Structure Determination of the Oxide Defect Zircon Structure: $ScVO_{3.94(2)}$

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AVO_4 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 In^{3+} and Sc^{3+}) 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 AVO_3 phase. The perovskite oxidizes directly back to AVO_4, whereas the bixbyite phase undergoes stepwise oxidation to metastable $AVO_{3.5+y}$ and metastable AVO_{4-x} phases. Figure 1 contrasts the distinct colours of the intermediate $ScVO_{3.70}$ (defect fluorite structure), the intermediate oxide deficient zircon structure $ScVO_{3.94(2)}$ and the fully oxidized stable zircon phase $ScVO_{4.00}$. 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 $ScVO_{3.94(2)}$ using powder neutron diffraction. Powder neutron diffraction data were collected on powder diffractometer C2 at room temperature. $ScVO_{4-x}$ is isostructural with $ScVO_4$ 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 $ScVO_{3.94}$. The oxygen stoichiometry was determined by means of thermal gravimetric analysis and the presence of paramagnetic V^{4+} was confirmed with d.c. bulk magnetic susceptibiliy and multinuclear solid state NMR.

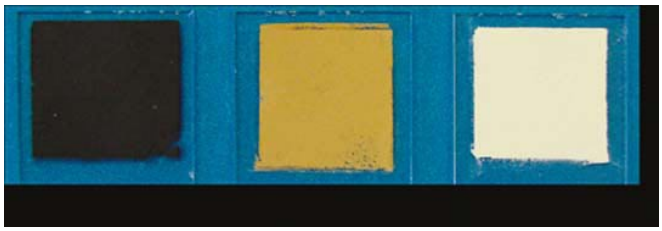

Fig. 1 Comparison of polycrystalline samples belonging to the Sc-V-O system, left: $ScVO_{3.70}$, center: $ScVO_{3.94}$, right: $ScVO_{4.00}$

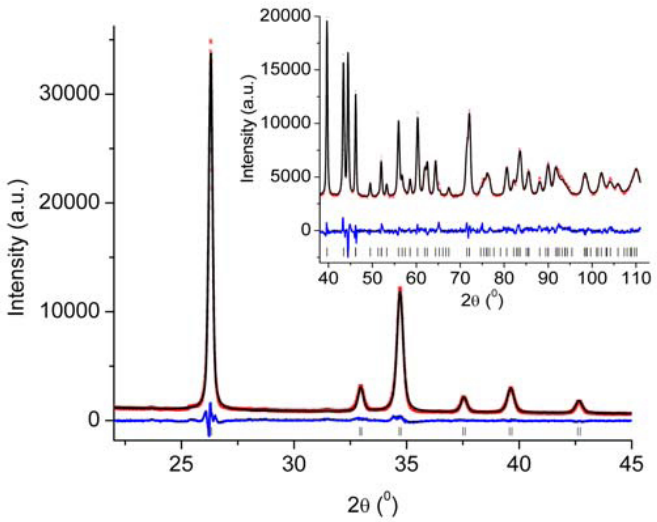

Fig. 2 $ScVO_{3.94(2)}$ zircon oxide defect structure. Rietveld plots of powder X-ray diffraction data with insert of neutron (λ = 1.3296Å) powder data. Black stars = experimental data, red line = best fit, blue line = intensity difference and tick marks = Bragg positions.

References

[1] Shafi, S.; Kotyk, M.W., Cranswick, L.M.D., Michaelis, V.K., Kroeker, S;, Bieringer, M; Inorganic Chemistry, 2009, 48(22) 10553-10559