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ABSTRACT OF DOCTORAL DISSERTATION

The investigation of influence of crystal field strength on relative sensitivity of Cr³⁺ doped nanocrystalline luminescent thermometers

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The main aim of the thesis is to investigate and understand the correlation between the material parameters of the host and the concentration of dopant ions on the spectroscopic properties and luminescence thermal quenching rates of the Cr³⁺ luminescence. Gaining such a knowledge enables the intentional development and design of the luminescent thermometers based on Cr³⁺ emission of the required parameters. This study focuses on a thorough analysis of the influence of crystal field strength on the relative sensitivity of Cr³⁺ doped nanocrystalline luminescent thermometers. For the purposes of this thesis, several approaches were developed that enabled to present the correlation between the crystal field strength and specific material parameters. The abovementioned approaches constitute the basis of the strategy of designing highly sensitive Cr³⁺-doped luminescent nanothermometers. Three of them involve examining the influence of host matrix stoichiometry and dopant ion concentration. On the basis of the performed research, it was shown that due to the increase of interionic distance between the metal and oxygen, in the matrix structure, the strength of the crystal field affecting the Cr³⁺ ions localized in the octahedral crystallographic sites was gradually reduced. The mentioned increase in the metal-oxygen distance was the result of substituting ions with a smaller ion radius (Al³⁺) with ions with a larger ion radius (Ga³⁺) in the analyzed Gd₃Al_{5-x}Ga_xO₁₂ host matrix. A similar effect was observed in the subsequent approach, where the increase in the concentration of Cr³⁺ ions contributed to the elongation of the average distance between the metal and oxygen, leading to a decrease in the strength of the crystal field. In both cases, the crystal field strength reduction resulted in the increase in relative sensitivity of luminescent thermometers based on the intensity of Cr³⁺ ion and operating in the ratiometric approach (Cr³⁺/Ln³⁺), where emission intensity of Ln³⁺ co-dopant ion was used as an internal luminescent reference signal. The obtained results confirmed that the luminescent thermometer based on the temperature-dependent change in the intensity of broadband Cr³⁺ emission attributed to the ${}^4T_{2(g)} \rightarrow {}^4A_{2(g)}$ transition is more suitable for precise, non-contact temperature determination than the one based on

narrowband emission attributed to ${}^2E_{(g)} \rightarrow {}^4A_{2(g)}$ transition. Additionally, the beneficial influence of the $Cr^{3+} \rightarrow Nd^{3+}$ energy transfer on the thermometric properties of the nanocrystalline luminescent thermometers co-doped with Cr^{3+} and Nd^{3+} ions, which contributed to increase the quenching rate of the Cr^{3+} ions luminescence and thus enhancing the relative sensitivity of the investigated luminescent thermometers, was confirmed. Moreover, it was shown that for nanocrystals co-doped with Cr^{3+} and Nd^{3+} ions, the useful range of Cr^{3+} ion concentration, i.e. the range in which emission bands derived from these ions were observed, was strongly narrowed in comparison to nanocrystals singly doped with Cr^{3+} ions. This resulted in a doubling of the relative sensitivity values, as exemplified by the $Y_3Al_2Ga_3O_{12}$ material, where an increase in relative sensitivity was observed from $S_R=1.3\%/^{\circ}C$ for $Y_3Al_2Ga_3O_{12}: 10\%Cr^{3+}$ to $S_R=2.2\%/^{\circ}C$ for $Y_3Al_2Ga_3O_{12}: 10\%Cr^{3+}, 1\%Nd^{3+}$ at $-50^{\circ}C$. In subsequent studies, a detailed investigations concerning the influence of the local environment of Cr^{3+} ions on their temperature dependent luminescence properties was performed. In the first steps, optimization of the stoichiometry of the $La_{3-x}Lu_xAl_{5-y}Ga_yO_{12}$ host matrix was accomplished, analyzing both the molar ratio of La^{3+} and Lu^{3+} cations incorporating into the dodecahedral sites as well as Al^{3+} and Ga^{3+} which occupies the octahedral sites in the matrix structure. In the course of conducted studies the $La_2LuGa_5O_{12}$ nanocrystals were selected as a host of the lower value of the crystals field strength and thus on the highest value of the relative sensitivity to temperature changes. This matrix was chosen for further analyzes examining the effect of both Cr^{3+} and Nd^{3+} dopant ions concentration. Obtained result confirmed the validity of considering both factors, namely host matrix stoichiometry and dopant concentration, since it has a substantial impact on the improvement of the relative sensitivity values of the analyzed luminescent thermometers. Furthermore, considering individual factors will enable the thoughtful and rational design of highly sensitive ones. In most previous cases, the Ln^{3+} co-dopant ions were used as an internal reference signal. However, in the course of the conducted research it was found that the structural changes induced by the incorporation of the Ln^{3+} ions may also significantly affect the thermal dependence of the Cr^{3+} emission intensity. In the $LaScO_3$ perovskite material it was demonstrated that the incorporation of lanthanide ion co-dopant affects the bond lengths of the $[CrO_6]^{9-}$ octahedra in the host matrix structure and thus, slightly impacts on the local crystal field around the Cr^{3+} ions. The changes in the crystal field strength led to the modification of the energy gap between the thermally coupled ${}^2E_{(g)}$ and ${}^4T_{2(g)}$ excited states of Cr^{3+} ions, which influence the thermal quenching behavior of their luminescence. The role of the host material composition was also investigated in the lifetime based luminescent thermometry by the analysis of the thermally induced shortening of the luminescence lifetime of ${}^2E_{(g)}$ excited state of Cr^{3+} ions. It was found that in the case of the nonexponential luminescence decay curves, the method of lifetime determination strongly affects the obtained relative sensitivity and usable temperature range of the lifetime based luminescent thermometer. Therefore, three different procedures of lifetime estimations were evaluated, namely average lifetime approach, doubleexponential fit and time-gated ratiometric approach. Additionally, taking into account the relative sensitivities derived from the average lifetime approach and

doubleexponential fit, their dependence on the crystal field strength was noticed. Those results confirmed the earlier conclusions that the highest relative sensitivity values were obtained for the material with the lowest crystalline field. In turn, a comparison of several methods of lifetimes determination highlighted that much more attention needs to be paid to the analysis procedure and obtained results affected by that. The performed investigations and the obtained results described in this dissertation enable the intentional design of the highly sensitive luminescent thermometers and constitute a significant step towards the widespread use of nanocrystalline materials doped with transition metal ions for remote temperature reading.

Acknowledgements

The "*High sensitive thermal imaging for biomedical and microelectronic application*" project is carried out within the First Team programme of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund.