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DFT CALCULATIONS ON ELECTRONIC PROPERTIES OF SLABS OF PbO2

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Introduction - Transparent conducting oxides (TCO) combine transparency and conductivity, properties that, generally, do not coexist. PbO2 has two main allotropic phases: ?-PbO2, columbite type orthorhombic structure belonging to the space group Pbcn (60), with cell constants a = 0.497 nm, b = 0.596 nm and c = 0.544 nm, and ?-PbO2, rutile type tetragonal structure belonging to space group P42/mnm (136), with cell constants a = 0.491 nm and c = 0.3385 nm. ?-PbO2 and ?-PbO2 are both considered highly covalent materials with strong hybridization between the 2p orbitals of O and 6s and 6p orbitals of Pb. ?-PbO2 is a narrow band gap semiconducting, which has received a great deal of attention lately due to their potential use as TCO. In this work it has been investigate the electronic structure of pure and Sn doped thin films of PbO2, aiming to contribute to a better understanding of the material behavior. Methodology - A quantum mechanical approach based on the periodic Density Functional Theory (DFT), with B3LYP hybrid potential, implemented in the CRYSTAL09 code has been used for the calculations. Results - From the calculations of band structures, it is suggested that the conducting behavior of ?-PbO2 is a intrinsic characteristic of the material that arises from the overlaping of the 6s orbital of the conducting band of Pb and the 2p orbital of the top of valence band of O. The charge density of the Pb cations in ?-PbO2 and ?-PbO2 is about half the formal ionic charge. The films present a small direct band gap. For ?-PbO2 VBM is situated at the ? point, with the conduction band minimum situated at the same point resulting in an direct band gap which change as a function of the film thickness. Films present a larger band gap than bulk material, with a little dependence on the terminal plane. The empty states are virtually composed of Pb 6p and 6s, with a predominance of 6p orbitals. Although Pb 6p and 6s contribute for both the empty and occupied states, there is a clear separation between them in every energetic region, indicating a small hybridisation between them. 2p states of oxygen atoms concentrate in the valence bond. While the structure of the conduction band is quite similar, with a great participation of the 6p orbitals of Pb and a minor participation of 6s orbitals, 6p orbitals of Pb are virtually missing of valence band. The material is highly covalent. Conclusions - The result suggest that PbO2 might have potentially more applications as films than in the bulk crystalline phase