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Nanoscale thermometry with fluorescent yttrium-based Er/Yb-doped fluoride nanocrystals

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ABSTRACT

We have synthesized fluorescent yttrium-based fluoride nanoparticles doped with Er^{3+} and Yb^{3+} ions. The nanocrystals, whose size can be adjusted from a few tens to a few hundreds of nanometers, exhibit a strong temperature-dependent fluorescence that makes them excellent candidates for nanoscale thermometry in the (25–100 °C) range. The temperature is determined by monitoring the intensity ratio of two visible fluorescence lines that are in thermal equilibrium. We discuss the thermal sensitivity of such probes and show that they can be indifferently excited at several wavelengths from the blue to the near-infrared part of the electromagnetic spectrum which makes them candidates of high potentials in many experimental environments.

1. Introduction

A strong effort has recently been devoted to the development of experimental techniques able to measure temperatures (T) at nanometer scales [1–3]. This effort is motivated by many applications in various domains including biology, chemistry, microfluidics, physics, and micro-electronics. In life sciences, monitoring and mapping the temperature in a cell can witness a chemical reaction or a structural change [4–8]. Measuring T at the scale of a cell is therefore relevant for studying the dynamics of these transformations. Similarly, determining accurately the temperature is often required to better control the reactions and the separation of proteins in the channels or capillaries of microfluidic devices and "labs-on-a-chip" [9,10]. Finally, in micro and nano-electronics, as the components size continuously shrinks, electrical current flows in smaller and smaller sections creating local temperature elevation and hot spots near defects that can degrade the devices. The observation of such effects is necessary to find the weaknesses of the devices and to improve their robustness [11–15].

A simple way to monitor thermal variations in a quantitative way is to use fluorescent nanoparticles. Indeed, for most solids or molecules, radiative de-excitations are very sensitive to temperature. In addition they can be used in various environments, such as in vacuum, gases, or liquids. Among the different materials that have been used for this purpose, organic dye molecules like rhodamine or green fluorescent protein (GFP) [8,10,16–18] showed strong temperature dependences, but their lack of robustness and stability limits the duration of their utilization. Inorganic materials like semiconductor quantum dots [19,20] or lanthanide-based nanocrystals [7,21–26] are more robust and functional in more difficult environments. Among lanthanides, erbium ions incorporated in a solid matrix have drawn much attention because *i)* they emit an intense fluorescence in the visible region during days without any photobleaching, and *ii)* two of their fluorescent lines are in thermal equilibrium. The relative importance of these two lines is therefore directly dependent on temperature. Measuring their fluorescence intensity ratio gives the absolute temperature of the surrounding local environment [7,21–27].

Er^{3+} ions can be incorporated into various matrices like oxides [23,24,26,27] or fluorides [7,25]. In a fluoride matrix, the large value of phonon energies limits non-radiative de-excitations and therefore increases fluorescence efficiency compared to other hosts. For thermal applications, the fluoride matrices that have mostly been used contain either Na and Y forming a NaYF compound [7,25] or Pb forming a PbF_2 compound [28,29] with cubic [7,29] or hexagonal [25] phases. In this article, we present a study of

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Table 1
Er and Yb concentration in the nanocrystals.

Nanocrystal type	Er composition (%)	Yb composition (%)
KY_3F_{10} (type A)	2	8
KY_3F_{10}/YF_3 (type B)	10	0
KY_7F_{22} (type C)	2	10
YF_3 (type D)	2	10

the temperature-dependent optical properties of nanocrystals with different chemical compositions and doped with Er^{3+} and Yb^{3+} ions: YF_3, KY_3F_{10} and KY_7F_{22}. These nanocrystals have different crystalline phases, and a size varying from a few tens to a few hundreds of nanometers. We will show that they can also be excited at different wavelengths in the visible and the near-infrared making them usable for many applications in various environments.

2. Synthesis and room-temperature optical characterization

2.1. Synthesis of the nanocrystals

We chose to synthetize nanocrystals with different sizes and chemical compositions. We show in Table 1 the Er and Yb doping rate associated to the different phases. The nanocrystals were synthesized by different methods depending on the required phase:

- Er/Yb-doped KY_3F_{10} nanocrystals (type A) were synthesized by a hydrothermal method at 180 °C (filling rate of 60%) for two days starting from a mixture of yttrium, ytterbium, erbium nitrates and potassium fluoride in stoichiometric amount dissolved in a solvent constituted of an excess of hydrofluoric acid and water. The as-synthesized nanocrystals were only washed by at least four dispersion-centrifugation cycles in water and dried at low temperature (60–80 °C) in a laboratory oven.
- The mixture of Er-doped YF_3 and KY_3F_{10} nanocrystals (type B) are obtained using a co-precipitation method. A solution of yttrium and erbium nitrates dissolved in water was prepared and added dropwise in a second solution constituted of hydrofluoric acid in excess, potassium fluoride and water. The as-obtained powder was washed by at least four dispersion-centrifugation cycles in water. The nanopowder is dried in a laboratory oven at 60 – 80 °C and finally annealed at 600 °C during 2 h under an atmosphere of dried argon to avoid the hydrolysis and/or oxidation of the fluorides.
- Er/Yb-doped KY_7F_{22} nanocrystals (type C) were synthesized using a coprecipitation method similar to the one used to obtain the KY_3F_{10}/YF_3 mixture. The washed and dried powder is annealed at 300 °C for 5 h under an atmosphere of dried argon. KY_7F_{22} decompose in the solid state above 400 °C to form KY_3F_{10} and YF_3.
- YF_3 nanocrystrals (type D) were synthesized by a hydrothermal method similar to the one used to obtain the type A nanocrystals from a mixture of yttrium, ytterbium, erbium nitrates in stoichiometric amount dissolved in a solvent constituted of an excess of hydrofluoric acid and water.

The goal is to compare the emission properties and the sensitivity to temperature variations of the different nanocrystals as a function of the size and the chemical composition. Scanning electron microscope (SEM) images of some nanocrystals deposited on a Si substrate are shown in Fig. 1. The size is 50–150 nm for KY_3F_{10}, 150–300 nm for the mixture of phases KY_3F_{10}/YF_3 and for KY_7F_{22}, and 600–900 nm for YF_3.

2.2. Room-temperature fluorescence

Lanthanide ions possess a lot of energy levels. Consequently, when Er^{3+} ions are incorporated in a matrix, they emit light at several wavelengths, the most intense being located at ~525 nm, ~550 nm and ~660 nm in the visible. They can also be excited in many spectral zones from near-UV to near-IR. In this article, in order to show the flexibility of the nanocrystals, we have chosen to excite the materials at three well-separated wavelengths: 450 nm, 658 nm and 975 nm. We show in Fig. 2 the absorption and de-excitation schemes of Er/Yb–codoped materials when excited at these three wavelengths. At 450 nm, absorption occurs from the

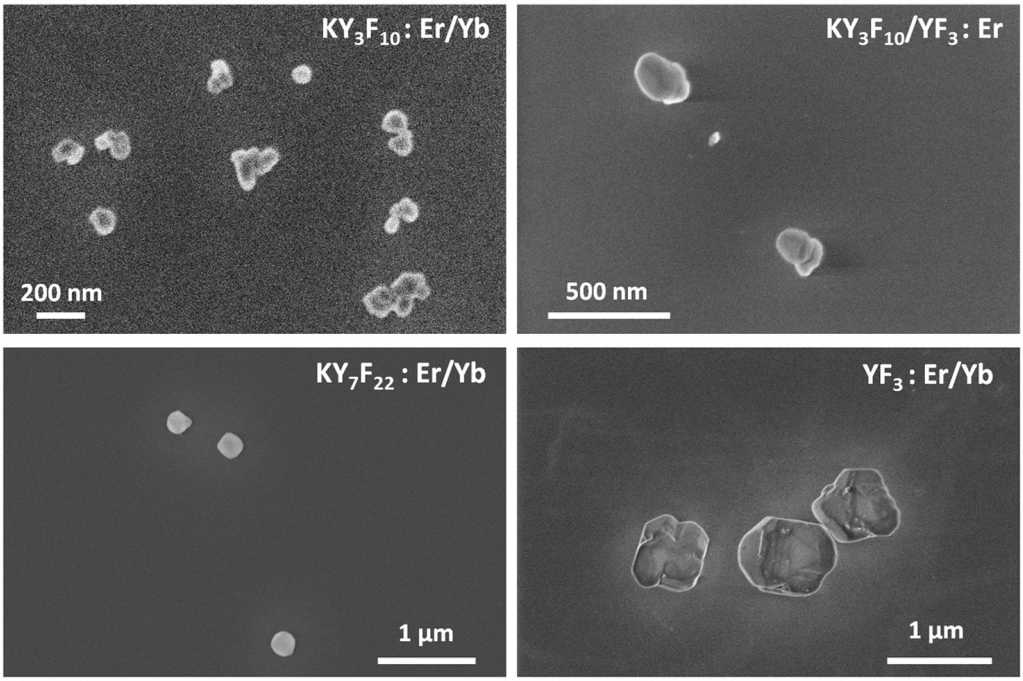

Fig. 1. SEM images of the nanocrystals.