First-Principles Study on optical and photoluminescence properties of Fe-doped montmorillonite clay

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Clay-based minerals have attracted attention due to their applications in many fields such as pharmaceutical, electrical appliances, and engineering applications. A further value-added market for smectite clay minerals is to make pillared clays, which are widely used for the development of catalysts and absorbent applications. The technological properties of these minerals rely on the internal structure of the constituent particles. Therefore, studying the structural and electronic features at the fundamental electronic properties is a permanent matter of interest. In this work, optical properties and the ground electronic state properties of Fe-doped montmorillonite nanoclay were investigated. To this end, we employ density functional theory (DFT) and density operator theory to explore absorption spectrum, density of states, partial density of states, charge carriers' relaxation dynamics, and photoluminescence (PL). To predict photoluminescence, charge carrier dynamics are obtained from non-adiabatic couplings between electronic orbitals and *ab initio* calculations. In this study, we assumed that the Fe is in its +3 oxidation state hypothetically and several spin multiplicities for the model were studied. We found that the bandgap of spin up is larger than spin down components for different spin multiplicities. Absorption spectra are interpreted in terms of transitions associated with orbitals localized on iron. The results of charge carrier dynamics indicate that for the low and intermediate spin multiplicities, the hole relaxes faster than the electron. Specifically, for high spin multiplicity, in the case of alpha spin under the considered range of low excitation energy, the electron tends to stay on the LUMO and never moves. The dynamics of excitation energy dissipation results for low and intermediate spin multiplicities show the most pronounced transition corresponds to HOMO to LUMO, while for high spin multiplicity there isn't any transition below the bandgap which is 4.62 eV in the alpha spin case. Four dominant transitions were explored for the beta component of high spin multiplicities in which the HOMO to LUMO orbital transition energy has the highest intensity in all cases.