

Luminescent thermometry and up-conversion in LiNbO₃ : Er crystals© A.P. Skvortsov¹, M.M. Voronov¹, A.B. Pevtsov¹, A.N. Starukhin¹, A.N. Reznitsky¹, K. Polgar²¹ Ioffe Institute, St. Petersburg, Russia² Wigner Research Centre for Physics of HAS,

1525 Budapest, Hungary

e-mail: a.skvortsov@mail.ioffe.ru

Received May 18, 2023

Revised July 18, 2023

Accepted October 30, 2023.

This paper presents the results of studying the temperature dependence of up-conversion „green“ photoluminescence (PL) in a congruent LiNbO₃ : Er³⁺ crystal excited by a laser diode operating at a wavelength of 808 nm. The study covers the temperature range from 77 to 413 K. Our results show that the temperature-dependent intensity ratio of green PL emitted by thermally bound states of the erbium ion (²H_{11/2} and ⁴S_{3/2}) can be used as a thermometric sensor. It is noteworthy that LiNbO₃ : Er³⁺ exhibits absolute temperature sensitivity (0.0044–0.0055 K⁻¹), which is one of the highest for materials activated by rare-earth ions, in the temperature range of 20–50°C, which is relevant for physiological measurements. This observation suggests that materials based on LiNbO₃ : Er³⁺ have great prospects for optical (contactless) temperature measurements in biological media.

Keywords: Photoluminescence, Erbium, Up-conversion, Thermometry.

DOI: 10.61011/EOS.2023.11.58023.5190-23

Phosphors activated by rare-earth ions (REI) are considered promising materials for the creation of nanoscale highly sensitive luminescent thermometers, the operation of which is based on the up-conversion transformation of exciting radiation [1–3]. An important advantage of such sensors is the opportunity of using them for non-invasive measurements of biological objects. Erbium-doped metal oxides, in which intense up-conversion photoluminescence (PL) in the green region of the spectrum is combined with high thermal sensitivity and increased stability of properties, are proposed as promising candidates for the implementation of up-conversion thermometry [4].

In this work, the effect of temperature on the intensity of up-conversion PL in congruent crystals LiNbO₃ : Er³⁺ (Li/Nb = 0.94 ratio), which were grown from a melt by the Czochralski method, was studied [5]. REI were added to the melt in the form of oxides. The concentration of Er³⁺ ions was 0.25% by mass. Oriented (1 × 5 × 10) mm³ samples were cut from bulk crystals. It should be noted that, although congruent crystals have a more disordered structure compared to stoichiometric ones, disorder does not lead to the disappearance of the fine structure of erbium lines. At the same time, congruent lithium niobate crystals are the most technologically advanced for growing [6].

Laser radiation at a wavelength of 980 nm is the most popular choice of pumping in up-conversion experiments on erbium ions (see, for example, [7,8]). The use of other wavelengths for pumping is less common (see review [3] and references are there), but can provide new insights into the spectroscopy of these materials. In this study, we use a semiconductor laser diode operating at a wavelength of 808 nm with a spectral half-width of 3 nm, the pumping power density did not exceed 10 W/cm². This choice of excitation makes it possible to simultaneously resonantly

excite under moderate pumping (< 10 W/cm²) not only the main transition ⁴I_{15/2} → ⁴I_{9/2}, but several more transitions to excited states (ESA, exciting state absorption, which are schematically shown by dashed arrows in Fig. 1, a). As a result, it becomes possible to obtain high-intensity radiation in a narrow spectral range corresponding to certain optical transitions [9]. It should be noted that we do not include in our consideration transitions to higher states (lying above the ²H_{9/2} level), since, as shown in our previous work [10], the contribution of these transitions to the green intensity“ up-conversion PL at moderate pumping levels is negligible. The spectra were recorded in photon counting mode using an automated complex assembled on the basis of a DFS-12 diffraction spectrometer.

In this work, we limited ourselves to studying up-conversion radiation in the green region of the spectrum, which is most often used in thermometric measurements. In the range (510–580 nm), there was an intense structured PL (Fig. 1, b), due to emission transitions from two closely spaced (thermally coupled) ion energy levels Er³⁺ [²H_{11/2} → ⁴I_{15/2} (520–540 nm) and ⁴S_{3/2} → ⁴I_{15/2} (545–580 nm)]. Temperature measurements were carried out in the range 77–413 K (Fig. 1, b). The temperature measurement error was 0.5%. It is clearly seen from the figure that with decreasing temperature the intensity of the short-wavelength PL band (²H_{11/2} → ⁴I_{15/2} junction) gradually decreases. At nitrogen temperature, this band practically disappears, which indicates the impossibility of thermal surges from the underlying level ⁴S_{3/2} to the level ²H_{11/2} ($\Delta E(0.09 \text{ eV}) \gg kT(0.00663 \text{ eV})$). In the temperature range relevant for biological research (20–100°C), the energy proximity ($\Delta E < kT$ of the states ²H_{11/2} and ⁴S_{3/2} at $T > 290 \text{ K}$ leads to specifying quasi-thermal equilibrium between these levels, determined by the Boltzmann factor

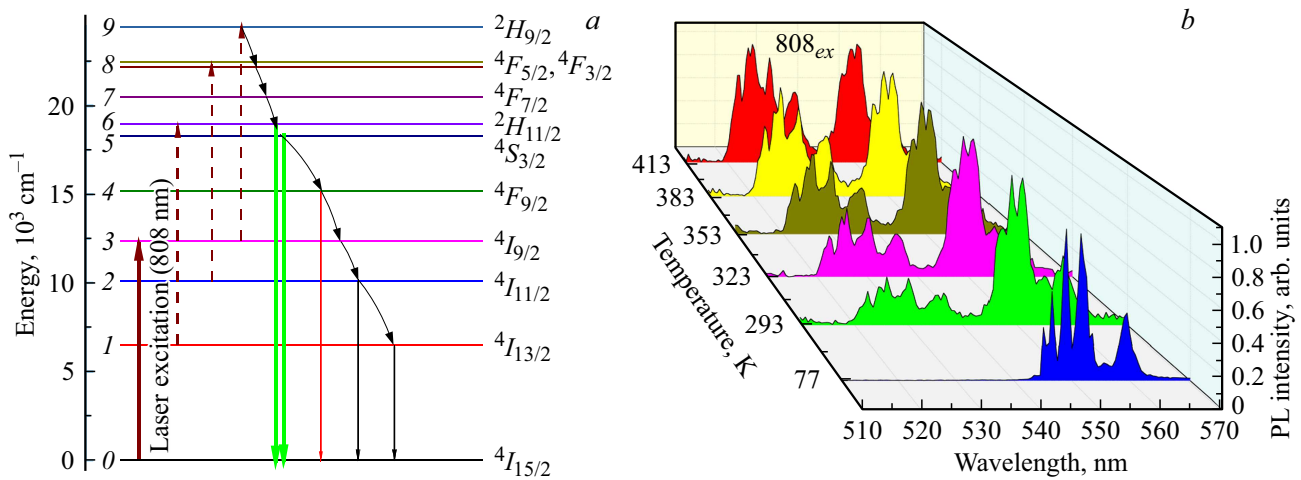


Figure 1. (a) Scheme of energy levels of the Er^{3+} ion and possible transitions between levels in the congruent LiNbO_3 crystal. Dashed lines indicate transitions to excited states (ESA transitions) that contribute to upconversion PL. (b) „Green“ PL spectra of the congruent crystal $\text{LiNbO}_3 : \text{Er}^{3+}$ measured at different temperatures. Excitation 808 nm.

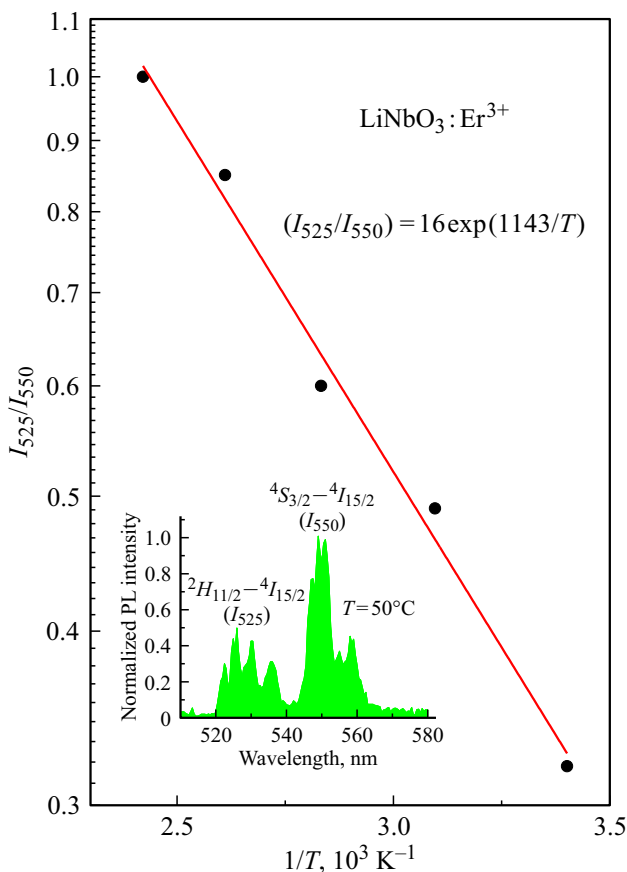


Figure 2. Logarithmic dependence on the inverse temperature of the intensity ratio of the green PL bands I_{525}/I_{550} corresponding to the transitions $2H_{11/2} \rightarrow 4I_{15/2}$ and $4S_{3/2} \rightarrow 4I_{15/2}$. Inset: example of the up-conversion PL spectrum of ($T = 50^\circ\text{C}$).

$[I_{525}(2H_{11/2})/I_{550}(4S_{3/2}) = C \exp(-\Delta E/kT)]$, which is confirmed by the linear nature of the experimental dependence

of I_{525}/I_{550} on the reciprocal temperature, constructed on a semi-logarithmic scale (Fig. 2). Here I_{525}/I_{550} — the ratio of the peak intensities of the „green“ PL bands centered in the spectral region of 525 and 550 nm and corresponding to the transitions $2H_{11/2} \rightarrow 4I_{15/2}$ and $4S_{3/2} \rightarrow 4I_{15/2}$. The validity of using peak (rather than integral) values follows from the fact that the shapes of the PL bands are similar at different temperatures (Fig. 1, b). Let us note that the value $\Delta E = 0.098 \text{ eV}$ determined in this way is in good agreement with the data on the energy difference between the excited levels of the erbium ion, $2H_{11/2}$ and $4S_{3/2}$, [11].

Let us now review the issue of specifying thermal equilibrium in the system of levels $2H_{11/2}$ and $4S_{3/2}$ in more detail. In the case of quasi-thermal equilibrium in a system of two nearby levels, the PL $4S_{3/2}/2H_{11/2} \rightarrow 4I_{15/2}$ spectra and absorption spectra $4I_{15/2} \rightarrow 4S_{3/2}/2H_{11/2}$ should obey the McCumber relation [12,13]: $\sigma_e(\nu) = \sigma_a(\nu) \exp[(\epsilon - h\nu)/kT]$, where $\sigma_e(\nu)$ and $\sigma_a(\nu)$ — emission and absorption cross sections, respectively, and the energy ϵ is determined by the number and location of sublevels and depends on temperature [13]. To test the efficiency of thermal coupling between the $2H_{11/2}/4S_{3/2}$ levels, we constructed the ratio $\sigma_e(\nu)$ and $\sigma_a(\nu)$ for two temperatures (293 and 413 K), which should be rectified on a semi-logarithmic scale (Fig. 3). As can be seen from the figure, in this case there is satisfactory agreement with the McCumber relation, which indicates a thermal connection in the $2H_{11/2}/4S_{3/2}$ level system and, as a consequence, the possibility of their use in luminescence thermometry in a fairly wide temperature range.

In conclusion, let us note that the parameter of the absolute thermometric sensitivity of the studied congruent crystals $\text{LiNbO}_3 : \text{Er}^{3+}$, defined as $S_a = [I_{525}(2H_{11/2})/I_{550}(4S_{3/2})] * (\Delta E/kT^2)$ [3], varied within the limits (0.0044–0.0055) K^{-1} at measurements in the temperature range (20–50) $^\circ\text{C}$ relevant for physiological studies. The obtained S_a values are among the top

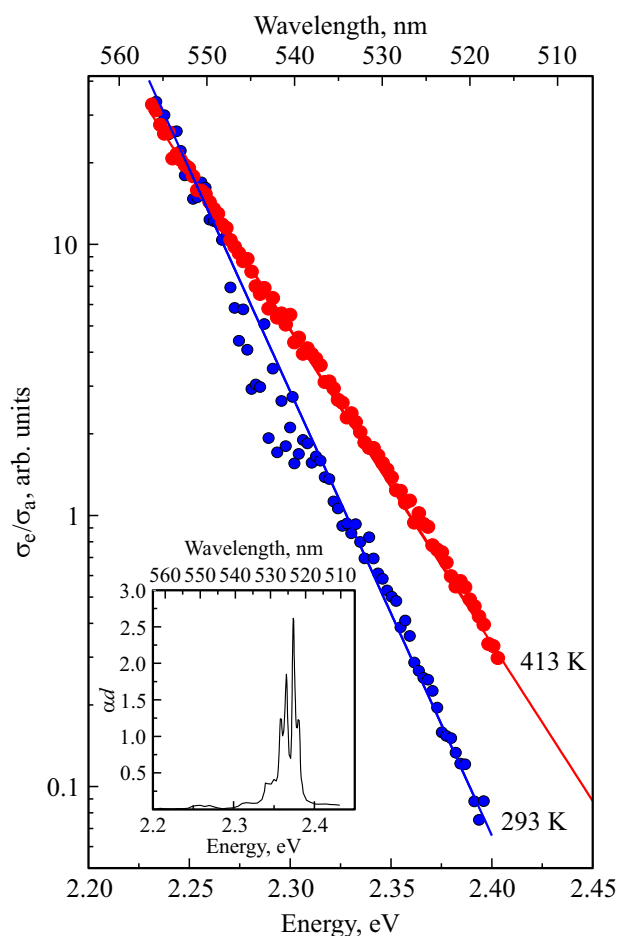


Figure 3. Checking the McCumber criterion. Circles — experimental values of the ratio $\sigma_e(\nu)$ and $\sigma_a(\nu)$ for two temperatures (293 and 413 K). Direct lines — least-squares fitting according to the relation: $\sigma_e(\nu)/\sigma_a(\nu) = \exp[(\epsilon - h\nu)/kT]$. At $T = 293$ K, $\sigma_e(\nu)/\sigma_a(\nu) = 5437 \exp((2.1 - h\nu)/0.0265)$; at $T = 413$ K, $\sigma_e(\nu)/\sigma_a(\nu) = 1000 \exp((2.1 - h\nu)/0.0375)$. Inset — absorbance spectrum of the congruent crystal $\text{LiNbO}_3 : \text{Er}^{3+}$ in the green region of the spectrum.

five among REI-activated materials used in luminescent thermometry [3]. Thus, the change in the intensity of up-conversion PL in $\text{LiNbO}_3 : \text{Er}^{3+}$ depending on temperature can be used as a sensitive temperature sensor.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by E.Potapova