Institute of Low Temperature and Structure Research
Polish Academy of Sciences

DOCTORAL DISSERTATION

Synthesis and analysis of the temperature influence on excited state absorption process in phosphors doped with Tb^{3+} and Pr^{3+} ions for applications in luminescence thermometry

in the form of a thematically coherent series of articles published in scientific journals

Joanna Stefańska

Supervisor

dr hab. Łukasz Marciniak, prof. ILTSR

Wrocław, 18.06.2021

ABSTRACT

The change in various luminescent properties of phosphors may result from the thermal activation of multiple radiative and nonradiative processes. Due to the dependence of the optical response of some materials on the temperature, it was possible to develop a whole field of luminescence thermometry, dedicated to the practical use of this phenomenon. A significant part of the descriptive section of this dissertation is devoted to the techniques related to such optical temperature measurements. The next part of this work focuses on the discussion of the results collected in the series of publications on novel materials doped with Tb^{3+} or Pr^{3+} ions, in which the influence of temperature on the excited state absorption (ESA) process was systematically studied. As the majority of optically active centers show a temperature quenching of luminescence, the results described in this dissertation are particularly interesting because the tested phosphors show an increase in emission intensity along with temperature, which is unusual. A large part of the results section was devoted to the description of the temperature-dependent optical processes optimization for applications in the luminescence thermometry. In the end, a summary of the conducted research was presented and general conclusions were drawn.

The important phase of the research involved the synthesis of many different phosphors doped with Tb^{3+} or Pr^{3+} ions in order to select those in which the ESA process can cause recordable luminescence. The most promising materials were selected for further analysis and the syntheses of series of phosphors of a given type with different dopant concentrations were carried out. In order to verify the universality of the conclusions drawn, the conducted research was carried out on different types of phosphors, ranging from nanomaterials, microcrystalline powders to glass. The following compounds were used in the research described in this dissertation: tetraphosphates, tungstates, oxyfluorotellurite glasses and fluorides. These materials were doped with varying concentrations of Tb^{3+} or Pr^{3+} ions, occasionally with the addition of Eu^{3+} or Cr^{3+} co-dopant.

During the research, a number of measurement techniques were used to provide a versatile characterization of the examined phosphors. Among them are: energy dispersive X-ray analysis, X-ray diffraction, transmission electron microscopy, Raman scattering, inductively coupled plasma-optical emission spectrometry, excitation, emission, transmittance, photoluminescence dynamics and quantum yield. It should be emphasized

that many of these measurements were carried out over a wide temperature range in order to thoroughly analyze the thermal dependence of the ESA process and evaluate the applicability of the chosen phosphors in luminescence thermometry.

The research also included the creation of proprietary software that allows for solving a system of dynamic rate equations, describing changes in the population of energy levels of Tb^{3+} ions. Thanks to the modeling of changes in parameters occurring in the equations, it was possible to predict their influence on the operation of the analyzed and similar lanthanide-based luminescent thermometers.

The first results, therefore, focused on comparing the experimental data with theoretical predictions in order to understand the influence of many thermally dependent processes on the emission of Tb^{3+} ions excited by the wavelength inducing the ESA process. The first single band ratiometric (SBR) luminescence thermometer based on temperature readout by measuring the relative intensity of a single emission band of Tb^{3+} ions, associated with $^5D_4 \rightarrow ^7F_3$ transition, with the use of excitation wavelengths matched to the transitions from the ground level $^7F_6 \rightarrow ^5D_4$ and excited level $^7F_5 \rightarrow ^5D_4$, respectively, was presented. In such an experimental setup, the observation of two luminescent signals in the same spectral range with opposite dependence of the emission intensity on the temperature was presented. Moreover, the possibility of involving interionic processes in order to improve the thermometric properties was also demonstrated. It was studied using excitation lines adjusted to the transitions to the $^5D_3$ level, which enabled the activation of the $\{^5D_3, ^7F_6\} \leftrightarrow \{^5D_4, ^7F_0\}$ cross relaxation process. In this case, it was possible to monitor the other emission band associated with the $^5D_4 \rightarrow ^7F_5$ transition of high branching ratio, which improved the signal-to-noise ratio. What is more, the theoretical modelling was carried out for Tb^{3+} ions, taking into account the influence of matrix parameters such as electron-phonon coupling, maximum phonon energy or stiffness, and the effect of dopant ion concentration. Certain trends in these properties were discovered and their influence on the thermometric properties of luminescent thermometers using the ESA process was broadly discussed.

In the further research, the influence of other temperature-dependent processes on the studied phenomenon of ESA was examined. The effect of dissipation of the emitting state energy into the conduction band or via a metal-to-metal energy transfer was investigated.

The beneficial influence of these processes on the thermometric results was demonstrated.

The emission of Tb^{3+} ions excited by means of the ESA-matched wavelength was also investigated in the emission-shape-based ratiometric approach with the use of an additional co-dopant luminescence. The focus was on an in-depth analysis of the energy transfer between two different dopant ions, and its resultant influence on the ESA process of Tb^{3+} ions. The knowledgeably selected representative of the lanthanide co-dopant ion was Eu^{3+}, while the transition metal co-dopant ion was chosen to be Cr^{3+}. It was shown that it is possible to achieve very high sensitivity of temperature readout by monitoring mutual changes in intensities of emission bands associated with Tb^{3+} and a co-dopant. Moreover, because of the strong variations in the emission color, the possibility of thermochromic measurement was also investigated.

The abovementioned research was extended to Pr^{3+} ions for which an analogous possibility of implementing luminescence thermometry in the SBR approach was investigated for the first time. By using the excitation wavelength inducing the $^3H_4 \rightarrow {}^3P_2$ transition from the ground level, a decrease in emission intensity was noted with the temperature elevation, while for the ESA-matched excitation associated with the $^3H_5 \rightarrow {}^3P_1$ transition, thermal enhancement of luminescence was observed. The phenomena governing the thermal dependence of both absorption processes turned out to be similar to those observed for Tb^{3+} ions. However, the unique configuration of Pr^{3+} ion energy levels that enable the occurrence of many different cross relaxation processes was shown to be of a crucial importance in this case. Therefore, special attention was paid to the influence of the dopant ion concentration on the spectral properties studied. In terms of SBR, the possibility of analyzing the Pr^{3+} emission bands in the red and yellow spectral ranges, and for the first time for this type of measurement – blue, was demonstrated.

This work is a source of comprehensive information on luminescence thermometry based on the use of the highly thermally dependent ESA process of lanthanide ions, derived from the results obtained for Tb^{3+} and Pr^{3+} ions. Thanks to an extensive and versatile analysis, it was possible to discover many important aspects, and to propose an interpretation of the influence of temperature on the processes under study. Various application possibilities were investigated and their advantages and disadvantages were indicated. Moreover, thanks to the modeling and a holistic view of all the obtained results, conclusions were drawn regarding possible paths for further development of the luminescence thermometry field.