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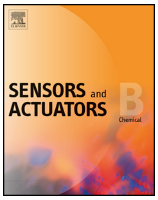

The impact of nanocrystals size on luminescent properties and thermometry capabilities of Cr, Nd doped nanophosphors

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ABSTRACT

Transition metal *d-f* emission based thermometry has recently proven to be an order of magnitude more sensitive than thermometers based on conventional *f-f* transitions in rare-earth ions. Little is known however about the susceptibility of these materials to nanoscale parameters, such as size or surface-to-volume ratio. Here we study the impact of nanocrystallite size on luminescent properties as well thermometry capabilities of CrNd co-doped $LiLaP_4O_{12}$ phosphors. In particular, we show that absolute emission intensity decreases (~0.81%/nm), emission band position blue shifts ($\Delta l \sim -0.066\,nm_{wave\ length}/nm_{grain\ size}$), temperature sensing range narrows (from 300 to 600 K at 240 nm down to 300–420 K at 20 nm), temperature sensitivity rises up (from 1%/K to ~5%/K) and temperature resolution drops (from ~0.3 °C down to 0.05 °C) gradually, when the size of NCs decreases from 240 down to 20 nm, respectively. As a consequence, proper design of host and dopants, enables finding optimal materials for many thermometry applications.

1. Introduction

Luminescence based thermometry at submicron scale is of great interest for applications in engineering and biology [1–3]. Owing to complex structure and spectroscopy of living tissues, theranostic (i.e. combined therapy and diagnostics) applications are the most demanding ones. In particular, interference of excitation light with tissue auto-fluorescence under short wavelength radiation, significant light scattering by heteregenous tissue components leads to shallow penetrations depths hindering the adoption of such remote thermometry for hyperthermia treatment, unless NIR excitation and NIR/Vis readout are available. Many thermosensitive phosphors have been proposed – different host materials, doping active ions, temperature sensitivity mechanism and readout schemes have been tested for that purpose [4]. While they are perfect candidates in terms of chemical and photo-stability, low toxicity and biofunctionalisation capability, the up-to-date sensitivity did no go beyond 1.5% K^{-1}, neither in upconverting (Yb/Er) [5–10] nor Stokes f-f transition [10–17] (e.g. Nd, Nd/Yb) which leaves space for further improvement. The recent studies from us [17] and other [18–22] demonstrated, that f-d transitions are more temperature sensitive than f-f ones, but we have also found out, that not only the sensitivity matters in nanothermometry, but also many other figures of merit, such as absolute intensity, photoexcitation intensity (especially for upconverting thermometers) or temperature resolution matters in real biological applications, which are affected by chosen phosphors.

Multifunctional luminescent nanoparticles found interest as (fluorescence/MRI/PET etc.) contrast agents or drug and monitoring delivery system. Another desirable functionality that multifunctional luminescent nanoparticle can offer for bioapplication, is fast and real time remote temperature sensing direct control of temperature at subtissue level allows for both monitoring biological processes as well as fast diagnosis. However, thinking about exploiting luminescent thermometer in real biological theranostics, a few requirements have to be met. First of all low cytotoxicity and high stability of nanoparticle used are desired, which can be achieved by using inorganic dielectric compounds. Their well known high physicochemical stability and their low cytotoxicity have been already confirmed in number of studies and reviewed [23]. Remote nano-bio-thermometry (RNBT) requires high emission efficiency of phosphors that facilitates reliable detection. Owing to fundamental physics behind luminescence (i.e. quantum efficiency of Stokes processes is usually at least one order of magnitude higher comparing to up-conversion), Stokes emission is thus preferred. Furthermore, excitation and emission spectral ranges are also of crucial significance, because high absorption and scattering as well as autofluorescence of biological tissue occurs in UV–vis

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range, which is prohibitive for many bio-related sensing applications. Therefore, NIR operating phosphors are beneficial for these purposes. On top of that, the key factor for RNBT is its sensitivity and resolution, which determines minimal temperature change that can be reliably detected. However, only few of the already proposed phosphors for luminescent thermometry met all these sophisticated requirements and high sensitivity is still a major challenge. Different approaches for enhancing of luminescent thermometers sensitivity have been already proposed, including host material optimization [4], wise optical active ions choice [19,24] and core/core shell architectures [11,13].

Recently, we have demonstrated a novel approach to optical thermometry, which exploits simultaneous photoexcitation of transition metal ions (Cr^{3+}), whose highly temperature dependent emission is related to much less temperature dependent (or ultimately independent) lanthanide ions (Nd^{3+}) emission. Such combination fulfilled the requirements of having excitation and emission readout in the NIR spectral region, high photostability and moreover improved the temperature sensitivity and absolute signal intensity by one order of magnitude. The mechanism behind temperature susceptibility is presented in Fig. 1a. Because emission of transition metal ions originates from *d-f* electron transition, where *d* orbital is not shielded from the influence of crystal field of the host matrix, their emission intensity and position of emission band are affected on the local ion's symmetry changes causing distortion of excited states ($^4T_2$ $^4T_1$ and ^2E) parabola in respect to the ground state one ($^4A_2$) (see Fig. 1b). The manifestation of this distortion results in the appearance of crossing point between ground end excited states parabolas. Therefore, the increase of temperature associated with increase of thermal energy of electrons, may decrease the excited state population via nonradiative transitions, if only the supplied thermal energy allows overcoming this crossing point energy (ΔE express energy difference between bottom of excited state parabola). Low value of ΔE facilitates thermal quenching of luminescence. From the other hand, the *f* orbitals of lanthanide ions are shielded by *5 s* and *5p* orbitals from local chemical environment, and hence, the influence of crystal field of the host on these *4f* orbitals is minimized, leading to negligible distortions of 4f energy states and lower thermal quenching of absolute emission intensity. Taking advantage from this fact, the emission intensity of lanthanide ion can be considered as a reference signal for self calibrated ratiometric RNBT luminescent thermometer. Following our previous studies, Cr^{3+} and Nd^{3+} ions are used as luminescence centers working in optical window of biological tissue. Excitation wavelength (665 nm) excited simultaneously and directly the Cr^{3+} and Nd^{3+} ions, leading to broad emission band centered at around 840 nm ($^4T_2 \rightarrow {}^4A_2$ transition of Cr^{3+} ions) and narrow emission band at 1048 nm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of Nd^{3+} ions) respectively. The luminescence intensity ratio (LIR) of these two bands can be used as a highly sensitive temperature sensor. Little is known however about the susceptibility of these materials to nanoscale parameters, such as size or surface-to-volume ratio. In this paper systematic studies of influence of grain size of $LiLaP_4O_{12}$:Cr, Nd nanocrystals on sensitivity of luminescent thermometer are investigated.

2. Experimental

$LiLaP_4O_{12}$:1%Cr^{3+}, 10%Nd^{3+} nanocrystals were successfully synthesized using previously described co-precipitation method [17]. Powder diffraction studies were carried out on PANalytical X'Pert Pro diffractometer equipped with Anton Paar TCU 1000 N Temperature Control Unit using Ni-filtered Cu $K\alpha$ radiation ($V = 40$ kV, $I = 30$ mA). The emission spectra was measured using 665 nm excitation line form laser diode (LD) and recorded using CCD camera from Stallarnet 1 nm spectra resolution. Temperature of the sample was controlled using heating stage from Linkam (0.1 °C temperature stability and 0.1 °C set point resolution).

The luminescence kinetics measurements were performed using Jobin-Yvon HR1000 monochromator equipped with R928P photomultiplier tube from Hamamatsu and using 532 nm line pulsed work (PW) from Nd:YAG laser as an excitation source. The decay profiles were collected using a LeCroy WaveSurfer 400 oscilloscope. In order to determine relative uncertainty of LIR ($\delta LIR/LIR$) maximal fluctuation of LIR value during 10 cycles of heating (50 °C) and cooling (0 °C) was choosen.

3. Results and discussion

Fig. 2a presents powder X-ray diffraction (XRD) patterns for samples annealed at different temperatures. As it can be noticed all diffraction peaks corresponds to the reference pattern of monoclinic $LiLaP_4O_{12}$ (ICSD 33241) structure. In this host there is only one La^{3+} site (C_1 point symmetry) which can be substituted by lanthanide/transition metal ions. The increase of annealing temperature causes narrowing of the full width at half maximum (FWHM) of diffraction peaks what originates from increasing size of the nanocrystals. The grain size varied between 20 nm to 240 nm, which was in good agreement with previously reported synthesis condition for $LiNdP_4O_{12}$ nanocrystals. Average size of the $LiLaP_4O_{12}$:Cr, Nd grains was determined from XRD patterns using Rietveld refinement technique (Fig. 2a).

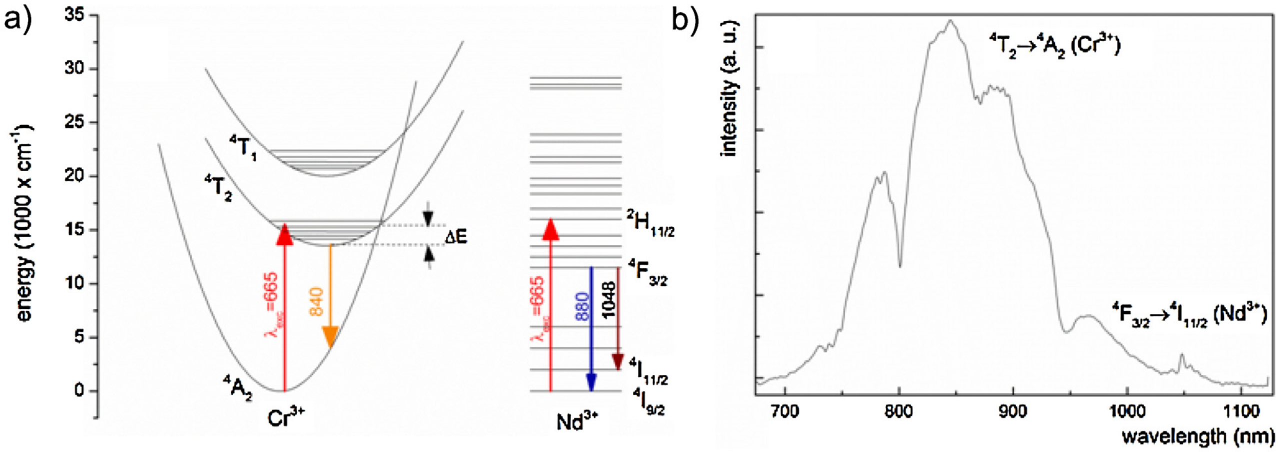

Fig. 1. Idea of lanthanide-transition metal ions based luminescent thermometer-a and simplified energy diagram of Cr^{3+} and Nd^{3+} ions in $LiLaP_4O_{12}$ host.