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Doctoral dissertation : „Relationship between chemical composition of garnet phosphor and its luminescence properties”

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Abstract

Garnets are an interesting group of chemical compounds. The structure of the first synthesized garnet was solved nearly 100 years ago. Despite such a rich history, the interest in this group of chemical compounds is not diminishing. This is due to the fact that the structure of garnet is rich in various crystallographic positions: dodecahedral, octahedral and tetrahedral. The presence of crystallographic sites with different coordination numbers and sizes allows obtaining garnets with nearly half of the elements of the periodic table. For this reason, garnets perfectly serve as a host in phosphors.

In the present work a series of germanate garnets doped with Ce^{3+} , Mn^{2+} or Eu^{3+} ions with the general formula $\text{A}_3\text{B}_2\text{Ge}_3\text{O}_{12}$, where A- Ca^{2+} , Sr^{2+} ; B- Al^{3+} , Sc^{3+} , Y^{3+} and yttrium aluminium garnet doped with Ce^{3+} ions were obtained. The latter phosphor is the most often studied phosphor with the garnet structure due to its widely use, e.g. as a scintillator or phosphor in white LED technology. Ce^{3+} and Mn^{2+} ions were selected for research due to their broadband emission, beneficial from the phosphors' point of view for LEDs.

Moreover, absorption and emission transitions in Ce^{3+} ions are allowed by selection rules, which ensures efficient absorption and emissions. Co-doping with Mn^{2+} ions allows the implementation of $\text{Ce}^{3+} \rightarrow \text{Mn}^{2+}$ energy transfer and simultaneous emission from both ions. It gives the possibility to synthesise phosphors with tuneable emission. Eu^{3+} ions were used as a structural probe, but also as a source of red light. Narrowband intensive emission from Eu^{3+} ions can complement the broad-band emission of phosphors and increase its brightness. Germanate garnets are relatively poorly researched; some have been synthesized and described for the first time.

The aim of the work was to determine how local symmetry and the chemical environment of the active ion in a phosphor affect the wavelength of its emission / absorption, and how structural factors affect occupancy of crystallographic positions in the hosts. The aim of the study

was also to investigate the efficiency and mechanism of $\text{Ce}^{3+} \rightarrow \text{Mn}^{2+}$ energy transfer in these hosts.

Single-phase germanium phosphors with a garnet structure were obtained using mainly a modified solid-state synthesis developed for the needs of this study. The obtained polycrystalline materials were examined by means of: powder diffractometry (XRD), absorption and emission spectroscopy in the UV-Vis range, including time-resolved spectroscopy, elemental analysis or Scanning Electron Microscopy.

It was shown that the wavelength of absorption / emission of active ions in these hosts depends on the chemical composition of the host and can be related to magnitude of deformation from cubic symmetry around active ions expressed by the d_{8g}/d_{8I} parameter. The radius of ions in the first and second coordination spheres influences the size of this parameter. It was also shown that electronegativity of the atoms that build the host is another important factor influencing the absorption / emission wavelength. It was determined how the active ions occupy different positions in the hosts using the Eu^{3+} or Ce^{3+} ions as a structural probe. The $\text{Ce} \rightarrow \text{Mn}$ energy transfer mechanism was studied and shown to be different for high and low unit cell. In addition, a synthesis method was developed and a modified YAG: Ce^{3+} was obtained, in which part of the oxygen atoms was replaced by nitrogen atoms ($\text{Y}_3\text{Al}_5\text{O}_{12-x}\text{N}_{2x/3}$). It was found that this structural modification alters the optical properties of the phosphor causing red shift and greater quantum yield of luminescence. The proposed method of synthesis allows an extremely high level of doping with Ce^{3+} ions (14%), while maintaining very intense emission from Ce^{3+} ions.