Abstract

In my thesis I am presenting my results in investigations of spectroscopic properties of Mn^{4+}-doped fluoride phosphors, based on the results from the following samples: $KNaSiF_6:Mn^{4+}$, $Rb_2GeF_6:Mn^{4+}$, $Na_3HTiF_8:Mn^{4+}$ and $Na_2(Si,Ge,Ti)F_6:Mn^{4+}$.

The aim of the research was understanding and description of interactions between the host lattice and Mn^{4+} dopants by investigating the influence of temperature and high pressure on the spectroscopic properties of fluoride phosphors.

The use of spectroscopic measurements as a function of temperature and pressure allowed to determine changes in energy structure (modification of crystal field strength parameter and parameters of interelectronic interaction) as well as change in radiative transition probability due to changes in characteristics of interaction within Mn^{4+} valence electrons and between Mn^{4+} ion and host lattice.

The main results of the thesis include:

(1) Development of quantum-mechanical model describing the influence of static symmetry distortions and antisymmetric oscillation modes in $[MnF_6]^{2-}$ complex on the probability of radiative transition in Mn^{4+} as a function of temperature. The model explains the observed properties of Mn^{4+} regarding the temperature evolution of the shape of the emission spectrum (relative decrease of the zero phonon line with respect to phonon sidebands) as well as unusual temperature dependence of the luminescence decay time.

(2) Determination of the values of parameter determining the energy structure of Mn^{4+} (crystal field parameter *Dq*, Racah parameters *B* and *C*) from optical spectra (including unique results of pressure dependence of luminescence excitation spectra). Based on these parameters, I have calculated the full energy structure of d^3 electronic configuration of Mn^{4+} with respect to pressure.

(3) Demonstration of the influence of the higher excited $^4T_2$ state on the radiative lifetime of ^2E emitting state. On this basis, a model was developed which uses spin-orbit interaction (treated as a perturbation) to explain the doublet-quartet emission transition $^2E \rightarrow {}^4A_2$. The model was used to explain the pressure evolution of $^2E \rightarrow {}^4A_2$ decay time, where it was extended by taking into account the influence of pressure on the electronic part of the ^2E emitting state wavefunction.

The thesis is based on the results of a few Mn^{4+}-doped fluoride phosphors, however, the conclusions drawn on this basis are general and applicable to a much broader group of phosphors.

The research described in this paper fall into the basic research category, but the obtained results are of practical value in the engineering of optical properties of other phosphors characterised by forbidden emission transitions.