Determination of Mn valence states in mixed-valent manganates by XANES spectroscopy

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ABSTRACT

The valence states of Mn in mixed-valent layer and tunnel structure manganese dioxides (MnO_2), usually referred to as phyllomanganates and tectomanganates, can be measured by X-ray absorption near-edge structure (XANES) spectroscopy with a precision and accuracy that are difficult to estimate owing to the paucity of well-characterized standards. A compilation of the Mn *K*-edge XANES spectra of most naturally occurring manganates, synthetic analogs of known structure and chemical composition, and pure-valence phase species is presented and made available as an open source. We intend this compilation to serve as a basis for the spectroscopic determination of the fractions of the Mn 2+, 3+, and 4+ valences in mixed-valent manganates and phase mixtures. The XANES derivatives of tectomanganates and phyllomanganates with no or little Mn^{3+} in the MnO_2 layer exhibit intensities, shapes, and relative energy positions of the main features characteristics of a particular valence composition. For these compounds, valence fractions can be derived using linear combination fitting analysis. Best quantitative results are obtained when the unknown spectrum is fit to a weighted sum of all reference spectra in the database with the fractions of species constrained to be non-negative (Combo method). The accuracy of the average valence is estimated to 0.04 v.u. in the range of 3+ to 4+, and decreases when the proportion of divalent Mn is higher than 15%. The accuracy of the method is also lower in (layer Mn^{3+}, Mn^{4+}) manganates, because the XANES features are affected non-additively by the amount and distribution of the Jahn-Teller Mn^{3+} cations. The merit of the Combo method for the determination of manganese valence sums relative to the methods based on calibration curves is discussed.

Keywords: XANES, valence determination, phyllomanganates, tectomanganates, manganese oxides