

## Hydrogen incorporation into pure and Nb-, Cr-, V-doped synthetic rutile at 600°C, 400MPa

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Rutile (TiO<sub>2</sub>) is a common accessory mineral in a variety of rock compositions and an important carrier of trace elements such as Nb, Ta, Zr, V, and Cr. Incorporation of trace amounts of hydrogen into the nominally anhydrous mineral occurs at variable contrasting physical conditions in nature (e.g. Hammer and Beran, 1991). This study explores hydrogen incorporation into large (~ 1 to 2 mm<sup>3</sup>) crystals of synthetic, pure and doped rutile of low initial hydrogen contents (< 3 ppm H<sub>2</sub>O equivalent) with 500 ppm Nb, or 2000 ppm Cr, or 2000 ppm V. The 'pure' rutile contains traces of Fe (< 10 ppm). Physical conditions in the hydration experiments (rutile + H<sub>2</sub>O sealed in an Au-capsule) were 600 °C and 400 MPa at fO<sub>2</sub> is close to the Ni-NiO buffer. Runtime varied between 14 days and 25 minutes in experiments with (nearly) pure rutile and were 14 days in experiments with doped rutile. We used Fourier Transform Infrared spectroscopy (FTIR) for quantification of hydrogen contents and UV-VIS for the exploration of colour changes.

All reacted samples (except V, which is nearly opaque) show a strongly polarized peak around 3278 cm<sup>-1</sup> in FTIR spectra. Calculated H<sub>2</sub>O equivalent of pure rutile in time series experiments varies between 271 and 365 ppm (using the absorption coefficient by Maldener et al. 2001) with an average value of 314 ± 50 ppm for all six runs, which is considered as the H<sup>+</sup> saturation level at given conditions. Core – rim zoning of the H<sub>2</sub>O contents or a clear trend to lower contents in the shorter experiments are absent, despite the lowest values of ~270 ppm occur in the 1h and 25 minutes experiments. The pure rutile changes colour from colourless or slightly reddish to deep blue in all samples. In the reacted samples there appears a polarized broad band at around 6400 cm<sup>-1</sup> (E<sub>||</sub>c > E<sub>⊥</sub>c), caused by electronic Ti<sup>3+</sup> + Ti<sup>4+</sup> → Ti<sup>4+</sup> + Ti<sup>3+</sup> intervalence charge-transfer (IVCT) transition. The band causes the blue colour and distinct dichroism.

In Nb- and Cr-doped rutile, distribution of H<sup>+</sup> is also uniform with ~240 ppm in Nb- and ~ 900 ppm in Cr-doped rutile. After hydration, the Nb-doped rutile changed its colour from light greenish-blue to deep blue. In both cases the colour is due to Ti<sup>3+</sup>/Ti<sup>4+</sup> IVCT pairs, which concentration significantly increases at the treatment. The Cr-doped rutile retained its red orange colour. The transparency of V-doped rutile is very low before and after the experiments. UV-VIS work on these runs is in progress. Reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup> causes the Ti<sup>3+</sup>/Ti<sup>4+</sup> IVCT transition and the blue colour in pure rutile (e.g. Khomenko et al. 1998) and hence a characteristic absorption band in the UV-VIS spectra. Diffusion of H<sup>+</sup> into the rutile structure ensures charge balance in the charge transfer reaction. It is fast enough to produce a uniform H<sup>+</sup> distribution in rutile even in 25 minutes. Volume diffusion of large cations (Ti, Cr, Nb) and oxygen in rutile can be excluded at given conditions. The deviation of H<sup>+</sup> contents in the doped rutile from the H<sup>+</sup> saturation level in pure rutile can be also explained by charge transfer including the possibly variable oxidation state of the trace elements.

### References:

- Hammer VMF, Beran A (1991) *Mineralogy and Petrology* 45:1-9
- Khomenko et al. (1998) *Physics and Chemistry of Minerals* 25:338-346
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