

K-edge XANES Spectroscopy on sulfur and phosphor in silicate minerals

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Although recently a series of investigations on sulfur speciation in natural and synthetic silicate glasses using X-ray near edge structure (XANES) spectroscopy at the S K-edge have been published or submitted [e.g. 1-10] the nature of sulfur in silicate structures is still only partly understood. The idea here is to see whether features from S K-edge XANES spectra of crystalline S-containing silicates where crystal structure data (e.g. from X-ray diffraction) include sulfur coordination can be assigned to S structural units. The comparison of spectral features between crystalline silicates and glasses will then help to identify and understand the sulfur coordination in silicate glasses where direct access to structural information via X-ray diffraction is not possible. But up to now only a few data exist about sulfur speciation in crystalline silicates [e.g. 11-13]. Hence, a study has been performed to systematically record S K-edge XANES spectra for neso-, soro-, phyllo- and tecto-silicates. Samples for S containing ring silicates have not been available and information about the existence of S-containing ino-silicates has not been found so far. S K-edge XANES spectra were measured in fluorescence mode at the SUL-X beamline of the synchrotron radiation source ANKA (KIT). Because samples were in most cases small spot sizes as low as $\approx 100 \times 100 \mu\text{m}^2$ have been used. The X-ray energy were calibrated to 2481.4 eV by a sulfate containing scotch tape. The spectra of the nesosilicates jasmundite, ternesite and ellestadite, the sorosilicate phosphoinnelite, and the phyllosilicates delhayelite and tuscanite exhibit a wide variety of shapes. Delhayelite and phosphoinnelite where sulfur is given just as SO_4^{2-} in the formula show additionally a complex pattern of resonances at energies below the sulfate resonance which means additionally reduced sulfur species are present. In the spectrum of jasmundite the broad resonance at about 2474.5 eV has been assigned to $[\text{SCa}_8]$ according to the crystal structure data. Additionally S^{6+} has been detected which is in contradiction to the chemical formula. Similar $[\text{SCa}_8]$ units might be present in Ca and Si rich blast furnace slags because their spectra show also the broad feature as known from the spectrum of jasmundite. In ternesite, ellestadite and tuscanite S^{6+} could be confirmed. Of course, sulfur speciation does not primary depend on the type of silicate but should be result of redox conditions during mineral formation. The most known sulfur containing silicates are the framework silicates of sodalite type with their cages that can host various anions in different oxidations states. Reduced sulfur species have been detected in the tectosilicates lazurite, hackmanite (sodalite variety), in helvines and in ultramarine color pigments. Phosphoinnelite, delhayelite, hackmanite and ultramarine spectra show pre-edges below 2470 eV. Their interpretation in terms of electron transitions is not yet understood. The "stability" of some minerals under the beam is limited. For instance, for the hackmanite pre-edge the main pre-edge intensity is increasing strongly and additional pre-edges occur. Because some of the minerals contain also phosphorus the study has been extended to P containing silicates, and first results will be presented.

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