

Optical absorption anisotropy of high-density, wide-gap, high-hardness SiO₂ polymorphs seifertite, stishovite, and coesite

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ABSTRACT

Dense, high-refractive index, ultra-hard, wide-gap polymorphs of SiO₂, recently discovered orthorhombic seifertite (space group 60 *Pbcn*), and earlier characterized tetragonal stishovite (space group 136 *P42/mnm*) and monoclinic coesite (space group 15 *C2/c*) were studied using advanced methods of electronic structure calculations involving full-potential linearized augmented plane wave density functional theoretical method (FP-LAPW-DFT) with spin polarization, orbital-dependent potentials, and modified Becke-Johnson potential (mBJ) for accurate account of the band gaps. Although these calculations yield an excellent account of many properties, we here focus on quantitative aspects of optical absorption and selection rules therein. Specifically, the valence-to-conduction band transition in seifertite is symmetry-allowed, and is symmetry-forbidden in stishovite and coesite. Theory is compared with published experimental data, and explanation is provided for weak pre-edge optical absorption in stishovite. Electronic structure and calculated properties of stishovite are also compared with those of the isostructural rutile TiO₂. Effective masses are calculated from the energy dispersion curves $E(\mathbf{k})$ at the valence band maximum for holes and conduction band minimum for electrons. In addition, we propose that splitting of the O2p valence-band in coesite and also observed in α -quartz is a general feature of polymorphs with tetrahedrally coordinated Si, in contrast with continuous valence bands in those with octahedral SiO₆ units such as seifertite and stishovite. Based on quantitative results obtained from the BVA theory, this difference originates from a high degree of covalence in the tetrahedral polymorphs as opposed to high ionicity in octahedral polymorphs.

Keywords: Theory, silica polymorphs, seifertite, stishovite, coesite, rutile, band structure, effective mass, optical absorption