Density functional calculations of the electronic structure and optical properties of aluminosilicate polymorphs (Al$_2$SiO$_5$)

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ABSTRACT

The density functional theory (DFT) based orthogonalized linear combination of atomic orbitals (OLCAO) method is used to study the electronic structure and spectroscopic properties of three alumino silicate polymorphs (Al$_2$SiO$_5$), andalusite, sillimanite, and kyanite. These polymorphs are precursors to mullite, which is an excellent refractory material. The electronic structure results include the band structure, total and partial density of states, bond order, and Mullikan effective charge (Q*), whereas the spectroscopic properties include X-ray absorption near-edge-structure (XANES), and the complex optical dielectric functions ($\varepsilon_1 + i\varepsilon_2$) for each polymorph. For the XANES calculations, we use a supercell approach and account for the electron-core hole interaction. Our calculations show that the polymorphs are insulators with direct band gaps of 5.05, 5.21, and 5.80 eV for andalusite, sillimanite, and kyanite, respectively. The calculated refractive indices (n) for each material are in agreement with experimental values from the literature. Results on the XANES spectral calculations (*K*-edge and *L*-edge) for all crystallographically nonequivalent ions in the polymorphs are presented. It is shown that to achieve excellent agreement with the experimentally measured spectrum, a weighted sum of the spectra from crystallographically inequivalent sites must be used. The analysis of the XANES spectra based on differences in the local bonding environments are provided.

Keywords: Aluminosilicate polymorphs, Al$_2$SiO$_5$, andalusite, sillimanite, kyanite, XANES, ELNES