

The effect of valence state and site geometry on Ti $L_{3,2}$ and O K electron energy-loss spectra of Ti_xO_y phases

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ABSTRACT

Titanium $L_{3,2}$ and O K electron energy loss near-edge structures (ELNES) of seven Ti oxides have been measured in a transmission electron microscope to obtain information on the valence state and site geometry of Ti. The coordination of Ti in all phases studied is octahedral, whereas the valence states occurring are Ti^{2+} , Ti^{3+} , and Ti^{4+} . Effects of polyhedra distortions are particularly observed for two oxides with mixed Ti^{3+} - Ti^{4+} valence state, i.e., the Magnéli phases Ti_4O_7 and Ti_5O_9 . A prominent pre-peak in the Ti L_3 edge is attributed to the orthorhombic polyhedra distortions in these compounds, leading to complex crystal field splitting. The effect of valence state manifests itself in a systematic chemical shift of Ti white lines by 2 eV per valence state. On the basis of collected Ti $L_{3,2}$ ELNES spectra we propose a new quantification technique for the determination of Ti^{4+}/Ti^{3+} ratios. Complementary O K ELNES spectra were well reproduced by Density Functional Theory calculation, revealing that the O K -edge is sensitive to the covalent bonding in all analyzed oxides.

Keywords: Electron energy loss spectroscopy, valence state of titanium, titanium oxides, density functional theory