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(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 iconicity in octahedral polymorphs.

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

INTRODUCTION

Dense, high-refractive index, ultra-hard, wide-gap polymorphs of SiO₂ are of a great interest not only owing to the history of discovery in extraterrestrial matter and their extraordinary physical properties, but also to the underlying chemical bonding and unusual coordination of the Si-O₂ structure-forming units and their arrangements. The most recently discovered and characterized polymorph of this type is orthorhombic seifertite (space group 60 Pbcn) (Dera et al. 2002; El Goresy et al. 2008), after tetragonal stishovite (space group 136 P42/mnm) was first synthesized in laboratory by Stishov and Popova (1961) and reported on its natural occurrence in Arizona meteor crater by Chao et al. (1962). The monoclinic coesite (space group 15 C2/c) was first synthesized by Coes (1953), its natural occurrence reported on its natural occurrence in Arizona meteor crater by Chao et al. (1962; El Goresy et al. 2008), after tetragonal stishovite (space group 136 P42/mnm) was first synthesized in laboratory by Stishov and Popova (1961) and reported on its natural occurrence in Arizona meteor crater by Chao et al. (1962). The monoclinic coesite (space group 15 C2/c) was first synthesized by Coes (1953), its natural occurrence reported on its natural occurrence in Arizona meteor crater by Chao et al. (1962) and crystal structure determined by Levien and Prewitt (1981) and Smyth et al. (1987). Some of the experimentally determined properties of the investigated silicas as well as of selected reference materials are summarized in Table 1.

The importance of these materials goes beyond their pure forms, especially as they serve as matrices holding impurities that impart on them new properties, both in nature and technology. For example, the exchange of 4H⁺ for Si⁴⁺; “the hydrogarnet substitution,” is considered to be one of the mechanisms for hydrogen storage in the deep Earth, stishovite being one of the vehicles for this storage as reported by Pawley et al. (1993) and Williams and Hemley (2001), the crystal structure of synthetic H-bearing aluminous stishovite having been reported by Smyth et al. (1995). Related to technology, diffusion of Cu⁺ in α-cristobalite was studied theoretically for possible implications to the functioning of nanoelectronic devices by Zelený et al. (2012), prompting an interest in general interaction of metals with the silica polymorphs. To advance the understanding of metal-support interactions at surfaces related to adhesion and catalysis, strength of bonding and agglomeration of Co and Ni on silica surfaces have been examined theoretically by Ma et al. (2000, 2001a), compared with those on alumina support by Ma et al. (2001b), and analyzed for periodic trends in interactions of the entire first-row transition metal series with the silica surface by Ma et al. (2002) on a slab model derived from β-cristobalite, using methods similar to those employed here, albeit focusing only on the ground-state properties.

Theory has now advanced to a level of high reliability and accuracy to attack both the fundamentals of electronic structure

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