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In-situ Monitoring of Vanadium Oxide Formation Using High Temperature XRD

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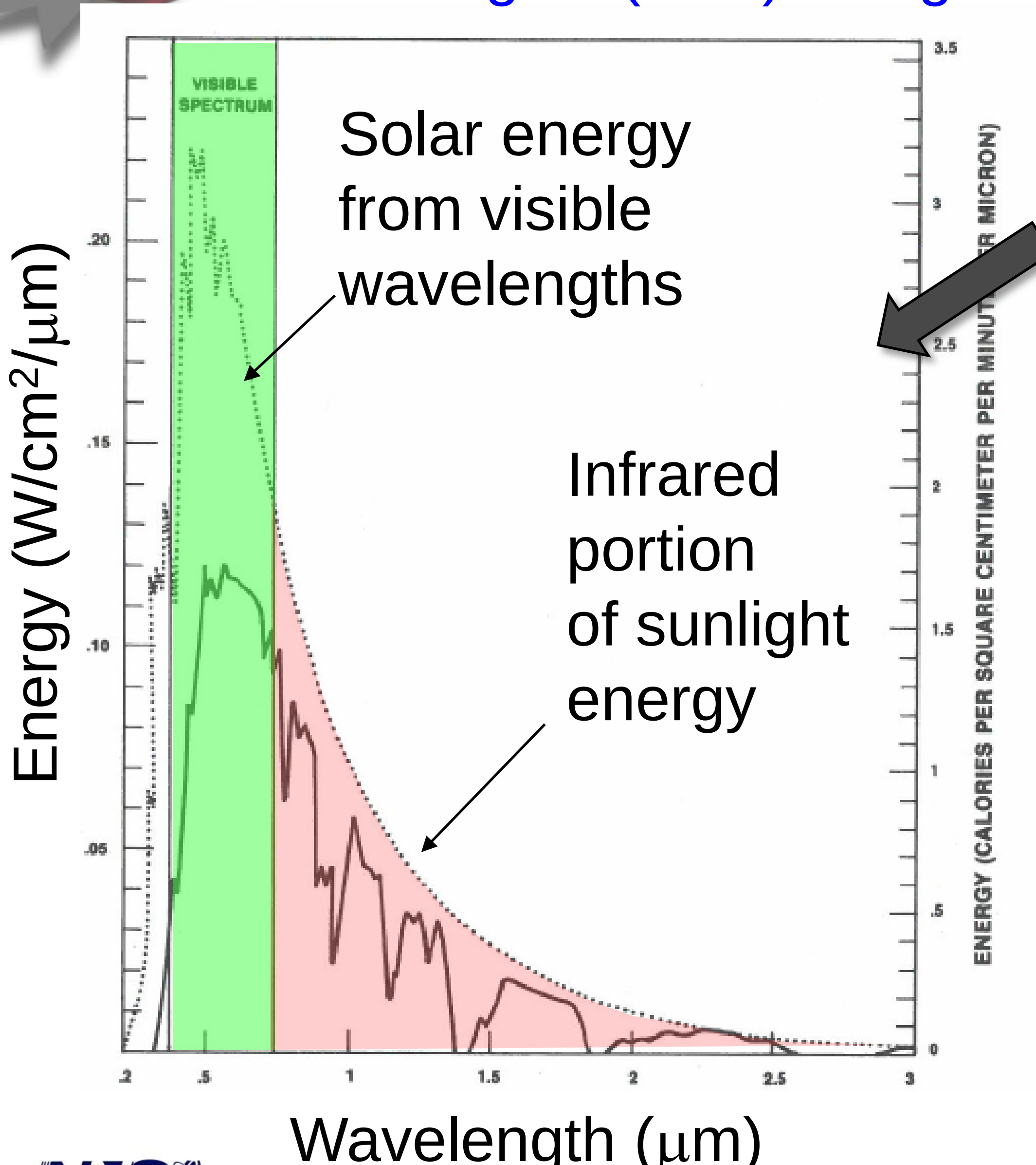
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Engineering of solar illumination (light) and thermal gain (heat) can greatly improve energy efficiency



This graph shows the energy distribution of sunlight as a function of wavelength

<u>Goal:</u>
Decouple light (visible) and IR (heat gain) via smart management of optical vs. thermal gain

E. Mazria, Passive Solar Energy Book

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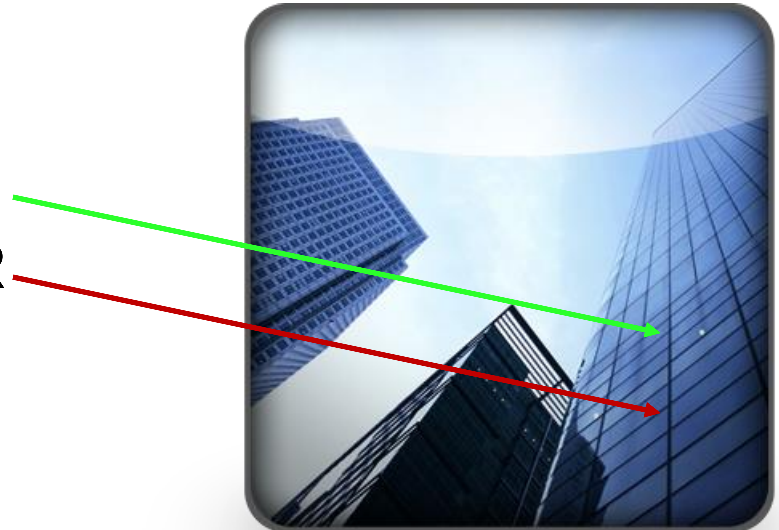
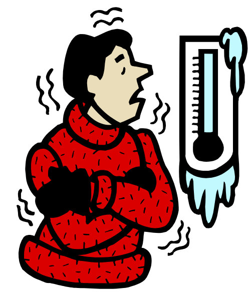
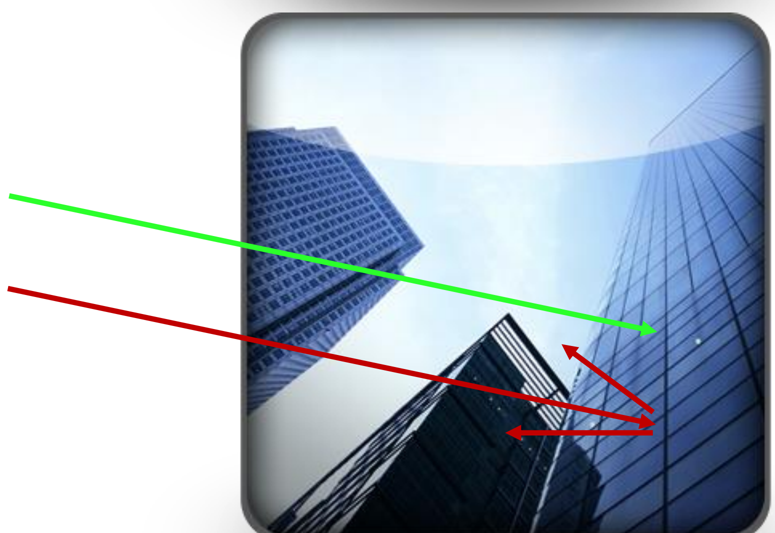
What if we could make a window coating that changes reflective behavior with temperature?

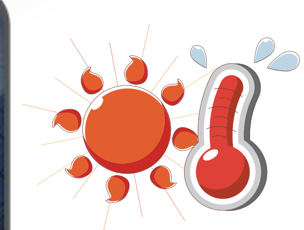
On cold days the window transmits light (visible) and IR (heat)





On *hot* days the window transmits light (visible) only (no IR)

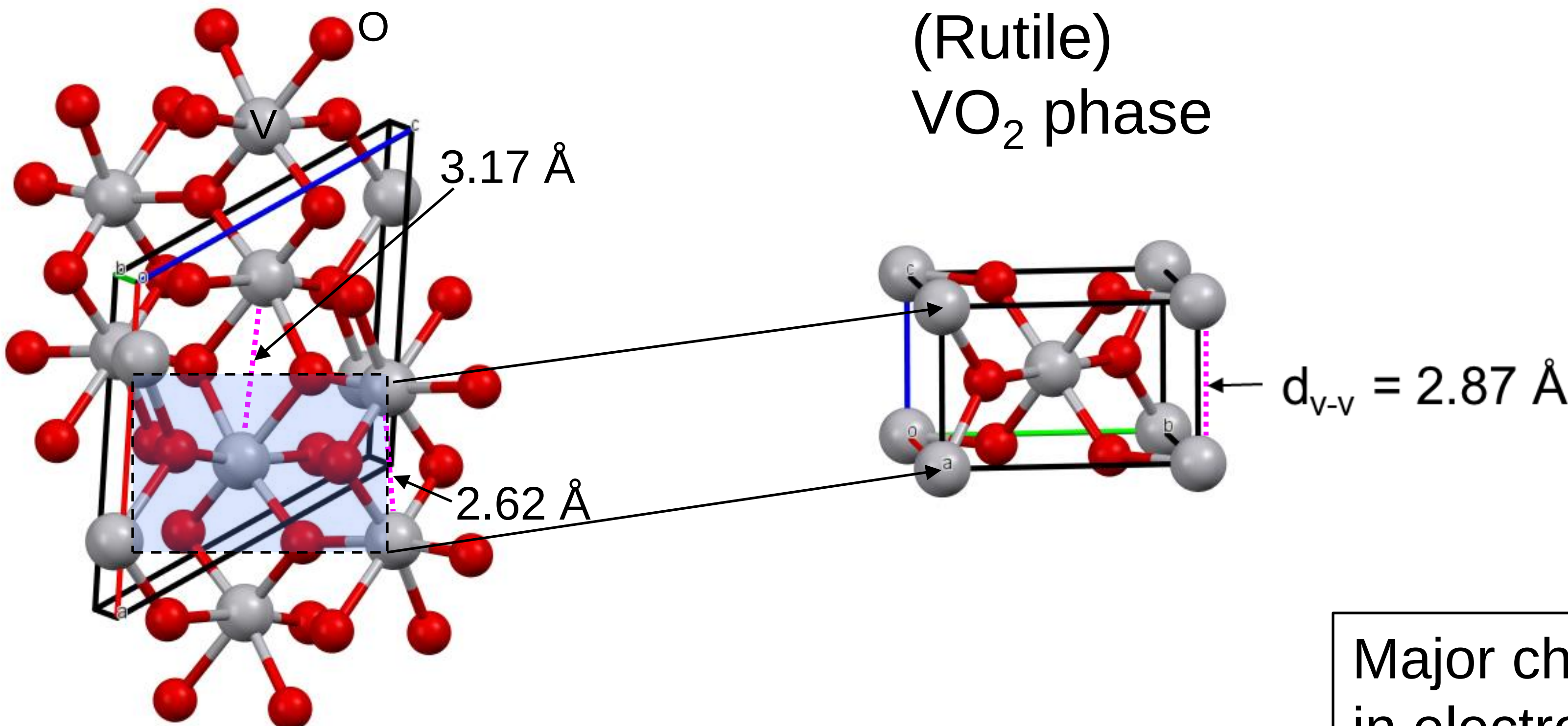


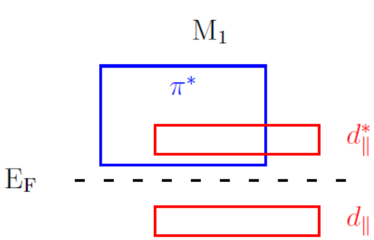


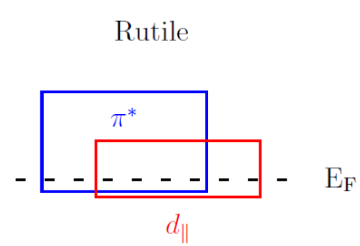
VO_2 demonstrates a significant structural change from monoclinic (M1) to tetragonal (rutile) at ~68ºC

Monoclinic (M1) VO_2

Tetragonal (Rutile) VO_2 phase



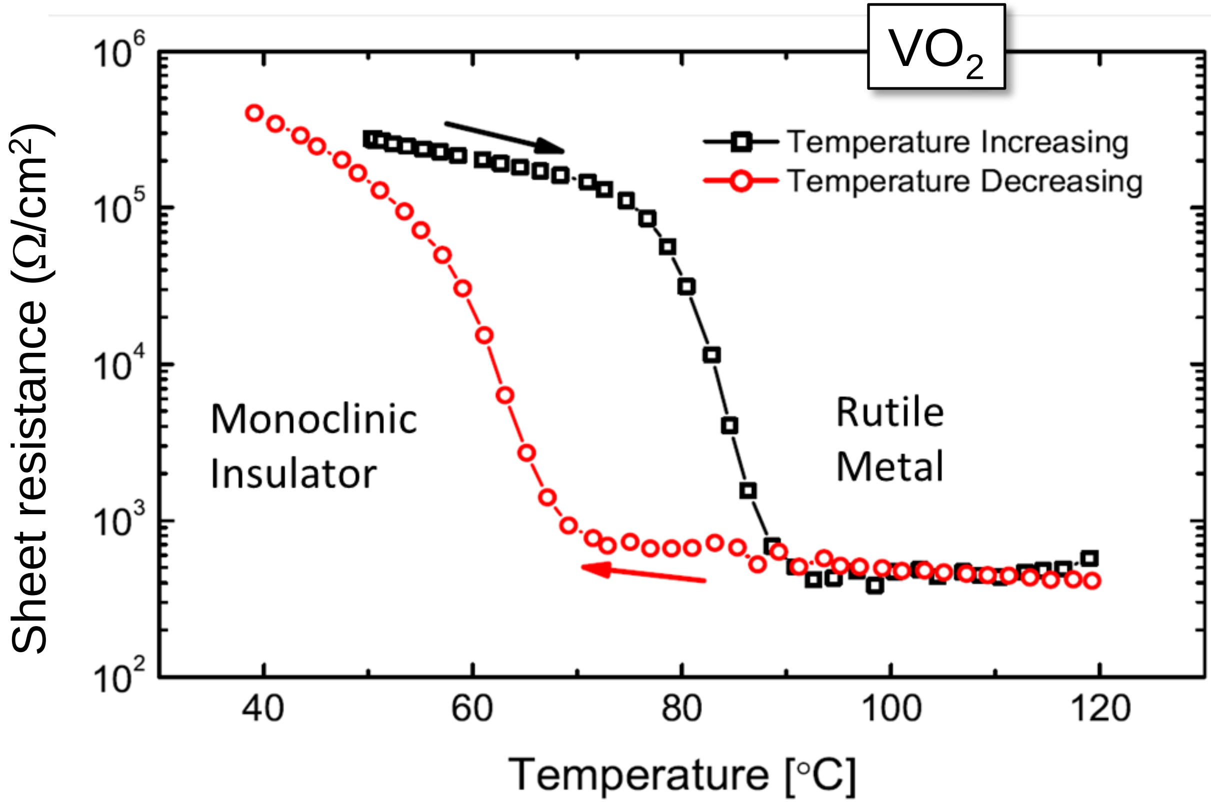




Major change in electronic structure with phase change

Lazarovits, *et al*. (2010). *Phys. Rev. B* **81**, 115117.

Intrinsic structural/electronic phase change of VO_2 has categorized it as a Metal-Insulator-Transition (MIT) Material



MIT materials display a very large change in resistivity at the transition temperature (T_c)

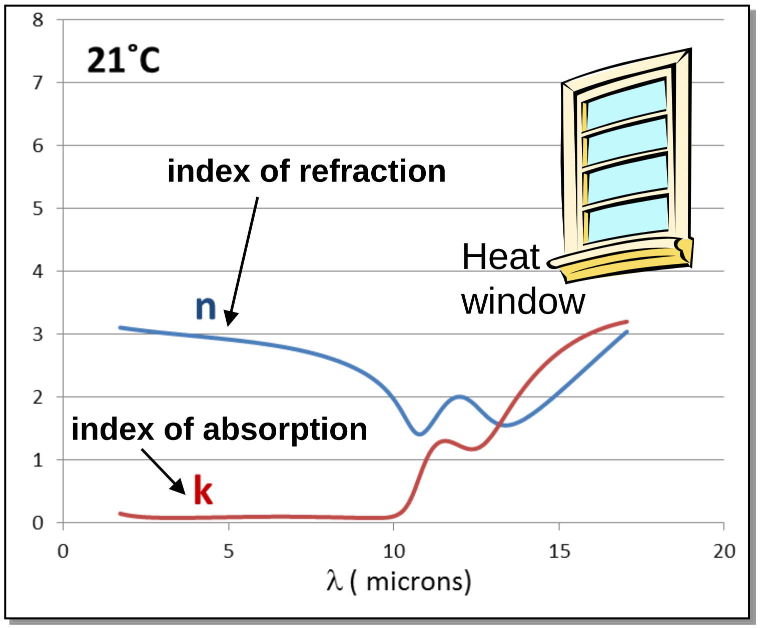
- Hysteresis effect

- Large area of research decades ago
  - optical shutters, switches
- More recently – “smart windows”

VO_2 refractive index $n^* = (n + ik)$ varies widely across monoclinic to tetragonal phase transition

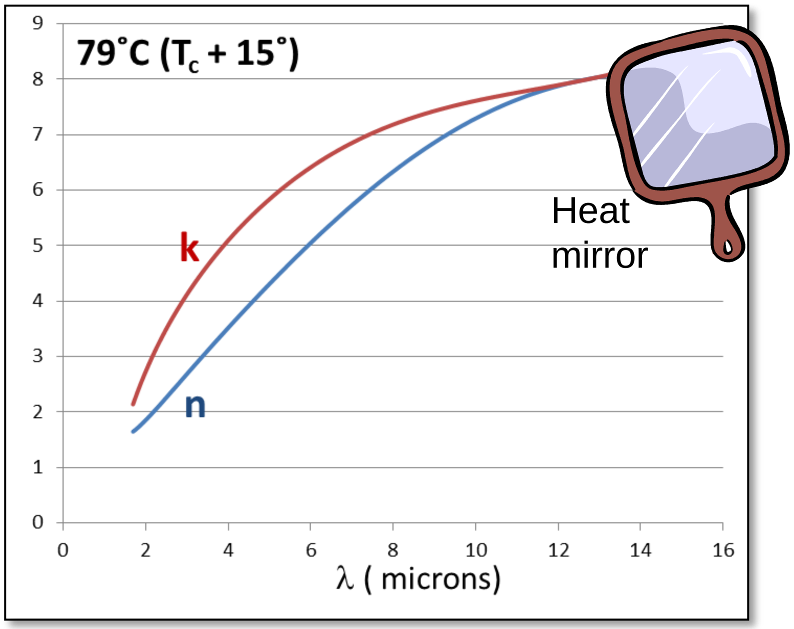
Monoclinic (M1) VO_2

- @ 21ºC, k ~ 0, **IR transparent**



Tetragonal (Rutile) VO_2

- @ 79ºC, k > n, **IR metallic**



Environmentally-switched IR transmission

Switching temperature is still too high, but it's a start.

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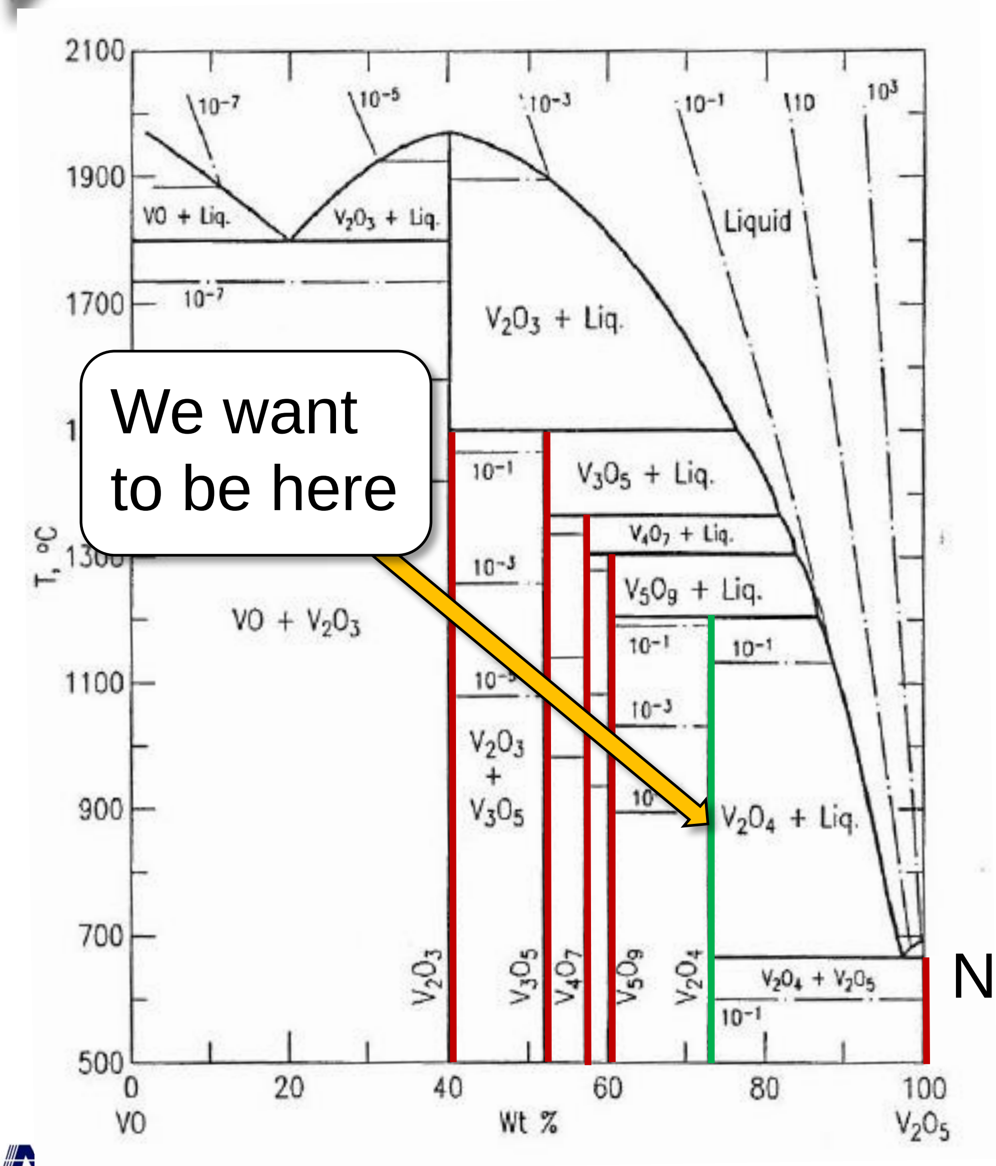
Forming tetragonal VO_2 is tricky due to the large number of possible VO_x compounds



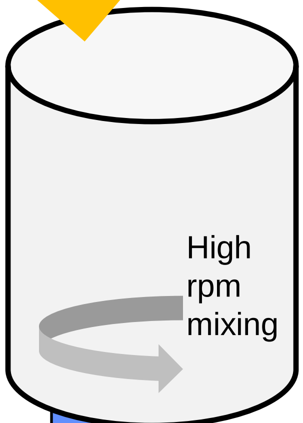
- VO_2 is a line compound
- Vanadium may has five common
valence states (0, +2, +3, +4, +5)
- Neighboring compounds have undesirable electrical properties:
  - V_2O_5 - insulator
  - V_nO_{2n-1} – no phase change
  - V_2O_3 - linear semiconductor

Need control of oxygen content

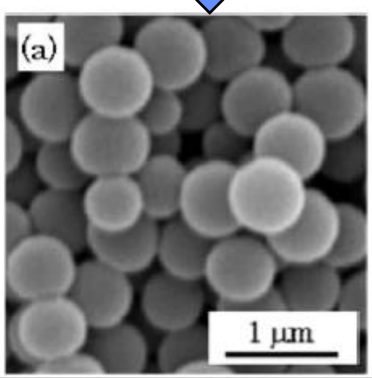
How can we synthesize tetragonal VO_2 at low temperatures with controlled pO_2?

In an inert environment….

acetone
pyridine
V-oxyisopropoxide
water

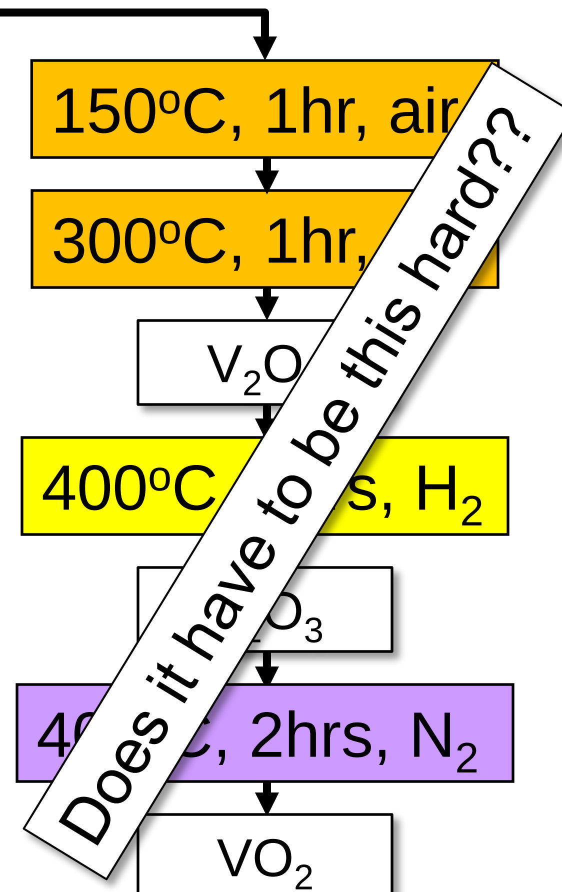


Monodisperse sub-micron spherical **Vanadium Oxide Precursor (VOP)** particles



S. Yamamoto, *et al.* (2009) *Chem. Mater*. **21** 198-200.

Tortured path to VO_2 formation

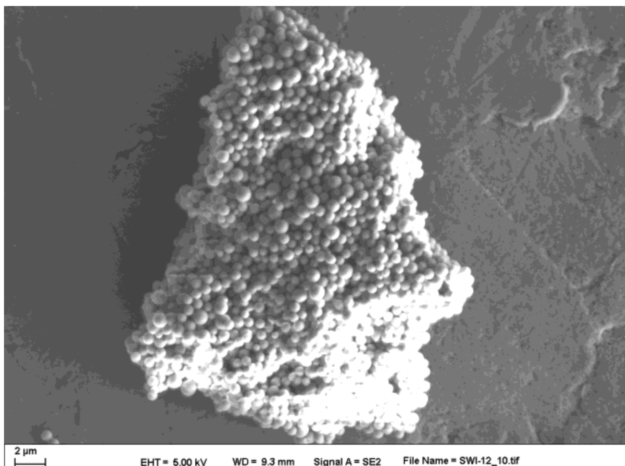


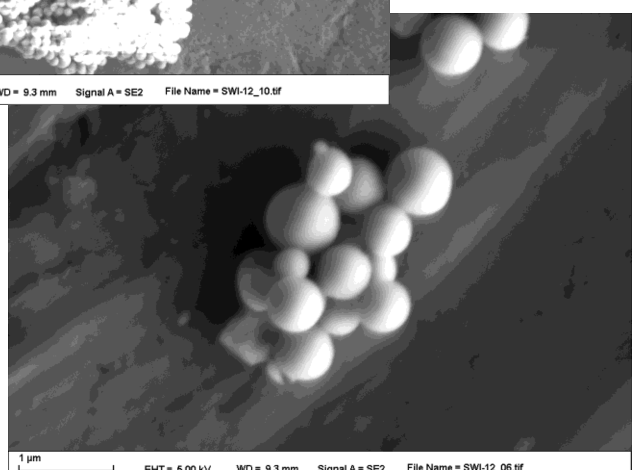
Lu, *et al.* (2011) *J. Mat. Chem.* **21** 14776.

Important observation: Monodisperse VOP particles must be collected rapidly after synthesis

SW1-12 – Collected after 3 hrs aging

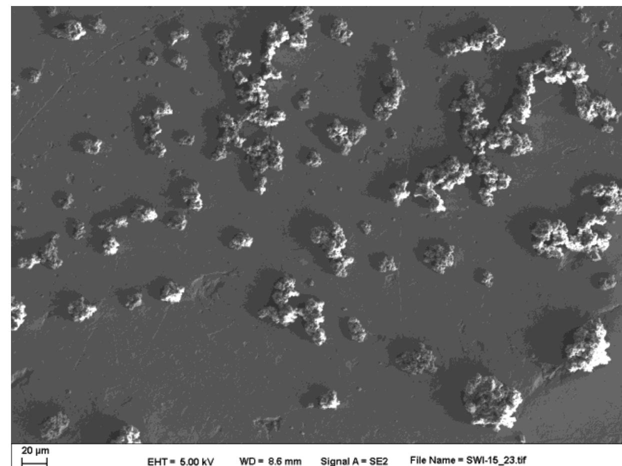
- Particles were opaque suspension, but were recovered easily.

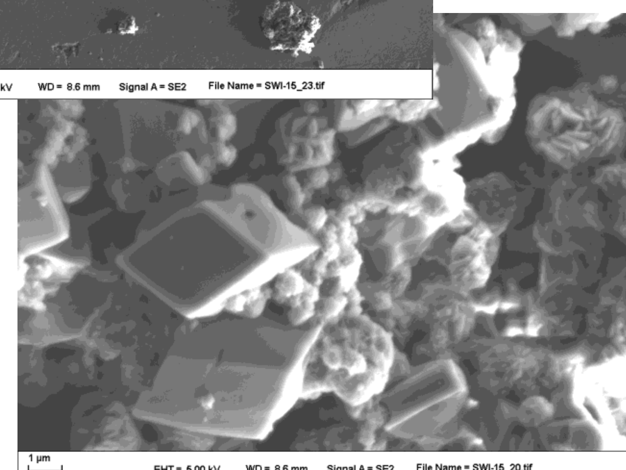




SW1-15 – Collected after 20 hrs aging

- Recrystallization with particle sedimentation





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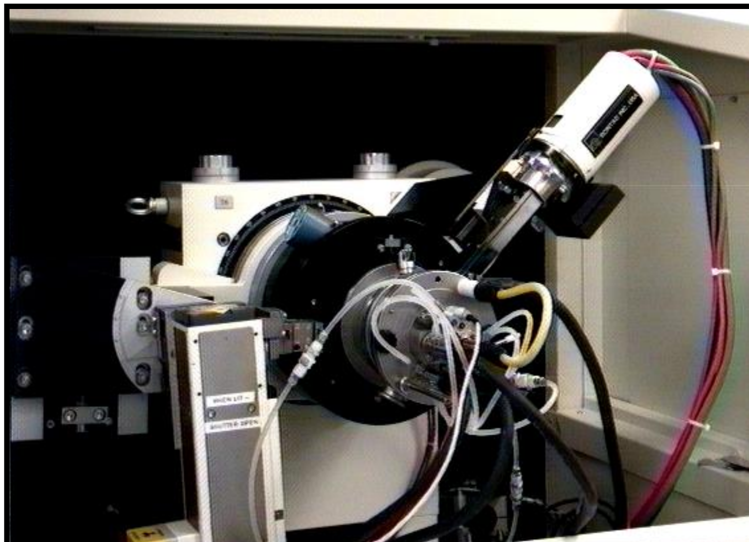
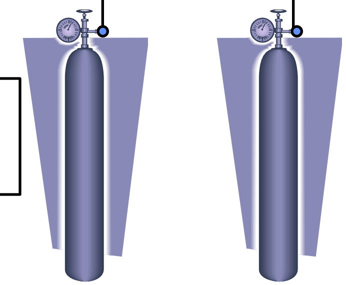
We monitored VOP using high temperature in-situ XRD analysis for VO_x phase evolution

Scintag PAD X diffractometer w/ Buehler HTK-1600 hot-stage



Gas flow control (mixing)

optional O_2 getter



UHP N_2 (or Helium)

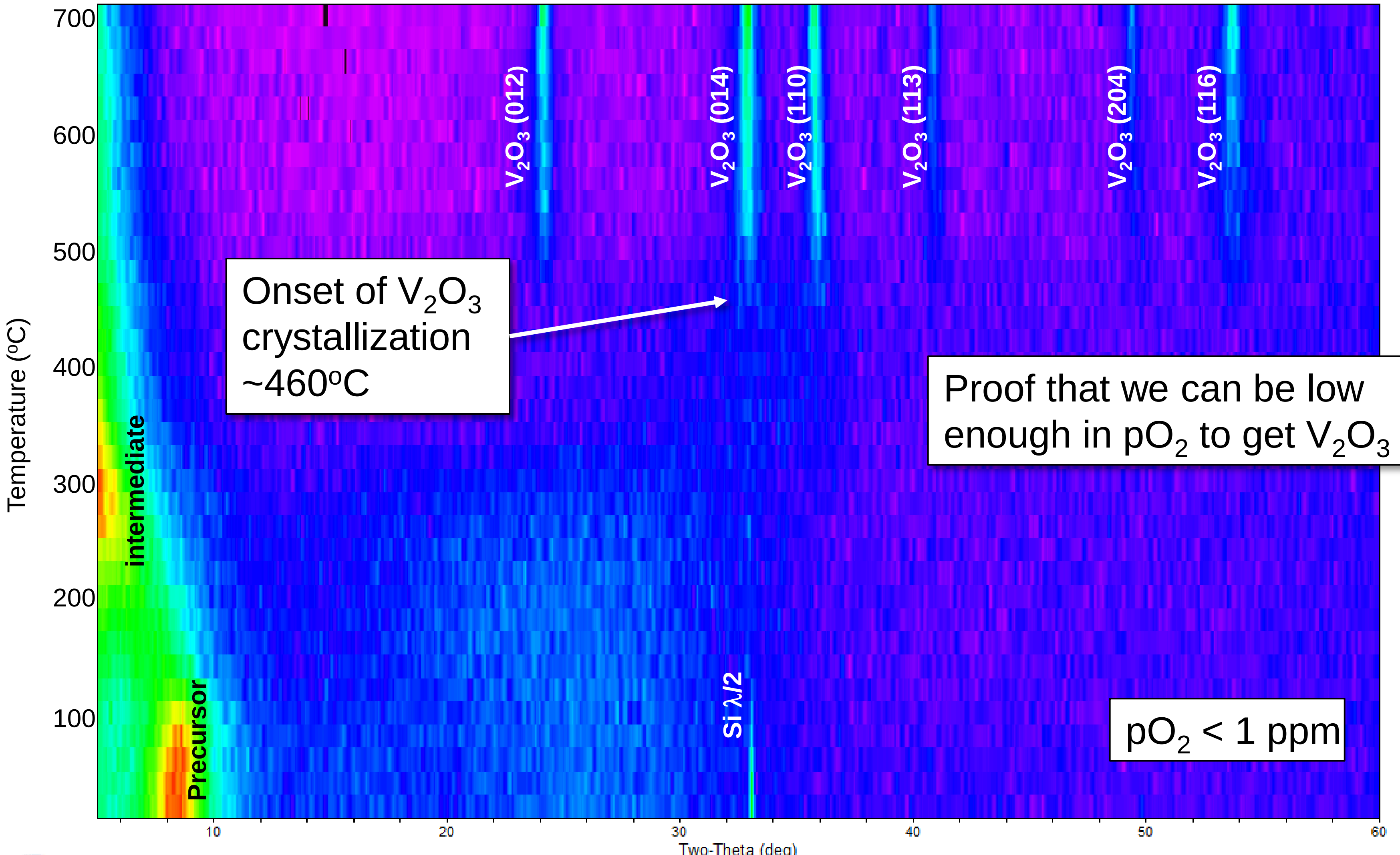
N_2 / 500 ppm O_2

pO_2 monitor

Computer control of temperatures and XRD scans

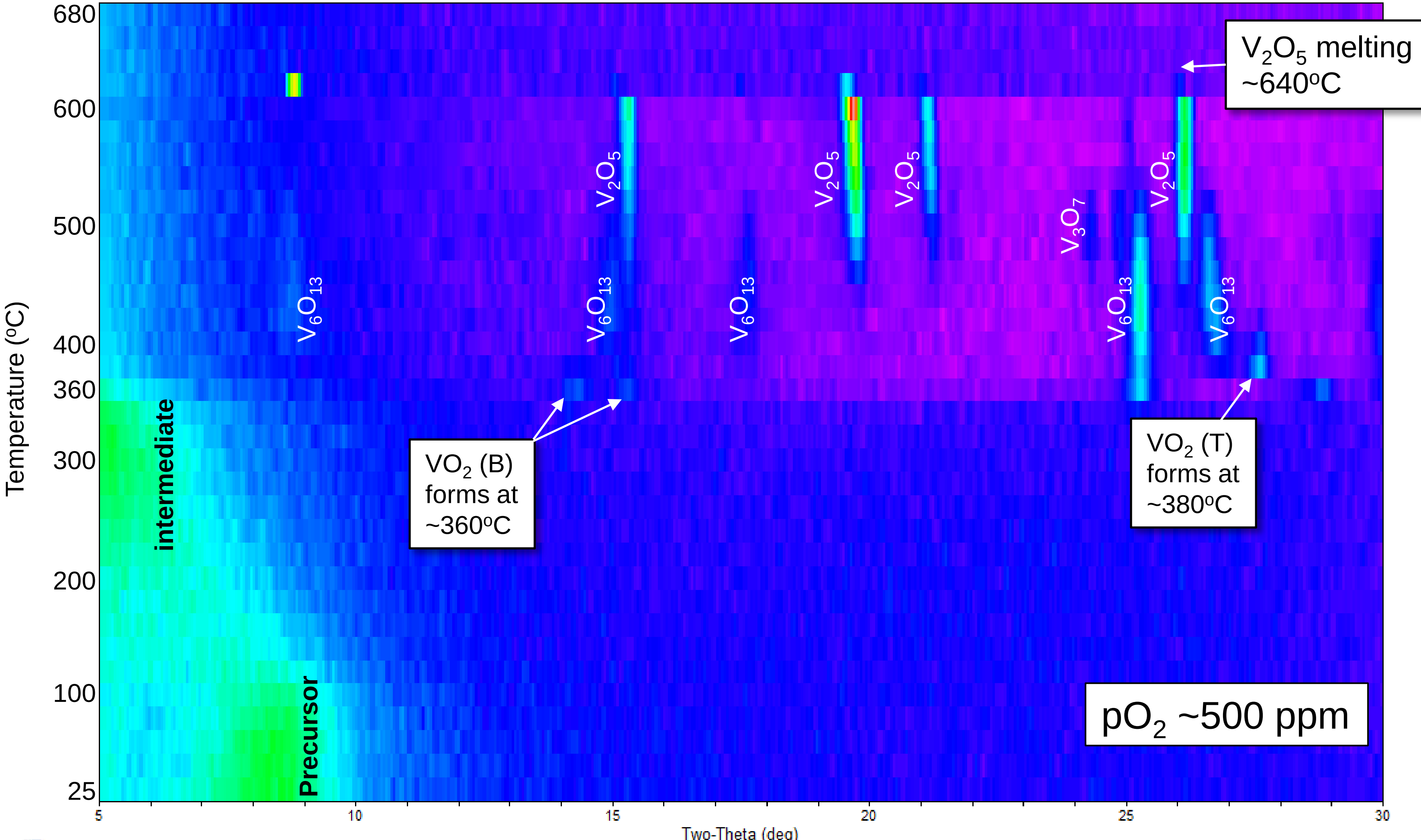
- VOP powder films dispersed on silicon substrates
- Temperature calibration performed using ThEx standards
- pO_2 monitor calibrated using certified mixed gases

First scan series employing gettered-Helium (< 1ppm O_2) revealed only V_2O_3 formation.



Scan series employing N_2/~500 ppm O_2 revealed **many** phases as a function of temperature.

Dial back pO_2



Zoomed 2θ range for simplicity

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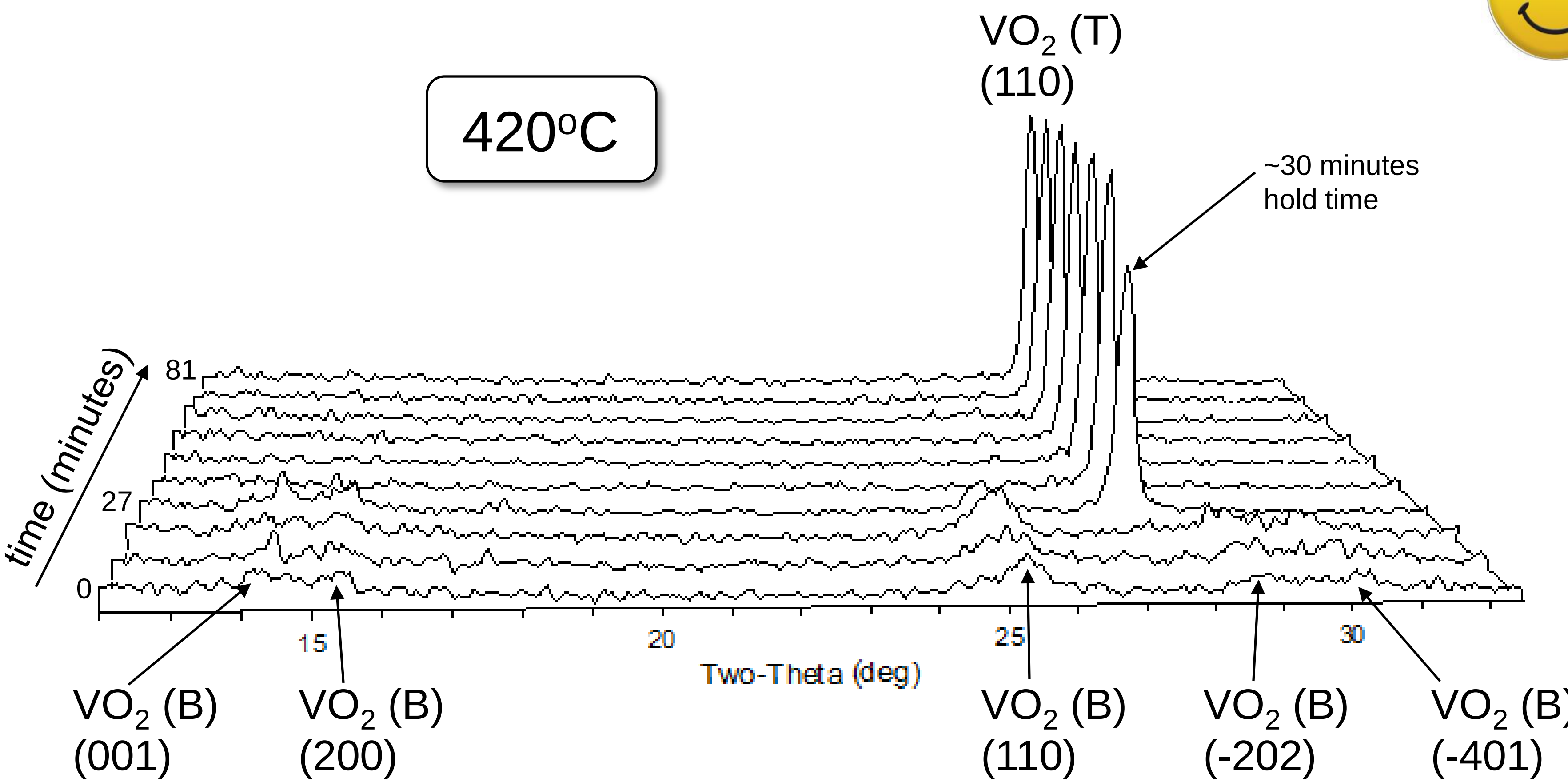
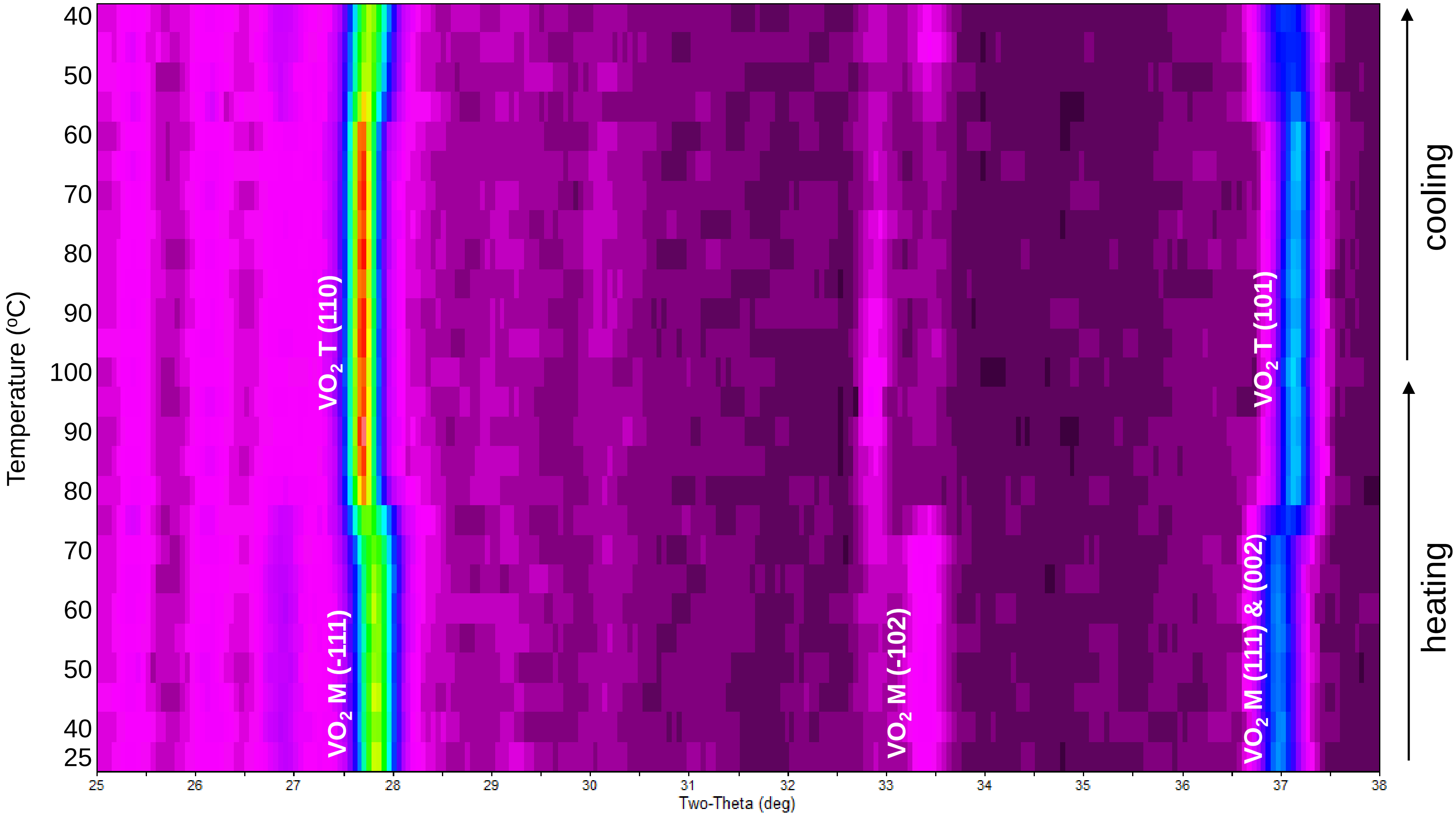
Isothermal hold at 420°C, ($10 < pO_2 < 500$ ppm) revealed fast conversion of VO_2 (B) to VO_2 (T)



Cycling from 25ºC to 100ºC and back down reveals VO_2 (M) to VO_2 (T) phase change with hysteresis.

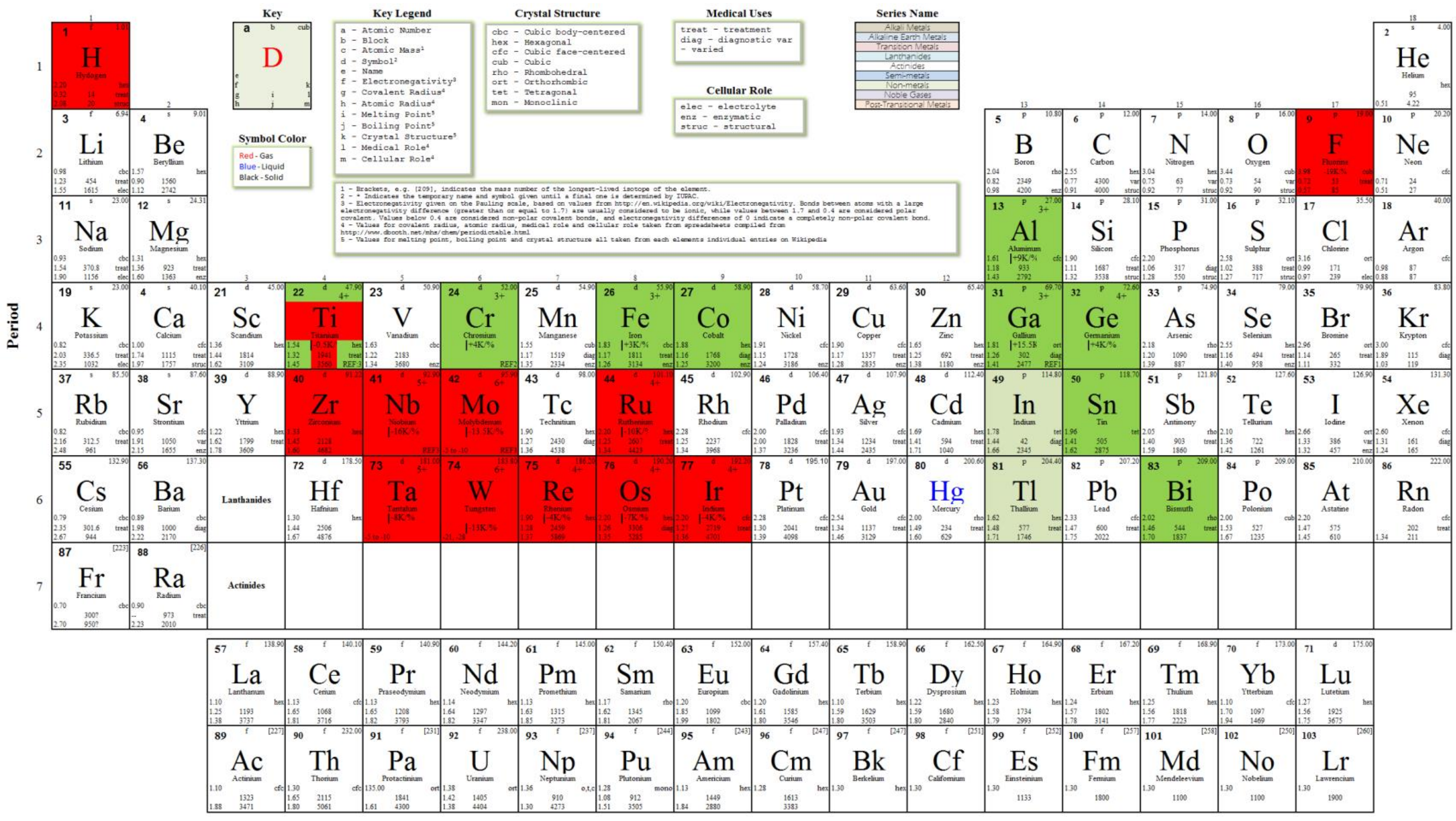


air atmosphere

Next step - doping to shift VO_2 phase transition (monoclinic → tetragonal)

Decrease T_c: large ionic radius, donor dopants

Increase T_c: small ionic radius, acceptor dopants



Summary

- Use of high temperature XRD has aided in the diagnosis of synthesis parameters for VO_2 (T) formation
- Vanadium oxide precursor (VOP) powders require harvesting to prevent recrystallization
- VOP powder shows conversion to the desired tetragonal VO_2 at 420^{o}C in **~30 min** with controlled pO_2.
- Clearly detectable VO_2 (M) to VO_2 (T) phase transition observed in 60 to 80^{o}C range.

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