

Features of Crystal Structure and Luminescent Properties of the $\text{La}_{1-(x+y)}\text{Eu}_x\text{Ca}_y\text{VO}_4$ Nanosized Compounds

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Among various types of optical materials orthovanadates are an important family of compounds those have actual and potential applications in the fields of laser hosts, catalysts, phosphors, sensors and polarizers. These compounds are chemically stable and non-toxic. Currently, some of mentioned applications require vanadate materials with improved efficiency of luminescence emission especially under excitation with light from near UV and violet spectral ranges. Now search for new vanadate compounds for these needs is carried out using variations of two and more cations in their composition including partial iso- and heterovalent substitutions. Intensities of luminescent emission of the RE activators in orthovanadate compounds can be effectively increased with the A^{2+} modifying cations. Properties of compositions with such heterovalent substitutions strongly depend on concentration ratios of the A^{2+} cations. Therefore, we expect that rare earth orthovanadate nanoparticles with heterovalent substitutions could bring an additional raise of luminescence intensity. We used the Ca^{2+} modifying impurities as first step of this elaboration.

In general, the orthovanadates compounds crystallize in two polymorphs, a tetragonal zircon-type structure (space group: I41/amd , $Z = 4$) and a monoclinic monazite-type (space group: P21/n , $Z = 4$). Compounds with small rare-earth cations, EuVO_4 e.g., have zircon-type structure. Compounds with a large rare-earth cation, LaVO_4 e.g., have monazite-type structure. The aim of this work was to synthesize and study their structural, morphological and other physical properties of the $\text{La}_{1-(x+y)}\text{Eu}_x\text{Ca}_y\text{VO}_4$ ($0.05 \leq x \leq 0.3$, $0.05 \leq y \leq 0.2$) compounds. The $\text{La}_{1-(x+y)}\text{Eu}_x\text{Ca}_y\text{VO}_4$ ($0.05 \leq x \leq 0.3$, $0.05 \leq y \leq 0.2$) samples were prepared by aqueous nitrate-citrate sol-gel synthesis route taking citric acid (CA) as a complexing agent. Phase compositions and crystal lattice parameters were determined using X-ray diffractometer DRON-3M ($\text{Cu}_{\text{K}\alpha}$ -radiation with a Ni filter). The diffraction patterns were taken at a step of $2^\circ/\text{min}$. The microstructure of the compounds was studied with a scanning electron microscope (SEM) Hitachi S – 2400. The pattern of the $\text{La}_{0.9}\text{Eu}_{0.05}\text{Ca}_{0.05}\text{VO}_4$, $\text{La}_{0.8}\text{Eu}_{0.1}\text{Ca}_{0.1}\text{VO}_4$ compounds fits well with monoclinic monazite-type, and $\text{La}_{0.65}\text{Eu}_{0.2}\text{Ca}_{0.15}\text{VO}_4$, $\text{La}_{0.5}\text{Eu}_{0.3}\text{Ca}_{0.2}\text{VO}_4$ samples crystallized in tetragonal zircon-type structure.

Luminescence spectra of the samples consist of narrow spectral lines in the 550 – 730 nm spectral range and the lines caused by the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ electron transitions in the Eu^{3+} ions. An addition of the Ca^{2+} ions increases intensity and changes spectra of the Eu^{3+} ions luminescence. The structure of the spectra also depends on the excitation light wave length. The carried out analysis has revealed that Eu^{3+} ions form at least two different types of emission centers in the studied materials. The assumption is made that I type centers are formed by the Eu^{3+} ions in their regular positions in the crystal lattice, while the II type centers have complex structure and they consists of Eu^{3+} ions, Ca^{2+} cations and oxygen vacancies. Correlations between luminescence properties and crystal structure of the samples were analyzed. The structure of the both types of emission centers had been analyzed. The samples of the $\text{La}_{0.9}\text{Eu}_{0.05}\text{Ca}_{0.05}\text{VO}_4$, $\text{La}_{0.8}\text{Eu}_{0.1}\text{Ca}_{0.1}\text{VO}_4$ compounds with monoclinic monazite-type are characterized by better efficiency of luminescence than $\text{La}_{0.65}\text{Eu}_{0.2}\text{Ca}_{0.15}\text{VO}_4$, $\text{La}_{0.5}\text{Eu}_{0.3}\text{Ca}_{0.2}\text{VO}_4$ samples with tetragonal zircon-type structures if excited from near UV and violet spectral ranges.