

# In situ X-ray scattering study of VO<sub>2</sub> formation from VOSO<sub>4</sub> precursor under solvothermal conditions

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Vanadium dioxide (VO<sub>2</sub>) is a correlated electron material known for its reversible insulator-to-metal transition (IMT) near room temperature [1]. In the ground state VO<sub>2</sub> exists in the monoclinic insulating phase VO<sub>2</sub>(M) and transitions to a metallic rutile phase upon thermal- or photoexcitation [2,3]. This IMT has been studied widely within the field of ultrafast science [3,4], and for different smart material applications [5,6,7]. However, the synthesis of phase-pure VO<sub>2</sub> is a challenge due to the many polymorphs of vanadium oxide, and the sensitivity of the VO<sub>2</sub>(M) phase formation to the synthesis conditions [7,8].

In this study, a synthesis route inspired by the TiO<sub>2</sub> synthesis from TiOSO<sub>4</sub> is explored [9]. This approach avoids toxic oxidizing agents such as hydrazine, often used during synthesis [7], by using a VOSO<sub>4</sub>-based precursor that avoids the need for a redox step during formation. Using a flow cell under hydrothermal conditions, a monoclinic VO<sub>2</sub>(B) phase is synthesized. *In situ* powder X-ray diffraction (PXRD) reveals that this metastable VO<sub>2</sub>(B) phase irreversibly transforms to the thermodynamically stable VO<sub>2</sub>(R) phase above 300 °C. The lifetime of the VO<sub>2</sub>(B) phase decreases with increasing temperature, indicating a kinetically activated solid-state transition mechanism. This is elucidated through Pair distribution function (PDF) analysis, to explore why the VO<sub>2</sub>(B) phase is formed initially. Based on these findings a synthesis is proposed for VO<sub>2</sub>-based materials.

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