An In-Depth Study of the Thermodynamics and Kinetics of the Structural Phase Transition of Hydrothermally Synthesized W/VO_2 Microparticles

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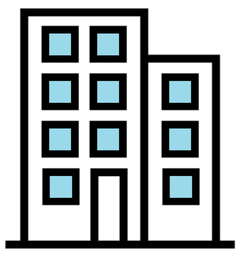
Introduction



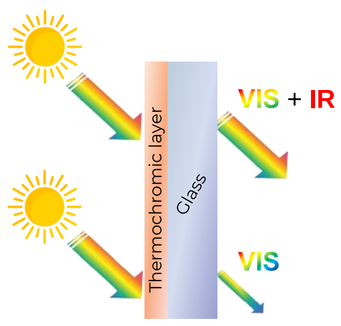
Buildings are responsible for about **1/3 of global energy use and CO_2 emissions.**

More than 50% of this energy used **for heating and cooling.** Where **windows alone account for over 30%** of a building's **total energy loss** or gain.

"Smart windows" *with thermochromic VO_2 coatings offer a passive solution.*

On a **cold day** the coating lets **solar infrared pass through**, providing passive heating.

On a **hot day** the coating **blocks solar infrared** radiation, passively cooling the buildings.



Switch temperature: ~20 °C (ambient)

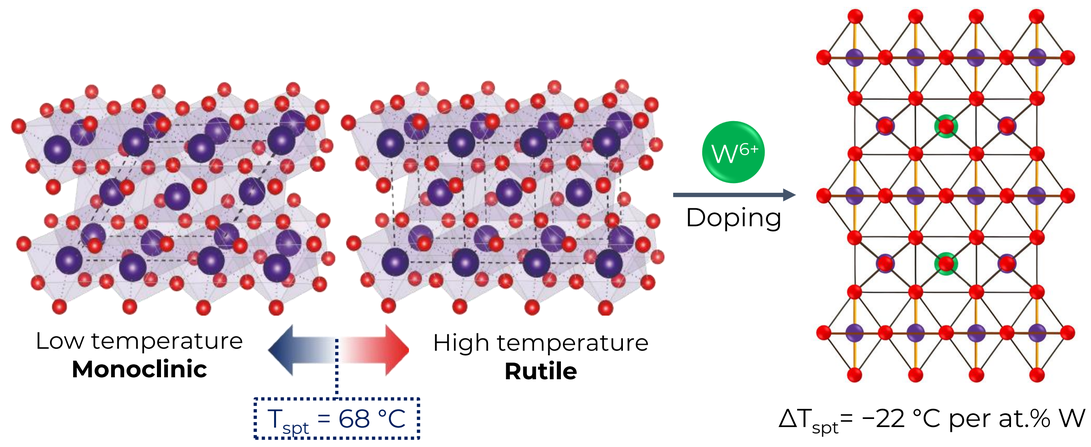
Research Aim

The natural phase transition temperature of VO_2 (~68 °C) is too high for smart window use. **Tungsten doping** lowers this temperature but also **alters the material's structure and transition dynamics**, which are still **not well understood for hydrothermally synthesized VO_2.**

This work aims to **reveal how W-doping and microstructure affect the thermodynamics and kinetics of the structural phase transition in VO_2** microparticles made by a non-harmful, scalable hydrothermal method.

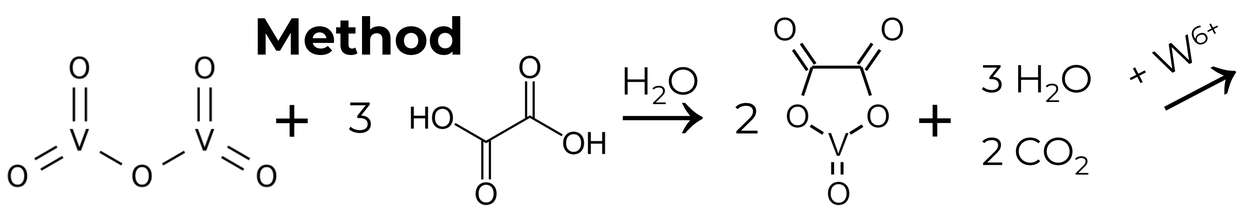
Theory

VO_2 structural phase transition (SPT)



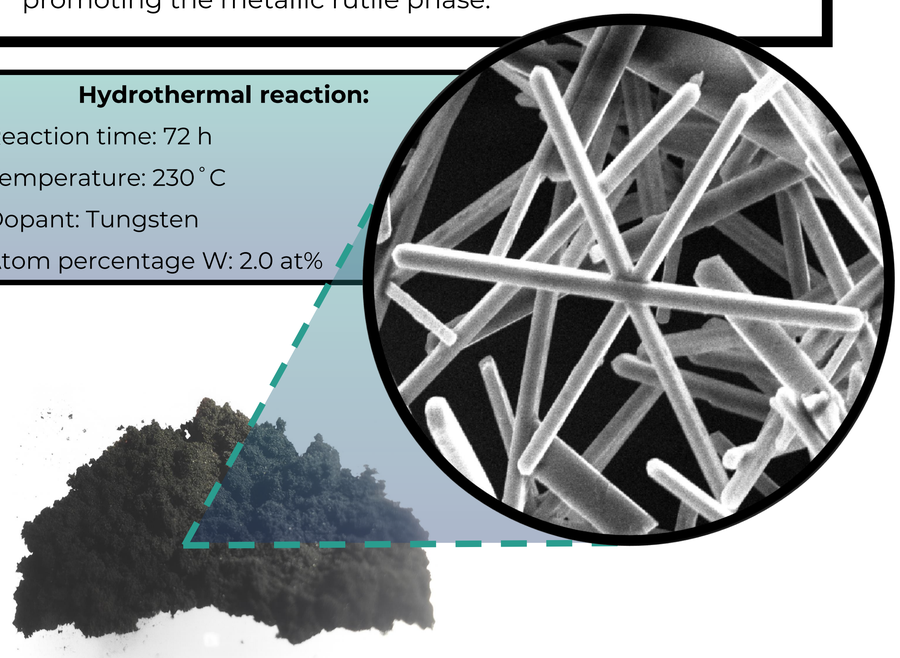
The SPT induces a change in the materials optical properties, from IR transparent to IR blocking. The temperature of the **SPT can be lowered using dopants such as tungsten**, as W^{6+} substitution for V^{4+} distorts the lattice and weakens V–V bonds, promoting the metallic rutile phase.

Method



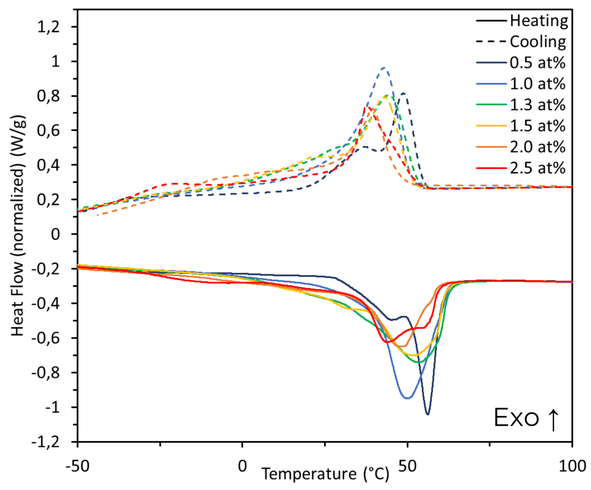
Hydrothermal reaction:

- Reaction time: 72 h
- Temperature: 230 °C
- Dopant: Tungsten
- Atom percentage W: 2.0 at%



Results and Discussion

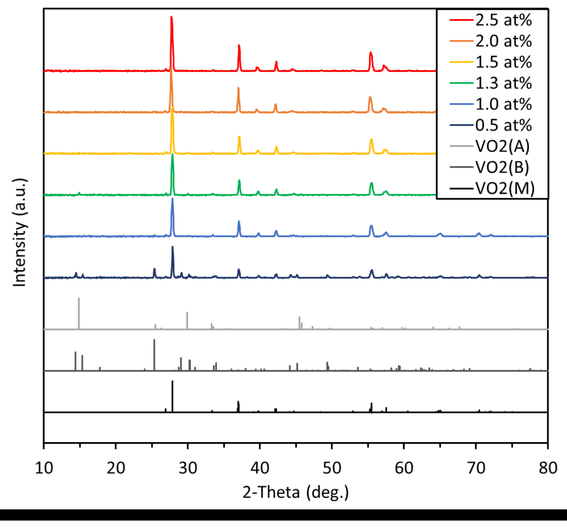
Importance of tungsten doping



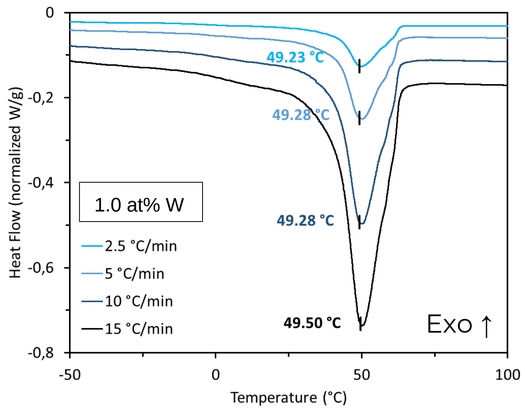
Increasing W content lowers the VO_2 switching temperature, though the reduction is smaller than expected due to:

- Inhomogeneous W incorporation: 0.1–1.8 at% among individual crystals in the 1.5 at% W sample. (TEM-EDX)
- Non-uniform crystal size and shape: rods (10.7 ± 2.3 µm), asterisks (arm length 12.8 ± 3.1 µm). (SEM)

W promotes crystallization of VO_2 in the monoclinic (M) phase. With more W, VO_2(B) peaks disappear and monoclinic peaks increase in intensity, confirming improved phase purity.

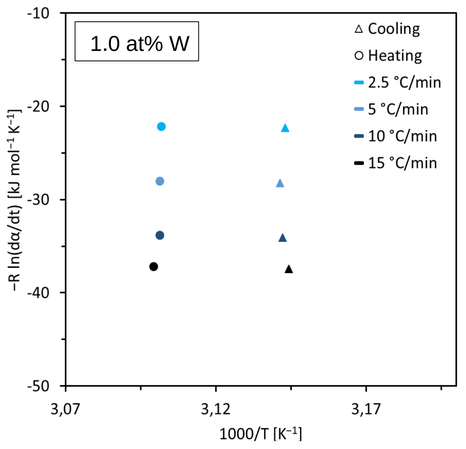


Kinetic analysis of the W-doped VO_2 phase transition



Friedman differential isoconversional method

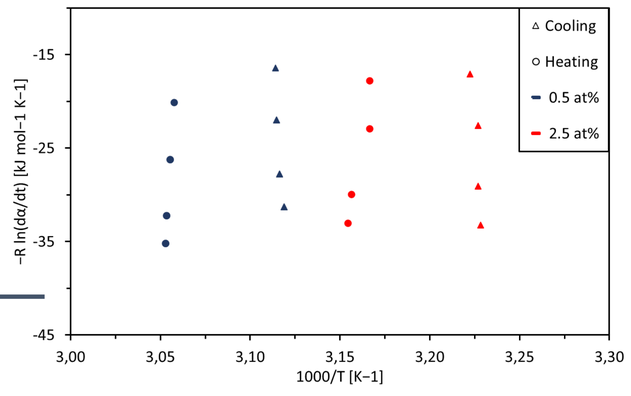
$$-R \ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = -R \ln(A_\alpha f(\alpha)) + \frac{E_\alpha}{T_{\alpha,i}}$$



DSC was performed at multiple heating rates (2.5 – 15 °C min^{-1}) for W-doped VO_2.

The running integral of the DSC signal was used to calculate conversion (α) vs T and time. At α = 0.5, the temperature ($T_{50\%}$) and conversion rate (dα/dt) were extracted.

Using the Friedman isoconversional method, plots of ln(dα/dt) vs 1/T yielded the activation energy (E_a).



The E_a trend with temperature remains unchanged, but higher W content shifts $T_{50\%}$ to lower temperatures.

Final Insights

1. The developed hydrothermal synthesis yields **highly crystalline, phase-pure monoclinic VO_2.** W doping promotes the formation of VO_2(M) and lowers transition temperature.
2. The **activation barrier/energy increases near the transition temperature**, causing phase switching to slow dramatically as the system approaches T_{spt}.
3. **Increasing W content shifts the 50% conversion point**, enabling control over the switching temperature to match different ambient climates or functional requirements.
4. The asymptotic activation behavior shows that **nucleation**, rather than phase growth, is the **rate-determining step** for both of the phase transitions.

References

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