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Multicolor-tunable emissions of YOF: Ln^{3+}/Yb^{3+} ($Ln^{3+} = Ho^{3+}, Er^{3+}, Tm^{3+}$) nanophosphors

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ABSTRACT

Color tuning of down-shifting and up-conversion emissions of YOF:Ln^{3+}/Yb^{3+} ($Ln^{3+} = Ho^{3+}$, Er^{3+}, Tm^{3+}) nanophosphors is demonstrated. Nanophosphors were prepared by the modified sol-gel Pechini method and characterized by the X-ray diffraction, transmission electron microscopy, and photoluminescence spectroscopy. Samples consist of 20 nm particles crystallized in the rhombohedral crystal structure. Depending on the Ln^{3+}/Yb^{3+} concentration ratio and the type of excitation (UV/VIS or NIR) color of the particle's emission varied from the blue to red. Commission Internationale de L'Eclairage chromaticity coordinates of emission colors are given for the range of Ln^{3+}/Yb^{3+} concentration ratios for both down-shifting and up-conversion luminescence. We showed that the emission color of these nanophosphors may be additional tuned by simultaneous excitation with UV-VIS and NIR radiation (in different proportion) which yields unique color labels for the anti-counterfeit and security applications.

1. Introduction

Lanthanide doped nanophosphors have been a matter of interest over the past years for their utilization in many important technologies, such as lasers, electronics, therapeutics, displays, solar cells, catalysis, medicine [1–5]. In addition, there is a growing interest for their use as bio-markers or nano-sensors, instead of traditional ones [6]. The application of these materials is based on their unique optical characteristics which arise from partially filled f-orbitals of lanthanide ions [7,8].

Multicolor luminescence of trivalent lanthanide (Ln^{3+}) doped nanomaterials can be realized using different ions whose f - f electronic transitions provide different-color emissions that span the complete visible–near-infrared spectral range. Also, it can be achieved by both types of excitation schemes, down-shifting (DS) and up-conversion (UC). In DS, the high-energy radiation (usually ultraviolet, UV) is used to excite phosphor's emission of lower energy photons. UC is an anti-Stokes emission process in which two or more low-energy photons (usually near-infrared, NIR) excite phosphor's emission of higher energy via multistep optical processess [2]. In both cases, phosphor luminescence is characterized by long-lived electronic excited states and narrow emission bands.

Materials doped with activator Ln^{3+} ions ($Ln^{3+} = Ho^{3+}$, Er^{3+}, Tm^{3+}, Tb^{3+}) in different concentration ratios with Yb^{3+} (sensitizer ion) may provide multicolor-tunable emissions in both DS and UC excitation schemes [9]. Several Ln^{3+}-activated nanophosphors with multi-color tunable emission have been reported so far, such as $GdVO_4$:Ln^{3+}/Yb^{3+} (Ln^{3+} = Ho, Er, Tm, Ho/Er/Tm), Ce^{3+}-Mn^{2+} doped $Y_7O_6F_9$, YOF:Ln^{3+}(Ln = Tb, Eu, Tm, Dy, Ho, Sm), lanthanide metal-organic frameworks, Cu (Mn)-doped ZnInS, $LuVO_4$:$Tm^{3+}/Dy^{3+}/Eu^{3+}$ [4,8,10–14]. However, to the best of our knowledge, there are no reports on the use of rare earth oxyfluorides for combined multi-color DS and UC emissions. These materials are promising hosts for preparation of phosphors due to their attractive chemical and physical properties which may be classified as in between characteristics of fluorides and oxides [1,15–17]. Alike fluorides, oxyfluorides have low phonon energy and high ionicity which leads to the efficient luminescence, while, on the other hand, these compounds have great chemical and thermal stabilities which resemble properties of oxides [2,3,18]. In addition, oxyfluoride nanomaterials are biocompatible and nearly nontoxic to live cells so they can be safely used for biomedical applications [5,19]. Zachariasen described oxyfluorides' (YOF and LaOF) crystal structures in 1950`s [20]. Generally, they can be found in three structural modifications: tetragonal, which is usually nonstoichiometric (REO_nF_{3-2}, $0.7 < n < 1$), rhombohedral, and cubic (β-YOF). The rhombohedral structure (r-YOF) is the stable one, and it is strictly stoichiometric ($n = 1$). The cubic β-YOF structure occurs as the result of

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Table 1
Sample names and concentration ratio (Ln^{3+}/Y^{3+}) for preparation of different YOF: Ln^{3+}/Yb^{3+} (Ln^{3+} = Ho^{3+}, Er^{3+}, Tm^{3+}) nanophosphors.

Samples name	Concentration ratio (mol %)	mmol
	Ho^{3+}/Y^{3+}	
0.005Ho	0.005/0.895	0.00125/0.224
0.01Ho	0.01/0.89	0.0025/0.222
0.015Ho	0.015/0.885	0.00375/0.221
0.02Ho	0.02/0.88	0.005/0.220
	Er^{3+}/Y^{3+}	
0.01Er	0.01/0.89	0.0025/0.222
0.015Er	0.015/0.885	0.00375/0.221
0.02Er	0.02/0.88	0.005/0.220
0.025Er	0.025/0.875	0.625/0.219
	Tm^{3+}/Y^{3+}	
0.02Tm	0.02/0.88	0.005/0.220
0.025Tm	0.025/0.875	0.00625/0.218
0.03Tm	0.03/0.87	0.0075/0.217

the phase transition from the rhombohedral YOF at temperature of 560–570 °C [1,21]. Nonstoichiometric compounds usually have a tetragonal crystal form, but additional studies have shown that these materials are more complex than it was previously assumed; one example are compound with general formula $RE_nO_{n-1}F_{n+2}$, $5 \le n \le 9$ such as $Y_5O_4F_7$, $Y_6O_5F_8$ and $Y_7O_6F_9$, which crystallize in an orto-rhombohedral form [10,19,22–25]. To prepare oxyfluorides, several methods can be employed: thermolysis method, sol-gel method, fluorolytic sol-gel, hydrothermal method, co-precipitation method, solid state synthesis, combustion synthesis, stearic acid method, urea based homogenous precipitation [4,16,23,26,27].

Here, the goal was to prepare Ln^{3+}/Yb^{3+}-doped YOF (Ln^{3+} = Ho^{3+}, Er^{3+}, Tm^{3+}) nanophosphors with multicolor-tunable DS and UC emissions under UV/VIS and NIR excitations. DS in Yb^{3+}/Ln^{3+} doped hosts is a considerably more complex process than DS in a single Ln^{3+} activated hosts. Yb^{3+},Ln^{3+} pairs offer a number of routes for the cross-relaxation between different Yb^{3+} and Ln^{3+} energy levels, depending on phonon energies of the host, temperature and excitation energy, which affect intensities of Ln^{3+} emissions (and sometimes providing Yb^{3+} emission via quantum-cutting) and consequently affect DS emission colors. In addition, we aimed to explore for the first time (to the best of our knowledge) the combined UV/VIS and NIR excitation of Yb^{3+}/Ln^{3+} to facilitate the luminescence coding with unique emission colors suitable for anti-counterfeiting and security applications. To achieve this goal, nanophosphors were prepared by the optimized and modified sol-gel Pechini method, and their structural and luminescence properties are studied in details.

2. Experimental

2.1. Reagents

All chemicals: yttrium(III) nitrate hexahydrate, $Y(NO_3)_3 \times 6H_2O$ (99.9%, Alfa Aesar), ytterbium(III) nitrate pentahydrate, $Yb(NO_3)_3 \times 5H_2O$ (99.9%, Alfa Aesar), holmium(III) nitrate pentahydrate, $Ho(NO_3)_3 \times 5H_2O$ (99.9%, Alfa Aesar), erbium (III) nitrate hydrate, $Er(NO_3)_3 \times nH_2O$ (n ˜ 5) (99.9%, Alfa Aesar), thulium(III) nitrate hydrate, $Tm(NO_3)_3 \times nH_2O$ (n ˜ 5) (99.9%, Alfa Aesar), ammonium fluoride, NH_4F (98%, Alfa Aesar), citric acid (99.6%, Acros Organics) and ethylene glycol (> 99%, Sigma Aldrich) were of the highest purity available and were used without any further purification.

2.2. *Syntheses of YOF and YOF: Ln^{3+}/Yb^{3+} (Ln^{3+} = Ho^{3+}, Er^{3+}, Tm^{3+}) nanophosphors*

The modified sol-gel Pechini method, previously described by Grzyb and co-workers [28,29], was used to prepare YOF:Ln^{3+}/Yb^{3+} (Ln^{3+} = Ho^{3+}, Er^{3+},Tm^{3+}) nanophosphors with different Ln^{3+}/Yb^{3+} concentration ratios. Concentration of Yb^{3+} was kept constant in all the samples (10 mol% (0.1), 0.025 mmol), while concentrations of other Ln^{3+} ions (see Table 1) were chosen based on the experience with similar nanophosphors.

The synthesis of undoped YOF nanophosphor. Weighted amount (0.25 mmol) of $Y(NO_3)_3$ was dissolved in 90 ml of water. Citric acid (as the chelating agent) and ethylene glycol (as complexing agent of Y^{3+} cations) were added into the solution. To prevent lanthanide fluorides from precipitating, a large excess of citric acid and ethylene glycol was used [1]. After the intense stirring of the solution at room temperature for 30 min, an aqueous solution of NH_4F (0.31 mmol NH_4F, 10 ml H_2O) was slowly added drop-wise into solution. Since NH_4F decomposes at 100 °C, the 25% excess to the stoichiometric amounts of nitrate precursor was used. The prepared mixture was additionally heated at 80 °C for 4 h (the time needed for the water evaporation and the gel formation). Final product was obtained through calcination of gel precursors at 700 °C in air for 4 h. After calcination, the sample was kept overnight in furnace to cool down to room temperature.

The synthesis of YOF:Ln^{3+}/Yb^{3+} (Ln^{3+} = Ho^{3+}, Er^{3+}, Tm^{3+}) nanophosphors. Lanthanide doped YOF were prepared in analogy to the procedure described for the undoped YOF system with only difference being the addition of the appropriate amount of the respective Ln-nitrates to the starting $Y(NO_3)_3$ solution (see Table 1).

2.3. *Characterization*

The X-ray diffraction (XRD) analysis of the obtained nanopowder samples was performed on Rigaku SmartLab system (Cu-Kα radiation, 30 mA current, 40 kV voltage) in the 2θ range from 10° to 90° (using continuous scan of 0.7 s^{-1}). JEOL JEM-2100 LaB_6 transmission electron

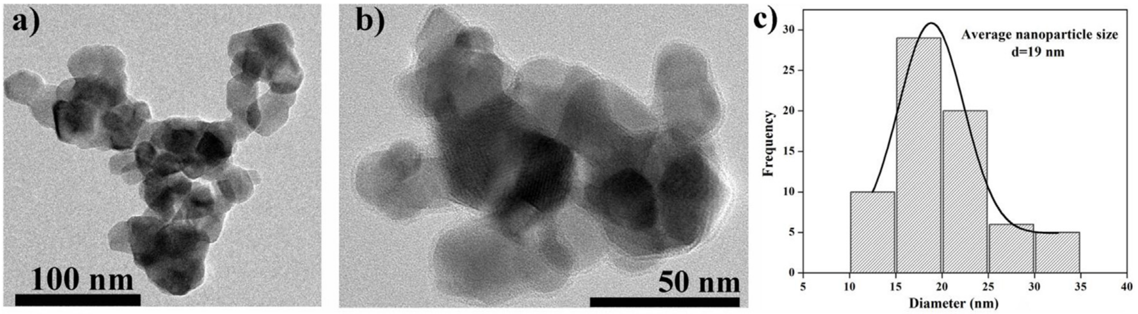

Fig. 1. a) and b) Typical TEM images for un-doped YOF nanoparticles at two different magnifications; c) size distribution histogram of YOF nanocrystals.