

Hydrogen diffusion in Cr-doped forsterite studied by XANES and FTIR

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The solubility and diffusion of hydrogen in synthetic Cr-doped forsterite has been studied as a function of oxygen fugacity, temperature and pressure (650-1000 °C, 10-25 kbar) in the piston cylinder apparatus. This Cr:forsterite (~160 ppm Cr) is grown for use in solid-state lasers, and contains both tetrahedral Cr⁴⁺ (lasing centre) but also octahedral Cr³⁺ as a contaminant.

1x1x1 mm cubes of the Cr:forsterite were annealed in Ag capsules containing a solid oxygen buffer (e.g. graphite, Ni-NiO, Fe₃O₄-Fe₂O₃, Re-ReO₂, Ag-Ag₂O), a solid silica activity buffer, and excess H₂O to achieve $p(\text{H}_2\text{O}) = P_{\text{total}}$. The resulting diffusion profiles of H were measured using FTIR spectroscopy, which quantifies the amount of H and distinguishes different O-H bonding environments. The valence states and coordination environments of Cr along the diffusion profiles were independently measured using Cr K-edge XANES, whose good spatial resolution also allows short diffusion profiles to be identified.

Diffusion of H utilises at least five pathways, each associated with its own point defect type. The difference between the fastest and slowest H diffusion coefficients in a single experiment, along one crystallographic axis, is up to three orders of magnitude. The fastest mechanism involves hydrogen-polaron exchange (i.e. reduction of chromium). The rate of diffusion along this pathway has a clear negative dependence on oxygen fugacity (faster at lower $f\text{O}_2$). The next fastest mechanisms both involve diffusion of M-site vacancies, either in isolation or associated with trivalent chromium. The diffusion rate of hydrogen along the M-site vacancy pathway is in good agreement with previous determinations of the same process. Slightly slower is a mechanism producing the hitherto undescribed 'Cr-clinohumite' point defect. This requires Cr⁴⁺ to move from tetrahedral to octahedral coordination, and become charge-balanced by two hydrogen on an adjacent tetrahedral site. The slowest mechanism involves rearrangement of both the tetrahedral and octahedral sublattices to equilibrate the Cr valence state at the very near edge (several micrometres) with the experimental conditions.