MAS NMR measurements and ab initio calculations of the $^{29}\text{Si}$ 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. (Al,□)Al$_4$(BO$_3$)$_2$Si$_2$O$_7$(O,OH)$_3$] 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. (Ta,Nb,□)Al$_4$(BO$_3$)$_2$(Si,Sb,As)$_2$O$_7$(O,OH,□)$_3$] from Szklary, Lower Silesia, Poland (WHF). 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 $^{29}\text{Si}$ 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., Q4 Si sites), and assigning the remaining three peaks to Si sites adjacent to vacant Al1 sites (i.e., Q3 Si sites). Due to the complexity of the dumortierite structure, clusters comprised of at least the first four shells of nearest neighbor atoms to the target Si atom are necessary to model Q4 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 WHF 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, $Z = 4$, $a = 4.6882(1)$ Å, $b = 11.7924(2)$ Å, $c = 20.1856(3)$ Å, and $V = 1115.97(4)$ Å$^3$ with $R_I = 0.0124$. 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 Al1-Al1 distance. Each sub-site is approximately ¼ occupied, suggesting that Al$^{3+}$ cations in individual face-sharing octahedral chains are ordered as □-Al1-Al1, 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 $a = 4.7001(7)$ Å, $b = 11.785(2)$ Å, $c = 20.277(3)$ Å. The spectrum of D34 showed two main peaks at –93 and –95 ppm, with minor peaks below –90 ppm and above –100 ppm. The spectrum of WHF showed one broad peak at –93 ppm, likely containing both Si1 and Si2 signals, and two minor peaks below –90 ppm.

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

INTRODUCTION

The dumortierite group of orthorhombic borosilicates comprises three isostructural minerals: dumortierite [c. (Al,□)Al$_4$(BO$_3$)$_2$Si$_2$O$_7$(O,OH)$_3$], magnesiodumortierite [c. (Mg,Ti,□)Al$_4$(BO$_3$)$_2$Si$_2$O$_7$(OH,□)$_3$], and holtite [c. (Ta,Nb,□)Al$_4$(BO$_3$)$_2$(Si,Sb,As)$_2$O$_7$(OH,□)$_3$]. Dumortierite is by far the most widespread of the three minerals and is second only to tourmaline as the most abundant borosilicate in pegmatites and aluminous metamorphic and metasomatic rocks (Grew 1996). In contrast, magnesiodumortierite has only been found in ultrahigh-pressure rocks of the western Alps (Chopin et al. 1995; Ferraris et al. 1995), and holtite in pegmatites at Greenbushes, Western Australia, Voron’i Tundry, Kola Peninsula, Russia, and Szklary, Lower Silesia, Poland (e.g., Pryce 1971; Voloshin et al. 1977; Pieczka and Marszałek 1996; Groat et al. 2009; Pieczka et al. 2011). In addition to several distinctive structural features such as face-sharing Al octahedra and vacancies at both cation and anion sites, dumortierite, and holtite are distinctive among aluminosilicate minerals because they incorporate not only substantial amounts of the high-field strength lithophile elements Nb and Ta substituting for Al at octahedral sites, but also significant quantities of the chalcophile elements As and Sb substituting for Si at tetrahedral sites with a change of coordination (e.g., Groat et al. 2001).

We undertook this study to investigate whether magic angle spinning nuclear magnetic resonance (MAS NMR) could provide new information about substitutions and vacancies around Si and Al in the crystal structures of dumortierite and holtite, and whether ab initio electronic structure calculations can be used to identify the structural environments responsible for the peaks seen in the spectra.