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Structure Sensitive Investigations on Mn-activated Perovskites and Rare-Earth-doped Aluminates

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Abstract

In this work optical, magnetic resonance, and optically-detected magnetic resonance measurement techniques were used to investigate the Mn-activated fluoroperovskites RbCdF_3 and LiBaF_3 as well as the rare-earth (RE) doped persistent phosphors SrAl_2O_4 and CaAl_2O_4 .

The photoluminescence (PL) of Mn-activated RbCdF_3 shows an emission band at 560 nm, which can be attributed to the Mn^{2+} dopant; the corresponding excitation bands are between 240 and 520 nm. After x-irradiation an increased Mn^{2+} emission can be observed and the excitation spectrum shows an additional intense broad band at 300 nm. Excitation at 300 nm leads to a decreasing intensity of the Mn^{2+} emission, whereas excitation at 240 nm leads to an increase in the PL intensity. Electron paramagnetic resonance (EPR) shows that the number of Mn^{2+} ions is reduced upon x-irradiation; the original Mn^{2+} level can be restored upon optical bleaching.

In LiBaF_3 it was possible to identify a luminescent oxygen vacancy complex emitting in the blue spectral region. The structure of that complex was investigated by PL and PL-detected electron paramagnetic resonance (PL-EPR). At 20 K the oxygen-related complex shows two luminescence bands peaking at about 430 and 475 nm, when excited at 220 nm. These bands can be attributed to an excited triplet state ($S = 1$) with the z -axis of the fine structure tensor parallel to the $\langle 110 \rangle$ direction. This complex is believed to be next to a Mn^{2+} impurity on a Ba^{2+} site and can be described by an oxygen on a fluorine lattice site with a nearest fluorine vacancy along the $\langle 110 \rangle$ direction.

Prior to x-irradiation the PL of Mn-activated LiBaF_3 shows a Mn^{2+} emission band at 710 nm; the corresponding excitation bands are between 210 and 620 nm. After x-irradiation the PL spectrum shows a new emission peaking at about 610 nm which is tentatively assigned to a perturbed Mn^{2+} emission; the intensity of all PL bands is increased. Structure sensitive investigations on the radiation-induced emission band were done by PL-EPR at a temperature of 1.5 K. The analysis of the angular dependent PL-EPR spectra, recorded for different orientations of the magnetic field, yielded that the 610 nm luminescence band is due to an excited triplet state ($S = 1$) of a Mn-related center with the z -axis of the fine structure tensor close to a $\langle 110 \rangle$ direction.

Single-crystals of MAl_2O_4 ($\text{M}=\text{Ca}$ and Sr) persistent phosphors that are nominally pure or doped with Eu and Nd or Dy, respectively, were investigated. Their recombination luminescence (RL) and microwave-induced changes in the RL in a high magnetic field (RL-EPR) were investigated after ultraviolet excitation at low temperatures. Wavelength dependent RL-EPR measurements indicate that only one intrinsic donor but at least two different intrinsic acceptors are involved in the recombination process. The donor-acceptor recombination energy is either emitted directly (undoped samples) or almost completely transferred to the RE activators (doped samples).