Compressibility and crystal structure of kyanite, Al$_2$SiO$_5$, at high pressure

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Abstract

The unit-cell dimensions and crystal structure of kyanite at various pressures up to 4.56 GPa were refined from single-crystal X-ray diffraction data. The bulk modulus is 193(1) GPa, assuming $K' = 4.0$. Calculated unit-strain tensors show that kyanite exhibits more isotropic compressibility than andalusite or sillimanite. The most and least compressible directions in the kyanite structure correspond approximately to the most and the least thermally expandable directions. The analysis of the distortion of the closest packing in kyanite indicates that the most compressible direction of the structure (along [012]) corresponds to the direction along which the closest-packed O monolayers are stacked. The bulk moduli for the Al1, Al2, Al3, and Al4 octahedra are 274(43), 207(14), 224(26), and 281(24) GPa, respectively, and those for the Si1 and Si2 tetrahedra are 322(80) and 400(95) GPa, respectively. Four AlO$_6$ octahedra that all become less distorted at higher pressures do not display clearly dominant compression directions. The average unshared O-O distance for each octahedron is considerably more compressible than the shared O-O distance. The high-pressure behaviors of the Al1 and Al4 octahedra are very similar but different from those of the Al2 and Al3 octahedra. Bulk moduli for the three Al$_2$SiO$_5$ polymorphs (kyanite, sillimanite, and andalusite), as well as those for the AlO$_6$ octahedra in their structures, appear to decrease linearly as their volumes increase. The significantly larger bulk modulus and more isotropic compressibility for kyanite than for andalusite or sillimanite are a consequence of the nearly cubic close-packed arrangement of O atoms and the complex edge-sharing among four distinct AlO$_6$ octahedra in the kyanite structure.

Introduction

The three Al$_2$SiO$_5$ polymorphs (kyanite, sillimanite, and andalusite) are of paramount importance in metamorphic and experimental petrology because of their abundance in metamorphosed pelitic rocks and relatively simple chemistry. Furthermore, they provide an interesting crystal-chemical system. On the one hand, all these structures have Si exclusively in tetrahedral coordination and one-half of the total Al in octahedral coordination. These AlO$_6$ octahedra share edges to form chains running parallel to the c axis. On the other hand, the remaining Al is fourfold, fivefold, and sixfold coordinated in sillimanite, andalusite, and kyanite, respectively. A knowledge of the crystal structures of these polymorphs as a function of pressure is therefore essential in understanding the stability relationships and phase-transition mechanisms within the Al$_2$SiO$_5$ system.

Relative to sillimanite and andalusite, kyanite is the high-pressure phase in the Al$_2$SiO$_5$ system. The crystal structure of kyanite was first deduced by Náray-Szabo et al. (1929) from the structure determination of staurolite and refined by Burnham (1963) from single-crystal X-ray diffraction data. It can be considered as a distorted cubic close-packed arrangement of O atoms, with 10% of the tetrahedral sites filled with Si and 40% of the octahedral sites filled with Al. The fact that kyanite is 12–14% denser than sillimanite and andalusite is partly attributable to this close-packing feature. There are four crystallographically distinct Al sites (Al1, Al2, Al3, and Al4) and two Si sites (Si1 and Si2) (Fig. 1). The Al1 and Al2 sites are in the zigzag edge-sharing octahedral chains. The chains are cross-linked by alternating SiO$_4$ tetrahedra and AlO$_6$ octahedra with Si1 and Al4 on one side and Si2 and Al3 on the other. The Al1 and Al3 octahedra share five edges with neighboring octahedra, whereas Al2 and Al4 share four edges with adjacent octahedra. Winter and Ghose (1979) studied the structural variations of kyanite, sillimanite, and andalusite with temperature. Ralph et al. (1984) determined the compressibility and the crystal structure of andalusite at pressures up to 3.7 GPa. Studies on the crystal structures of the three Al$_2$SiO$_5$ polymorphs have been summarized by Papke and Cameron (1976), Winter and Ghose (1979), Ribbe (1980), and Kerrick (1990). In this paper, we compare our high-pressure structure study of kyanite (up to 4.56 GPa) with other studies of andalusite at high pressures to better understand the crystal chemistry of the Al$_2$SiO$_5$ system at high pressure.