Mn impurities in CaZnOS: insight from luminescence spectroscopy and density functional theory

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Manganese is a well-known optical dopant. It can adapt different charge states of which the divalent, Mn^{2+}, featuring a $3d^5$ electron configuration, and the tetravalent, Mn^{4+}, featuring a $3d^3$ electron configuration are most abundant in luminescence literature. Both these charge-states of Mn can show efficient luminescence, originating from intraconfigurational 3d transitions, having the emission in the visible spectral range. Excitation of the luminescence can be achieved by exciting the $3d^N$ manifold directly or sensitized by exciting the host compound with subsequent energy transfer.

This study concentrates on the oxysulfide CaZnOS [1]. This polar compound is built of alternating monolayers of ZnS and CaO, and forms a peculiar host for Mn^{2+}. It has been proposed as LED phosphor as well as mechanoluminescent pressure gauge [2, 3]. This material was synthesized by a solid-state reaction and the luminescent properties were characterized in detail. The ability of this material to store energy through the trapping of charge carriers is assessed from thermoluminescence measurements.

To get a thorough understanding of the properties of this phosphor, the electronic structure of the doped and undoped compound is analyzed in detail. First principles calculations on charged supercells within the framework of density functional theory (DFT) are combined with semi-empirical crystal field theoretical (CFT) calculations to obtain the multiplet structure of the $3d^5$ manifold, phonon energies of the Mn defect and the location of the impurity levels in the single-particle energy gap of the CaZnOS host. This particular phoshor is used as an example to demonstrate the complementarity of different types of energy level schemes [4].

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