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

GIANNANTONIO CIBIN,1,2,* ANNIBALE MOTTANA,1,2† AUGUSTO MARCELLI,2 GIANFELICE CINQUE,2,* WEI XU,3 ZIYU WU,3,2,4 and MARIA FRANCA BRIGATTI5

1Dipartimento di Scienze Geologiche, Università degli Studi Roma Tre, Largo S. Leonardo Murialdo 1, I-00146 Roma, Italy
2Istituto Nazionale di Fisica Nucleare, Laboratori Nazionali di Frascati, Via E. Fermi 30, I-00040 Frascati RM, Italy
3BSRF, Institute of High Energy Physics, Beijing 100049, P.R. China
4NSRL, University of Science and Technology of China, Hefei 230026, P.R. China
5Dipartimento di Scienze della Terra, Università di Modena e Reggio Emilia, Via S. Eufemia 19, I-41100 Modena, Italy

ABSTRACT

We recorded angle-dependent XANES (AXANES) spectra at the potassium K-edge for three compositionally intermediate polythionite-siderophyllite trioctahedral 1M-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: Polythionite, siderophyllite, X-ray absorption pleochroism, XAFS, XANES, MXAN

INTRODUCTION

X-ray absorption fine spectroscopy (XAFS) is a very efficient method to study local properties (e.g., oxidation state) and environment (i.e., coordination number) of an atom, since it is both chemically selective and independent of the aggregation state of the probed material. Moreover, being a synchrotron radiation (SR) based technique it takes additional advantage of the properties of the source. The high brilliance of the source gives rise to high sensitivity allowing to detect atomic concentrations to the trace (ppm) level. It also allows for high-resolution spectroscopy, which enables discriminating fine structures present in the signal. Finally, the strong polarization of the synchrotron beam with over 90% of the e vector lying in the orbital plane of the storage ring (Bassett 1988) accounts for a sensitivity towards the anisotropy of the studied material.

* Present address: Diamond Light Source, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, U.K.
† E-mail: mottana@uniroma3.it

XAFS anisotropy (i.e., the dependence of the absorption signal on the polarization of the X-ray beam relative to the crystal axes) is particularly relevant at the atom absorption K-edge. This is due to the transitions of the 1s state to the final local empty p-states, which reflect highly directional bonds (Bradley et al. 1985). All this wealth of orientation-dependent information makes XAFS (particularly in its near-edge region, XANES) the method of choice for studies where not only the oxidation state and local coordination of an atom are in question, but also its site distortion, i.e., the way its ligands deviate from their expected symmetric positions due to the inequality of the bond lengths and angles which they actually form with the probed absorber atom (Bunker and Stern 1984; Koningsberger and Prins 1988). In brief, XAFS is very effective in the study of strongly anisotropic structures (e.g., Brown et al. 1977; Poumellenc et al. 1990; etc.). Micas, the most widespread minerals showing layered morphology, are thus well suited to studies aiming at testing the effectiveness of angle-resolved (viz. polarized) XAFS.

The mica structure [cf. Mottana et al. (2002a) and Fleet (2003)]