American Mineralogist, Volume 91, pages 29–34, 2006

The real topological configuration of the extra-framework content in alkali-poor beryl: A multi-methodological study

G. DIEGO GATTA,[1,2,*] F. NESTOLA,[2] G.D. BROMILEY,[2,3] AND S. MATTAUCH[4]

[1]Dipartimento di Scienze della Terra, Universita' degli Studi di Milano, Via Botticelli 23, I-20133 Milano, Italy
[2]Bayerisches Geoinstitut, Universitaet Bayreuth, Universitaet Str. 30, D-95447 Bayreuth, Germany
[3]Department of Earth Sciences, Cambridge University, Downing Street, Cambridge CB2 3EQ, U.K.
[4]Forschungszentrum Jülich, D-52425 Jülich, Germany

ABSTRACT

The crystal structure of alkali/water-poor beryl ($H_2O + Na_2O + Cs_2O < 1.2$ wt%) was reinvestigated by means of laser ablation inductively coupled plasma mass spectroscopy, thermogravimetric analysis, neutron diffraction, and polarized infrared spectroscopy to determine the real topological configuration of the extra-framework content in the six-membered ring channels. Analysis of the nuclear density Fourier map suggests that the (water) oxygen is located along the sixfold axis at the 2*a* site (0,0,1/4), whereas the (water) protons are at –0.028(7), –0.071(3), 0.332(1). The hydrogen atoms are distributed in 6×2 equivalent positions, above and below the oxygen site. Geometrical configuration of the water molecule is well defined: the O-H bond distance is 0.949(18) Å and the H-O-H bond angle is 106.9(2.2)°. The H···H vector is oriented at ~4° from [001]. This configuration is completely different from that found in alkali-rich beryl, where the H···H vector is perpendicular to [001]. Na is probably located, with the H_2O oxygen, at the 2*a* site. According to the chemical analysis, which shows that the amounts of other alkali and earth-alkali cations are negligible (Rb, K, Mg, Mn ≤ 110 ppm, Ca ≤ 225 ppm, Cs ≤ 430 ppm), no effect of other cations on the extra-framework population was observed in the structural refinement. The final agreement index (R_1) of the structural refinement was 0.037 for 34 refined parameters and 160 unique reflections with $F_o > 4\sigma(F_o)$. The topological configuration of the H_2O molecule into the channel is confirmed by the spectroscopic investigation. Polarized single-crystal IR spectra show that the H_2O molecule is oriented with the molecular symmetry axis perpendicular to the hexagonal axis and H···H vector parallel (or quasi-parallel) to [001].

Keywords: Chemical mineral analysis, L-A-ICP-MAS, crystal structure, single-crystal neutron diffraction, water-poor beryl, polarized IR-spectra, trace elements, REE