

Spectroscopic properties of Mn²⁺ and Fe³⁺ dopants

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Mn²⁺ ions in solids exhibit luminescence in the spectral regions between green and far red, depending on the local environment and distances between central ions and ligands. The basic optical properties of this dopant are well described by the crystal field theory for d⁵ electronic configuration. According to this theory, all optical transitions at ambient conditions occur between the ⁶A₁ ground state and higher energy excited states with a different spin, thus being strongly spin-forbidden, having very small transition probability and long decay times of luminescence. Fe³⁺ ions with the same d⁵ electronic configuration as Mn²⁺ ions show very similar optical properties. Usually, the optical transitions, especially between the ground and the first excited level are also strongly coupled with the lattice, thus both absorption and luminescence spectra are broad, often without 0-phonon lines, even at very low temperatures. An externally applied pressure may strongly influence the spectral position of luminescence as well as the luminescence decay kinetics of the ions with a d⁵ electronic structure. High-pressure luminescence experiments may help to distinguish between possible valence states of Mn ions.

Both Mn²⁺ and Fe³⁺ may substitute other ions in the sites with tetrahedral and octahedral symmetry with coordination numbers 4 and 6, respectively. In this different coordination, they exhibit different electron-phonon coupling, which is reflected in their luminescence properties, especially by the appearance of sharp zero-phonon lines in the spectra. Relatively weak electron-phonon coupling is observed in a tetrahedral environment.

Fe dopant ions for a long time were considered as the luminescence quenchers. Indeed, in some materials, the luminescence of Fe ions is not observed, although their presence is undoubtful there. Recently, there have been many publications devoted to the properties of Fe³⁺ ions in various hosts.

In this presentation results of optical studies of several compounds doped with Mn²⁺ and Fe³⁺ ions will be presented, showing their particular properties in different hosts, including Gd(Zn,Mg)B₅O₁₀:Mn, LiGaO₂:Fe, and some others. The difficulties in the interpretation of the optical spectra will be discussed.

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