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Synthetic Ag-rich tourmaline: Structure and chemistry

DAVID LONDON,[1,*] ANDREAS ERTL,[2] JOHN M. HUGHES,[3] GEORGE B. MORGAN VI,[1] ERIC A. FRITZ,[4] AND BRIAN S. HARMS[1]

[1]School of Geology and Geophysics, University of Oklahoma, 100 East Boyd Street, Room 810 SEC, Norman, Oklahoma 73019, U.S.A.
[2]Institut für Mineralogie und Kristallographie, Geozentrum, Universität Wien, Althanstrasse 14, 1090 Vienna, Austria
[3]Department of Geology, Miami University, Oxford, Ohio 45056, U.S.A.
[4]Gemological Institute of America, 5345 Armada Drive, Carlsbad, California 92008, U.S.A.

ABSTRACT

Ag-rich tourmaline crystals were synthesized at 750 °C, 200 MPa H_2O, and f_{O_2} = log (NNO) – 0.5, starting with an oxide mix of dravite composition to which various reagents, including AgF and AgCl, were added. Tourmaline containing up to 7.65 wt% Ag_2O was synthesized, and this is the first time a tourmaline is described that contains significant amounts of Ag at the ninefold-coordinated X site. Crystal structure refinement and chemical analysis (EMPA) give the optimized formula $^{X}(Na_{0.58}Ag_{0.18}\square_{0.24})$ $^{Y}(Al_{1.54}Mg_{1.46})$ $^{Z}(Al_{5.34}Mg_{0.66})$ $^{T}(Si_{5.90}Al_{0.10})O_{18}$ $(BO_3)_3$ $^{V}(OH)_3$ $^{W}(O_{0.53}F_{0.47})$, with a = 15.8995(4) and c = 7.1577(4) Å, and R = 0.036 for a crystal (~20 × 100 μm) with approximately 2.2 wt% Ag_2O. Refining Na ↔ Ag at the X site clearly indicates that Ag occupies this site. The X-O2 distance of ~2.52 Å is slightly longer than tourmaline with ~$(Na_{0.6}\square_{0.4})$, reflecting the slightly larger ionic radius of Ag compared to Na. Releasing the occupancy at the Y site gives ~$Al_{0.98}$ (~12.7 e^-), which can be explained by occupation of Mg and Al. On a bond-angle distortion vs. <Y-O> distance diagram, the Ag-rich olenite-dravite lies approximately on the V site = 3 (OH) line in the figure, defining the relation between bond-angle distortion (σ_{oct}^2) of the ZO_6 octahedron and the <Y-O> distance. No H could be found at the O1 site by refinement, in agreement with the Mg-Al disorder between the Y site and the Z site. Synthetic tourmaline contains no Ag when only AgCl is added; the compatibility of Ag in tourmaline, therefore, is largely a function of the F/Cl ratio of the fluid medium. A positive association of Ag at the X site with Al at the Y site and with F suggests that tourmaline might be useful for exploration in Cornwall-type polymetallic ore deposits associated with F-rich peraluminous granites or at other Ag-, F-, and B-enriched deposits such as Broken Hill, Australia. Preliminary electron microprobe analyses of tourmaline from Cornwall and Broken Hill, however, failed to detect Ag at the 3σ detection level of 0.08 wt% Ag_2O.

Keywords: Tourmaline, silver, crystal synthesis, crystal structure