

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 Q⁴, Q³, Q², some Q¹ silicates, and amorphous materials have ELNES similar to that of α -quartz, and the Q⁰ and some Q¹ silicates have ELNES different from that of α -quartz. A “coordination fingerprint” is defined for Q⁴, Q³, and Q² 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 XO₄⁻ (X = Al, Si, S, and P) series attests to a common molecular-orbital picture of their bonding. For Q⁰ and some Q¹ 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 SiO₄ 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 ²⁹Si 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 Qⁿ. For silicates with isolated SiO₄ 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 -Fe₂SiO₄ have FeO₆ bonded to SiO₄ and exhibit similar ELNES. Topaz, dumortierite, staurolite, and kyanite have similar Si L_{2,3} ELNES, with AlO₆ bonded to the SiO₄. Their edge shapes are distinct from those of silicates with SiO₄ bonded to AlO₄, 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.