American Mineralogist, Volume 95, pages 1084–1094, 2010

The interlayer structure of trioctahedral lithian micas: An AXANES spectroscopy study at the potassium *K*-edge

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Abstract

We recorded angle-dependent XANES (AXANES) spectra at the potassium *K*-edge for three compositionally intermediate polylithionite-siderophyllite trioctahedral 1*M*-micas using polarized synchrotron radiation. We evaluated the experimental spectra for both their in-plane and out-of-plane component fractions of the electric dipole contribution using the analytical formulae of Brouder (1990), referring to theory to extract the origin of their multiple-scattering pathways of Natoli et al. (2003). This analysis was extended to a fourth lithian mica studied previously and allowed characterization of the local environment and ordering around the potassium atoms in the interlayer of the entire set of micas. The AXANES in-plane components are notably similar to the XANES spectra recorded on randomly oriented powders, provided these are oriented at the "magic angle" (Pettifer et al. 1992). Most observed contributions arise from multiple-scattering interactions of the photoelectron ejected from the potassium absorber colliding with atoms located in the interlayer itself. Note that this includes not only interactions with other coplanar potassium and/or alkali atoms distributed along the interlayer plane, but also with their near- and next-nearest neighboring oxygen atoms which lie on the basal planes of the tetrahedral sheets facing the interlayer. By contrast, the AXANES out-of-plane component suggests that several multiple-scattering pathways cross the energetic and structural barrier represented by the tetrahedral sheets. They reach not only the X anions that are located on the upper level of the octahedral sheets, at the center of the open cavity in the tetrahedral sheet, but also the metal cations centering the octahedral sheet itself. Therefore, the out-of-plane components provide indirect information on the number of independent octahedral sites, the cation oxidation state, and the *trans*- vs. *cis*-orientation of the anionic sites.

Keywords: Polylithionite, siderophyllite, X-ray absorption pleochroism, XAFS, XANES, MXAN