American Mineralogist, Volume 98, pages 7–18, 2013

Coupled H and Nb, Cr, and V trace element behavior in synthetic rutile at 600 °C, 400 MPa and possible geological application

Friedrich Lucassen,[1,2,*] Monika Koch-Müller,[2] Michail Taran,[3] and Gerhard Franz[1,†]

[1]Technische Universität Berlin, Ackerstrasse 71-76, 13355 Berlin, Germany
[2]Deutsches GeoForschungsZentrum, Telegrafenberg, 14473 Potsdam, Germany
[3]National Academy of Sciences, Palladin Avenue, 34, 03680 Kyiv-142, Ukraine

Abstract

We performed hydration experiments of pure and Nb-, Cr-, and V-doped synthetic dry (H_2O < 3 ppm) single rutile crystals. They were equilibrated with pure H_2O in hydrothermal experiments at constant conditions of 600 °C, 400 MPa, and f_{O_2} near the Ni-NiO buffer, run time between ~25 min and 14 days. Slabs cut parallel to (110) of the reacted single crystals (1 to 2 mm^3) were analyzed for H^+ by FTIR. Hydration occurs almost spontaneously and the H_2O-equivalent is uniformly distributed in the samples, but depends extremely on trace element contents. In pure rutile, the average H_2O-content is 314 ± 50 ppm, the saturation level at these conditions. Rutile doped with 500 ppm Nb has a lower average H_2O content of ~235 ppm, rutile with 2000 ppm Cr has ~900 ppm H_2O, and rutile with 2000 ppm V does not incorporate H_2O. During stepwise heating at atmospheric pressure of a reacted Nb-doped rutile, H^+ is quickly released between 450 and 550 °C. UV-VIS spectra of unreacted colorless and reacted deep blue pure rutile show the rutile-characteristic sharp absorption edge in the UV spectra. The reacted rutile has a broad absorption band at 6500 cm^{-1} wavenumber attributed to intervalence charge transfer transition $Ti^{3+}+Ti^{4+} \rightarrow Ti^{4+}+Ti^{3+}$. The reduction of Ti^{4+} to Ti^{3+} is charge balanced by the incorporation of H^+. The Nb-doped rutile changed its color from light greenish-blue (untreated) to deep blue. In the untreated Nb rutile, the UV-VIS absorption band at 6500 cm^{-1} indicates that Nb^{5+} is charge balanced by Ti^{3+}. In the reacted Nb-rutile the absorption band is more intense, but compared with the pure rutile, H^+ incorporation is lower by the equivalent of Ti^{3+} reduced in the untreated rutile. Reacted Cr-rutile almost retains its brownish-orange color, but the spectrum shows a prominent Ti^{3+}/Ti^{4+} IVCT band at ~6400 cm^{-1} with moderate intensity considering the high-H_2O contents of ~900 ppm. The high-H^+ contents are best explained by the reduction of Cr^{4+} to Cr^{2+}. The UV-VIS spectra of the dark-blue to opaque V-doped rutile show a very strong absorption toward low energies, which is likely caused by reduction of Ti^{4+} to Ti^{3+} for charge balance of V^{5+}. This forms a deep narrow window of transmittance in the range 25 000–20 000 cm^{-1}, which causes the dark-blue color.

To explore the possible use of H-in-rutile as a geohygrometer, geothermobarometer, and oxybarometer, we measured the H^+ content in a natural rutile crystal from a retrograded eclogite with a zoned trace element (Fe, Nb, and Zr) content. The crystal reveals a slight correlation between the variable H_2O (~200 to 900 ppm) and its trace element concentrations. The observations indicate that the preservation of H^+ contents in this natural rutile is a complicated interplay of diffusive reequilibration of fast H^+, slower Fe and very slow other trace elements. An interpretation of the H_2O contents of the natural crystal in terms of f_{O_2} or a_{H_2O} is not possible.

Keywords: Experimental petrology, rutile, NAM, UV-VIS spectroscopy