Chemical bonding and electronic structures of the Al$_2$SiO$_5$ 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$_2$SiO$_5$: 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$_2$SiO$_5$ polymorphs is relatively featureless compared to those observed from α-SiO$_2$ and α-Al$_2$O$_3$, suggesting that the orbital overlaps span a greater range in energy. The observed band gap energy for Al$_2$SiO$_5$ (sillimanite) was ~9.1 eV, a value in between those for α-SiO$_2$ (~8.6 eV) and α-Al$_2$O$_3$ (~9.6 eV). The conduction band feature of Al$_2$SiO$_5$ was experimentally compared to those of α-SiO$_2$ and α-Al$_2$O$_3$, and shown that it is indeed intermediate between the α-SiO$_2$ and α-Al$_2$O$_3$ phases.

Keywords: Al$_2$SiO$_5$ polymorphs, X-ray photoelectron spectroscopy, low electron energy loss spectroscopy, valence- and conduction band structures, andalusite, sillimanite, kyanite

INTRODUCTION

The three polymorphs of Al$_2$SiO$_5$, sillimanite, andalusite, and kyanite, are geologically important minerals, whose crystal structures, and physical and thermodynamic properties have been extensively investigated (Kerrick 1990 and references therein). Crystal structures of sillimanite, andalusite, and kyanite were refined by Burnham (1963a), Burnham and Buerger (1961), and Burnham (1963b), respectively, following the structure determinations of kyanite by St. Naray Szabo et al. (1929), and sillimanite and andalusite by Taylor and Hey (1931). Further refinements of the sillimanite and andalusite structures were carried out using single-crystal neutron diffraction methods (Finger and Prince 1972). Winter and Ghose (1979) determined the thermal expansion and the structural changes of all three polymorphs as a function of temperature up to 1000 °C. The crystal structures of all three polymorphs have also been refined at high pressure [andalusite, Ralph et al. (1984); kyanite, Yang et al. (1997a) and Comodi et al. (1997); and sillimanite, Yang et al. (1997b)].

Sillimanite and andalusite are orthorhombic with space groups Pmn21 and Pnma, respectively, whereas kyanite is triclinic with P1. The crystal structures of the three polymorphs have one feature in common, namely, half of the Al atoms occur in sixfold (octahedral) coordination forming chains of edge-shared [AlO$_6$] octahedra parallel to the crystallographic c-axis. The differences in their stability relations depend critically on the differences in the chemical bonding of the remaining Al atoms in each polymorph: Al is in fourfold (tetrahedral) coordination in sillimanite (stable at low P and high T), fivefold coordination (trigonal bipyramidal) in andalusite (stable at low P and low T), and sixfold coordination (octahedral) in kyanite (stable at high P and high T). The Si atom is in fourfold (tetrahedral) coordination in all three polymorphs. The reader is referred to the paper by Winter and Ghose (1979) for the details of the crystal structures of all three polymorphs.

Lattice dynamical studies of these minerals, including experimental measurements of phonon dispersion relations, density of states (DOS), and theoretical shell model calculations of their vibrational and thermodynamic properties, have been made by Rao et al. (1999). The electron density distributions in all three polymorphs have been determined experimentally from multipole refinements based on high resolution single crystal X-ray diffraction data collected at 100 K by a CCD detector (Dahaoui et al. 2001), and theoretically by ab initio quantum mechanical calculations using the LAPW method (Iglesias et al. 2001). The electric field gradient tensors at the 27Al sites in all three polymorphs calculated from the experimentally and theoretically derived electron density distributions match the values obtained from single-crystal 27Al NMR measurements (Raymond and Hafner 1970; Hafner et al. 1970; Hafner and Raymond 1967; Bryant et al. 1999).

The differences in the chemical bonding and electronic structures of the three Al$_2$SiO$_5$ polymorphs are fundamental to the understanding of their thermodynamic properties and