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Research Article

Temperature sensitivity of Nd^{3+}, Yb^{3+}:YF_3 ratiometric luminescent thermometers at different Yb^{3+} concentration

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ABSTRACT

Nd^{3+} (0.5 mol.%), Yb^{3+} (1.0, 2.0, 3.0, 4.0, and 8.0 mol.%):YF_3 phosphors were synthesized using a co-precipitation method with subsequent hydrothermal treatment and annealing in vacuum. The Nd^{3+}, Yb^{3+}:YF_3 phosphors are orthorhombic phase nano-crystals. Luminescence intensity ratio (LIR) of Nd^{3+} ($^4F_{3/2} - {}^4I_{9/2}$, ~866 nm) and Yb^{3+} ($^2F_{5/2} - {}^2F_{7/2}$, ~980 nm) emissions was chosen as temperature-dependent parameter. The energy exchange between $^4F_{3/2}$ (Nd^{3+}) and $^2F_{5/2}$ (Yb^{3+}) is phonon-assisted which explains the temperature dependence of LIR. There are Nd^{3+} to Yb^{3+} energy transfer (ET), Yb^{3+} to Nd^{3+} back energy transfer (BET) and energy diffusion (ED) between Yb^{3+} ions. The probability of BET decreases with the increase of Yb^{3+} concentration which leads to LIR dependence on Yb^{3+} concentration. The maximum absolute temperature sensitivity (S_a) was achieved for Nd^{3+} (0.5%), Yb^{3+} (1.0%):YF_3 ($S_a = 0.0018\ K^{-1}$ at 148 K). The studied samples demonstrate high stability after 8 cooling-heating cycles. The Nd^{3+} (0.5%), Yb^{3+} (1.0%):YF_3 phosphors are very promising for temperature sensing.

1. Introduction

Luminescence thermometry based on the use of inorganic phosphors allows determining the local temperature of an object with a sub-micrometric spatial resolution which is much in demand for fundamental biology, medicine, and industry [1–9]. In some cases, the luminescence thermometry provides contactless temperature measurements in the depth of an object [4]. The temperature determination can be performed by detecting and analyzing a temperature-dependent luminescence signal (intensity, lifetime, band shape, bandwidth, polarization, and spectral position) [10,11]. In this case, two of the main characteristics of the temperature-sensitive phosphor are absolute temperature sensitivity (further – S_a [luminescence parameter unit of measure/K]) and relative temperature sensitivity. The sub-micrometric spatial resolution can be achieved by using special nanosized materials that operate in ultraviolet and/or visible and/or near-infrared spectral range. The operation in these spectral ranges allows increasing the Rayleigh diffraction limit of resolution (rough estimation ~ $\lambda/2$) in comparison to thermal cameras operating mostly in the long-wavelength infrared (7–14 μm) spectral range [10,11].

For accurate temperature measurements, suitable phosphors should be used. The choice of the phosphors is usually a compromise between temperature sensitivity, desirable excitation, and emission wavelengths, chemical stability, temperature-dependent parameter, etc. Among a large variety of candidates for luminescence thermometry, the rare-earth (RE)-doped fluoride materials have a special role because of their high temperature sensitivity, excellent photostability, long luminescent lifetimes, sharp emission bands, high brightness, high melting point, chemical stability, and low toxicity [2,9,12].

There are many physical mechanisms of temperature sensitivity of RE-doped phosphors. For instance, some doping ions such as Pr^{3+} [14–16], Dy^{3+} [17,18], Er^{3+} [3,19], Eu^{3+} [10,11], and Nd^{3+} [20,21] have thermally coupled electron levels which share their electronic populations according to the Boltzmann law. Here the luminescence intensity ratio (LIR) of two emissions from the thermally coupled electron levels is taken as a temperature-dependent parameter. For some phosphors, the luminescence intensity is strongly dependent on temperature [22]. This phenomenon is usually explained by an increase of luminescence quenching processes efficiency and/or an increase of multiphonon nonradiative decay probability with an increase of temperature [22]. However, the above-mentioned systems have some disadvantages. They are not effective below 120 K [23]. In the case of ions having thermally coupled electron levels, it is impossible to manipulate and/or increase temperature sensitivity by varying external parameters

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