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Synthesis of luminescent KY_3F_{10} nanopowder multi-doped with lanthanide ions by a co-precipitation method

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Abstract: A series of KY_3F_{10} nanophosphors doped with Gd^{3+}, Ce^{3+} and Eu^{3+} ions were obtained with the use of a co-precipitation method. The resulting products were white precipitates, consisting of spherical particles with diameter about 150–200 nm, which was confirmed using transmission electron microscopy (TEM) technique. Powder X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX) measurements confirmed appropriate structures of the nanoparticles obtained. Spectroscopic properties of the products were examined on the basis of the measured excitation/emission spectra and luminescence decay curves. The synthesized samples showed orange-red luminescence, characteristic for Eu^{3+} ions. The reaction process was performed in required alkaline pH adjusted with the use of ethylenediaminetetraacetic acid (EDTA) and potassium hydroxide. The samples containing large amounts of Gd^{3+} dopant ions exhibited a tendency to form products with different morphologies.

Keywords: fluorides; co-precipitation; nanophosphors; luminescence; nanopowders; Ce^{3+}/Gd^{3+}/Eu^{3+} doping; rare earths

Luminescent properties of lanthanide ions, Ln(III), make them a subject of many studies and possible applications, including inorganic luminescent nanomaterials[1–8]. Inorganic luminophores doped with Ln(III) show intense, multicolour emission, long luminescence lifetime and narrow emission bands resulting from the forbidden 4f-4f transitions[9–11]. Inorganic character of nanophosphors results in their high resistance against photobleaching, thermal degradation, high-energy radiation, etc. This leads to stable and efficient luminescence, which is especially important for their bioanalytical applications. Other benefits for the use of such lanthanide doped luminescent nanomaterials are their biocompatibility and possibility of formation of more complex, functional materials[12–18].

One of the simplest and characterized by very intense luminescence group of nanomaterials are matrices based on fluorides, e.g., LaF_3 YF_3, CeF_3, GdF_3, $NaYF_4$, KY_3F_{10}, Sr_2LnF_7, etc.[19–22]. In general, lanthanide fluorides reveal very low phonon energy of crystal lattice (≈350 cm^{-1} for LaF_3[23]), resulting in relatively high quantum yields of luminescence, related to negligible nonradiative relaxation of their excited states[24].

The un-doped or doped KY_3F_{10} can be obtained as single crystals and micro-/nanocrystals[25,26]. However, preparation methods are usually quite problematic in their use because of complexity and difficulties in reproducibility of the product, they require hydrothermal conditions or high temperature calcination as well[25,27,28].

In this study we focused on the synthesis, structural, morphological and spectroscopic characterization of luminescent KY_3F_{10} nanopowders doped with lanthanide ions (Ce^{3+}/Gd^{3+}/Eu^{3+}). The method used for the synthesis was based on the co-precipitation of components in the presence of ethylenediaminetetraacetic acid (EDTA), acting as an anti-agglomerating and complexing agent. EDTA worked also as a buffer, which maintained an alkaline environment during the reaction.

1 Experimental

1.1 Synthesis

Materials: Aqueous solutions of $Gd(NO_3)_3$, $Y(NO_3)_3$ and $Eu(NO_3)_3$ were obtained by dissolving respectively Gd_2O_3, Y_2O_3 and Eu_2O_3 oxides (Stanford Materials, 99.99%) in a concentrated HNO_3 (POCh S.A., pure, p.a.). $CeCl_3$ solution was obtained by dissolving $CeCl_3{\cdot}7H_2O$ salt in deionized water. As a source of fluoride ions potassium tetrafluoroborate, KBF_4 (Sigma-Aldrich, ≥96%) was used. KOH (pure p.a., 85%) was purchased from POCh S.A., whereas ethylenediaminetetraacetic acid-EDTA (ACS reagent, 99.4%–100%) was from Sigma-Aldrich. Deionized water was used for all experiments.

Syntheses were performed to get each time 0.5 g of the product. Steps of the synthesis procedure were as follows: 0.5 g of ethylenediaminetetraacetic acid was added to 40 mL of deionized water and heated to 60 ºC. Next, to this solution, mixed with a magnetic stirrer was added dropwise

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with a solution of KOH until pH 8 was reached, after that stoichiometric amount of KBF_4 (relative to Ln^{3+} ions) was added. Subsequently, the solution of lanthanide ions (mixed at the desired molar ratio) in 40 mL of water was prepared. Both of the solutions were mixed together and heated to 60 ºC. Afterwards the pH was raised to 8.5 with KOH (except of the synthesis with 97% of Gd^{3+}, where the pH was adjusted to 9.5). The reaction was continued for 20 h with stirring and heating at 60 ºC. The obtained white precipitates were collected and dried in an oven overnight, at 80 ºC. In the whole article the percentage values (x) are molar percentage (mol.%).

It has been observed, that with an increasing amount of the Gd^{3+} ions, the yield of the synthesis decreased. This observation was the reason for adjusting of higher reaction pH (approx. 9.5) for the sample with 97% of the Gd^{3+} ions (at pH=8.5 no product has precipitated). This also suggests that synthesis of the KLn_3F_{10} nanopowders is strongly dependent on the reaction pH.

1.2 Characterization

TEM measurements were performed with a Philips CM200FEG electron microscope operating at 200 kV, equipped with an EDAX analyzer. Luminescence measurements, i.e., excitation/emission spectra and luminescence decay curves were conducted on a Hitachi F-7000 spectrofluorometer. The recorded spectra were corrected for the apparatus response. XRD patterns were collected with a Bruker AXS D8 Advance diffractometer, using Cu Kα radiation (λ=0.15406 nm).

2 Results and discussion

2.1 Structure and morphology

Comparison of the measured XRD patterns (Fig. 1) with the reference pattern (ICSD 108778) confirms a successful preparation of KY_3F_{10}. Synthesized samples crystallized in a cubic system, *Fm*-3*m* space group. Moreover, all of the reflexes are broadened because of the nanocrystallinity of the products synthesized. During the synthesis of the products highly doped with Gd^{3+} ions, the isostructural KGd_3F_{10} nanocrystals are formed, having similar structural and luminescent properties. This effect is due to the replacement of Y^{3+} ions by larger Gd^{3+} ones.

TEM images of the three samples of KY_3F_{10}:2%Ce^{3+}, 1%Eu^{3+},x%Gd^{3+}, where x=0% (a, b), 30% (c, d), 97% (e, f) are shown in Fig. 2. All of the synthesized KY_3F_{10} prod

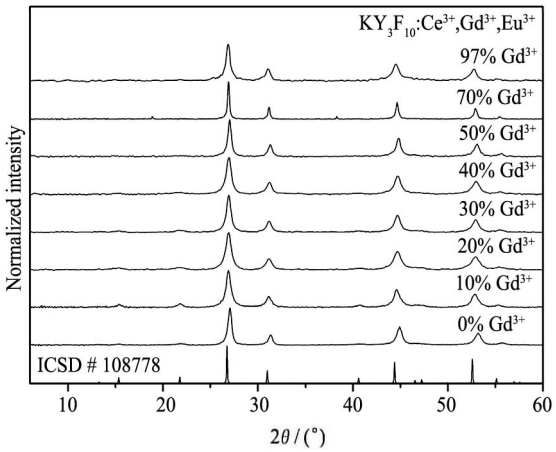

Fig. 1 XRD patterns of KY_3F_{10}:2%Ce^{3+},1%Eu^{3+},x%Gd^{3+}, x=0%, 30%, 97% Gd^{3+} ions

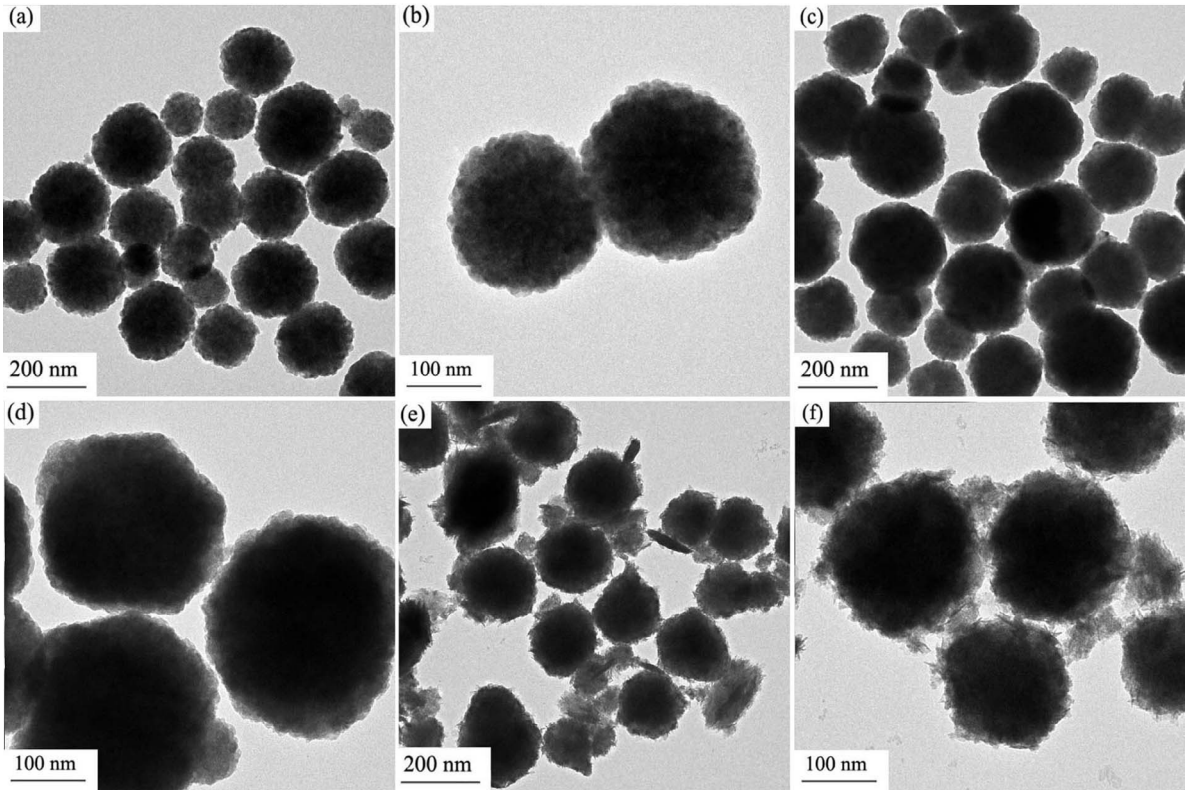

Fig. 2 TEM images of KY_3F_{10}:2%Ce^{3+},1%Eu^{3+},x%Gd^{3+}, where x=0% (a, b), 30% (c, d), 97% (e, f)