



62th Annual Denver X-ray Conference

SAND2013-6616C

Westminster, Colorado

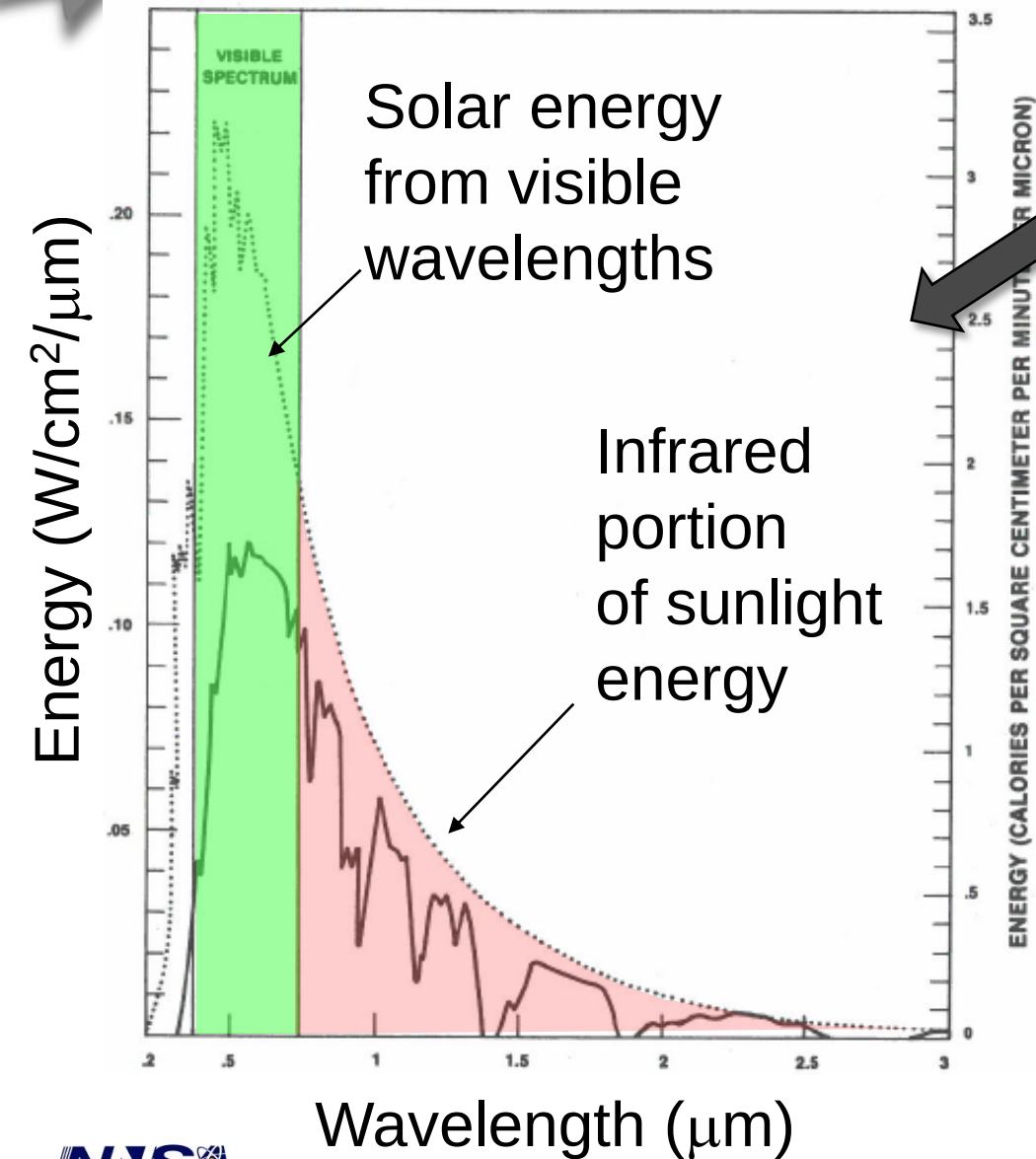
In-situ Monitoring of Vanadium Oxide Formation Using High Temperature XRD

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



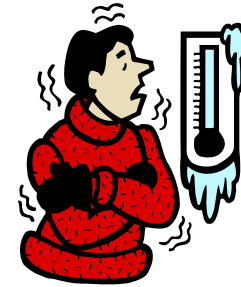
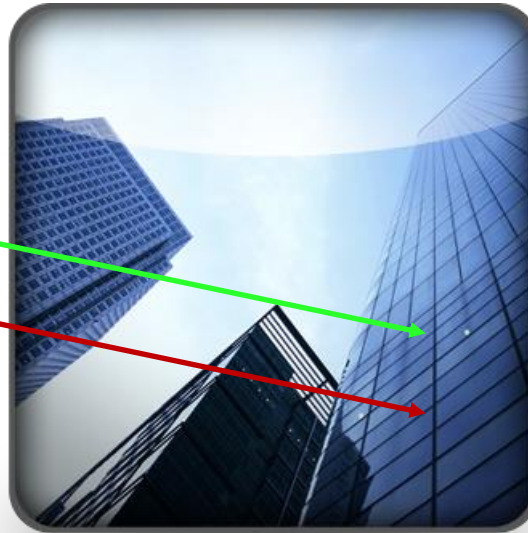
This graph shows the energy distribution of sunlight as a function of wavelength

Goal:

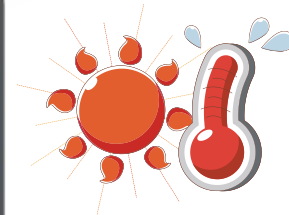
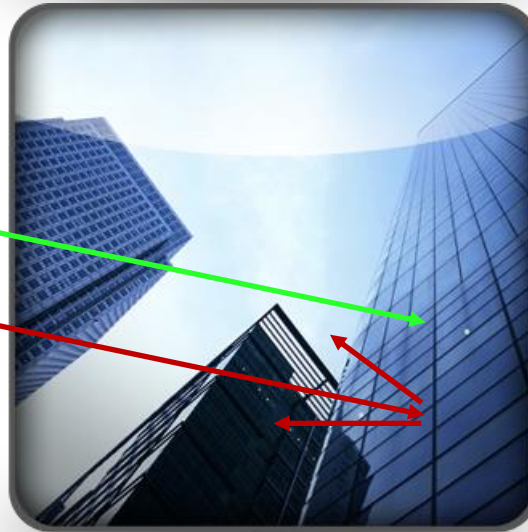
Decouple light (visible) and IR (heat gain) via smart management of optical vs. thermal gain

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)

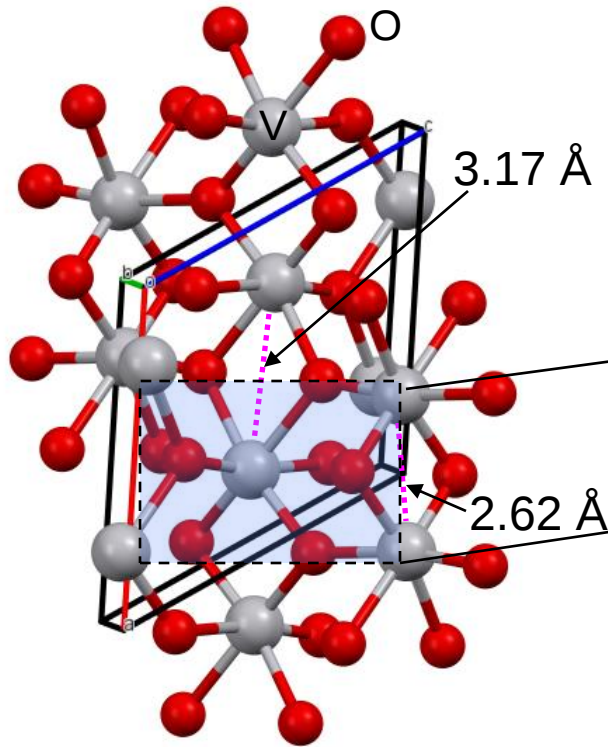


On *hot* days
the window
transmits light
(visible) only
(no IR)

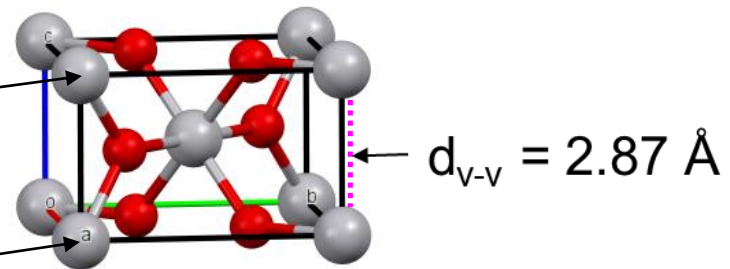


VO₂ demonstrates a significant structural change from monoclinic (M1) to tetragonal (rutile) at ~68°C

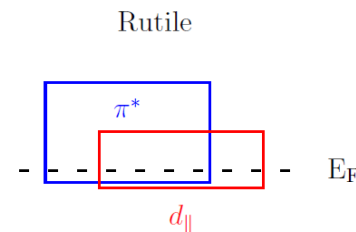
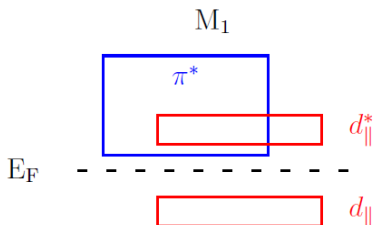
Monoclinic (M1) VO₂



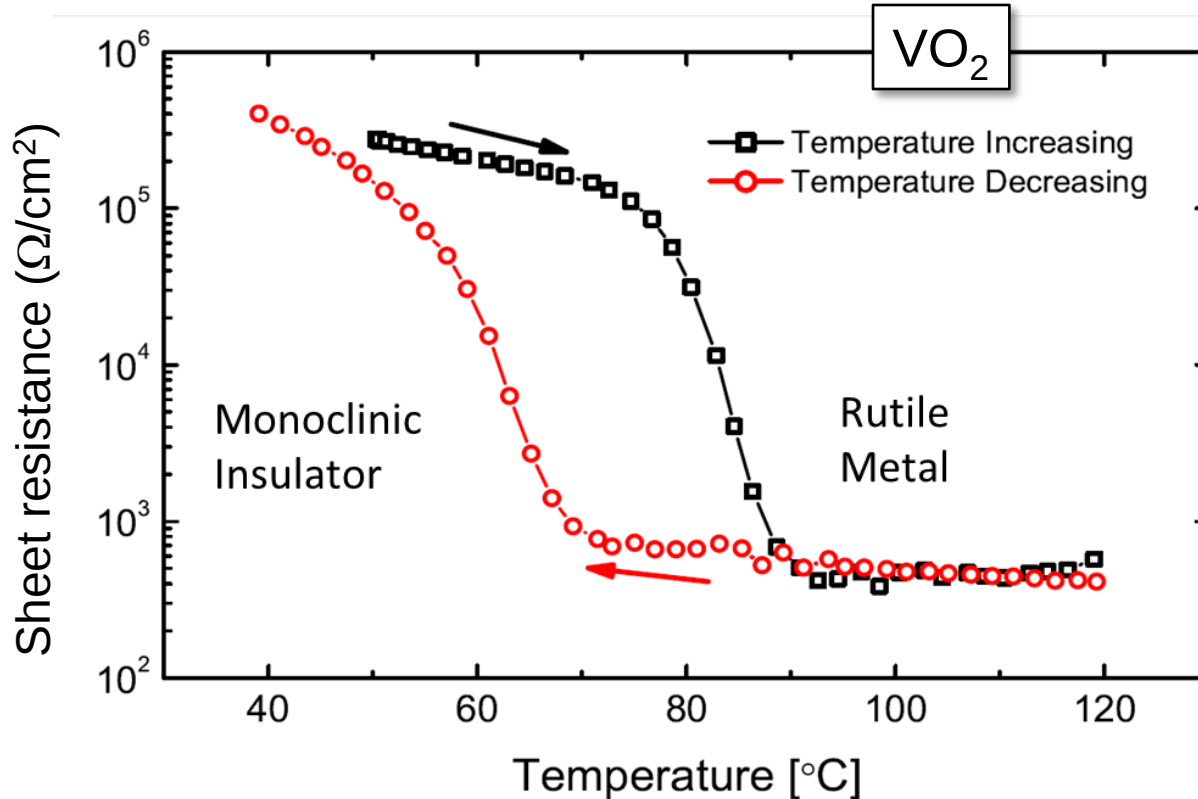
Tetragonal
(Rutile)
VO₂ phase



Major change
in electronic
structure with
phase change



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)

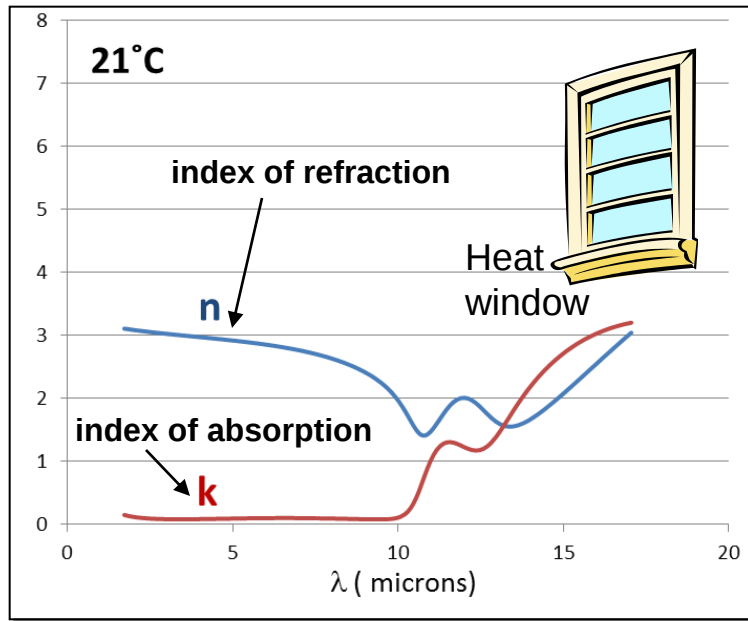
- Hysteresis effect

- 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

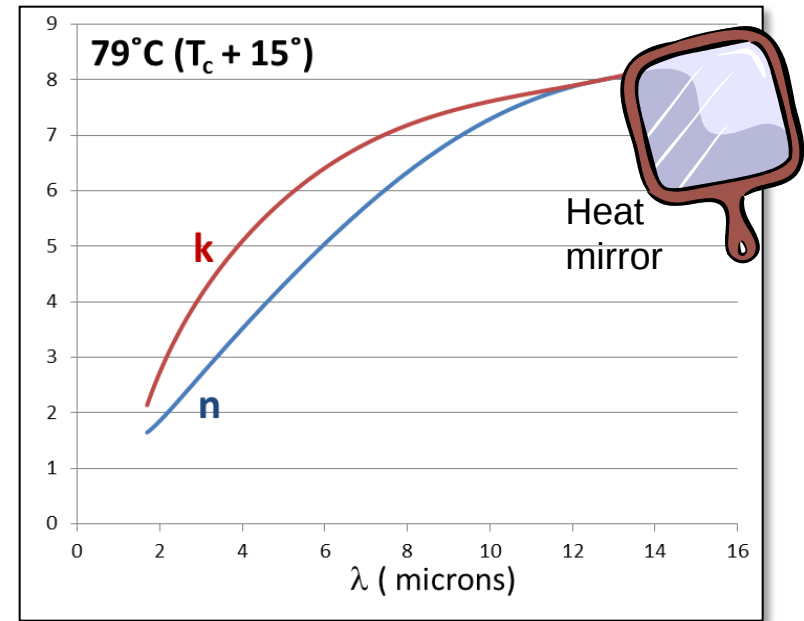
Monoclinic (M1) VO_2

- @ 21°C, $k \sim 0$, IR transparent



Tetragonal (Rutile) VO_2

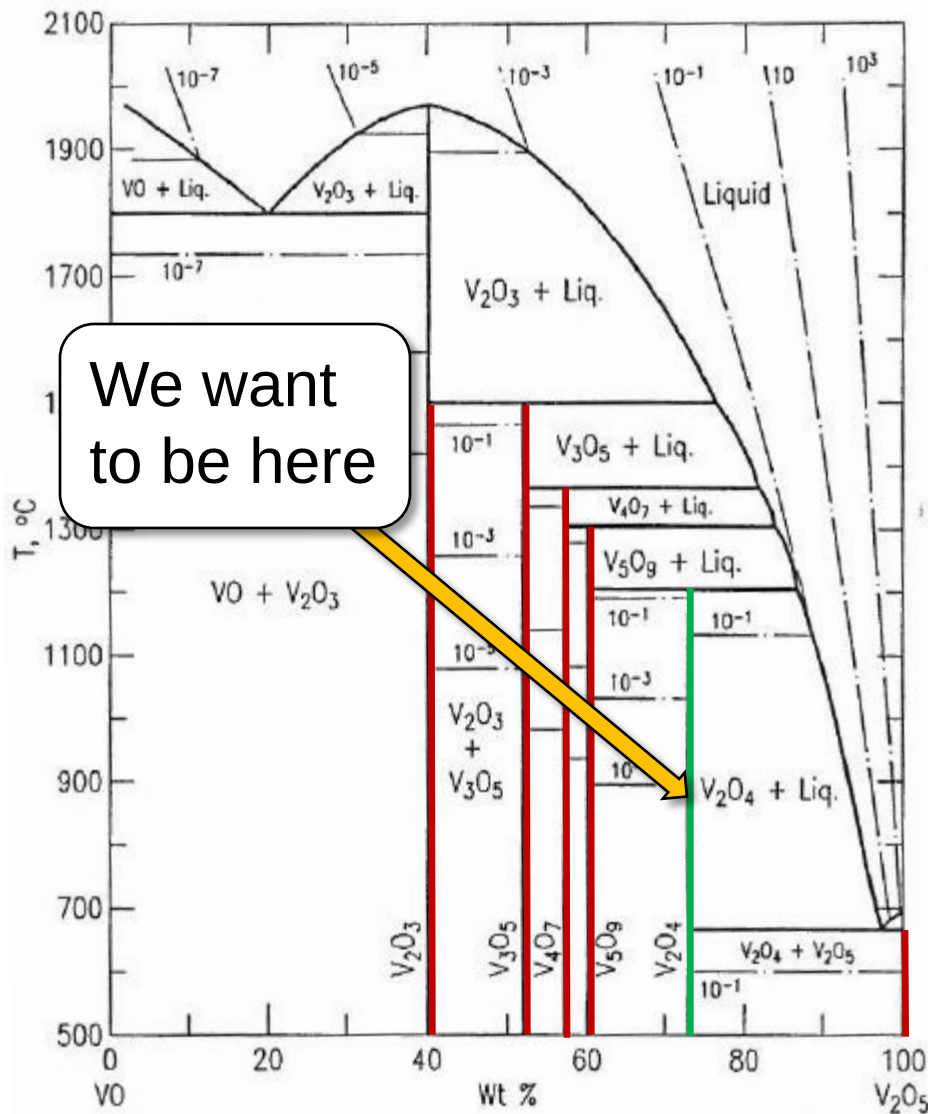
- @ 79°C, $k > n$, IR metallic



Environmentally-switched IR transmission

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

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



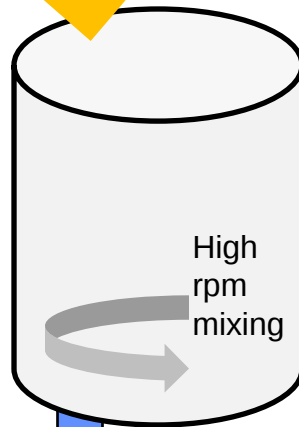
- VO_2 is a line compound
- Vanadium may have five common valence states (0, +2, +3, +4, +5)
- Neighboring compounds have undesirable electrical properties:
 - V_2O_5 - insulator
 - $\text{V}_n\text{O}_{2n-1}$ - no phase change
 - V_2O_3 - linear semiconductor

Need control of oxygen content

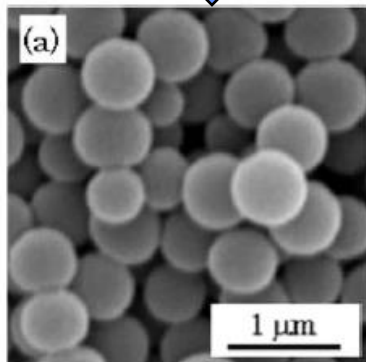
How can we synthesize tetragonal VO_2 at low temperatures with controlled pO_2 ?

In an inert environment....

acetone
pyridine
V-oxyisopropoxide
water



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



Tortured path to VO_2 formation

150°C, 1hr, air

300°C, 1hr,

V_2O_5

400°C, 2hrs, H_2

VO_3

400°C, 2hrs, N_2

VO_2

Does it have to be this hard??

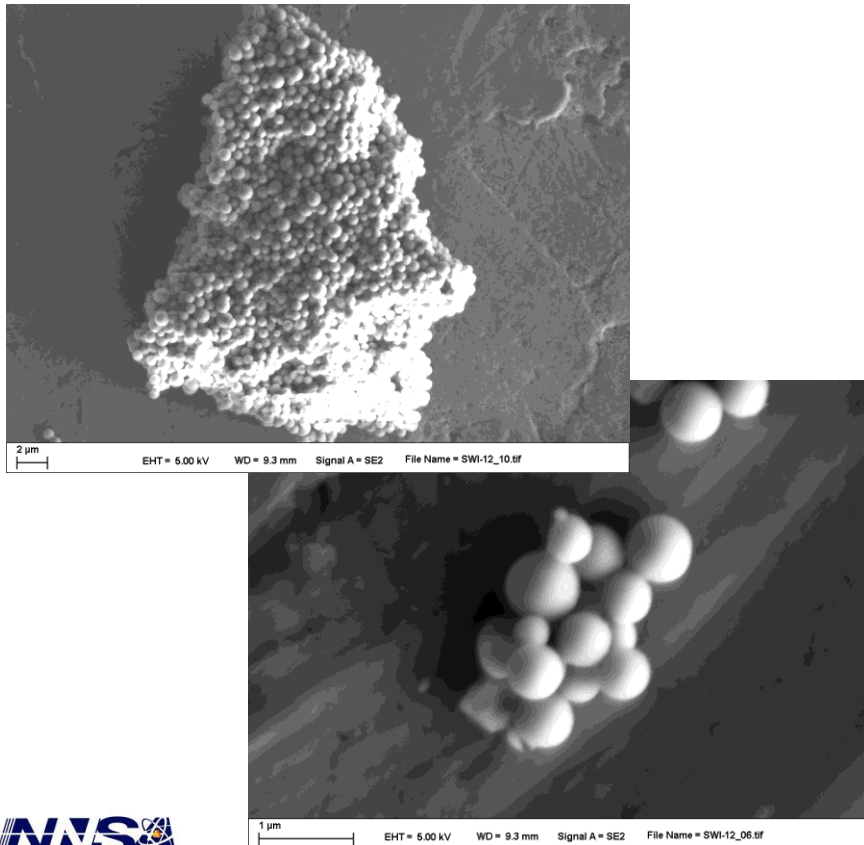
S. Yamamoto, et al. (2009) *Chem. Mater.* **21** 198-200.

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

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

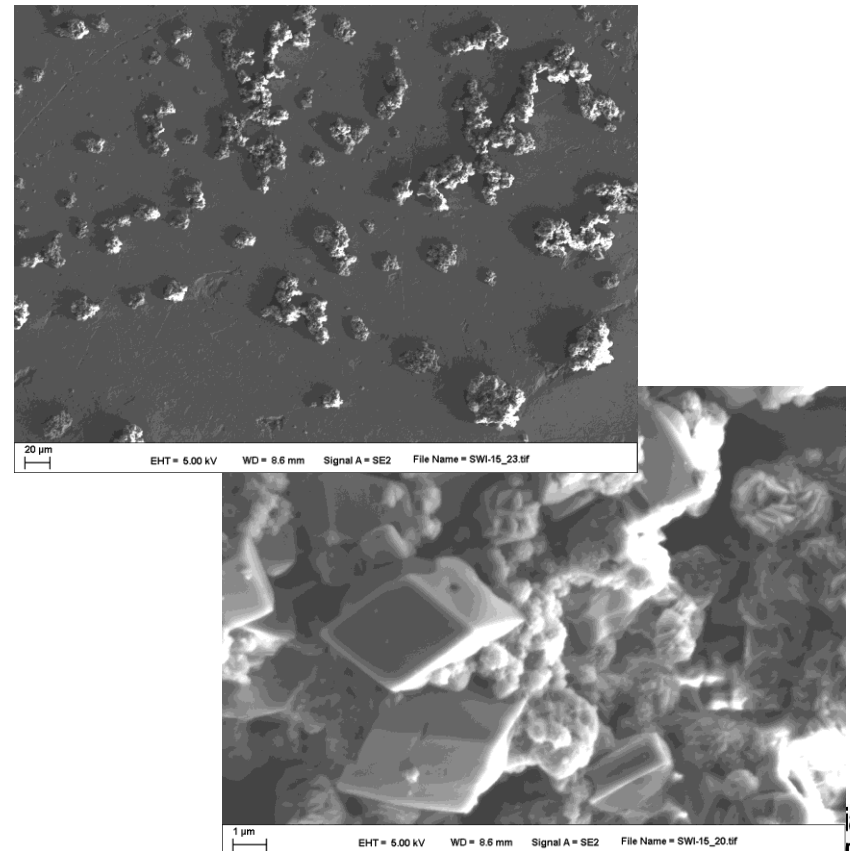
SW1-12 – Collected after 3 hrs aging

- Particles were opaque suspension, but were recovered easily.



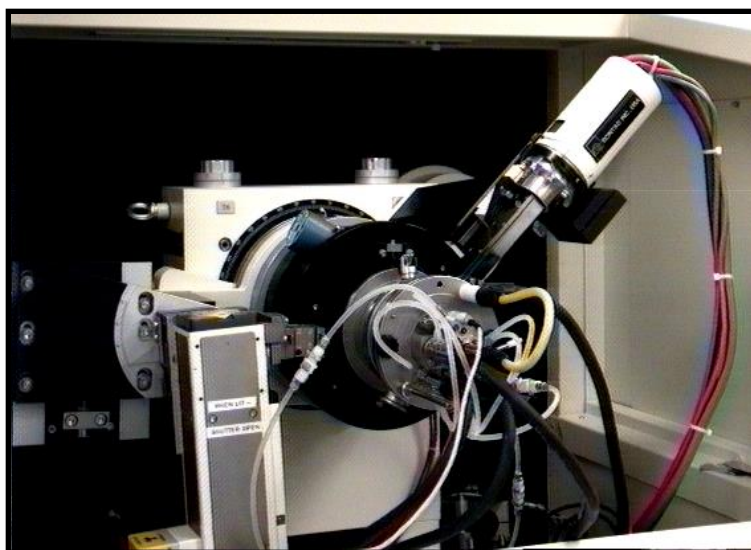
SW1-15 – Collected after 20 hrs aging

- Recrystallization with particle sedimentation



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



Computer control
of temperatures
and XRD scans

Gas flow
control
(mixing)

optional
 O_2 getter

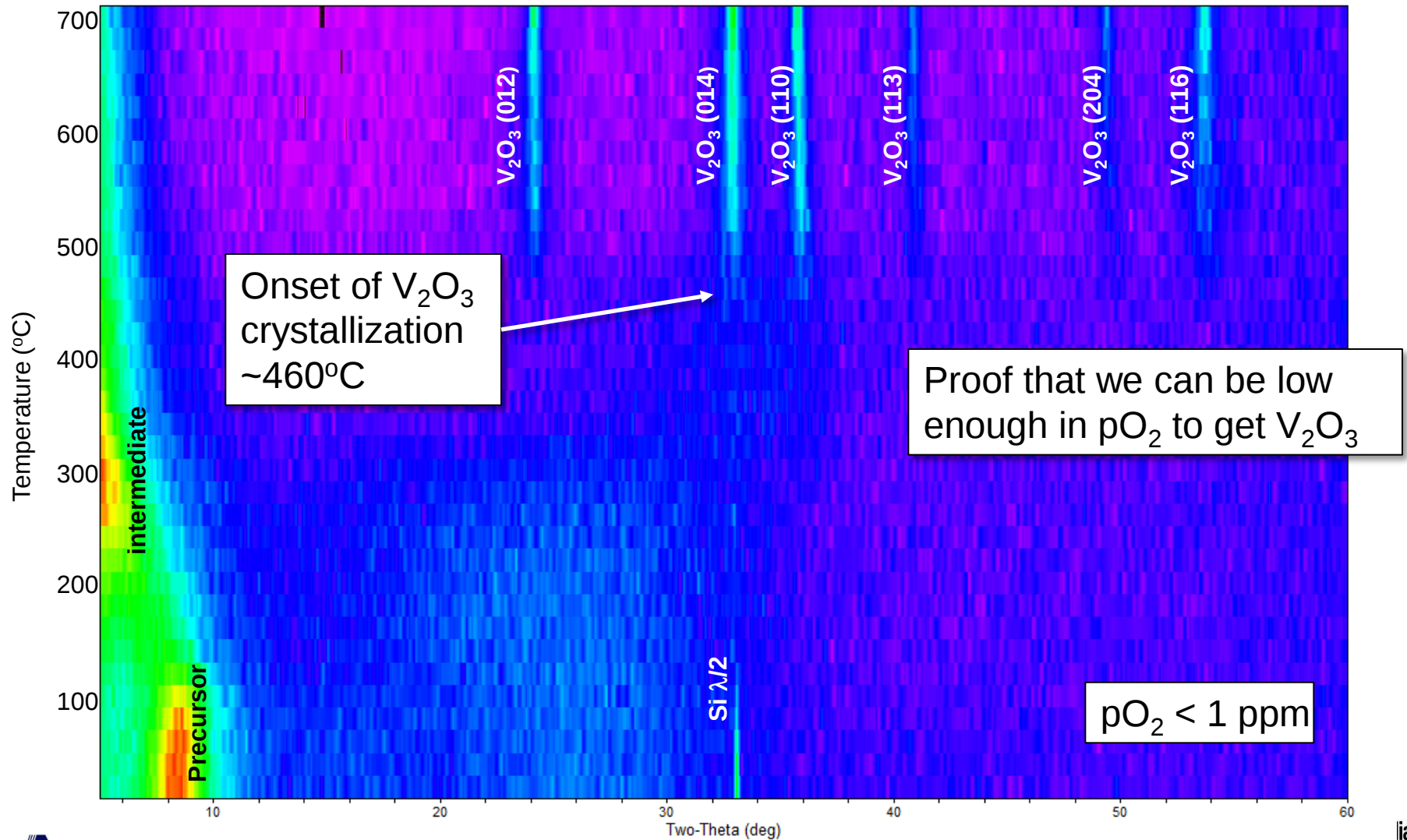
UHP N_2
(or Helium)

N_2 / 500 ppm O_2

pO_2
monitor

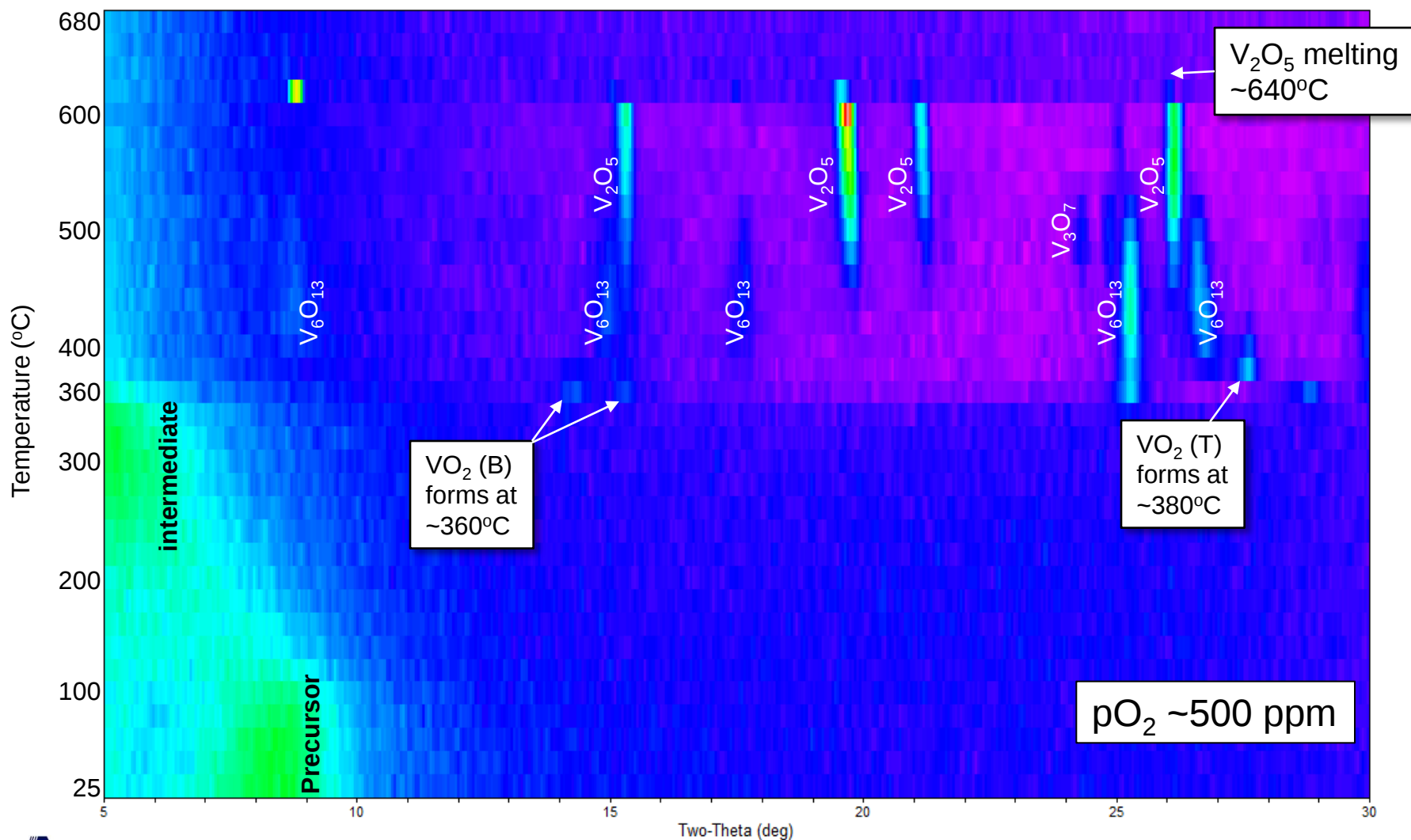
- VOP powder films dispersed on silicon substrates
- Temperature calibration performed using ThEx standards
- pO_2 monitor calibrated using certified mixed gases

First scan series employing gettered-Helium ($< 1\text{ppm O}_2$) revealed only V_2O_3 formation.

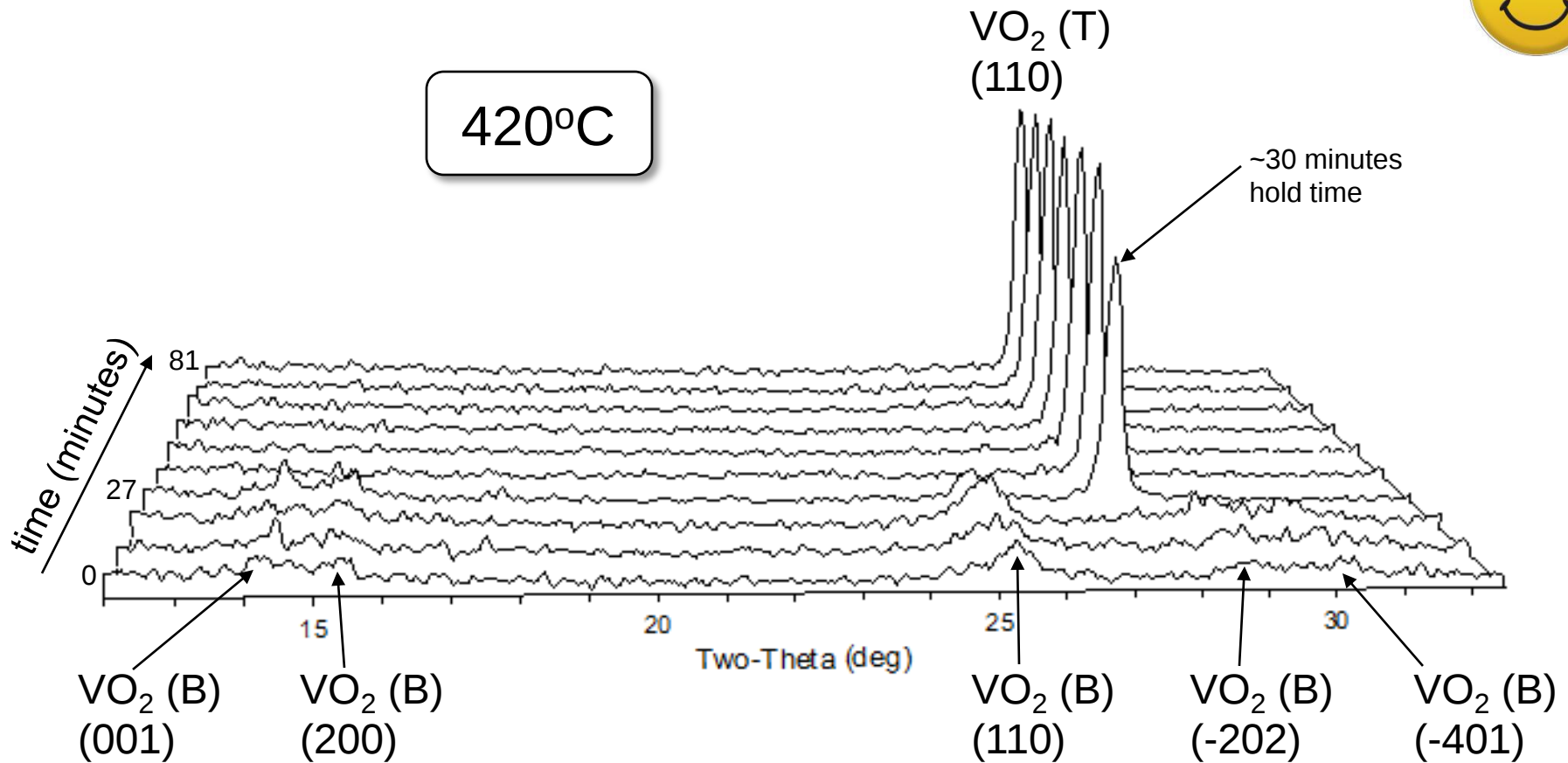


Scan series employing $\text{N}_2/\sim 500 \text{ ppm O}_2$
revealed **many** phases as a function of temperature.

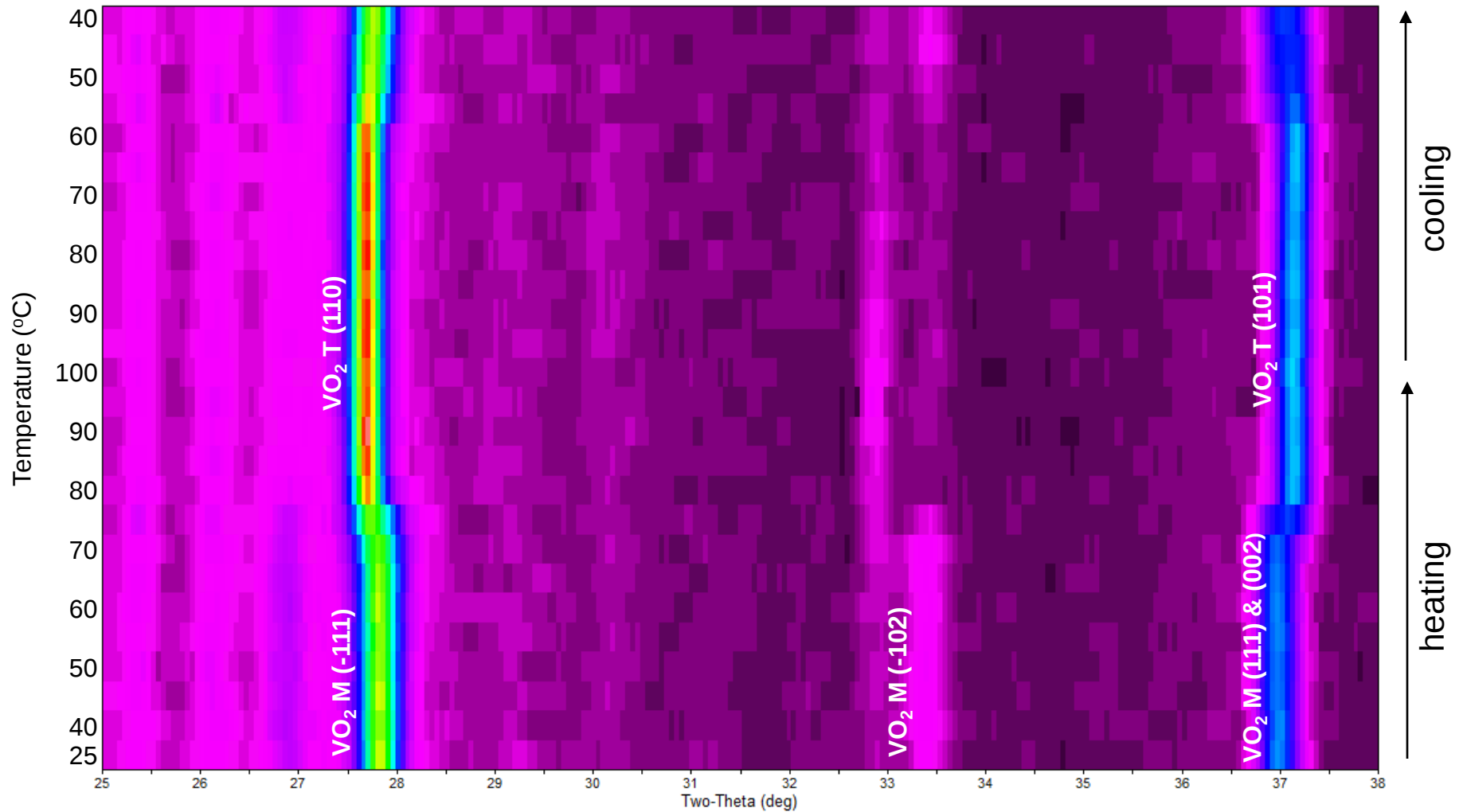
Dial back pO_2



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



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



air atmosphere

Next step - doping to shift VO₂ phase transition (monoclinic → tetragonal)

Decrease T_c: large ionic radius, donor dopants

Increase T_c: small ionic radius, acceptor dopants

Key		Key Legend		Crystal Structure		Medical Uses		Series Name	
H D		a - Atomic Number b - Block c - Atomic Mass¹ d - Symbol¹ e - Name f - Electronegativity² g - Covalent Radius² h - Atomic Radius³ i - Melting Point³ j - Boiling Point³ k - Crystal Structure³ l - Medical Role⁴ m - Cellular Role⁵		chc - Cubic body-centered hex - Hexagonal ofc - Cubic face-centered d - Cubic rho - Rhombohedral ort - Orthorhombic tet - Tetragonal mon - Monoclinic		treat - treatment diag - diagnostic var - varied		Alkali Metals Alkaline Earth Metals Transition Metals Lanthanides Actinides Inner Metals Non-metals Noble Gases Post-Transition Metals	
Symbol Color Red - Gas Blue - Liquid Black - Solid						Cellular Role elec - electrolyte enz - enzymatic struc - structural			
1 - Indicates, e.g. [29], indicates the mass number of the longest-lived isotope of the element. 2 - - Brackets the temporary name and symbol given until a final one is determined by IUPAC. 3 - Electronegativity given on the Pauling scale, based on values from http://en.wikipedia.org/wiki/Electronegativity. Bonds between atoms with a large electronegativity difference (greater than or equal to 1.7) was usually considered to be ionic, while values between 1.7 and 2.4 are considered polar covalent. Values below 0.4 are considered nonpolar covalent bonds, and electronegativity difference of 0 indicates a completely nonpolar covalent bond. 4 - ⁴ Values for covalent radius, atomic radius, medical role and cellular role taken from spreadsheets compiled from http://www.docubox.net/news/news/periodictable.html 5 - ⁵ Values for melting point, boiling point and crystal structure all taken from each elements individual entries on Wikipedia									

1	2																	18				
1	H																	He				
2	Li	Be															B	C	N	O	F	Ne
3	Na	Mg															Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
6	Cs	Ba	Lanthanides		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	Rn				
7	Fr	Ra	Actinides		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			



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°C in **~ 30 min** with controlled $p\text{O}_2$.
- Clearly detectable VO_2 (M) to VO_2 (T) phase transition observed in 60 to 80°C range.



Acknowledgments

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