AVO₄ compounds with A = rare earth, Y, In and Sc crystallize in zircon type structures. Upon reduction of the pentavalent vanadium to trivalent vanadium either a cation disordered bixbyite structure (for In³⁺ and Sc³⁺) or a cation ordered orthorhombic perovskite structure (for all rare-earth) is formed. Oxidation of the trivalent vanadites follows different pathways depending on the structure of the AVO₄ phase. The perovskite oxidizes directly back to AVO₄, whereas the bixbyite phase undergoes stepwise oxidation to metastable AVO₃.₅⁺ and metastable AVO₄⁺ phases. Figure 1 contrasts the distinct colours of the intermediate ScVO₃.₇₀ (defect fluorite structure), the intermediate oxide deficient zircon structure ScVO₃.₉₄(2) and the fully oxidized stable zircon phase ScVO₄. The metastable stable phases were identified by means of in-situ powder X-ray diffraction. This experiment focused on the investigation of the oxide defect zircon structure ScVO₃.₉₄(2) using powder neutron diffraction. Powder neutron diffraction data were collected on powder diffractometer C2 at room temperature. ScVO₄₋ₓ is isostructural with ScVO₄ and shows evidence of oxide anion clustering and strongly supports defect disorder. Variations of the unit cell dimensions supported the existence of oxide defects. The structure refinements were carried out with GSAS using two neutron diffraction patterns (λ = 2.37Å and λ = 1.33Å) and one powder X-ray diffractogram. Figure 2 shows selected Rietveld plots of ScVO₃.₉₄. The oxygen stoichiometry was determined by means of thermal gravimetric analysis and the presence of paramagnetic V⁴⁺ was confirmed with d.c. bulk magnetic susceptibility and multinuclear solid state NMR.

References