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

SITARAM ARYAL,* PAUL RULIS, AND W.Y. CHING

Department of Physics, University of Missouri-Kansas City, Kansas City, Missouri 64110, U.S.A.

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 aluminosilicate 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 ($\varepsilon_{i}$, $\varepsilon_{i}^*$) 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

INTRODUCTION

Sillimanite, andalusite, and kyanite are three polymorphs of Al$_2$SiO$_5$, which are important ceramic and refractory materials. All are raw materials for high alumina refractory products that are used in glass furnaces, cement kilns, combustion chambers, and in various ceramic products such as spark plugs, acoustic tiles, high tension insulators, brake linings, and so on. They are also very important from a fundamental crystal structural point of view because they are precursors to mullite. Mullite is a refractory and ceramic material and in recent years it has become a promising candidate for structural and functional ceramics due to its low thermal expansion, low thermal capacity, and excellent creep resistance along with high-temperature strength and stability under severe chemical environments (Schneider et al. 2005). Mullite has a very complex structure (Al$_{4-2x}$Si$_{2+2x}$O$_{10-4x}$) of varying degree of disorder in which x varies from 0.18 to 0.88. When x = 0, the structure reduces to Al$_2$SiO$_5$ polymorphs. In mullite, the Al sites are either octahedrally or tetrahedrally coordinated and Si is tetrahedrally coordinated similar to sillimanite. However, experimental determination of the tetrahedral cation sites is difficult. They are always presented as partial occupation by Al or Si.

These polymorphs are found commonly in metamorphic rocks and are geologically important materials since they provide information about pressure and temperature at their time of formation and the type of metamorphism (Klein et al. 1993; Donna et al. 2002). Among these three polymorphs, andalusite is a low-pressure and low-temperature phase, whereas sillimanite and kyanite are high-temperature and high-pressure polymorphs.

Numerous reports exist that refine the crystal structures of these three polymorphs under various physical conditions (Ralph et al. 1984; Yang et al. 1997a, 1997b; Hexiong et al. 1997) but very little work has been done on their electronic and optical properties. The experimental studies are mostly confined to the X-ray absorption near edge structure (XANES) (Brydson et al. 1992; Froba et al. 1995; Li et al. 1995), chemical bonding and electronic structures using X-ray photoelectron and electron energy loss spectroscopy (Ohuchi et al. 2006) and electric field gradients (Dahaoui et al. 2001). Similarly there are very few theoretical calculations on these polymorphs as a whole so far. Iglesias et al. (2001) calculated electronic structure of andalusite and focused their discussion on the electric field gradient (EFG). They assumed the DOS features in other polymorphs are similar to andalusite. Since all the existing experimental and theoretical studies on these three polymorphs appear to be scattered so that a combined and a comparative study in connection with their structural characteristics will be very useful. Furthermore, it provides the first step toward understanding the structure and properties of the more complex mullite phases.

Brief accounts of crystal structures and method of calculations...