

MAS NMR measurements and ab initio calculations of the ^{29}Si chemical shifts in dumortierite and holtite

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ABSTRACT

Three samples from the dumortierite group of minerals were examined with magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR): a dumortierite [c. $(\text{Al}, \square)\text{Al}_6(\text{BO}_3)_2\text{Si}_3\text{O}_{13}(\text{O}, \text{OH})_2$] consisting of dark blue euhedral crystals from Madagascar (D34); a fine-grained pale blue dumortierite from Island Copper mine, British Columbia, Canada (D12); and a creamy white holtite [c. $(\text{Ta}, \text{Nb}, \square, \text{Al})\text{Al}_6(\text{BO}_3)_3(\text{Si}, \text{Sb}, \text{As})_3\text{O}_{12}(\text{O}, \text{OH}, \square)_3$] from Szklary, Lower Silesia, Poland (WPH). Restricted Hartree-Fock ab initio electronic structure calculations were performed on model clusters with the goal of matching local environments of Si atoms to peaks in the ^{29}Si MAS NMR spectra. The spectrum of D34 showed five resolved peaks at -95.2 , -92.6 , -91.3 , -89.1 , and -86.5 ppm with deconvoluted peak area contributions of 57, 19, 7, 10, and 7%. Electronic structure calculations, cross-polarization MAS NMR measurements and relative intensities support assigning the peaks at -95.2 and -92.6 ppm to Si2 and Si1 sites, respectively, adjacent to fully occupied Al1 sites (i.e., Q^4 Si sites), and assigning the three remaining peaks to Si sites adjacent to vacant Al1 sites (i.e., Q^3 Si sites). Due to the complexity of the dumortierite structure, clusters composed of at least the first four shells of nearest neighbor atoms to the target Si atom are necessary to model Q^4 sites. The spectrum of D12 showed two main peaks at -93 and -95 ppm, with minor peaks below -90 ppm and above -100 ppm. The spectrum of WPH showed one broad peak at -93 ppm, likely containing both Si1 and Si2 signals, and two minor peaks below -90 ppm.

Single-crystal X-ray diffraction and structure refinement on D34 shows orthorhombic symmetry, $Pnma$, $Z = 4$, $a = 4.6882(1)$, $b = 11.7924(2)$, $c = 20.1856(3)$ Å, and $V = 1115.97(4)$ Å³ with $R_1 = 0.0124$. Three distinct sub-sites of the face-sharing octahedral chain site Al1 were distinguished corresponding to sites with one vacancy above, with one vacancy below, and between two occupied sites; the vacancy-adjacent sites have the cation displaced to increase the Al^{3+} - Al^{3+} distance. Each sub-site is approximately $\frac{1}{4}$ occupied, suggesting that Al^{3+} cations in individual face-sharing octahedral chains are ordered as \square -Al-Al-Al, although cations from chain to chain are disordered, preserving $Pnma$ symmetry.

Powder X-ray diffraction measurements were performed on both D34 and D12. The unit cell of D12 was found to be $a = 4.7001(7)$, $b = 11.785(2)$, $c = 20.277(3)$ Å.

Keywords: Dumortierite, holtite, nuclear magnetic resonance, borosilicates, ab initio, single-crystal X-ray diffraction, powder X-ray diffraction, electron microprobe