Thesis:

The detection of lead-free fluoride nanocrystals dispersed in sol-gel materials using X-ray diffraction as well as microscopic and spectroscopic techniques

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Abstract:

Nowadays, the development of researches concentrated on synthesis and characterization of oxyfluoride glass-ceramics doped with rare earth ions is a forefront direction in current materials engineering. The glass-ceramics are the class of innovative optical materials, which contain the fluoride nanocrystals dispersed in oxide amorphous matrices. Such materials combine good mechanical strength and chemical durability of oxide hosts with high luminescence efficiency of rare earth ions incorporated into low-phonon fluoride crystals. Generally, the oxyfluoride glass-ceramic materials are commonly fabricated via controlled heat-treatment of glasses derived by conventional melt-quenching method. Alternatively, such materials can be successfully prepared via sol-gel technique, which is based on polycondensation reaction in liquids phase. Due to the fact that the heat-treatment of xerogels could be conducted at significantly lower temperatures compared with melting of glass-forming components, the sol-gel method seems to be a particularly attractive technique to fabricate the oxyfluoride glass-ceramic materials dedicated for optoelectronic applications.

In this doctoral dissertation, the Eu^{3+}-doped glass-ceramic materials containing MF_2 (M = Ca, Sr, Ba) or MF_3 (M = Y, La, Gd) nanocrystals were synthesized via sol-gel method and characterized. The studied materials were fabricated by controlled heat-treatment of silicate xerogels and the structural changes within sol-gel hosts were verified using IR-ATR spectroscopy. The individual fluoride crystal phases were identified by XRD measurements and the received results were confirmed by high resolution mode in transmission electron microscope HR-TEM. The structural changes during controlled heat-treatment of precursor xerogels were also evaluated based on unique spectroscopic behavior of optically active Eu^{3+} ions, which results from the nature of their intra-configurational $4f^6$-$4f^6$ transitions. Due to the significant decrease of R/O-ratio values after conducted heat-treatment process as well as observable splitting of emission bands, the partial incorporation of Eu^{3+} ions into precipitated MF_2 (M = Ca, Sr, Ba) and MF_3 (M = Y, La, Gd) fluoride nanocrystals was confirmed. Moreover, the change in character of registered decay curves of the $^5D_0$ excited state from mono-exponential (xerogels) to bi-exponential (glass-ceramics) clearly evidenced the distribution of Eu^{3+} ions between sol-gel hosts and fluoride nanocrystals. In summary, the above techniques allow for the full characterization of the glass-ceramic materials, with particular emphasis on the crystallization of fluoride phases in nanometric range.