

Comparative Electron Energy-Loss Near-Edge Fine Structure Investigations Of Titanium Oxides

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Near-edge fine structures in electron energy-loss spectroscopy (ELNES) contain information about the local bonding and environment of atoms in solids. These fine-structure arise because the final states of the excitation process may be appreciably modified by chemical bonding [1]. A pragmatic approach to ELNES is collecting “fingerprints” from elements in similar compounds and to identify common features in order to derive bonding information [2].

For this study we have collected ELNES-data from different titanium oxides with varying stoichiometry. Special attention was paid to the low loss region, as well as to the Ti L_{2,3} and O K edges of the compounds TiO₂ (rutile, brookite and anatase), Ti₂O₃, TiO_x (with x varying from 0.8 to 1.2) and Ti₂O. The spectra have been acquired on a 200 kV Philips CM20 + GIF, operated with an undersaturated LaB₆ cathode. The energy resolution in these spectra was found to be ~0.7 eV (FWHM at the zero loss peak) during 1s exposure time and never exceed 0.9 eV for an acquisition time of 30 seconds.

TiO₂ forms three distinct polymorphs: rutile and anatase with a tetragonal structure and orthorhombic brookite. The crystal structure of Ti₂O₃ on the other hand is trigonal. TiO_x is cubic and exists within a stoichiometric range from TiO_{0.58} to TiO_{1.33}. In all these compounds the titanium atoms are surrounded by six oxygen atoms. These coordinating oxygen octahedra are slightly distorted and the distortion decreases from TiO₂ (≤0.06 Å for the Ti-O distances) to TiO_x [3]. Trigonal Ti₂O exhibits ordered arrangements of the oxygen atoms in the octahedral voids of hcp titanium and shows no octahedral coordination of the oxygen around the titanium atoms.

FIG. 1. shows the low loss spectra of the analyzed compounds. One can see increased separation of the second feature (10-25 eV; originating from interband transitions) going from Ti₂O to the TiO₂ modifications which is accompanied by a change from metallic (Ti₂O and TiO) to semiconducting (Ti₂O₃) to insulating (TiO₂) behavior. There is also a shift of the M_{2,3} edge (48 eV) to lower energy-loss with decreasing titanium valence state.

The left part of FIG. 2 represents the Ti L_{2,3} edges of the different titanium oxides. The octahedral ligand-field causes the five degenerated d states in the conduction band to split into the twofold e_g states, and the threefold t_{2g}. The presence of distortions from octahedral symmetry causes further splitting (e.g. the L₃-e_g feature of the TiO₂-modifications). Going from top to bottom the ligand-field splitting decreases and both L edges shift to lower energies.

Like the Ti L_{2,3} edge the O K edge (right side in FIG. 2) is effected by the octahedral ligand-field as well. The splitting into t_{2g}- and e_g-features is reduced with decreasing oxygen content and the O K edge shifts to higher energy loss [4].

The aim of this work was to systematically study the influence of different oxidation states as well as the influence of the environment of particular crystallographic sites on the ELNES for the above mentioned ionization edges [5].

References

- [1] R Brydson, EMSA Bulletin 21 (1991) 57
- [2] F. Hofer and P. Golob, Ultramicroscopy 21 (1987) 379
- [3] R.W.G. Wyckoff, Crystal Structures vol 1, Wiley-Interscience, New York, 1960
- [4] M. Yoshiya et al., J. Phys.: Condens. Matter 11 (1999) 3217
- [5] We gratefully acknowledge financial support by the Austrian Science Foundation (FWF) within the Special Research Program ‘Electroactive Materials’ and E. Krautz, Institute of Solid State Physics, Graz University of Technology, for sample preparation.

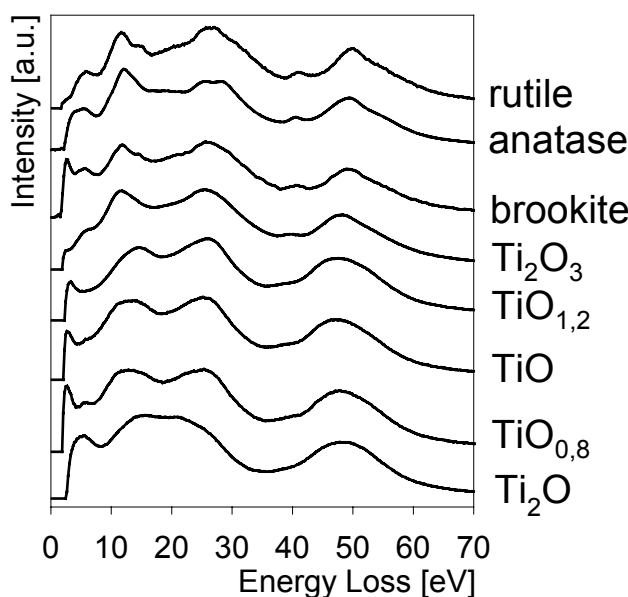


FIG. 1 Low loss spectra of different titanium oxides (all spectra are Fourier log deconvoluted)

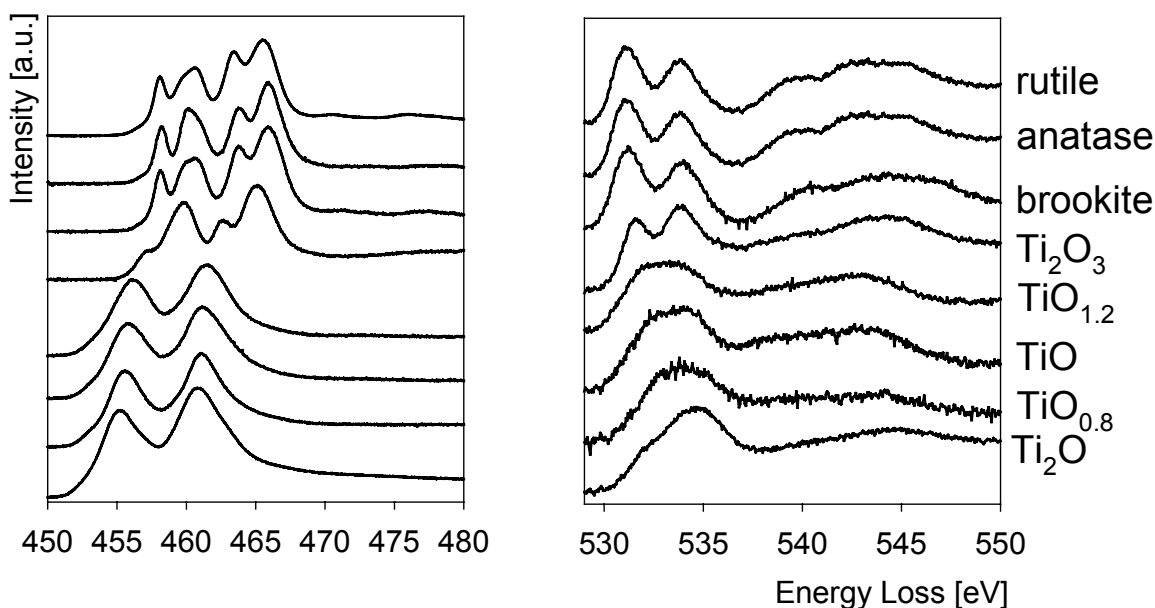


FIG. 2. Ti L_{2,3} and O K edge spectra of different titanium oxides (all spectra are Fourier ratio deconvoluted)