American Mineralogist, Volume 91, pages 740–746, 2006

Chemical bonding and electronic structures of the Al_2SiO_5 polymorphs, andalusite, sillimanite, and kyanite: X-ray photoelectron- and electron energy loss spectroscopy studies

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ABSTRACT

We have undertaken a detailed analysis of the X-ray photoelectron spectra obtained from the three polymorphs of Al_2SiO_5; andalusite, sillimanite, and kyanite. Comparison of the spectra was made based on the chemical bonding and structural differences in the Al- and Si-coordination within each polymorph. The spectra for Si(2p) for all three polymorphs are nearly identical, consistent with the fact that all the Si atoms are in 4-fold (tetrahedral) coordination, whereas the binding energies, peak shapes, and peak widths for Al(2p) vary depending on the type of polymorph. The upper-valence band for all three polymorphs is characterized by four main features derived from O(2p), Al(3s), Al(2p), Si(3s), and Si(3p), and the differences in their contributions are observed. The density of state of the Al_2SiO_5 polymorphs is relatively featureless compared to those observed from α-SiO_2 and α-Al_2O_3, suggesting that the orbital overlaps span a greater range in energy. The observed band gap energy for Al_2SiO_5 (sillimanite) was ~9.1eV, a value in between those for α-SiO_2 (~8.6eV) and α-Al_2O_3 (~9.6eV). The conduction band feature of Al_2SiO_5 was experimentally compared to those of α-SiO_2 and α-Al_2O_3, and shown that it is indeed intermediate between the α-SiO_2 and α-Al_2O_3 phases.

Keywords: Al_2SiO_5 polymorphs, X-ray photoelectron spectroscopy, low electron energy loss spectroscopy, valence- and conduction band structures, andalusite, sillimanite, kyanite