

Institute of Low Temperature and Structure Research
Polish Academy of Sciences



DOCTORAL DISSERTATION

**Synthesis and investigation of spectroscopic properties of
nanocrystalline phosphors doped with vanadium – V^{3+} , V^{4+} , V^{5+}
ions and iron Fe^{3+} ions for applications in luminescent
thermometry**

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

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Abstract of doctoral dissertation

This doctoral dissertation describes a thorough analysis of the impact of structural and morphological parameters of the host material on the temperature-dependent spectroscopic properties of V^{n+} ($n = 5, 4, 3$) and Fe^{3+} ions, with particular emphasis on the possibility of their use in luminescence thermometry. This technique of thermal sensing and imaging continually attracts attention due to its numerous advantages, among which the remote readout mode, fast response and submicrometer spatial resolution should be mentioned. Unlike the thermovising infrared camera, luminescence thermometry allows to real temperature measurement of an entire object, not only of its surface. Among different types of contactless luminescence thermometers, the inorganic nanomaterials doped with optically active ions attract immense attention, due to their high thermal, chemical and mechanical stability, perfect photostability and the lack of photo-blinking effect. In turn, the small size, falling within the ambit of nanoscale, significantly broadens the range of their applicability, including medicine, engineering and microelectronic.

For this reason, the luminescence thermometry can be considered as a promising alternative for conventional methods used for temperature measurement. Considering, new approaches are sought, in order to improve the temperature-sensing capabilities of luminescence thermometers, including the relative sensitivity and usable temperature range. Therefore, the presented doctoral dissertation enters in new perspective, exploiting the phenomenon of stronger temperature vulnerability of transition metal ions luminescence compared to the luminescence of lanthanide ions, which is a research hypothesis of this thesis. Thus, the spectroscopic properties of transition metal ions, including emission intensity, the spectral position of the emission bands and luminescence lifetime pose a temperature probe. The crucial advantage of transition metal ions -based luminescence thermometers is the possibility of the effective modification of their thermally-affected spectroscopic properties, such as the luminescence thermal quenching rate and the spectral range of temperature-induced optical response via wise selection of the inorganic host material composition and its properties. This feasibility observed for transition metal ions results from the direct exposition of valence electrons in $3d$ orbitals to external conditions, including lattice composition and crystallographic surrounding of the optically active ions in contrary to the $4f$ orbitals of lanthanide ions, which are shielded with $5s$ and $5p$ ones. Concerning the described method of thermal readout, the aim of the present doctoral dissertation is the investigation of

temperature-susceptible luminescence of vanadium (V^{3+} , V^{4+} , V^{5+}) and iron (Fe^{3+}) ions in order to develop new contactless nanocrystalline luminescence thermometers. The research work, performed within the doctoral thesis involves the synthesis of the nanocrystalline phosphors, their structural and morphological characterization, measurement and the analysis of their spectroscopic properties. The crucial part of the doctorate dissertation refers to the determination of thermal dependence of V^{n+} and Fe^{3+} luminescence as well as to the investigations and verification of proposed approaches in order to improve the temperature-sensing capabilities of analysed luminescence thermometers.

The nanocrystalline phosphors doped with V^{n+} and Fe^{3+} ions were successfully synthesized by means of the modified Pechini method, using different concentrations of the optically active ions. As a result, the powder form of phosphors was obtained. In order to investigate the impact of structural and morphological properties on luminescence of V^{n+} and Fe^{3+} ions the annealing process was carried out at different temperatures, involving various calcination time duration. The synthesis parameters were deliberately selected and optimized, depending on the host material composition in order to enable the formation of well-crystallized materials with high phase purity, determined by appropriate structural and morphological characterization.

Aiming at the development of new luminescence thermometers different inorganic lattices were taken into account as host materials, namely $Y_3Al_5O_{12}$, $LaGaO_3$ and $Y_3Al_4GaO_{12}$, $Y_3Al_3Ga_2O_{12}$, $Y_3Al_2Ga_3O_{12}$, $Y_3AlGa_4O_{12}$, $Y_3Ga_5O_{12}$ ($Y_3Al_{5-x}Ga_xO_{12}$) in the case of V^{n+} ions, whereas $LiAl_5O_8$, $Y_3Al_5O_{12}$, $Y_3Ga_5O_{12}$, $Lu_3Ga_5O_{12}$, $Gd_3Ga_5O_{12}$, $MgAl_2O_4$, $MgGa_2O_4$, $CaAl_2O_4$, $CaGa_2O_4$, $SrAl_4O_7$, $CaAl_4O_7$, $BaAl_4O_7$ for Fe^{3+} ions. The thermal dependence of luminescence was determined in $-150^\circ C - 300^\circ C$ and $-150^\circ C - 310^\circ C$ (considering $MgAl_2O_4$, $MgGa_2O_4$, $CaAl_2O_4$, $CaGa_2O_4$ materials) temperature ranges.

It was found that three vanadium oxidation states are present in the nanocrystalline host materials, namely V^{5+} , V^{4+} and V^{3+} , which are localized in different part within the nanocrystals, namely V^{5+} ions are located mainly on the surface of particles, whereas the V^{4+} and V^{3+} preferentially occupy their interior. Moreover, they vary in the spectral position of the emission bands and thermal quenching rate of the luminescence intensity. Hence, it was found that by changing the particle size their spectroscopic properties can be modulated. The $d-d$ emission spectral range of V^{3+} and V^{4+} ions (600 nm – 800 nm) is interesting from the biological applications perspective, since it overlaps with biological optical windows. With the enhancement of particle size the charge-transfer emission intensity of V^{5+} ions (~ 500 nm) is reduced with respect to the luminescence intensity of V^{3+} and V^{4+} ions. It results from the fact,

that the growth of crystal grain size leads to the lowering of the surface-to-volume ratio. Moreover, it was demonstrated that the emission of V^{4+} ions in the nanoscaled phosphors is observed for the host material composition with octahedral crystallographic position of Ga^{3+} ions. Three types of V^{n+} ions based luminescence thermometers were proposed. The first one is based on the temperature susceptible emission intensity of single V^{n+} ion in garnets - $Y_3Al_5O_{12}$, $Y_3Al_{5-x}Ga_xO_{12}$ and perovskite - $LaGaO_3$ host materials. The second type is represented by a ratiometric temperature sensor, using the ratio between emission intensities of two vanadium ions within the same phosphor. In turn the third type refers to the ratiometric approach, basing on the ratio between temperature-dependent V^{n+} emission intensity and the luminescence intensity of lanthanide ions, barely influenced by temperature changes (internal reference signal). It was found, that the incorporation of lanthanide ions as co-dopants, namely Nd^{3+} , Dy^{3+} and Eu^{3+} ions, significantly enhances the relative sensitivity and usable temperature range of V^{n+} - based luminescence thermometers. It was concluded that the performance of V^{n+} singly doped – or V^{n+} , Ln^{3+} - co-doped nanocrystals to thermal sensing can be further improved by the optimization of their size, dopant concentration, Ga^{3+} content in the lattice and thus by the host material stoichiometry. The growing number of the V^{4+} ions associated with the increase of the Ga^{3+} ions concentration in the garnet structures increases the probability of $V^{5+} \rightarrow V^{4+}$ phonon-assisted energy transfer, which is a dominant effect, being responsible for the modification of temperature-sensing properties of V^{n+} - based $Y_3Al_{5-x}Ga_xO_{12}$ luminescence thermometers. Additionally, since three vanadium oxidation states (V^{5+} , V^{4+} and V^{3+}) are simultaneously present in $LaGaO_3$ lattice, the methods of their stabilization were proposed, namely the charge compensation method, citric acid - assisted synthesis method of the nanomaterials as well as grain size tuning by the use of various annealing temperatures. The most effective one was the method basing on the particle size changes, since the V^{n+} ions are located in different parts of the nanocrystals. Considering the charge compensating method, the use of Mg^{2+} as charge compensating ions leads to the most effective stabilization of V^{4+} ions luminescence.

The thermally-dependent $d-d$ emission of Fe^{3+} ions, taking place from tetrahedral and octahedral emitting centres were demonstrated as a temperature sensing probe. It was found that the intense red luminescence of six-fold coordinated Fe^{3+} ions in $LiAl_5O_8$ host materials, covering with the spectral range of the first biological optical window ($\lambda_{em} = 660$ nm), has potential to be applied to monitor the temperature of biological systems. It results from the biocompatibility of Fe^{3+} -doped $LiAl_5O_8$ nanocrystals verified by cytotoxicity assessment. Moreover, the impact of dopant concentration and particle size on Fe^{3+} optical properties and

their thermal-vulnerability was examined. Three types of Fe^{3+} - based luminescence thermometers were presented, namely **i)** – the one exploiting the thermally-dependent single emission of Fe^{3+} ion, **ii)** – the ratiometric luminescence thermometers and **iii)** – luminescence lifetime – based ones. Furthermore, the thermally-susceptible luminescence of tetrahedrally coordinated Fe^{3+} ions ($\lambda_{\text{em}} \sim 800$ nm), which dominates in the emission spectra of $\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{Y}_3\text{Ga}_5\text{O}_{12}$, $\text{Lu}_3\text{Ga}_5\text{O}_{12}$, $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ host materials, reveals temperature sensing capability. It was proposed, that by the crystal field modification via an appropriate selection of host material composition and the introduction of Cr^{3+} ions to activate the $\text{Fe}^{3+} \rightarrow \text{Cr}^{3+}$ phonon-assisted energy transfer, the optical response to temperature changes of considered Fe^{3+} luminescence can be significantly improved. Owing to thermally-dependent Fe^{3+} and Cr^{3+} emission intensities, the ratiometric temperature sensor was developed, exploiting the luminescence intensity ratio of Fe^{3+} and Cr^{3+} ions as a thermometric parameter. It was found that with the lowering of the crystal field strength, i.e. by the elongation of metal-to-oxygen distance, the spectral position of the emission band of fourfold coordinated Fe^{3+} ions can be shifted towards longer wavelengths, while their luminescence lifetime becomes shortened. Considering the ratiometric approach, the Nd^{3+} luminescence was used as an internal reference signal, simultaneously providing further enhancement of temperature sensing accuracy and relative sensitivity (up to 5.90%/°C for $\text{Lu}_3\text{Ga}_5\text{O}_{12}$ at 100°C). The modification of crystal field strength and the local ions symmetry induced by appropriate choice of host material composition was successfully applied in order to modulate the luminescence thermal quenching rate and the spectral position of the emission band of the octahedrally coordinated Fe^{3+} ions ($\lambda_{\text{em}} \sim 700$ nm) in MgAl_2O_4 and MgGa_2O_4 nanomaterials as well as tetrahedrally coordinated Fe^{3+} ions ($\lambda_{\text{em}} \sim 800$ nm) in CaAl_2O_4 , and CaGa_2O_4 nanocrystals. The reduction of the local point symmetry from O_h to C_1 and the increase of crystal field strength, i.e. the shortening of metal-to-oxygen distance, enhances the performance of Fe^{3+} luminescence to temperature sensing, simultaneously causing the redshift of the Fe^{3+} emission band. It was proved, that the inorganic lattices with low point symmetry of cationic sites, being occupied by Fe^{3+} ions, are favourable from the thermometric perspective. Thus, this approach enables the development of a highly sensitive Fe^{3+} - based luminescence thermometer, in which relative sensitivity and usable temperature range can be adjusted by the intentional design of the host material composition. In turn, for these lattices compositions the use of Tb^{3+} ions luminescence as an internal reference signal in the ratiometric approach enables the improvement of the reliability of the temperature readout of Fe^{3+} - based luminescence thermometers. The low local point symmetry (C_1) of cationic sites, substituted by fourfold coordinated Fe^{3+} ions and the

enhancement of crystal field strength significantly improves the thermometric properties of Fe³⁺-doped SrAl₄O₇, CaAl₄O₇, BaAl₄O₇ phosphors, with simultaneous red-shift of the maximum emission band. The strong temperature dependence of the intensity of the near infrared (NIR) - located Fe³⁺ emission band allowed to create intensity – based luminescence thermometers. Furthermore, in order to improve the reliability of temperature sensing via Fe³⁺ emission intensity, the luminescence lifetime and ratiometric approaches were successfully implemented. Considering the latter, two thermally-affected luminescence intensity ratios were used, **i)** – exploiting the emission intensity ratio of Fe³⁺ ions localized in two crystallographic positions of Al³⁺ ions in the BaAl₄O₇ host materials and **ii)** – taking advantage of the internal reference signal represented by Tb³⁺ luminescence.

The demonstrated results considerably complement and broaden the knowledge of vanadium and iron ions spectroscopy in a wide temperature range. Furthermore, the performed investigations enter into main global trends concerning the applicability of nanoscaled phosphors, particularly concerning the development of transition metal ions based temperature sensors. It should be noticed, that these are the first scientific works where Vⁿ⁺ and Fe³⁺ luminescence are investigated in terms of thermal sensing. The growing significance of luminescence thermometry in plenty of areas enforces the importance of the presented research. The obtained results are included in eight papers published in international journals of the Philadelphia list.

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