

# Electronic structure of ZrTiO<sub>4</sub>, HfTiO<sub>4</sub>, FeTiO<sub>3</sub> and MgTiO<sub>3</sub> titanates: Theoretical calculations and x-ray spectroscopy studies

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The modified augmented plane wave (APW) method as incorporated in the WIEN2k code [1] and/or cluster FEFF8 program [2] have been used to calculate total and partial densities of states of the constituent atoms in FeTiO<sub>3</sub>, MgTiO<sub>3</sub>, ZrTiO<sub>4</sub> and HfTiO<sub>4</sub> titanates, prospective materials for their application in the field of microwave communication and dynamic random access memory (DRAM) devices and they are indispensable components used intensively in wireless-communication systems (e.g. in the mobile phones satellite communications), catalysts in some oxidation reactions, humidity sensors, optical devices, and high-*k* gate insulator.

To verify the theoretical results, in the present work, the X-ray emission Ti *Lα*, Fe *Lα*, Zr *Lβ<sub>2,15</sub>* and O *Kα* bands representing the energy distribution of mainly the Ti 3*d*-, Fe 3*d*-, Zr 4*d*- and O 2*p*-like states, respectively, as well as the X-ray photoelectron (XPS) valence-band and core-level spectra have been measured for FeTiO<sub>3</sub>, MgTiO<sub>3</sub>, ZrTiO<sub>4</sub> and HfTiO<sub>4</sub> oxides.

The theoretical APW/FEFF8 data reveal that the valence band of the above oxides under consideration is dominated by contributions of the O 2*p* states. These states contribute throughout the whole valence-band region; however their maximum contributions occur in the upper portion of the band. The calculations render that the bottom of the conduction band of FeTiO<sub>3</sub>, MgTiO<sub>3</sub>, ZrTiO<sub>4</sub> and HfTiO<sub>4</sub> is dominated by contributions of the Ti 3*d*\* states. The experimental data were found to be in good agreement with the theoretical results for all the compounds studied.

Measurements of XPS core-level binding energies for the constituent atoms of the ZrTiO<sub>4</sub> to HfTiO<sub>4</sub> titanates indicate that Ti and Zr(Hf) atoms are in the formal valence states +4. When going from ZrTiO<sub>4</sub> to HfTiO<sub>4</sub>, the XPS Ti 2*p* and O 1*s* core-level binding energies do not alter within the accuracy of the present measurements.

## References

1. P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties, Karlheinz Schwarz, Technical Universität Wien, Austria, 2001 (ISBN 3-9501031-1-2).
2. A.L. Ankudinov, B. Ravel, J.J. Rehr, S.D. Conradson, Phys. Rev. B 58 (1998) 7565-7576.