



# Luminescent thermometry based on $\text{Ba}_4\text{Y}_3\text{F}_{17}:\text{Pr}^{3+}$ and $\text{Ba}_4\text{Y}_3\text{F}_{17}:\text{Pr}^{3+}, \text{Yb}^{3+}$ nanoparticles



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## ABSTRACT

New effective luminescence thermometers based on novel host  $\text{Ba}_4\text{Y}_3\text{F}_{17}$  doped with  $\text{Pr}^{3+}$  and  $\text{Pr}^{3+}/\text{Yb}^{3+}$  in 80–320 K temperature range were studied. The absolute temperature sensitivity ( $S_a$ ) of both  $\text{Ba}_4\text{Y}_3\text{F}_{17}:\text{Pr}^{3+}$  (0.1 mol %) and  $\text{Ba}_4\text{Y}_3\text{F}_{17}:\text{Pr}^{3+}$  (0.1 mol.%):  $\text{Yb}^{3+}$  (10.0 mol.%) nanothermometers based on luminescence intensity ratio (LIR) between two  $\text{Pr}^{3+}$  emission bands ( ${}^3\text{P}_1\text{-}{}^3\text{H}_5$  and  ${}^3\text{P}_0\text{-}{}^3\text{H}_5$ ) demonstrate a notable value ( $0.011 \text{ K}^{-1}$  at 300 K) in the 200–320 K range. The  $\text{Ba}_4\text{Y}_3\text{F}_{17}:\text{Pr}^{3+}$  (0.1 mol.%):  $\text{Yb}^{3+}$  (10.0 mol.%) nanothermometers based on LIR between  ${}^3\text{P}_0\text{-}{}^3\text{H}_4$  of  $\text{Pr}^{3+}$  and  ${}^2\text{F}_{5/2}\text{-}{}^2\text{F}_{7/2}$  of  $\text{Yb}^{3+}$  emission bands demonstrate high  $S_a$  into the 80–200 K range with maximal  $S_a = 0,0778 \text{ K}^{-1}$  at 100 K. The stability of the phosphors was revealed by thermo-cycling experiments.

## 1. Introduction

Luminescence nanothermometry allows determining the local temperature of an object with a sub-micrometric spatial resolution which is highly important for fundamental biology, medicine, and industry [1–5]. The temperature determining can be performed by detecting and analyzing a temperature-dependent luminescence signal [6,7]. The sub-micrometric spatial resolution can be achieved by using special nano-sized materials that operate in ultraviolet and/or visible and/or near-infrared spectral range. The sensors operating in the physiological temperature region are highly required for hypothermia [8] and thermometry of living cells [9]. The sensors operating in the higher temperature regions are effective in temperature mapping of microcircuits [10]. The cryogenic temperature sensors are very important for applications in energy storage industries, aerospace, and cryogenic equipment [11–14]. Such kinds of chemically stable thermometers are highly required for cryogenic temperature range where rapid change of temperature can destroy the thermometers. However, the chemical compositions of the host as well as doping ion(s) play an important role in thermometric applications.

In luminescence nanothermometry, the temperature determining is performed by analyzing of luminescence signal parameter. There are six key parameters that are used for the luminescence emission characterization, namely, intensity, lifetime, band shape, bandwidth, polarization, and spectral position [6,15]. Some of these parameters can

strongly depend on the temperature in a particular temperature range. Among a large variety of candidates for luminescence thermometry, the rare-earth-doped fluoride materials have 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 [16–21].

One of the most important characteristics of the thermometers is an absolute temperature sensitivity  $S_a$ . The high  $S_a$  provides high-resolution, precise and easy temperature reading. According to the literature data [5], the  $\text{NaYF}_4:\text{Er}^{3+}, \text{Yb}^{3+}$  up-conversion nanoparticles having  $S_a 0.0026 \text{ K}^{-1}$  at 300 K are applicable in intracellular temperature sensing [5]. However, searching for higher sensitive luminescence thermometers is a very relevant scientific task, because higher  $S_a$  provides more precise measurements as well as allows simplifying measuring setup. Moreover, in some specific temperature ranges, such as cryogenic one, most of the existing luminescence thermometers are non-effective. The search for new cryogenic thermometers is an urgent task. One of the ways to temperature sensitivity enhancing is using thermometers containing two or even more doping ions. In this case, the complex and temperature-dependent energy transfer processes can provide huge temperature sensitivity in a specific temperature range.

The mechanisms of temperature sensitivity of rare-earth-doped fluoride nanoparticles are different. For example, the physical background of systems containing one doping ion such as  $\text{Pr}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Er}^{3+}$  doped materials is based on the presence of thermally coupled electron

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