

Bonding in silicates: Investigation of the Si $L_{2,3}$ edge by parallel electron energy-loss spectroscopy

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ABSTRACT

The Si $L_{2,3}$ core-loss edge can be used to probe the crystal chemistry around Si, providing information on the s- and d-like partial density of unoccupied states of the Si-O bonds. We present Si $L_{2,3}$ edges from 59 silicates, glasses, and amorphous materials acquired by parallel electron energy-loss spectroscopy (PEELS) with a transmission electron microscope (TEM) at an energy resolution of 0.7 eV. The Si $L_{2,3}$ edge spectrum of α -quartz is interpreted using the results of a recent pseudopotential band-structure calculation. A combination of Si s- and d-like partial density of states derived from this calculation resembles the Si $L_{2,3}$ energy-loss near-edge structure (ELNES) of α -quartz. The Si $L_{2,3}$ ELNES of the silicates are interpreted using the results of the band-structure calculation of α -quartz. The Si $L_{2,3}$ edges of Q^4 , Q^3 , Q^2 , some Q^1 silicates, and amorphous materials have ELNES similar to that of α -quartz, and the Q^0 and some Q^1 silicates have ELNES different from that of α -quartz. A “coordination fingerprint” is defined for Q^4 , Q^3 , and Q^2 Si $L_{2,3}$ ELNES because of their similarity to the α -quartz spectrum. The similarities between the $L_{2,3}$ core-loss edge shapes of the third-row XO_4^- ($X = Al, Si, S,$ and P) series attests to a common molecular-orbital picture of their bonding. For Q^0 and some Q^1 spectra a “structure fingerprint” is defined because the Si $L_{2,3}$ -edge shapes are indicative of the number, distribution, and nature of the non-nearest-neighbor atoms. Spectra of olivine glasses and metamict zircon more closely resemble the α -quartz spectrum than their crystalline analogs. In contrast to previous studies, we show that distortion of the SiO_4 tetrahedron is of secondary importance as an ELNES-modifying parameter. Polyhedral distortions become less important with increase in polymerization. There is a positive linear correlation between the energies of the Si $L_{2,3}$ -edge onsets and polymerization, Si 2p and 2s binding energies, and the ^{29}Si NMR isotropic chemical shifts. The shift to higher energies of the edge onsets with polymerization corresponds to an increase in effective charge on the Si atom with higher Q^n . For silicates with isolated SiO_4 tetrahedra, increases in $L_{2,3}$ -energy onsets correlate with increases in polarizing power of the next-nearest-neighbor cations. The Si $L_{2,3}$ -edge shapes are affected by the types and coordinations of the next-nearest-neighbor cations. For example, andradite, ilvaite, fayalite, and γ - Fe_2SiO_4 have FeO_6 bonded to SiO_4 and exhibit similar ELNES. Topaz, dumortierite, staurolite, and kyanite have similar Si $L_{2,3}$ ELNES, with AlO_6 bonded to the SiO_4 . Their edge shapes are distinct from those of silicates with SiO_4 bonded to AlO_4 , as in the feldspars. A comparison of the Al and Si $L_{2,3}$ and Al, Si, O, and F K core-loss edges of topaz illustrates the influence of neighbor effects and mixing of unoccupied states. This mixing illustrates the limitations of *ab initio* methods that model core-loss edges that neglect non-nearest-neighbor interactions.