Journal of Alloys and Compounds 731 (2018) 478–488

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Size influence on temperature sensing of erbium-doped yttrium oxide nanocrystals exploiting thermally coupled and uncoupled levels' pairs

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ARTICLE INFO

Article history:
Received 23 June 2017
Received in revised form
13 September 2017
Accepted 14 September 2017
Available online 7 October 2017

Keywords:
Nanothermometry
Rare earth
Yttrium oxide
Fluorescence intensity ratio

ABSTRACT

The performance of Y_2O_3 nanocrystals with three distinct sizes, doped with 2 mol% of Er^{3+} ions, as nanothermometers, exploiting two different methodologies is investigated. We found that the sensitivity of the temperature sensor using such crystals is high and this magnitude depends strongly on the crystallite size. For nanothermometers based on fluorescence intensity ratio (FIR) from thermally coupled levels ($^2H_{11/2}$, $^4S_{3/2}$), the sensitivity is higher for larger nanocrystals. On the other hand, when using FIR from levels which are not thermally coupled ($^2H_{11/2}$, $^4F_{9/2}$), highest sensitivities were obtained for the smaller nanocrystals. Moreover, the values of absolute and relative sensitivities measured for these samples are among the highest reported so far in literature. These results indicate that Er^{3+}-doped Y_2O_3 nanocrystals are promising materials for temperature sensing in nanoscale and that the choice of nanocrystals' size and FIR methodology may improve the sensing performance aiming a specific application.

1. Introduction

In the last decades, there has been an intense interest in the development of materials and methods that would allow temperature measurements at nanoscale [1,2]. In different technological areas, nanothermometry has emerged as a very important tool for the comprehension of physical [3], chemical [4] and biological phenomena [5,6] of micrometric and nanometric systems, as well as a useful performance controller for microelectronic [7] and nanophotonic devices [8]. Among the myriad of proposed methodologies, luminescence-based nanothermometers have been intensively investigated. Exploiting the highly localized light emission of quantum dots [9,10], nanodiamonds [11] and rare earth-doped nanocrystals (REDONs) [12], very accurate and sensitive temperature nanosensors have been developed.

Interesting enough is the versatility of rare earth-doped materials aiming luminescent temperature sensing. Indeed, exploiting several aspects of the rare earth ions emissions, highly efficient thermal nanoscopes have been proposed. One of the most common approaches using REDONs is called fluorescence intensity ratio (FIR). Originally designed for temperature sensing using doped optical fibers and bulk materials [13–16], this principle can be directly transposed to nanoscale [17]. Basically, this method uses the ratio of the luminescence intensity related to two thermally coupled energy levels to detect temperature. In this context, two levels are considered in thermal quasi-equilibrium whenever the energy gap between them is smaller than 2000 cm^{-1} [18]. Assuming that I_2 and I_1 are the luminescence intensities from the upper and lower energy levels, respectively, and that ΔE is the energy gap between them, the FIR can be written as

$$FIR(T) = I_2/I_1 = Bexp(-\alpha/T) \quad (1)$$

In this equation, B and α are constants that can be obtained directly from the measured spectra and are related to the experimental conditions and characteristics of the rare earth emission properties within a specific solid host. Namely, $\alpha = \Delta E/k_B$ and $B = (\varphi_2/\varphi_1)$, where k_B is the Boltzmann constant and φ_i is a constant that depends on the fluorescence collection efficiency, as well as the branching ratios and luminescence quantum efficiency of the energy level i [19].

The performance of this device can be evaluated quantitatively

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https://doi.org/10.1016/j.jallcom.2017.09.156
0925-8388/

by defining the sensor absolute (S_a) and relative sensitivities (S_r) as

$$S_a = \partial(FIR)/\partial T = FIR\ \alpha \Big/ T^2 \quad (2)$$

and

$$S_r = S_a/FIR. \quad (3)$$

The absolute sensitivity varies with the temperature, presenting a maximum value, S_{max}, at $T = T_{max} = \alpha/2$. On the other hand, the relative sensitivity decreases for measurements of higher temperature values. The value of S_{max} can be employed as a quantity to compare the performance among sensors based on this band-shape methodology. However, the relative sensitivity, S_r, is the most important comparative parameter among temperature sensors of the same kind or that exploit different approaches. It varies with the environment temperature but its magnitude is determined by the value of the empirical constant α.

This methodology have been investigated exploiting different solid-state hosts doped with a single rare earth specie, such as Er^{3+} [17,20] and Nd^{3+} [21,22] or a combination of co-dopants, such as Yb-Er [23–35], Yb-Er-Cr [36], Yb-Er-Zn [37], Er-Mo [38,39], among others [40–48]. In the case of Er-doped materials based sensors, the most usual approach involves the green luminescence provided by the radiative transition from the $^2H_{11/2}$ and $^4S_{3/2}$ excited states to the $^4I_{15/2}$ ground state of erbium ions. Typically, the energy gap between those excited levels is about 1100 cm^{-1}, which is smaller than 2000 cm^{-1} limit to allow thermal coupling among them. On the other hand, the energy gap between these levels to the energetic closest level ($^4F_{9/2}$) is larger than that 2500 cm^{-1}. Plus, the solid host is always chosen to have low cut-off phonon energy (<1000 cm^{-1}). Due to these facts, the nonradiative decay rate from the $^2H_{11/2}$ and $^4S_{3/2}$ to lower levels can be very small. Neglecting these relaxation channels, the green emission from erbium can be modelled simply as a three levels' system, in which the excited states are thermally coupled as required by the FIR model.

It must be emphasized that different effects can cause a deviation of the measured luminescence intensity ratio from the Boltzmann distribution or a slight difference on the obtained value of the constant α. For instance, in bulk materials, it has been observed that the FIR signal differs from Eq. (1) due to the overlapping of the luminescence the peaks associated to the thermally coupled levels [14]. On the other hand, in submicron [23] and nanoscale [17], there has been observed that the value of α and, consequently, S_r can vary with the size of the host. These changes were associated to presence of impurity's species near the nanoparticles' surface. Indeed, the smaller the nanophosphor, the more important the contribution of the emitting ions on the particle's surface to the overall emission. The presence of organic molecules adsorbed to the surface of the nanocrystals provides extra nonradiative relaxation channels to the emitting ions. This modifies the nonradiative decay rate of the nanophosphor, affecting mainly the nanocrystals of smaller sizes. Moreover, while in nanoscale the relative sensitivity increased with the raise of the $BaTiO_3$ nanocrystals' size [17], the size effect reported for submicron particles was the opposite, and the value of the parameter α was the largest for the microspheres with the smallest diameter (700 nm) [23].

Nevertheless, temperature-dependent luminescence is not always related to a pair of thermally coupled levels. Rare-earth doped solid-state materials can exhibit multiwavelength luminescence associated to electronic transitions from different excited state levels. This is a very rich set of excitation/relaxation mechanisms, which may vary with the excitation conditions, rare earth ions species and concentration, presence of impurities, as well as the host crystalline structure [49]. For most of the investigated systems exhibiting frequency upconversion, the excitation processes involving single-doped or multi-doped materials are not entirely composed by resonant transitions. For these cases, light absorption, emission and energy transfer mechanisms are also possible due to phonon-assisted processes, which are intrinsically temperature dependent [50–53]. Due to this fact, the luminescence observed from different rare-earth doped systems might vary with temperature [25,54–56]. Moreover, this dependence can be different if you compare emissions from distinct excited states of rare-earth ions. Therefore, even when the emitting levels are not thermally coupled, it would be possible, in principle, to evaluate the temperature experienced by the material by analysing the relative emission from that exited states.

Exploiting this rational, recently, it was demonstrated that the FIR methodology can be applied even when the condition of thermal coupling between the emitting levels is not observed [24,25] or the emitting levels are associated to different ions species (DIS) [41–45,47,54]. In these works, the temperature dependence of the analysed luminescence was related to phonon assisted processes: light absorption, energy transfer and nonradiative decay, which are strongly affected by the environment temperature [50–52,57,58]. Although it is possible to achieve very high sensitivities using these approaches [42], modelling the operation principle of this kind of sensor is not an easy task. The number of possible excitation and de-excitations processes that plays important roles to the observed phenomena can be huge and an accurate analytical solution of the rate equation system that describes the whole phenomena is not easily obtained. Even when an approximate solution can be evaluated [54], it may not present the simplicity of Eq. (1).

Nonetheless, empirical mathematical expressions were proposed and applied satisfactorily to describe the operation of FIR sensors based on thermally uncoupled levels' pair. Lojpur et al. analysed the temperature sensing performance of thermally uncoupled erbium levels in the range of 10–300 K using Y_2O_3:Yb, Er nanocrystals [24]. In their study, they analysed the FIRs of the green emission associated to the $^4S_{3/2}$ level to the red emission from $^4F_{9/2}$ level, to the blue emission related to the $^2H_{9/2}$ and to the sum of emission from $^2H_{9/2}$, $^4F_{9/2}$ and $^2H_{11/2}$ levels. It was observed that all those FIRs presented an approximate exponential growth with the measured temperature for this system. They showed that the fluorescence intensity ratio of the investigated thermally non-coupled levels' pair (FIR^{NC}) dependence on temperature could be described by

$$FIR^{NC} = Aexp(T/C), \quad (4)$$

where A and C are constants. However, they could not elucidate the relation of these empirical constants with the physical properties of the nanophosphors. Following this approach, the sensor's absolute and relative sensitivities can be written as

$$S_a^{NC} = FIR^{NC} \Big/ C \quad (5)$$

and

$$S_r^{NC} = 1/C. \quad (6)$$

Alternatively, Zheng et al. [25] proposed that Eqs. (1)–(3) could also be applied to the case in which the emitters' levels are not thermally coupled. In their work, they exploited FIR between ultraviolet emissions from the thermally uncoupled $^2I_{11/2}$ and $^4D_{7/2}$ levels of erbium ions. Again, the excitation mechanisms of those excited levels involved non-radiative relaxation and energy transfer processes which are temperature dependent. This was the origin of the temperature variation displayed by the investigated