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Abstract

Given doctoral thesis is devoted to the structural, morphological, and spectroscopic characteristics of microcrystalline materials activated with Pr^{3+} or Eu^{2+} in selected inorganic matrices. The main purpose of the work was to develop and characterize thoroughly new optical temperature sensors based on the 5d→4f transition of the Pr^{3+} or Eu^{2+} ion operating in a wide temperature range (11 - 700 K) and offering high temperature sensitivity combined with low uncertainty (high resolution) of temperature measurement (<0.1 K). Luminescent thermometers were examined for the first time, systematically monitoring the effect of 5d→4f transitions for the quality of their operation. This characteristic was supplemented with the thermoluminescence analysis of selected thermometers in the range of 303 - 773 K.

In order to perform the above tasks, a number of luminescent materials based on $Sr_2(Ge_{0.75},Si_{0.25})O_4:Pr^{3+}$, $Sr_2(Ge_{0.50},Si_{0.50})O_4:Pr^{3+}$, $Lu_2(Ge_x,Si_{1-x})O_5:Pr^{3+}$, $Y_2(Ge_x,Si_{1-x})O_5:Pr^{3+}$ and $SrB_4O_7:Eu^{2+}$, where x = 0; 0.10; 0.25; 0.50; 0.75; 1.00 were synthesized. In the case of Pr^{3+} activated phosphors, the substitution of silicon (Si) with germanium (Ge) was aimed to reduce the forbidden energy gap of the material host lattice in order to fine-tune important thermometric parameters.

Luminescence and thermometric analysis showed that bandgap engineering enables the control and management of the temperature range of 5d→4f luminescence detection. This, in turn, appears to be very useful in precise modeling of the operating range of the thermometer, as well as the temperature range in which it is most sensitive. Using the 5d→4f/4f→4f emission intensity ratio, a high value of the relative thermometric sensitivity (S_r = 3.54%/K) was obtained at cryogenic temperature (17 K) for the $Lu_2(Ge_{0.75},Si_{0.25})O_5:Pr^{3+}$, while for $Lu_2SiO_5:Pr^{3+}$ the same value was obtained at 350 K. In addition, the engineering of the bandgap also allows for precise control of thermometric parameters, using the 5d → 4f luminescence kinetics. This makes it possible to create luminescent thermometers operating in a dual-mode (based on the ratios of the intensity of the emission bands and, independently, luminescence decay time).

Moreover, studies of the $SrB_4O_7:Eu^{2+}$ phosphor as a luminescent thermometer in the range 11 – 600 K were carried out. The temperature dependencies of both the 5d→4f/4f→4f emission intensity ratio and the emission decay time result from the same

physical effect, *i.e.,* the thermal coupling of the lowest $5d_1$ excited level of Eu^{2+} and the $^6P_{7/2}$ excited level of the $4f^7$ dopant configuration. Such thermal coupling changes the contribution of emissions from these levels in response to a temperature change, however, without significant thermal quenching of the luminescence. This advantageous situation allows the measurement of spectra with a high signal-to-noise ratio over the entire measuring range while obtaining high thermometric sensitivity. The research has shown that using the $5d \rightarrow 4f$ emission of Pr^{3+} or Eu^{2+} allows the design of very sensitive luminescent thermometers offering excellent measurement resolution and operating in a wide temperature range. It is an innovative and very successful contribution to the development of this research area.