

Impact of substituent size and electronegativity on the band gap of TiO₂ polymorphs

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The semiconductor polymorphs of TiO₂ are promising materials in photovoltaics and optics. These polymorphs have been studied with a variety of experimental and computational methods, which aim at tuning the electronic structure, in particular, the band gap value of the crystalline solid. Several experimental studies report that the addition of a substituent into the structure of TiO₂ decreases its band gap value, but the reasons for this phenomenon are unknown. Possible explanations for the change in band gap involve the substituent atom's crystal radius or its electronegativity. Understanding the cause of the band gap value change will provide great insight in designing new materials. Our hypothesis is that larger crystal radii of substituent atoms will result in a decrease in the band gap of TiO₂. In this project, atoms of differing crystal radii and electronegativity were selected for substitution into the three polymorphic forms of TiO₂, which are rutile, anatase, and brookite. Our computational approach utilizes the linearized-augmented plane-wave (LAPW) approach of density functional theory (DFT), in the WIEN2k software, to determine the band gap and density of states for each polymorph. Preliminary results indicate that there is a more prominent trend in the electronegativity's effect on band gap than the crystal radius.