Effect of Incommensurate Structural Modulations in Fresnoite Framework Structures on High-Resolution ELNES Spectra

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Compounds adopting the fresnoite framework structure (Ba₂TiSi₂O₈, Ba₂TiGe₂O₈, and Sr₂TiSi₂O₈ will be considered here) host incommensurate structural modulations. For Ba₂TiGe₂O₈ (BTG) and Sr₂TiSi₂O₈ (STS), corresponding satellite reflections are very pronounced and allow for complete refinements of their modulated structures (in (3+1) dimensions in the case of BTG, [1] and in (3+2)-D for STS, [2]). Structural modulations in Ba₂TiSi₂O₈ (BTS), however, are much weaker. The full solution of the modulated structures of BTG and STS can be used to analyze distortions of coordination polyhedra in great detail. Such analyses revealed that beyond the rigid-unit-mode picture, there are significant changes of bond lengths and bond angles of the titanium surroundings associated with the formation of the structural modulation. High-energy resolution (ΔE~0.4 eV) Ti-L₂,₃ and O-K electron energy loss near-edge structures (ELNES) of single-crystalline BTG, STS, and BTS are juxtaposed and interpreted in terms of distorted TiO₅ square pyramids. ELNES spectral features are discussed on the basis of molecular-orbital Xα cluster calculations (in the local density approximation) of unoccupied Ti(3d) orbitals [3,4] and multiple-scattering calculations of the O-K ELNES [5]. In these calculations, approximants of the modulated structure of both BTG and STS were used to describe differently distorted titanium and oxygen environments. Therewith, it is shown that the broadening of spectral features in both Ti-L₂,₃ and O-K ELNES of BTG and STS is caused by deformations of coordination polyhedra accompanying incommensurate structural modulations. As such higher-order coordination effects only become apparent at sufficiently high spectral resolution, the results give a foretaste of the tremendous explorative power of ELNES spectroscopy utilising monochromated electrons.

References