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# Nanocrystalline rare earth fluorides doped with $Pr^{3+}$ ions

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**Abstract:** Praseodymium(III) doped $CeF_3$, $CeF_3$:Gd, $LaF_3$, $GdF_3$ and $YF_3$ inorganic fluorides were precipitated in an aqueous, surfactant-free solution, using $NH_4F$ as a source of fluoride ions. The as-prepared products were subjected to a hydrothermal treatment, which led to the formation of crystalline nanoluminophores, composed of spherical (≈30 nm) and elongated (≈40–200 nm) nanostructures. Due to the presence of $Pr^{3+}$ ions, the synthesized nanomaterials showed yellow luminescence under a blue light irradiation. The nanoluminophore based on the $YF_3$ host revealed the most promising spectroscopic properties, i.e., bright and intensive emission, hence it was investigated in detail. The photophysical properties of the nanomaterials obtained were studied by powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and spectrofluorometry, i.e., measurements of excitation/emission spectra and luminescence decay curves.

**Keywords:** yellow luminescence; lanthanide fluorides; $Pr^{3+}$ doping; nanocrystals; hydrothermal post-treatment; $Ce^{3+}$ quenching; rare earths

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Luminescent nanomaterials have been intensively investigated over the last decade[1–5]. Such materials are composed of nano-sized particles, whose at least one dimension is in the size range of 1–100 nm[6]. Two major groups of luminescent, solid nanomaterials are semiconductive quantum-dots and lanthanide doped luminophores. Their main advantages over the organic fluorescent compounds are resistance to photo-bleaching/oxidation and the ability to formation of stable aqueous colloids[7–10]. These features are crucial in bioapplications of nanoparticles, e.g., bio-imaging and drug-delivery[11,12]. However, the ultra-small nanoparticles based on heavy metal ions, such as CdSe, CdTe and PbS quantum dots are often eco- and cytotoxic, which limits their possible applications[13,14].

The luminescent rare earth nanocrystals, like inorganic oxides, fluorides, phosphates, vanadates and borates are usually non-cytotoxic, eco-friendly and biocompatible materials[3,15–17]. Appropriate doping with lanthanide ions ($Ln^{3+}$), makes them efficient luminophores, which can generate intense visible emission in a broad range of colours, under UV or IR excitation (up-conversion)[18–21]. Moreover, they exhibit narrow emission bands, long radiative lifetime resistance to photo-degradation, biocompatibility, stability of the colloids formed and facile surface modification[3,16,19–22]. That is why lanthanide doped inorganic nanomaterials seem to fulfil all requirements of modern phosphors, which makes them important for industrial and biomedical applications, such as new light sources, luminescent tracers, document security agents, biomarkers, etc.[23–26]

Here we reported hydrothermal synthesis and photophysical characterization of rare earth fluorides, doped with $Pr^{3+}$ ions, $REF_3:Pr^{3+}$ (RE=Y, La, Ce, Gd). The products obtained were composed of small nanocrystals (30–50 nm) exhibiting yellow luminescence under a blue light irradiation (≈440 nm). The use of $Pr^{3+}$ ion as a luminescence activator is due to its interesting spectroscopic properties, i.e., specific energy level structure and rarely observed yellow colour of emission.

## 1 Experimental

### 1.1 Synthesis

Materials: $La_2O_3$, $Gd_2O_3$, $Y_2O_3$ and $Pr_6O_{11}$ oxides (Stanford Materials, 99.99%) were separately dissolved in a concentrated $HNO_3$ (POCh S.A., pure. p.a.) to obtain $La(NO_3)_3$, $Gd(NO_3)_3$, $Y(NO_3)_3$ and $Pr(NO_3)_3$ aqueous solutions, respectively. $CeCl_3\cdot 7H_2O$ (99.9%) was purchased from Sigma-Aldrich. Ammonium fluoride, $NH_4F$ (ACS grade, ≥98%) was purchased from POCh S.A., and used as a source of fluoride ions. For all syntheses, the deionized water was used.

All of the syntheses were performed to obtain 1 g of the product. A typical synthesis procedure was as follows: an aqueous solution of $Pr(NO_3)_3$ was mixed together with the given solution of rare earth salt, i.e., $CeCl_3$, $La(NO_3)_3$, $Gd(NO_3)_3$ or $Y(NO_3)_3$, in an appropriate molar ratio. The formed solution was filled with water up to 100 mL. The second solution was prepared by dissolving 50% molar excess of $NH_4F$ in 100 mL of water. Subsequently, the

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solution containing rare earth ions was added dropwise to the solution containing fluoride ions. During the synthesis process, the reaction system was intensively magnetically stirred, and heated up to 60 ºC. When the reaction was completed, the resultant white, colloidal precipitate of the given REF$_3$:Pr$^{3+}$ was centrifuged and washed with water several times. In order to increase crystallinity of the products, the purified colloidal precipitates were transferred into the Teflon lined vessel, and hydrothermally treated in a microwave autoclave for 2 h (180 ºC, 40 bar). When the process was finished, the final nanomaterials were collected and dried overnight, in an oven (80 ºC).

### 1.2 Characterization

Powder X-ray diffraction patterns were recorded with a Bruker AXS D8 Advance diffractometer, using Cu Kα radiation ($\lambda$=0.15406 nm). Electron microscopy images were acquired using a transmission electron microscope JEM 1200 EXII, JEOL, operating at accelerating voltage 80 kV. The excitation spectra were measured using a Hitachi F-7000 spectrofluorometer, whereas the emission spectra and luminescence decay curves were measured with the use of the QuantaMasterTM 40 spectrophotometer equipped with an Opolette 355LD UVDM tunable laser, which had a repetition rate of 20 Hz, as an excitation source and a Hamamatsu R928 photomultiplier as a detector. The excitation and emission spectra were appropriately corrected for the apparatus response.

## 2 Results and discussion

### 2.1 Structure and morphology

The products synthesized were analysed using a powder XRD technique, which confirmed their expected crystal structures. In the whole article the content of Ln$^{3+}$ ions ($x$) are molar percentage (mol.%). Fig. 1 presents XRD patterns of the REF$_3$:1%Pr$^{3+}$ (RE=La, Ce, Gd, Y), and Fig. 2 shows XRD data for YF$_3$:$x$Pr$^{3+}$ ($x$=0.1%–5%), which were synthesized as a series of compounds doped with different amounts of Pr$^{3+}$ ions (because of the most intense luminescence of the doped YF$_3$, in comparison to the other hosts). The recorded diffractograms fit the corresponding reference patterns of the given REF$_3$ host, namely: LaF$_3$:1%Pr$^{3+}$ crystallises as hexagonal LaF$_3$, in a space group *P*-3*c*1 (JCPDS card No. 032-0483); both CeF$_3$:1%Pr$^{3+}$ and CeF$_3$:49.5%Gd$^{3+}$,1%Pr$^{3+}$ were assigned to hexagonal CeF$_3$, space group *P*-3*c*1 (070-0002); GdF$_3$:1%Pr$^{3+}$ has a structure of orthorhombic GdF$_3$,

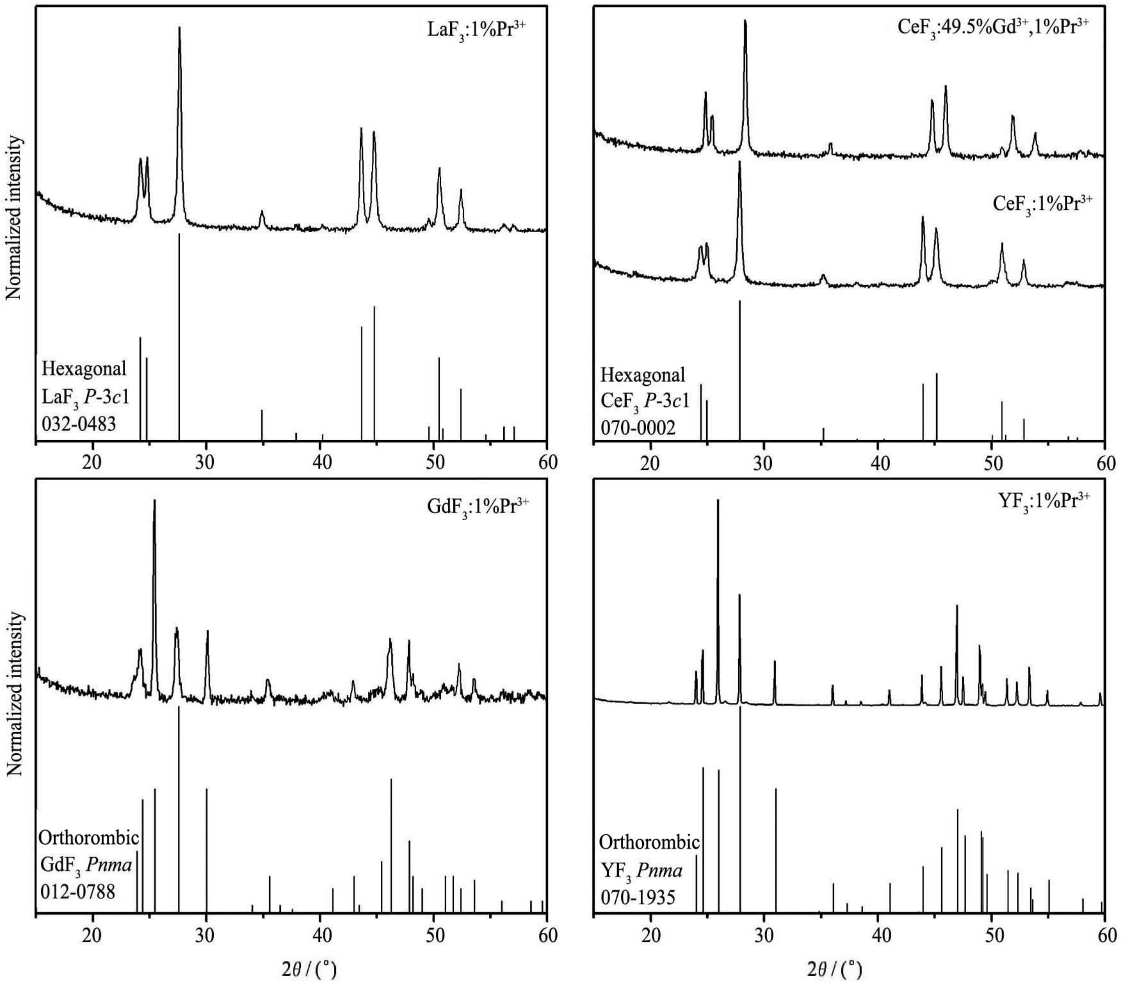

Fig. 1 XRD patterns of REF$_3$:1%Pr$^{3+}$ (RE=La, Ce, Gd, Y)