INTRODUCTION

Previous studies of boron contents in tourmaline have yielded different results for different tourmaline species. Structural studies of Mg-rich tourmalines show that B contents are close to stoichiometric composition with no evidence for $[4]B$ (MacDonald and Hawthorne 1995; Taylor et al. 1995; Bloodaxe et al. 1999; Ertl et al. 2001). Also, no $[4]B$ could be detected with $^{11}B$ magic-angle-spinning (MAS) nuclear magnetic resonance (NMR) spectra by Wodara and Schreyer (1997), Tagg et al. (1999), and by Schreyer et al. (2000) in Mg-rich natural tourmaline (dravite).

Compositions containing excess boron have been reported by Dyar et al. (1994, 1998). Recent crystal structure studies of Al-rich and Li-bearing tourmalines (olenite and elbaite) (for the classification scheme, see Hawthorne and Henry 1999) showed that B substitutes for Si to significant amounts at the tetrahedral site in natural tourmaline (Ertl et al. 1997; Hughes et al. 2000; Hughes et al. 2001; Schreyer et al. in preparation). A $^{11}B$ MAS NMR spectroscopic study of Al- and Li-rich natural tourmaline by Schreyer et al. (1999), and by Schreyer et al. (2000) in Mg-rich natural tourmaline (dravite).

As the excess-boron olenite from Stoffhütte, Koralpe, Styria, Austria (Ertl et al. 1997; Ertl and Brandstätter 1998; Hughes et al. 2000) has the highest boron content among all known natural tourmalines, it was in particular interesting to investigate this mineral by $^{11}B$ MAS NMR spectroscopy. The (simplified) formula of this colorless olenite is given by Hughes et al. (2000) as $X(Na_{0.40}Ca_{0.29}Si_{0.31})Y(Al_{2.42}Li_{0.36}Si_{0.22})Z(Al_{5.92}Si_{0.08})B_{3.00}T(Si_{4.86}B_{1.06}Al_{0.08})O_{27}[F_{0.06}(OH)_{3.31}O_{0.63}]$, which has been determined by optimization from the chemical data in combination with refinement of the site scattering. Ertl et al. (1997) and Hughes et al. (2000) noted that this olenite contains only traces of Fe, Mn, and Ti, and low concentrations of transition elements are desirable for optimal NMR resolution. A spectroscopic investigation by nuclear magnetic resonance spectroscopy is complementary to crystal structure determination, and provides a confirmation of the results of site scattering refinement using the latter method. As has been shown by Schreyer et al. (2000), replacement of Si by B at the T position of synthetic olenite has a considerable influence on the interactions of the OH groups with surrounding atoms. To investigate the influence of tetrahedrally coordinated boron on the hydrogen bonds the Koralpe olenite was examined by IR spectroscopy.

Nuclear magnetic resonance and infrared spectroscopic study of excess-boron olenite from Koralpe, Styria, Austria

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ABSTRACT

Significant amounts of boron in both trigonal and tetrahedral coordination have been found through $^{11}B$ magic-angle-spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy of natural olenite (aluminum-rich tourmaline) from Stoffhütte, Koralpe, Styria, Austria. The $^{11}B$ MAS NMR spectrum consists of a superposition of two quadrupolar MAS peaks. A broad peak with $\delta_{pp} = 18.3$ ppm, $\nu_0 = 1410$ KHz, and $\eta = 0.11$ demonstrates the trigonal-planar environment of the BO$_3$ group (relative area ratio = 80%). The narrow symmetrical peak ($\delta_{pp} = 0.0$ ppm, $\nu_0 = 300$ KHz, $\eta = 0.00$) represents tetrahedral BO$_4$ groups (relative area ratio = 20%). An infrared spectrum shows hydroxyl stretching bands at low wavenumbers indicating that underbonded O atoms of the hexagonal ring (due to a partial replacement of $[6]Si$ by $[4]B$) form relatively strong hydrogen bonds with the protons of the hydroxyl groups. A $^{29}Si$ MAS NMR spectrum shows a peak consisting of a main signal at $-90$ ppm and a shoulder at about $-85$ ppm. The main signal originates from Si atoms connected (via oxygen bridges) to two other Si atoms in the hexagonal ring, and the minor signal is from Si atoms connected to one Si and one B atom. No signal corresponding to $[6]Si$ was detected in this natural olenite sample.

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