

Abstract

The aim of the thesis was investigation of the influence of host modification on the spectroscopic properties of europium-doped phosphors from the phosphate family. Chapters 1 to 6 contains the existing theoretical background regarding the subject of the thesis. Chapters 7 to 11 present the experimental results along with analyses and interpretation of the results. To accomplish the objective of the thesis three series of materials based on $\text{Ca}_9\text{Y}(\text{PO}_4)_7$ and $\beta\text{-NaCaPO}_4$ crystal matrices were prepared using the Pechini method involving two-step synthesis strategy (calcination and reduction). In all crystal matrices the europium ion activator (5 mol. %) was intentionally substituting the calcium sites. Two matrix modification strategies were employed. First strategy, applied in the case of $\text{Ca}_9\text{Y}(\text{PO}_4)_7$, was to change the stoichiometric ratio of Y^{3+} ions (from 0.5 to 2 mol.) and Ca^{2+} (from 8 to 9.5 mol.). Second strategy involved heterovalent substitution of codopant ions in the anionic sublattice, e.g. Al^{3+} in place of P^{5+} in $\text{Ca}_9\text{Y}(\text{PO}_4)_7$ and Si^{4+} in place of P^{5+} in $\beta\text{-NaCaPO}_4$. The concentration of codopants spanned 0, 5, 10 mol. % Al^{3+} and 0, 5, 15 mol. % Si^{4+} . XRD analysis showed, that all prepared samples were single phase. Spectroscopic results have shown that not the modification strategy itself, but type of point defects created as the result of matrix modification influences the luminescent properties of the materials. A confirmation of this observation comes from the investigation of series of calcium-yttrium orthophosphates, where both the decrease of $[\text{Y}]/[\text{Ca}]$ concentration ratio as well as substitution of Al^{3+} ions into P^{5+} sites have a similar effect on the properties of the obtained phosphors. The observed changes were attributed to the presence of the same type of defects regardless of the modification strategy. Additionally, detection of an additional, atypical Eu^{2+} ions emission band was explained by the change in crystal field strength due to appearance of $V_{\text{O}}^{\bullet\bullet}$ defect in the vicinity of Eu^{2+} ions. The emission spectra of reduced samples contain emission bands of Eu^{3+} ions of in the 580-710 nm wavelength range, which intensity is altered by the performed matrix modifications. Stabilization of Eu^{3+} ions under the reducing conditions was explained by assuming the presence of chemically induced defects (Ca'_{Y} , Al''_{P} , Si'_{P}) compensating the excess charge appearing after introducing the Eu^{3+} ions in the Ca^{2+} sites ($\text{Eu}^{\bullet}_{\text{Ca}}$). It was also observed that matrix modification applied in the study allowed facile modification of the emission colour of obtained phosphors.