

## VACUUM ULTRAVIOLET, PHOTOEMISSION AND THEORETICAL STUDIES OF THE ELECTRONIC STRUCTURE OF $\text{Al}_2\text{O}_3$ UP TO $1000^\circ\text{C}$

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The high temperature properties of  $\text{Al}_2\text{O}_3$  are important to the processing of this material, for understanding its conductivity and mass transport behavior for sintering, and to the high temperature applications of the material as an optical and structural material. We report the results of a study of the electronic structure of single crystal  $\alpha\text{-Al}_2\text{O}_3$  using results of vacuum ultraviolet and X-ray photoelectron spectroscopies, and pseudofunction band structure calculations of the room- and high-temperature electronic structure, incorporating the lattice expansion and electron-phonon interaction. The optical direct band gap is found to decrease linearly from 8.8 eV at room temperature to 7.2 eV at 1763 K with a temperature coefficient of  $-1.1$  meV/K. The effect of thermal expansion and the electron-phonon interaction, on the band gap, is found to be linear in this temperature range. The valence-band width is constant with temperature, while the unoccupied conduction band states broaden and shift toward the valence band.

$\text{Al}_2\text{O}_3$  and other ceramic materials are finding greater applications as structural, electronic and optical materials. All of these applications rely on high temperature fabrication, high operating temperatures, or specific optical and electronic properties. There is an increasing need to understand the electronic properties of ceramics under these unique conditions. For example the electronic and ionic defect creation energies (for formation of electrons, polarons, vacancies and interstitials) in  $\text{Al}_2\text{O}_3$  are of the same magnitude [1], while the electronic defects have greater mobility than do the ionic defects. Therefore both defect types play critical roles in the diffusion, mass transport, and sintering behavior of  $\text{Al}_2\text{O}_3$ . The goal of this work has been to develop interactive experimental and theoretical techniques to determine the valence and conduction band electronic structure, both experimentally and theoretically, of ceramics.

The first area we have addressed is the temperature dependence of the electronic structure of  $\text{Al}_2\text{O}_3$  [2]. The electronic structure of ionic ceramics exhibits a much greater temperature dependence than the covalent semiconductors, and can not be studied by the experimental or

theoretical techniques which have been applied with success to silicon. Therefore we have developed high temperature vacuum ultraviolet spectroscopy to measure the band gap and joint density of states at high temperatures, pseudofunction band structure techniques to calculate the contributions of lattice expansion and the electron-phonon interaction and high temperature valence band photoemission to measure the valence band structure and broadening with temperature.

Vacuum ultraviolet spectroscopy as a function of temperature [3] was used to study the band gap and higher lying transitions in single crystal  $\alpha\text{-Al}_2\text{O}_3$ . The absorption edge position is found to lie at 8.8 eV and fits either a direct or Urbach type absorption edge shape, as determined from room temperature transmission measurements taken from 4.5 to 15 eV. The reflectance from 7 to 15 eV as a function of temperature, from room temperature up to 1573 K, was then measured. The exciton peak observed at 9 eV at room temperature is shown to lie on top of the fundamental absorption edge, allowing us to identify the room temperature optical band gap to be 8.8 eV. From band structure calculations we can

identify the band gap as arising from O 2p to Al 3s transitions, while the peak at 13 eV at room temperature arises from O 2p to Al 3p transitions. These three features in the reflectance are found to shift to lower energy with increasing temperature as follows; O 2p to Al 3s (band gap)  $-1.1$  meV/K, exciton  $-1.0$  meV/K, O 2p to Al 3p  $-0.7$  meV/K. For comparison the band gap temperature coefficient for Si is  $-0.22$  meV/K while for Ge it is  $-0.44$  meV/K. This leads to a decrease in the band gap from 8.8 eV at room temperature to 7.6 eV at 1573 K and by extrapolation, the optical band gap at 1763 K is 7.2 eV. The temperature dependence of the band gap of Al<sub>2</sub>O<sub>3</sub> is linear. When modeled by an equation of the form  $E_g^0(T) = E_g^0(300\text{ K}) + \beta(\text{abs. edge})T + \gamma(\text{abs. edge})T^2$  where  $\beta$  and  $\gamma$  are the linear and quadratic temperature coefficients,  $\beta$  is  $-1.1$  meV/K and  $\gamma$  is less than  $-1 \times 10^{-4}$  meV/K<sup>2</sup>.

The temperature dependence of the electronic structure of Al<sub>2</sub>O<sub>3</sub> was computed using ab initio self-consistent local density calculations by the pseudofunction method [4]. These calculations use a local density potential for exchange and correlation. Two types of calculations were undertaken to model the respective contributions of lattice expansion and the electron-phonon interaction on the temperature dependence of the electronic structure.

The energy bands of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at room temperature show a direct band gap of 6.3 eV at the zone center  $\Gamma$  while experimentally the gap is found to be 8.8 eV; an underestimate of the band gap is expected for local density calculations. The calculated band gap must be multiplied by 1.4 to obtain agreement with experiment, and we have also used this factor to correct all subsequent calculated band gap energies. To calculate the temperature dependence of the band gap we have used experimentally determined values for the lattice expansion as a function of temperature [5] to calculate the lattice expansion contribution. The electron-phonon contribution is then modeled by use of distorted lattice calculations, in the high temperature thermally expanded lattice, where specific phonon vibrations are modeled using amplitudes determined from high

temperature experimental Debye-Waller factors. The phonon modes chosen were symmetry conserving  $xy$  and  $z$  modes.

The lattice expansion contribution to the temperature dependence is found to be linear from room temperature to 1763 K, and is computed to be  $-0.43$  meV/K. The electron-phonon interaction leads to a computed temperature dependence of  $-0.35$  meV/K. Therefore we can see that the lattice expansion contribution is 55% of the temperature dependence of the band gap. Lattice expansion contributes only 15% and 35% of the temperature dependence of Si and Ge respectively, so we can see that the ionic nature of the bonding, and the localization of the charge, leads to a larger lattice expansion effect, in addition to producing a larger overall band gap temperature dependence. We calculate that lattice expansion leads to a small decrease in the valence-band width, even though simultaneously the band gap is decreasing. This valence-band width decrease due to lattice expansion is counteracted by a broadening of the valence band due to the electron-phonon interaction. The net effect of both terms is to produce no change in the valence-band width with increasing temperature. This observation was then tested with valence band XPS measurements.

Valence band XPS, as a function of temperature up to 1273 K, was used to determine the valence band density of states, and the band broadening and shift. The valence band XPS spectra were obtained with an hemispherical analyzer equipped with a position sensitive detector. The incident X-ray was a monochromatized Al-K $_{\alpha}$  radiation (1486.7 eV). The resolution function of the spectrometer is a Gaussian with a full width at half maximum (FWHM) of 0.7 eV obtained with Au (4f<sub>7/2</sub>) line. A charge neutralization electron gun was used to compensate for the differential charging commonly observed in insulators.

The valence band XPS results allow us to confirm the results of the band structure calculations. The upper valence band consists of two peaks, O 2p at the valence band maximum, and Al-O hybridized levels below it. The lower valence band arises from O 2s states. The valence

band features and width agree with the density of states of the pseudofunction calculation. With increasing temperature, up to 1273 K, there was no change in the valence-band width or structure. This confirms the result of the pseudofunction calculation, that the occupied valence band states are relatively unaffected by temperature, while the dramatic temperature dependence of this band gap must arise from changes in the unoccupied conduction band states.

We find that Al<sub>2</sub>O<sub>3</sub> demonstrates a much larger temperature dependence of the band gap than previously reported for the covalent semiconductors. 55% of the temperature dependence arises from lattice expansion while the rest is due to the electron-phonon interaction. The valence-band width is constant with increasing temperature, and therefore the conduction band minimum must be shifting towards the valence band. In addition the Al 3s and Al 3p conduction bands have different temperature coefficients. Therefore there is considerable broadening of the unoccupied conduction band states with increasing temperature, coupled with their shift towards the valence band. This detailed perspective on the effects of increasing temperature on the electronic structure of a ceramic material is only possible due to the complementary application of vacuum ul-

traviolet, and valence band XPS spectroscopies with pseudofunction band structure calculations.

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