American Mineralogist, Volume 98, pages 1624–1630, 2013

Neutron diffraction in gemology: Single-crystal diffraction study of brazilianite, $NaAl_3(PO_4)_2(OH)_4$

G. Diego Gatta,[1,*] Pietro Vignola,[1] Martin Meven,[2,3] and Romano Rinaldi[4]

[1]Dipartimento di Scienze della Terra, Università degli Studi di Milano, Via Botticelli 23, I-20133 Milano, Italy
[2]Institut für Kristallographie, RWTH Aachen, Jägerstrasse 17-19, D-52056 Aachen, Germany
[3]Jülich Centre for Neutron Science, Forschungszentrum Jülich GmbH, Outstation at FRM II, Lichtenbergstrasse 1, D-85747 Garching, Germany
[4]Dipartimento di Scienze della Terra, Università degli Studi di Perugia, Piazza Università 1, I-06123 Perugia, Italy

Abstract

The chemical composition and the crystal structure of a gem-quality brazilianite from the Telírio pegmatite, near Linópolis, Minas Gerais, Brazil, [$NaAl_3(PO_4)_2(OH)_4$, a = 11.2448(5) Å, b = 10.1539(6) Å, c = 7.1031(3) Å, β = 97.351(4)°, V = 804.36(7) Å^3, space group $P2_1/n$, Z = 4], have been reinvestigated by means of electron microprobe analysis in wavelength-dispersive mode, single-crystal X-ray and neutron diffraction. The chemical analysis shows that brazilianite from Telírio Claim approaches almost ideal composition. The neutron anisotropic structural refinement was performed with final agreement index R_1 = 0.0290 for 211 refined parameters and 2844 unique reflections with $F_o > 4\sigma(F_o)$, the X-ray refinement led to R_1 = 0.0325 for 169 refined parameters and 2430 unique reflections with $F_o > 4\sigma(F_o)$. The building-block units of the brazilianite structure consist of chains of edge-sharing $AlO_4(OH)_2$ and $AlO_3(OH)_3$ octahedra. Chains are connected, via corner-sharing, by P-tetrahedra to form a three-dimensional framework, with Na atoms located in distorted cavities running along [100]. Five independent H sites were located, here labeled as H(1), H(2a), H(2b), H(3), and H(4). The configuration of the OH groups, along with the complex hydrogen-bonding scheme, are now well defined. The O-H distances corrected for "riding motion" range between ~0.992 and ~1.010 Å, the O···O distances between ~2.67 and ~2.93 Å, and the O-H···O angles between ~151° and ~174°. The H(2a) and H(2b) are only ~1.37 Å apart and mutually exclusive (both with site occupancy factor of 50%). The differences between the crystal structure of brazilianite and wardite [ideally $NaAl_3(PO_4)_2(OH)_4 \cdot 2H_2O$] are discussed. This work fulfills the need for accurate crystal-chemical data for this gem mineral.

Keywords: Brazilianite, crystal chemistry, single-crystal neutron diffraction, hydrogen bonding