Electronic and Optical Properties of TiO₂

A. Ferreira da Silva[1]; N. Souza Dantas[1,2,7]; E. F. da Silva, Jr.[3]; I. Pepe[1]; M. O. Torres[1]; C. Persson[4]; T. Lindgren[5]; J. Souza de Almeida[6] and R. Ahuja[6]

[1] Instituto de Física, Universidade Federal da Bahia, Ondina 40 210- 340 Salvador, BA, Brazil

[2] Departamento de Física, Universidade Estadual de Feira de Santana, BA, Brazil

[3] Departamento de Física, Universidade Federal de Pernambuco, 50670 901 Recife, PE, Brazil

[4] Department of Material Science and Engineering, Royal Institute of Technology, SE–100 44 Stockholm, Sweden

[5] Department of Material Science, Uppsala University, SE–751 21 Uppsala, Sweden

[6] Department of Physics, Uppsala University, SE–751 21 Uppsala, Sweden

[7] Instituto Nacional de Pesquisas Espaciais, LAS//INPE, S. J. dos Campos, SP, Brazil

Abstract. The electronic and optical properties of the rutile titanium dioxide compound have been investigated experimentally by absorption measurements and theoretically by a full-potential linearized augmented plane wave (FPLAPW) method within the local density approximation (LDA). The thin films for the absorption measurements were prepared by DC magnetron sputtering. The theoretical results for the absorption compared qualitatively well with the experimental findings. The dielectric functions and band-structure have also been calculated, and the LDA band-gap energy is corrected by an on-site Coulomb potential.

INTRODUCTION

The compound titanium dioxide (TiO₂) has been recognized as very promising material with a variety of technological applications, such as for instance, coatings and gas sensors. Here the calculations for *absorption*, total real and imaginary parts of the dielectric function, as well as the optical band gap energy are made for the TiO₂ rutile phase and they were based on the density function theory within the local density approximation (LDA), employing the full-potential linearized augmented plane wave (FPLAPW) method [1,2]. The thin films for the absorption measurements were prepared by DC magnetron sputtering. The polycromatic beam used in the absorption measurements was varied from 850 to 300 nm corresponding to phonon energies from about 1.5 to 4.0 eV. The theoretical results for the absorption compares qualitatively well with the experimental finding. The features of the dielectric functions and the band structure are presented.

OPTICAL PROPERTIES

The calculation of optical properties of rutile TiO₂ was based on a FPLAPW [1,2] within the LDA, using the exchange-correlation of Perdew and Wang [3]. The underestimated LDA band-gap energies need to be corrected. We therefore employ the LDA+U model with $U_d = 10$ eV on the Ti d-states (e.g., LDA plus an on-site, angular-dependent Coulomb potential [4]. The dielectric function was calculated in the momentum representation, which requires matrix elements of the momentum, p, between occupied and unoccupied eigenstates. To be specific the imaginary part of the dielectric function, $\varepsilon_2(\omega) = \mathrm{Im}[\varepsilon(q = 0,\omega)]$, was calculated as

$$\varepsilon_2^{ij}(\omega) = \frac{4\pi^2 e^2}{\Omega m^2 \omega^2} \sum_{knn'\sigma} \langle kn\sigma|p_i|kn'\sigma\rangle\langle kn'\sigma|p_j|kn\sigma\rangle \times$$

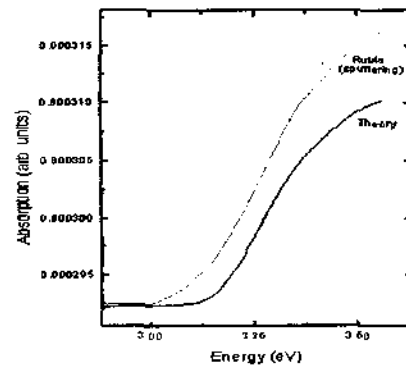$$\times f_{kn}(1-f_{kn'})\delta(e_{kn'} - e_{kn} - \hbar\omega).$$

FIGURE 1. Absorption spectra for TiO₂.

The imaginary part of the dielectric function, $\varepsilon_2(\omega)$, in the long wavelength limit has been obtained directly from the electronic structure, using the joint density-of-states and the optical matrix overlap [2]. In the expression above, e is the electron charge, m its mass, Ω is the crystal volume and $f_{k,n}$ is the Fermi distribution. The real part of the dielectric function, $\varepsilon_1(\omega)$, is obtained from $\varepsilon_2(\omega)$ using the Kramers-Kronig transformation and the absorption coefficient, $\alpha(\omega)$, is obtained directly from the above relations [2].

In Figure 1, we show the calculated and measured experimental absorption spectra. As one can observe, the calculaed (3.2 eV) and experimental (3.0 eV) absorption edges have a good agreement and they also compared well with previous experimental result (E_g =3.0 eV) [5]. The electronic structure of TiO_2 is shown in Fig. 2. The conduction-band minimum is located at Γ point (|k| = 0 in the figure) and the calculated band gap energy is already corrected by the on-site Coulomb potential. The calculated total real ε_1 and imaginary ε_2 part of the
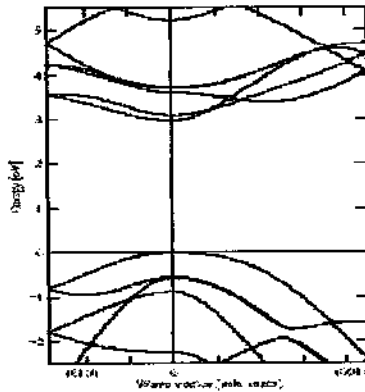

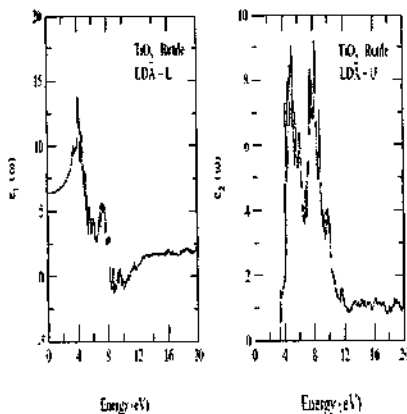FIGURE 2. The electronic structure of rutile TiO_2

FIGURE 3. Calculated total real and imaginary dielectric function for rutile TiO2.

dielectric function are shown in Fig. 3. The calculations are described in Ref [2]. The imaginary part ε_2 starts at 3.2 eV, associated with the direct transitions at Γ point, corresponding to the fundamental band gap. It also displays mainly two peaks positioned around 5 and 8 eV. The complete description of the origin of these peaks will be presented elsewhere. The calculated low-frequency dielectric constant (not including the optical phonon contribuition to the screening) is $\varepsilon = 6.7$.

CONCLUSIONS

We have investigated the optical absorption, band structure and the dielectric function of rutile TiO_2 using the measured optical absorption and theoretically using the FPLAPW method with the on-site Coulomb correction. We show that the LDA+U can produce accurate band-gap energy for this oxide. Our calculated and experimental values of the band-gap energies present a reasonable agreement between them.

ACKNOWLEDGMENTS

REFERENCES

1. Blaha, P., Schwarz, K., Madsen, G. K. H., Kvasnicka D., and Luitz, J., WIEN2k, An APW + Local Orbitals Program for Calculating Crystal Properties (K. Schwarz, Techn. Univ. Wien, Austria), 2001. ISBN 3-9501031-1-2.

2. Ferreira da Silva, A., Pepe, I., Persson, C., de Almeida, J. S., Araújo, C. M., Ahuja, R., Johansson, B., An, C. Y., and Guo, J-H., Phys. Scripta T109, 180 (2004).

3. Perdew, J. P. and Wang, Y., Phys. Rev. B 45, 13244 (1992).

4. Nova' k, P., Boucher, F., Gressier, P., Blaha, P., and Schwarz, K., Phys. Rev. B 63, 235114 (2001).

5. Landolt-Börnstein, Numerical Data and Functio-nal Relationship in Science and Technology, New Series, Vol. III/17a,b, edited by O. Madelung et al., (Springer Berlin. 1982).