

Electronic structure of ZrTiO₄, HfTiO₄, FeTiO₃ and MgTiO₃ titanates: Theoretical calculations and x-ray spectroscopy studies

A.A. Lavrentyev,^a B.V. Gabrelian,^a P.N. Shkumat,^a I.Y. Nikiforov,^a E.I. Kopylova,^b
T.N. Bondarenko,^b O.Y. Khyzhun^b

^a*Don State Technical University, 1, Gagarin Sq., Rostov-on-Don, 344010, Russian Federation, e-mail:
alavrentyev@dstu.edu.ru*

^b*Frantsevich Institute for Problems of Materials Science of National Academy of Sciences of Ukraine,
3, Krzhyzhanovsky Str., Kyiv, 03680, Ukraine, e-mail: khyzhun@ipms.kiev.ua*

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 FeTiO₃, MgTiO₃, ZrTiO₄ and HfTiO₄ 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_{2,15}* 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 FeTiO₃, MgTiO₃, ZrTiO₄ and HfTiO₄ 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 FeTiO₃, MgTiO₃, ZrTiO₄ and HfTiO₄ 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 ZrTiO₄ to HfTiO₄ titanates indicate that Ti and Zr(Hf) atoms are in the formal valence states +4. When going from ZrTiO₄ to HfTiO₄, 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.