American Mineralogist, Volume 91, pages 1150–1162, 2006

Angular dependence of potassium *K*-edge XANES spectra of trioctahedral micas: Significance for the determination of the local structure and electronic behavior of the interlayer site

GIANNANTONIO CIBIN,[1,2] ANNIBALE MOTTANA,[1,2,*] AUGUSTO MARCELLI,[2]
AND MARIA FRANCA BRIGATTI[3]

[1]Dipartimento di Scienze Geologiche, Università degli Studi Roma Tre, Italy
[2]Istituto Nazionale di Fisica Nucleare, Laboratori Nazionali di Frascati, Italy
[3]Dipartimento di Scienze della Terra, Università di Modena e Reggio Emilia, Italy

ABSTRACT

The X-ray absorption angle-dependent behavior at the potassium *K*-edge has been determined for two end-members and two intermediate trioctahedral micas, which are representative of the $Fe^{2+}Mg_{-1}$, $Fe^{3+}Al_{-1}$, $SiAl_{-1}FeLi_{-1}$, and $F_{-1}OH$ exchange vectors, using horizontally polarized synchrotron radiation. Experimental spectra are interpreted by the multiple scattering theory following decomposition according to the angular dependence approach of Brouder (1990). The experimental spectra sum up anisotropic effects deriving from in-plane and out-of-plane photoelectron interactions with the potassium near- and next-near neighbors up to the fifth/sixth coordination sphere. For the first time, the absorption edge of a low Z atom is decomposed so as to produce two partial patterns giving, respectively, the full in-plane absorption spectrum ($\sigma_{\parallel}$) and the full out-of-plane spectrum ($\sigma_{\perp}$). They fully describe the complete X-ray absorption dichroic behavior of layered compounds, of which mica is a prototype. $\sigma_{\parallel}$ essentially reflects the arrangement of the atoms located in the mica interlayer space and facing tetrahedral sheets. Differences among the four micas depend on structural changes induced by the adaptation of their tetrahedral sheets to the increasing sizes of their octahedral sheet due to chemical substitutions (i.e., the $Fe^{2+}Mg_{-1}$ vector, mainly) and to chemical changes at the octahedral anion site ($F_{-1}OH$ vector). By contrast, $\sigma_{\perp}$ reflects multiple-scattering interactions entering deep into the mica structure, beyond the tetrahedral sheet and well into the octahedral sheet. Such contributions reflect both changes in the anions coordinating the octahedral cations and increasing total amount of heavy atoms (essentially Fe), and differ based on electronic properties such as oxidation states (e.g., Fe^{2+} and Fe^{3+}). Therefore, angle-dependent XANES spectroscopy is one of the rare spectroscopic techniques able not only to detect, but also to quantify structural effects in the atoms at the medium- to long-range order.

Keywords: Mica, XAS, polarized XANES, potassium *K*-edge, trioctahedral micas, crystal structure