Fingerprints of order and disorder in the electronic and optical properties of crystalline and amorphous TiO_2

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We have investigated the structural and electronic properties as well as the linear optical response of amorphous TiO2 within density functional theory and a numerically efficient density-functional based tight-binding approach as well as many-body perturbation theory. The disordered TiO2 phase is accurately modeled by molecular dynamics. The equivalence to experimentally characterized amorphous phases is demonstrated by atomic structure factors and radial pair-distribution

functions. By density functional theory calculations, using both the standard semilocal Perdew-Burke-Ernzerhof functional and the non-local Heyd-Scuseria-Ernzerhof screened hybrid functional, the electronic band gap is found to be larger than in the crystalline TiO2 phases rutile, anatase, and brookite if temperature induced effects on the atomic structure are neglected. The quasiparticle

band gap is determined to be 3.7 eV, while the optical gap is estimated to 3.5 eV. A similar sized electronic mobility gap of 3.7 eV is obtained from analysis of the degree of localization of electronic states through the inverse participation ratio and the information entropy of the charge density distributions. The frequency dependent optical constants, calculated from the complex dielectric function, have been determined in independent particle approximation. Besides similar absorption characteristics between the most common crystalline phases and amorphous TiO2, we find distinct differences in the optical spectra in the energy region between 5 eV and 8 eV. These differences can be assigned to the loss of symmetry in the local atomic structure of the disordered material. While the composition of the crystalline phases rutile, anatase, and brookite is well described by periodic arrangements of distorted TiO6 octahedra building blocks, the amorphous phase is characterized by partial loss of this octahedral coordination and the formation of disorder-induced under- and over-coordinated Ti ions. This leads to the absence of the crystal-field splitting of the unoccupied Ti-3d states into e_g and $t2_g$ like sub-bands. The amorphous phase is interpreted as a superposition of building blocks that reflect the various local symmetries of the manifold of synthesizable crystalline TiO2 phases. The linear optical properties, calculated within the independent particle approximation, are found to be in excellent agreement with the available experimental data.

Further prospects for applying this approach on tailoring high quality thin film metal-oxide optical coatings will be described and respective examples will be presented.