</sup>/Er<sup>3+</sup> NCs have been proposed as nanoprobes for dual-modal in vivo upconversion fluorescence and long-lasting X-ray computed tomography bioimaging. Multifunctional BaGdF<sub>5</sub> nanospheres are considered as drug carriers [16], whereas graphene oxide-BaGdF5 nanocomposites have been recently proposed for multi-modal imaging and photothermal therapy [17]. On the other hand, some doubts on interpretation and conclusions presented therein [5-17] are cast by the fact that individual barium yttrium fluoride - 'BaYF5' or barium gadolinium fluoride - 'BaGdF5' compounds do not exist on the hitherto reported phase diagrams [18], and what is called "BaREF<sub>5</sub>" (RE - rare earth element or combination thereof) should be more properly named as a cubic fluorite-type  $Ba_{0.5}RE_{0.5}F_{2.5}$  phase, since it presents not a compound but a specific composition among more general cubic fluorite-type  $Ba_{1-x}RE_xF_{2+x}$  phase of variable composition [19-21]. Erroneous designation of Ba0.5RE0.5F2.5 phase as so-called

ions [5–13]. In one case the reported [14] luminescence intensity of the active-core/active-shell BaGdF<sub>5</sub>:Yb<sup>3+</sup>/Er<sup>3+</sup> was, remarkably, about four times as high as that of  $\beta$ -NaYF<sub>4</sub>:Yb<sup>3+</sup>/Er<sup>3+</sup> NCs. In other

Erroneous designation of Ba<sub>0.5</sub>RE<sub>0.5</sub>F<sub>2.5</sub> phase as so-called 'BaYF<sub>5</sub>' compound by some authors may be a consequence of neglecting recognition of phase equilibria in BaF<sub>2</sub>-YF<sub>3</sub> system and may take its origin from the mere assignment of 'BaYF<sub>5</sub>' composition to product obtained from 1:1 BaF<sub>2</sub>-YF<sub>3</sub> melt, as discussed by Fedorov et al. [19,20]. On the other hand results of Fedorov et al.





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[19,20] are based on X-ray diffraction studies of nanofluoride phases formed in the BaF<sub>2</sub>-YF<sub>3</sub> system during the course of precipitation from aqueous solution, whereas other authors reported on nanocrystals of 'BaYF<sub>5</sub>' composition with grain size as small as 5–10 nm, obtained by thermolysis of lanthanide trifluoroacetates in high boiling organic solvents. The latter non-equilibrium conditions are much different from those during co-precipitation from aqueous media at room temperature, which may affect structure and morphology of resulted nanocrystals. However, there are no systematic studies of barium-yttrium nanofluoride phases obtained by thermolysis.

One should be aware that whether 'BaYF<sub>5</sub>' is a compound or a solid state solution is not only a problem of a correct nomenclature. If the cubic fluorite-type  $Ba_{1-x}Y_xF_{2+x}$  phase of variable composition exists then it is likely that x = 0.5 is not the optimal composition in regard of morphological or luminescent properties. Yet, to the best of our knowledge, compositions other than x = 0.5 have not been probed in the studies of so-called 'BaYF<sub>5</sub>' or 'BaGdF<sub>5</sub>'.

In this paper we report the results of systematic studies of nanophases formed in BaF<sub>2</sub>-YF<sub>3</sub> system synthesized using the thermal decomposition method. Besides the X-ray diffraction (XRD) the photoluminescence (PL) spectroscopy was employed for characterization of samples doped with optically active Eu<sup>3+</sup> and Er<sup>3+</sup> ions. The spectroscopic properties of oleic acid (OA) capped NCs are compared with those of ligand-free NCs co-precipitated from aqueous solution. Moreover, we indicate that intensity of upconversion emission observed under excitation at 980 nm for the Ba<sub>1-x</sub>Y<sub>x</sub>F<sub>2+x</sub> phase co-doped with Yb<sup>3+</sup> and Er<sup>3+</sup> ions is strongly composition dependent and, interestingly, its maximum does not correspond to x = 0.5. To the best of our knowledge, this study is the first in which PL spectroscopy is used to identify phases formed in BaF<sub>2</sub>-YF<sub>3</sub> system.

#### 2. Experimental section

#### 2.1. Chemicals and materials

Lanthanide oxides were purchased from Stanford Materials and were of 99.99% purity grade. Oleic acid (90%, technical), octadec-1en (90%, technical) and all other chemicals (ACS purity grade) came from Sigma—Aldrich and were used for samples preparation without any purification.

#### 2.1.1. Preparation of trifluoroacetates precursors

Trifluoroacetic acid salts were prepared by dissolution of appropriate lanthanide oxide (or barium hydroxide octahydrate) in excess of trifluoroacetic acid at 90 °C. After total reconstitution of substrates the excess of acid was evaporated near to dryness and the beakers were placed in vaccum desiccator over  $P_2O_5$  for 2 days.

#### 2.1.2. Synthesis of oleic acid (OA) capped nanoparticles

Appropriate amounts of trifluoracetates (2 mmol in total; e.g. 363.0 mg of Ba(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>, 289.1 mg of Y(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>·3H<sub>2</sub>O, 203.6 mg of Yb(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>·3H<sub>2</sub>O and 22.4 mg of Er(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>·3H<sub>2</sub>O were used for preparation of Ba<sub>0.50</sub>Y<sub>0.30</sub>Yb<sub>0.18</sub>Er<sub>0.02</sub>F<sub>2.5</sub>) were placed in a three neck round bottom flask and 20 cm<sup>3</sup> of a mixture of oleic acid and octadec-1-en (1:1 vol) was added. The flask was placed in a heating mantle and the solution was degassed in vacuum at 100–110 °C for 1 h with periodic Ar refills. Afterwards the flask was placed in a heating salt bath (KNO<sub>3</sub>:NaNO<sub>3</sub>, 1:1 weight ratio) preheated to 360 °C. 30 min after trifluoroacetates decomposition (which occurs at 280–290 °C) the flask was pulled out of the bath and left to cool down naturally. Nanoparticles were precipitated with excess of ethanol, centrifuged and washed five times by means of dissolution in toluene and precipitation with ethanol (about 1:10–1:8 v/v).

#### 2.1.3. Synthesis of ligand-free nanoparticles

 $Ba_{1-x-y}Y_xEu_yF_{2+x+y}$  nanoparticles without any surface ligands were prepared according to the method described in Ref. [22]. Appropriate amounts of BaCl<sub>2</sub> and Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (2 mmol in total, e.g. 1.00 mmol of BaCl<sub>2</sub>, 0.98 mmol of Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and 0.02 mmol  $Eu(NO_3)_3 \cdot 5H_2O$ were used for preparation of of  $Ba_{0.50}Y_{0.49}Eu_{0.01}F_{2.5}$ ) were dissolved in 15 cm<sup>3</sup> of water in a teflon bottle. Afterwards 10% excess (5.5 mmol), relative to stoichiometry. of NH<sub>4</sub>F was added and the bottle was placed on a heating mantle with a magnetic stirrer and heated to 90 °C. After 30 min the bottle was sealed with a cap and left for 24 h in these conditions. Fluorides were collected by means of centrifugation and washed three times with water and once with ethanol and dried in the air.

#### 2.2. Characterization

XRD experiments were carried out on Bruker D8 Advance diffractometer equipped with Cu X-Ray lamp and Vantec detector. Patterns were collected in temperature series from 25 °C to 1000 °C in argon atmosphere and the samples were placed on Pt/Rh heater. Lattice parameters were calculated using Bruker TOPAS software. Corrected emission and excitation spectra were recorded on an Edinburgh Instruments FLSP 920 spectrofluorimeter.

#### 3. Results and discussion

#### 3.1. Structure and morphology

TEM images shown in Fig. 1 indicate that all samples are composed from non-aggregated particles with average size ranging from 5 to 15 nm. At the same time the morphology and dispersity of NCs synthesized under the same conditions strongly depend on REF<sub>3</sub> content in the initial composition.

The selected area diffraction patterns (SAED, Fig. 1) and the XRD patterns (Fig. S1, Supplementary data) confirm that all  $Ba_{1-x}Y_xF_{2+x}$  (x = 0.20–0.90) samples are composed of single cubic fluorite type phase only. In Fig. 2 the lattice parameters *a* determined for OA-capped NCs are presented as a function of YF<sub>3</sub> content and compared with those previously reported [20] for ligand-free samples precipitated from aqueous solution. The plot for OA-caped NCs clearly reveals two regions of linear dependence between *a* and YF<sub>3</sub> content (x): the *a* constant decreases monotonically between x = 0.20 and x = 0.40, as well as between x = 0.40.

For samples with relative YF<sub>3</sub> content from 45 to 75 mol% the linear trend obtained for OA-caped NCs matches very well that recognized for NCs precipitated from aqueous solution [20]. By analogy to results of Fedorov et al. [20] the cubic phases corresponding to the first (YF<sub>3</sub> content up to ~47-48 mol%) and the second (YF<sub>3</sub> content from ~47 to 48-~75 mol%) region of linear dependence in Fig. 1 will be denoted as F-phase and F<sub>1</sub>-phase, respectively. If YF<sub>3</sub> content is larger than 80 mol% formation of F<sub>1</sub>phase is accompanied by precipitation of the second cubic phase depicted in Ref. [20] as (H<sub>3</sub>O)Y<sub>3</sub>F<sub>10</sub>·nH<sub>2</sub>O. Some discrepancy between our results for OA-caped NCs and those presented therein [20] for ligand-free NCs occurs only in the composition region up to 30 mol% of YF<sub>3</sub>. This is due to the fact that in aqueous solutions BaF<sub>2</sub> precipitates as the second phase besides the F-phase, the latter having the constant lattice parameter value a = 5.933 Å. Since formation of BaF<sub>2</sub> is not observed in the procedure used by us for synthesis of OA-capped NCs the lattice parameters for single cubic fluorite type phases formed in this region vary monotonically and the obtained linear correlation matches well the trend found using data of [20] for co-precipitated samples with 43 and 35 mol% YF<sub>3</sub>, and data of [21] for sample with 25 mol% YF<sub>3</sub> synthesized by solid



**Fig. 1.** TEM images of  $Yb^{3+}/Er^{3+}$  co-doped (left panel) or  $Eu^{3+}$  doped (right panel) nanocrystalline samples with different total REF<sub>3</sub> content a)  $Ba_{0.7}Y_{0.18}Er_{0.02}F_{2.5}$  (30% REF<sub>3</sub>), c)  $Ba_{0.5}Y_{0.32}Eu_{0.01}F_{2.5}$  (40% REF<sub>3</sub>), c)  $Ba_{0.5}Y_{0.32}Eu_{0.01}F_{2.5}$  (40% REF<sub>3</sub>), c)  $Ba_{0.5}Y_{0.32}Eu_{0.01}F_{2.5}$  (50% REF<sub>3</sub>), d)  $Ba_{0.67}Y_{0.32}Eu_{0.01}F_{2.5}$  (33% REF<sub>3</sub>) e)  $Ba_{0.5}Y_{0.49}Eu_{0.01}F_{2.5}$  (50% REF<sub>3</sub>) and f)  $Ba_{0.34}Y_{0.65}Eu_{0.01}F_{2.5}$  (66% REF<sub>3</sub>). Insets present selected area diffraction patterns (SAED).



**Fig. 2.** The plot of lattice parameter a as a function of YF<sub>3</sub> content. The borderline between phases are adopted from Fig. 3 in Ref. [20].

state reaction.

The observed linear correlation between the lattice constant a and the YF<sub>3</sub> content in the sample indicates unambiguously that

nanophases formed in the  $BaF_2-YF_3$  system during thermolysis of metal trifluoroacetate precursors in a OA/ODE solvent are solid state solutions, analogous to those obtained by precipitation from aqueous solution [20] or solid state reaction [21]. In contrast, if any stoichiometric compound would be formed, a discontinuity in the liner dependence should be expected, which is not the case.

To reveal the possible formation of any ordered and stoichiometric phases under elevated temperature conditions, the temperature dependent XRD studies have been carried out. The XRD patterns were recorded in 25-1000 °C range for ligand-free NCs heated in Ar atmosphere with a heating rate of 3 °C/min. The phase diagram of BaF<sub>2</sub>-YF<sub>3</sub> system [18] predicts the existence of BaY<sub>2</sub>F<sub>8</sub> (monoclinic, C2/m [23]) and Ba<sub>4</sub>Y<sub>3</sub>F<sub>17</sub> (rhombohedral, R-3 [24]) phases. Fig. 3a demonstrates that the non-equilibrium phase with BaF<sub>2</sub>:YF<sub>3</sub> molar ratio of 1:2 (67 mol% of YF<sub>3</sub>) can be converted to the equilibrium monoclinic BaY<sub>2</sub>F<sub>8</sub> phase during heating at 750 °C, which corroborates with previous reports [25]. The same main product was observed for sample with 60 mol% YF<sub>3</sub>, although in this case  $BaF_2$  and  $Ba_4Y_3F_{17}$  were identified as by-products with XRD. The pure Ba<sub>4</sub>Y<sub>3</sub>F<sub>17</sub> phase was recognized in the XRD pattern for samples with 43 mol% YF<sub>3</sub> (BaF<sub>2</sub>:YF<sub>3</sub> molar ratio of 1:2) heated to 750 °C.

In contrast, heating of the sample with  $BaF_2$ :YF<sub>3</sub> molar ratio of 1:1 (50 mol% YF<sub>3</sub>), corresponding to the so-called 'BaYF<sub>5</sub>' composition, has not led to its conversion to any other phase. The XRD patterns recorded in the temperature range up to 750 °C correspond to the single F<sub>1</sub>-phase (Ba<sub>0.5</sub>Y<sub>0.5</sub>F<sub>2.5</sub>) of fluorite-type cubic



Fig. 3. X-ray diffraction patterns of the BaF<sub>2</sub>-YF<sub>3</sub> samples with 67 mol% of YF<sub>3</sub> (a) and with 50 mol% of YF<sub>3</sub> (b) as-precipitated from aqueous solutions (top panels) and after heating at 750 °C at Ar atmosphere (bottom panels).

structure and the only noticeable effect is narrowing of diffraction peaks due to the increase of grain sizes. The sample of this composition heated at or above 750 °C undergoes partial decomposition, as is evidenced by appearance of additional phases identified as  $BaF_2$  and  $Ba_4Y_3F_{17}$  in the XRD pattern (Fig. 3b). In a control experiment a sample with 50 mol% YF<sub>3</sub> was annealed for 72 h at 700 °C in Ar atmosphere. Also in this case, any other phase than cubic F<sub>1</sub>-phase could be detected in the XRD diagram.

In contrast to phases precipitated from aqueous solution, heating of OA-capped NCs in Ar atmosphere led to their decomposition at 750 °C, regardless of their initial stoichiometry. One of the decomposition product is BaF<sub>2</sub>, and the second depends on the relative content of YF<sub>3</sub> in the initial sample. XRD patterns reveal Y<sub>2</sub>O<sub>3</sub> as the second decomposition product for samples with lower relative content of YF<sub>3</sub> (e.g. for sample with BaF<sub>2</sub>:YF<sub>3</sub> molar ratio of 2:1, corresponding to 33 mol% of YF<sub>3</sub>), whereas those with larger content of YF<sub>3</sub> (e.g. sample with BaF<sub>2</sub>:YF<sub>3</sub> molar ratio of 1:2, corresponding to 67 mol% of YF<sub>3</sub>) decompose to BaF<sub>2</sub> and YOF. Formation of Y<sub>2</sub>O<sub>3</sub> or YOF as the second decomposition product is also confirmed by PL and PL excitation spectra recorded for samples doped with Eu<sup>3+</sup> (Fig. S2, Supplementary data). The different decomposition products may be also easily discerned visually since samples which yields Y<sub>2</sub>O<sub>3</sub> or YOF appear after heat-treatment as white or dark-grey powders, respectively.

It is worth to notice that formation of oxo-derivative products does not result from presence of oxygen traces in a furnace atmosphere, since such products are not observed during analogous experiments with ligand-free NCs. Therefore, formation of Y2O3 or YOF during heat treatment results from the presence of OA ligands on the NCs surface. This is additionally proved by a control experiment in which most of the OA ligands was removed from the NCs surface by annealing the sample with 67 mol% of YF<sub>3</sub> (BaF<sub>2</sub>:YF<sub>3</sub> molar ratio of 2:1) in melted ammonium bifluoride (NH<sub>4</sub>F<sub>2</sub>H) for 1 h. Detaching of OA from NC's surface could be easily detected by appearance of an oleic phase, which was separated and discarded. The obtained solid mixture of NCs in NH<sub>4</sub>F<sub>2</sub>H was subsequently heated in Ar stream, initially at 350 °C to remove NH<sub>4</sub>F and HF, and then at 750 °C. In this case the main product identified in the XRD diagram was  $BaY_2F_8$ , with only small admixture of  $Ba_4Y_3F_{17}$ , whereas neither Y<sub>2</sub>O<sub>3</sub> nor YOF were observed.

At present, we are not in position to propose the mechanism explaining the formation of  $Y_2O_3$  or YOF depending on the relative content of YF<sub>3</sub> in the initial sample. The NMR spectra recorded for nanoparticles dispersed in CDCl<sub>3</sub> (Fig. S3, Supplementary data) do not reveal any differences in chemical composition of ligands present on the surface of  $Ba_{1-x}Y_xF_{2+x}$  NCs with different *x* value. Similarly, no significant differences were observed in IR spectra measured for samples corresponding to F-phase (40 mol% YF<sub>3</sub>) and F<sub>1</sub>-phase (50 or 67 mol% YF<sub>3</sub>) – Fig. S4 (Supplementary data). The band occurring for all samples at 1546 cm<sup>-1</sup> corresponds to the assymetric stretching mode of COO<sup>-</sup> group and signifies the formation of metal-carboxylate species [26]. The symmetric COO<sup>-</sup> stretch is observed at 1462 cm<sup>-1</sup>. The separation of 84 cm<sup>-1</sup> between those bands indicates bidendate chelating coordination of COO<sup>-</sup> group to NCs surface [26]. The band positions of ligands coordinated to NC's surface are very similar to those of oleate ligand in yttrium oleates (Fig. S4, Supplementary data).

Also thermogravimetry-differential thermal analysis (TG-DTA) measurements do not reveal significant differences in thermal stability of samples with 33, 50 or 67 mol% YF<sub>3</sub>, which during heating to 600 °C exhibit loss of 68.1, 78.4 and 73.6 wt% of their initial weight, respectively (Fig. S5, Supplementary data). For samples with the smaller relative content of YF<sub>3</sub> the decrease of mass occurs in rather continues manner, whereas for those containing larger amounts of YF<sub>3</sub> more distinct steps can be discerned in TG curve (Fig. S6, Supplementary data).

#### 3.2. Photoluminescence spectra

The previous XRD studies revealed existence in BaF<sub>2</sub>-YF<sub>3</sub> system of two different phases, F and F<sub>1</sub>, which may be attributed to the formation of the different type defects in the crystal lattice of Ba<sub>1-x</sub>Y<sub>x</sub>F<sub>2+x</sub> [19,20]. If so, one may expect appropriate composition dependence of PL spectra measured for optically active Ln<sup>3+</sup> ions doped into Ba<sub>1-x</sub>Y<sub>x</sub>F<sub>2+x</sub> phases. For this purpose Eu<sup>3+</sup> ion was chosen as the most suitable dopant to take advantage of its luminescence as a structural probe [27]. The PL spectra were recorded for ligand-free Ba<sub>1-x-y</sub>Y<sub>x</sub>Eu<sub>y</sub>F<sub>2+x+y</sub> samples where y = 0.01 and x = 0.32, 0.36, 0.42, 0.49, 0.66 and 0.74, which corresponds to relative content of REF<sub>3</sub> (YF<sub>3</sub> + EuF<sub>3</sub>) of 33, 37, 43, 50, 67, 75 and 90 mol%, respectively.

Based on their mutual similarity the obtained PL spectra may be grouped into three sets, and the representative member of each set is presented in Fig. 4. The first group consists of the spectra



**Fig. 4.** The PL spectra recorded for ligand-free  $Ba_{1-x-y}Y_xEu_yF_{2+x+y}$  samples with a) 33, b) 75 and c) 90 mol% of REF<sub>3</sub> (YF<sub>3</sub> + EuF<sub>3</sub>) under excitation at 394 nm.

recorded for samples with 33, 37 and 43 mol% of REF<sub>3</sub>. The second group encompasses spectra of samples containing 67 and 75 mol% REF<sub>3</sub>. The spectrum obtained for sample with 90 mol% of REF<sub>3</sub> differs markedly from others and thus should be included into a separate group.

The shape of the spectra evolves gradually with increasing REF<sub>3</sub> content and it is not straightforward to establish the exact composition borderline between each group. For example, the structure of the spectrum obtained for sample with 50 mol% content of REF<sub>3</sub> is very similar to that of 43 mol% REF<sub>3</sub> sample, which may suggest that both should be included into the same group. On the other hand some differences in relative intensity of bands observed in both spectra may be discerned, rising doubts about such classification. Therefore, the I<sub>0-4</sub>/I<sub>0-2</sub> intensity ratio of the  $^5D_0 \rightarrow \, ^7F_4$  and  $^5D_0 \rightarrow \, ^7F_2$  emission transitions of Eu  $^{3+}$  is chosen as a suitable parameter allowing to present in a more quantitative manner changes in PL spectra as a function of REF<sub>3</sub> content (here we used I<sub>0-4</sub>/I<sub>0-2</sub> instead of more commonly applied I<sub>0-1</sub>/I<sub>0-2</sub> intensity ratio since intensity of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition cannot be precisely determined owing to its overlap with the  ${}^{5}D_{1} \rightarrow {}^{7}F_{3}$ transition).

Two regions of linear correlation between  $I_{0-4}/I_{0-2}$  intensity ratio and mol% of REF<sub>3</sub> may be distinguished in Fig. 5a for ligand-free NCs precipitated from aqueous solution. They mark out concentration ranges, extending below and above about 47 mol% REF<sub>3</sub>, which match well those determined from XRD studies (Fig. 2) and, accordingly, should be assigned as corresponding to F- and F<sub>1</sub>phases, respectively. With the increase of REF<sub>3</sub> content the  $I_{0-4}/I_{0-2}$ intensity ratio increases for F-phase, whereas the opposite trend is observed for F1-phase. Based on established trends in the I0-4/I0-2 ratio the spectrum of sample with 50 mol% REF<sub>3</sub> should be unequivocally attributed to phase F<sub>1</sub>, in spite that its structure is more alike to those of samples with 33, 37 and 43 mol % REF<sub>3</sub>. The I<sub>0-4</sub>/I<sub>0-2</sub> ratio for sample with 90 mol% REF<sub>3</sub> deviates significantly from both linear trends. Moreover, the number of lines is larger than observed in spectra of other samples (Fig. 5), which suggests that this spectrum is actually a combination of two overlapping spectra. This conclusion is in accordance with results of XRD studies [20] showing that the mixture of F1-phase and (H3O)Y3F10·nH2O phase precipitates for YF<sub>3</sub> content larger than 80 mol%.

The  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  emission decay time decreases with increasing of YF<sub>3</sub> content (Fig. 5b). In the plot presenting the dependence of the emission decay time on the YF<sub>3</sub> content two regions of linear correlation with different slopes may be easily distinguished and their composition ranges match well those identified on the basis of the  $I_{0-4}/I_{0-2}$  intensity ratio. The point at 90 mol% YF<sub>3</sub> (presumably corresponding to the mixture of  $F_1$ -phase and  $(H_3O)Y_3F_{10} \cdot nH_2O$  phase) deviates much less from the trend obtained for F<sub>1</sub>-phase than it was observed while comparing intensity ratio (Fig. 5a). This may suggest that emission decay time of Eu<sup>3+</sup> ions in the REF<sub>3</sub> reach F<sub>1</sub>phase is similar to that in  $(H_3O)Y_3F_{10}$  nH<sub>2</sub>O phase or, what is more likely, that Eu<sup>3+</sup> emission in the latter is strongly quenched and the main contribution to the decay curve comes from Eu<sup>3+</sup> ions in F<sub>1</sub>phase. For samples with lower concentration of REF<sub>3</sub> the rise time is observed in Eu<sup>3+ 5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>1</sub> emission transients. The rise time values decrease monotonically along the increase of REF<sub>3</sub> content for samples comprising F-phase (inset in Fig. 5b). The point for sample with 50 mol% REF<sub>3</sub> evidently deviates from the above trend, confirming precipitation of F1-phase for this composition. However, in the region of the F<sub>1</sub>-phase the correlation between the rise time and REFF<sub>3</sub> content cannot be established, because the rise time gradually diminish for more YF<sub>3</sub> abundant samples and finally becomes unobserved for those with REF<sub>3</sub> content larger then 65 mol%.

Fig. 6 compares emission spectra of OA-capped and ligand-free



**Fig. 5.** a) The  $I_{0-4}/I_{0-2}$  intensity ratio of the  ${}^5D_0 \rightarrow {}^7F_4$  and  ${}^5D_0 \rightarrow {}^7F_2$  emission transitions of  $Eu^{3+}$  in OA-capped and ligand-free  $Ba_{1-x}Y_xF_{2+x}$  NCs as a function of REF<sub>3</sub> (YF<sub>3</sub> + EuF<sub>3</sub>) content. b) The  ${}^5D_0 \rightarrow {}^7F_1$  emission decay time of  $Eu^{3+}$  in ligand-free  $Ba_{1-x}Y_xF_{2+x}$  NCs as a function of REF<sub>3</sub> (YF<sub>3</sub> + EuF<sub>3</sub>) content. The inset presents dependence of rise time values observed in  ${}^5D_0 \rightarrow {}^7F_1$  emission transients on REF<sub>3</sub> content for ligand-free  $Ba_{1-x}Y_xF_{2+x}$  NCs.



Fig. 6. PL spectra of OA-capped and ligand free  $Ba_{1-x}Y_xF_{2+x}$  NCs doped with  $Eu^{3+}$  ion.

NCs doped with Eu<sup>3+</sup> ion recorded for samples with 67 mol % REF<sub>3</sub>. The relative intensity of the  ${}^5D_0 \rightarrow {}^7F_0$  and  ${}^5D_0 \rightarrow {}^7F_2$  transitions (normalized to  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  magnetic dipole transition) is much larger for OA-capped than for ligand-free NCs, which indicates the lower local symmetry of dopant ions in the former ones. This is expected, since due to their smaller grain sizes OA-capped NCs posses a more developed surface area, causing that number of the low symmetry surface sites accessible for dopant ions is larger than in the case of bigger nanocrystals precipitated from aqueous solution. More disturbed environment of Eu<sup>3+</sup> ions manifests itself also in broadening of emission bands that leads to loss of some fine structure details. Hence, the variation in the shape of emission spectra recorded for Eu<sup>3+</sup> doped OA-capped NCs with different REF<sub>3</sub> content is less pronounced than in the case of ligand-free samples. Nevertheless, two regions of linear relationship between the  $I_{0-4}/I_{0-2}$  intensity ratio and REF<sub>3</sub> molar fraction are obviously visible, reflecting the composition ranges in which F- and F1-phases occur (Fig. 5a). Note that for ligand-free samples the  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ transition is more intense than the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition ( $I_{0-4}/I_{0-1}$  $_2 > 1$ ), while opposite ( $I_{0-4}/I_{0-2} < 1$ ) is true for OA-caped NCs. Interestingly, the evolution of the  $I_{0-4}/I_{0-2}$  intensity ratio as a function of REF3 content follow opposite trends for OA-capped and ligand-free NCs (Fig. 5a).

Fig. 7 presents UC emission spectra recorded for OA-capped NCs doped with Yb<sup>3+</sup> and Er<sup>3+</sup> ions under excitation with laser diode at 980 nm. The green emission bands at 540 and 520 nm are due to de-excitation of  ${}^{4}S_{3/2}$  and thermalized  ${}^{2}H_{11/2}$  levels, respectively. At about 654 nm the red  ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$  emission is observed. The inset (black triangle) in Fig. 7 shows the dependence of the green-to-red emission intensity ratio (G/R), corresponding to  ${}^{2}H_{11/2} + {}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$  and  ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$  transitions, respectively, on the relative percentage content of REF<sub>3</sub> in the sample.

If mechanisms leading to population of the  ${}^{4}F_{9/2}$  red emitting level through multiphonon relaxation of the  ${}^{4}S_{3/2}$  green emitting level become more efficient, a decrease of the green-to-red intensity ratio is expected. Thus, this ratio may mirror the contribution of non-radiative relaxation processes, but may also indicate changes in the mechanism of excitation processes. For example, alteration in local surroundings may influence the efficiency of cross-relaxation processes  $|{}^{4}I_{15/2}, {}^{4}S_{3/2} > \rightarrow |{}^{4}I_{13/2}, {}^{4}I_{9/2} > and |{}^{4}I_{15/2}, {}^{4}S_{3/2} > \rightarrow |{}^{4}I_{9/2}, {}^{4}I_{13/2} > occurring between two Er^{3+} ions.$ 

Inset in Fig. 7 reveals that two regions of liner dependence may



**Fig. 7.** Upconversion emission spectra recorded under excitation with laser diode at 980 nm for OA-capped Ba<sub>1-x</sub>Y<sub>x</sub>F<sub>2+x</sub> NCs doped with Yb<sup>3+</sup>(18%) and Er<sup>3+</sup>(2%) ions, with total REF<sub>3</sub> content of 40% (solid line) and 50% (dot line). The inset show the dependence of the green-to-red, G/R,  $({}^{2}H_{11/2}+{}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$  to  ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ ) emission intensity ratio (black triangle) and the relative intensity of UC emission (bars) on the relative percentage content of REF<sub>3</sub> in the sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

be distinguished on the plot of the green-to-red intensity ratio, corresponding to the area of occurrence of F- and F1-phases identified in Figs. 2 and 5. Due to a sudden drop of upconversion intensity the green-to-red intensity ratio can not be determined for samples containing more than 60 mol% of REF<sub>3</sub>. Bars in the inset in Fig. 7 show that intensity of UC emission increases with increasing of REF<sub>3</sub> in the region of F-phase, whereas the opposite trend is evident for F<sub>1</sub>-Phase. This phenomenon may be related with different kind of defects and clusters formed in both phases [20] and certainly warrants further experimental study. Interestingly, UC emission is at least sixteen times more intense for 40 mol% REF<sub>3</sub> sample as compared to that of 50 mol% REF<sub>3</sub> (1:1 stoichiometry). At the same time the TEM images show that morphology of both Fand F1-phases depends on the sample composition. Hence, although it is not clear whether sample morphology or specific BaF<sub>2</sub>-YF<sub>3</sub> stoichiometry is the main factor causing that the highest intensity is observed for 40 mol% REF<sub>3</sub> sample, the obtained trend indicates unequivocally that the most intense UC emission is expected for REF<sub>3</sub> reach region of F-phase.

#### 4. Conclusions

In this paper PL spectroscopy was used as a convenient and reliable tool for discrimination of nanofluoride phases formed in BaF<sub>2</sub>-YF<sub>3</sub> system during thermolysis of metal trifluoroacetates in high boiling organic solvents. Analysis of i) the I<sub>0-4</sub>/I<sub>0-2</sub> intensity ratio and ii) emission decay times for Eu<sup>3+</sup> doped samples as well as iii) relative intensity of UC emission and iv) the green-to-red intensity ratio for Yb<sup>3+</sup>/Er<sup>3+</sup> co-doped samples as a function of REF<sub>3</sub> content leads to unambiguous conclusion that two Ba<sub>1-x</sub>RE<sub>x</sub>F<sub>2+x</sub> phases with cubic fluorite-type structure are formed for samples with 35–75 mol % of REF<sub>3</sub>. Results of PL measurements corroborates well with those of XRD study. The correlation between lattice constants or spectroscopic parameters and the percentage of REF<sub>3</sub> content is the same irrespective of whether BaF<sub>2</sub>-YF<sub>3</sub> nanophases are obtained by thermolysis – yielding OA-capped NCs, or precipitated from aqueous solution – yielding ligand-free NCs.

However, in none of our experiments was there any evidence for formation of so-called 'BaYF<sub>5</sub>' nanocrystals. Instead, our results demonstrate that also during thermolysis a solid state solution is formed for 1:1 BaF<sub>2</sub>-YF<sub>3</sub> stoichiometry, analogously as it has been observed during XRD analysis of phases precipitated in aqueous solution [19,20]. Therefore, the formed nanofluorides should be designated as a cubic fluorite-type  $Ba_{0.5}Y_{0.5}F_{2.5}$  phase, and in neither case it should be called as the 'BaYF<sub>5</sub>' compound.

This finding bears some important practical implications. Owing to assumption of existence of the specific 'BaYF5' compound in most, if not all, studies hitherto reported, only the phase with x = 0.5 (1:1 BaF<sub>2</sub>-YF<sub>3</sub> stoichiometry) has been probed among broad range of possible composition of Ba<sub>1-x</sub>RE<sub>x</sub>F<sub>2+x</sub> phases. However, this is not necessarily the optimal composition in regard of nanoparticles morphology or emission properties. Indeed, in present studies the most intense UC emission is obtained for Yb<sup>3+</sup>/Er<sup>3+</sup> codoped sample with 40 mol% REF<sub>3</sub>. For sample with 50 mol% of REF<sub>3</sub> (1:1 BaF<sub>2</sub>-YF<sub>3</sub> stoichiometry) the UC emission is more than sixteen times less intense, whereas it is totally quenched for those containing more then 60 mol% REF<sub>3</sub>. Possibly, the optimal composition may depend on the specific protocol employed for synthesis of OAcapped NPs. However, bearing in mind that solid Ba<sub>1-x</sub>RE<sub>x</sub>F<sub>2+x</sub> solutions of variable composition, rather then specific stoichiometric compounds, are formed in BaF2-YF3 system, one may be much more flexible while choosing possible compositions for experiments.

#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jallcom.2016.02.255.

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