ON THE GROWTH AND POST-TREATMENT OF NANOSTRUCTURED VANADIUM DIOXIDE (VO_2) PHASES USING HYDROTHERMAL SYNTHESIS

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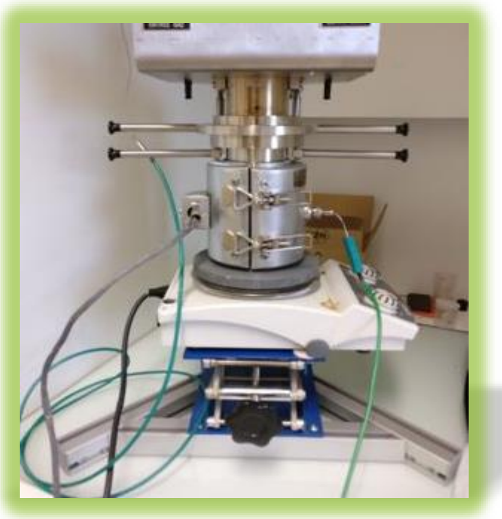
HYDROTHERMAL SYNTHESIS

Reduction of V^{5+} in V^{4+}

NON- ASSISTED



T_{max} = 250°C

PTFE tubes

Synthesis parameters:

control on phase
and
on morphology

- ❑ $[V^{5+}]$
- ❑ T (°C)
- ❑ t (hours)
- ❑ pH
- ❑ Filling %
- ❑ Heating Rate

MICROWAVE-ASSISTED

Quartz tubes

T_{max} = 300°C

Nanostructure

MAIN OBJECTIVES

Development of "beyond CMOS" devices for digital signal processing with high steep slope in the 10mV/decade. One-dimensional (1D) nanostructures, such as nanorods and nanowires, have considerable interest due to both their fundamental research importance and the wide range of potential applications in nanodevices. In that way, synthesizing VO_2 nanowires and probing their intrinsic properties are critical to assess their possible role in new Ultra-Fast electronic devices based on Metal Insulator phase Transition (MIT) in VO_2.

T < 68 °C
Monoclinic M (Insulating)

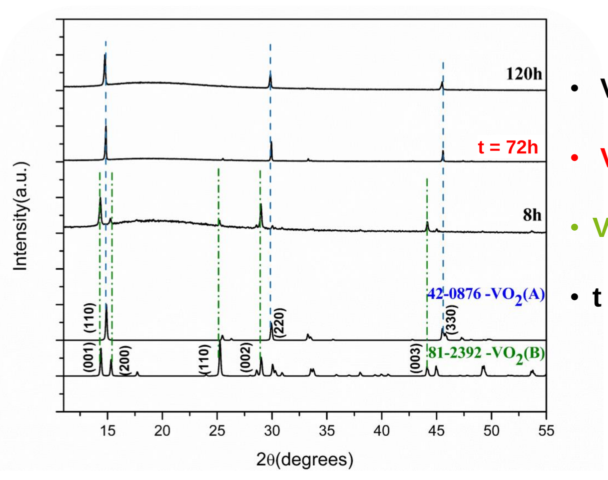
T > 68 °C
Rutile R (Metallic)

Here, we synthesize VO_2 nanowires using Hydrothermal or Microwave Assisted Hydrothermal synthesis. The composition and morphology of as-obtained samples were characterized using XRD, SEM, FT-IR correlated with LCAO-DFT calculations. We also show that it is possible to form $VO_2(M)$ phase by peculiar post-treatments.

NANOSTRUCTURE AND STRUCTURE

NON- ASSISTED

- t > 8h : Nanobelts ⇨ Nanowires



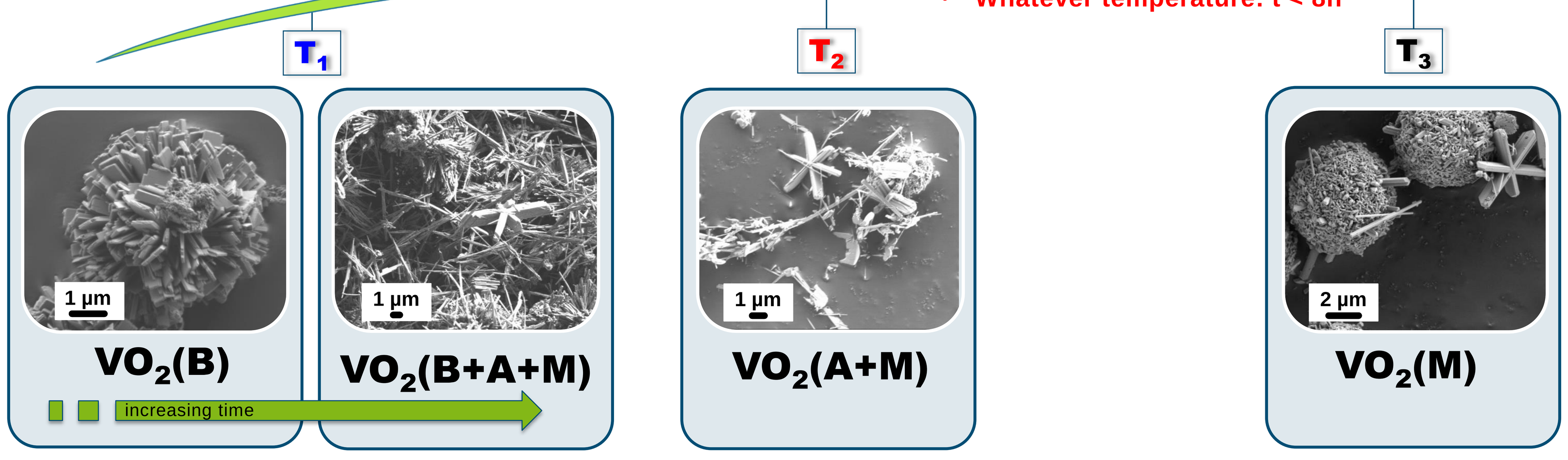
- $VO_2(A)$ starts fading up
- $VO_2(A)$
- $VO_2(B)$
- t < 8h : V_3O_7

- 8h required to produce VO_2
- At least 72h necessary to convert $VO_2(B)$ ⇨ $VO_2(A)$

MICROWAVE (MW)-ASSISTED

increasing temperature

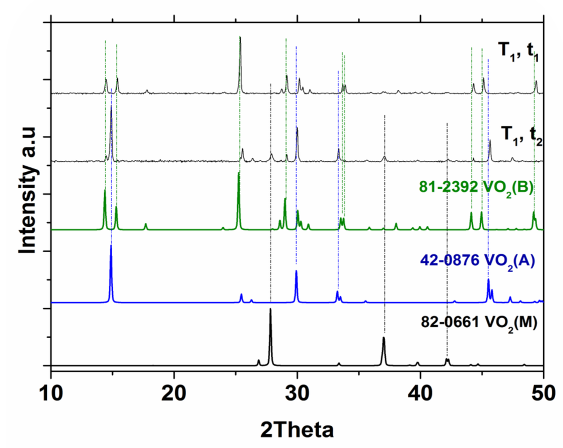
- Whatever temperature: t < 8h



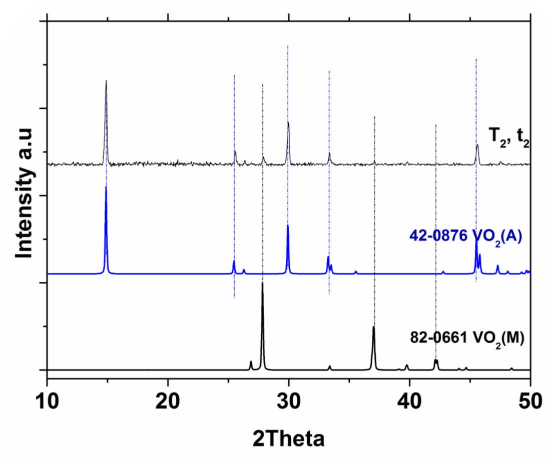
Nanobelts

Nanowires + Snowflakes

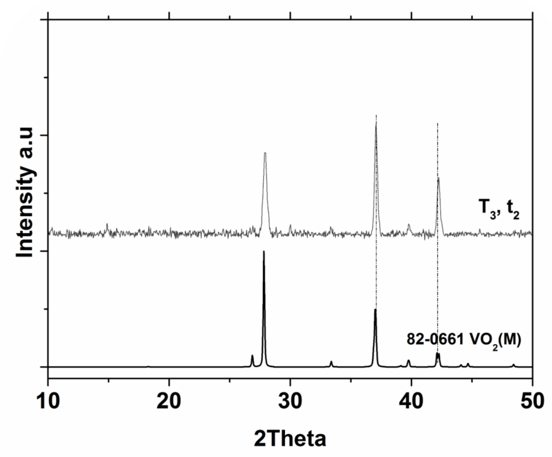
Microspheres + Snowflakes



- For shorter time, $VO_2(A)$ + ε $VO_2(B)$
- For longer time, mixture of $VO_2(B+A+M)$



- For higher temperature, % $VO_2(M)$ ⇗



- Major phase $VO_2(M)$ + ε $VO_2(A)$

FT-IR CHARACTERIZATION

LCAO-DFT CALCULATIONS

3 steps Kohn & Sham - Density Functional Theory (KS-DFT) study:

1. Structure and geometry optimization in **CRYSTAL14** ①
2. Electronic structure calculations: Density Of States (DOS) and band diagrams
3. **Modelling of IR absorption spectrum within the harmonic approximation** ②③ with respect to equilibrium structure

① R. Dovesi, R. Orlando, A. Erba, C. M. Zicovich-Wilson, B. Civalleri, S. Casassa, L. Maschio, M. Ferrabone, M. De La Pierre, P. D'Arco, Y. Noel, M. Causa, M. Rerat, B. Kirtman, *Int. J. Quantum Chem.* 114, 1287 (2014)
② F. Pascale, C.M. Zicovich-Wilson, F. Lopez Gejo, B. Civalleri, R. Orlando, R. Dovesi, *J. Comput. Chem.* 25, 888-897 (2004)
③ C.M. Zicovich-Wilson, F. Pascale, C. Roetti, V.R. Saunders, R. Orlando, R. Dovesi, *J. Comput. Chem.* 25, 1873-1881 (2004)

Mode n°	Calculation ω (cm^{-1})	Assignment
VO_2 (B) *C2/m space group*		
1	466	Bu/Au
2	491	Bu
3	665	Au
VO_2 (A) HT *I4/m space group*		
1	453	Eu
2	596	Au
3	899	Eu
VO_2 (A) LT *P4/ncc space group*		
1	388	A2u
2	508	Eu
3	630	A2u
4	875	Eu
VO_2 (M1) *$P2_1/C$ space group*		
1	486	Au
2	597	Bu/Au
3	775	Bu/Au

***Atomic Orbitals* (AOs) basis set and B3LYP density functional were used**

Crystallographic parameters: results match well with experimental data (<1%)

method validated for the study of IR spectra

EXPERIMENTAL

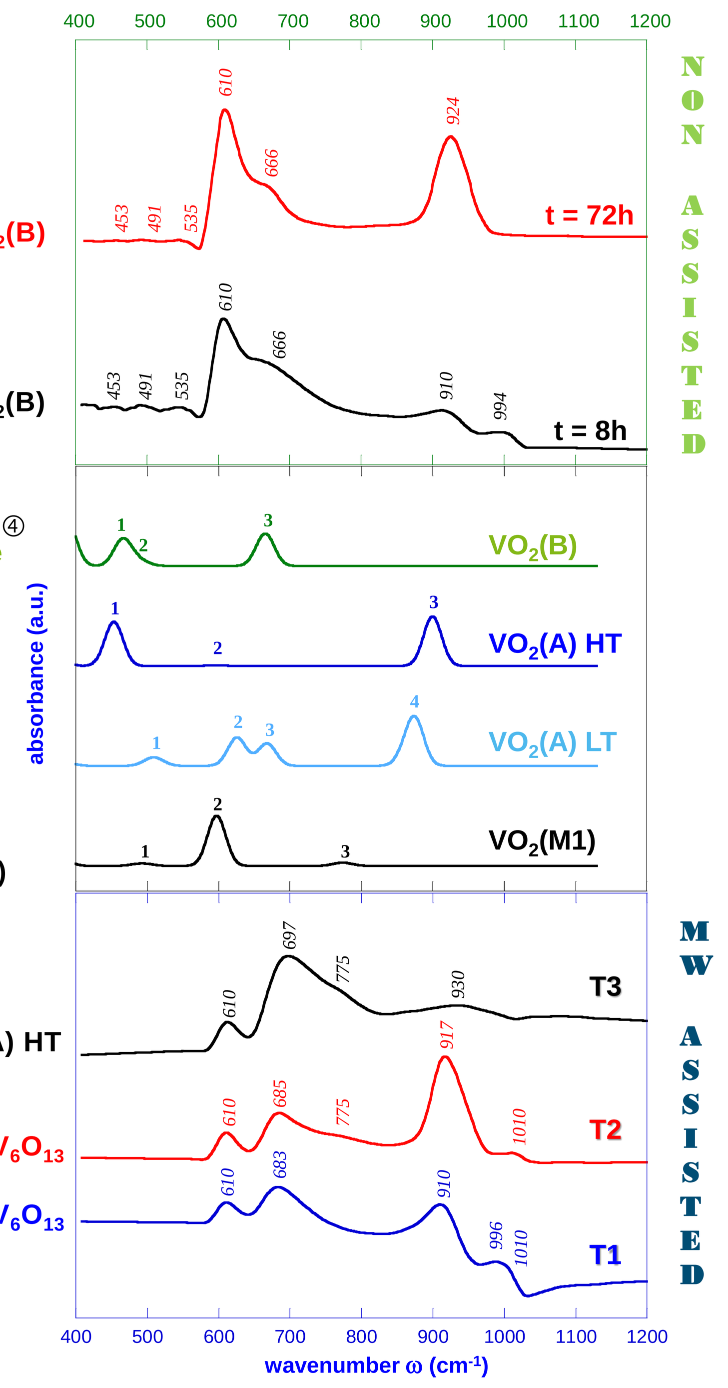
ATR mode

- $VO_2(A)$ LT + $VO_2(A)$ HT + $VO_2(B)$
- $VO_2(A)$ LT + $VO_2(A)$ HT + ε $VO_2(B)$
- Problem for $VO_2(B)$ calculated spectrum, indeed experimental results in agreement with literature ④

Compound	Wavenumbers (cm^{-1})
V_6O_{13}	1010, 995, 950, 895, 861, 770, 543
$VO_2(B)$	997, 931, 875, 771, 534

④ J.-C. Valmalette, J.-R. Gavarri, *Mater. Sci. Eng.* **B54** (1998) 168-173

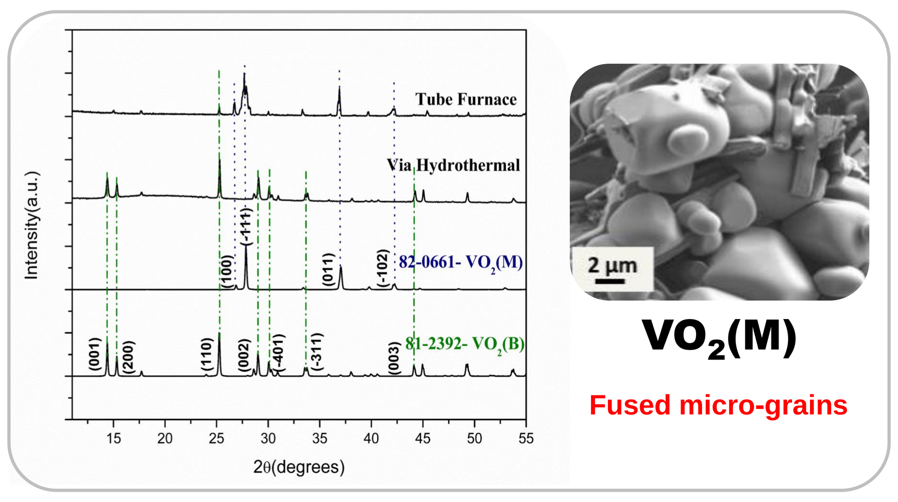
- $VO_2(M1)$ simulated spectrum probably shifted to lower ω due to temperature (0K)
- $VO_2(M)$ + $VO_2(A)$ HT
- $VO_2(A)$ HT + $VO_2(M)$ + V_6O_{13}
- $VO_2(A)$ HT + $VO_2(B)$ + V_6O_{13}



- Theory allows to assign vibrational modes
- LCAO-DFT calculations match with measurements
- Absorption bands of various VO_2 phases in agreement with phases detected in DRX

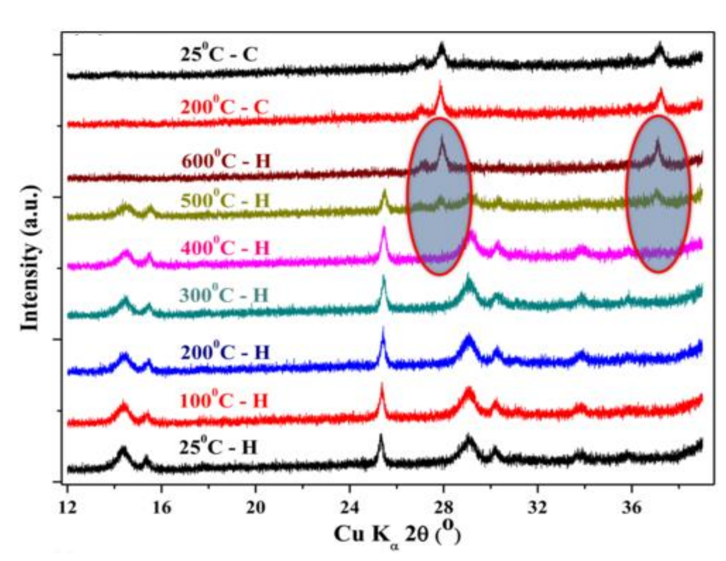
PHASE CONVERSION

ANNEALING FOR 2h AT 700°C, Ar FLOW



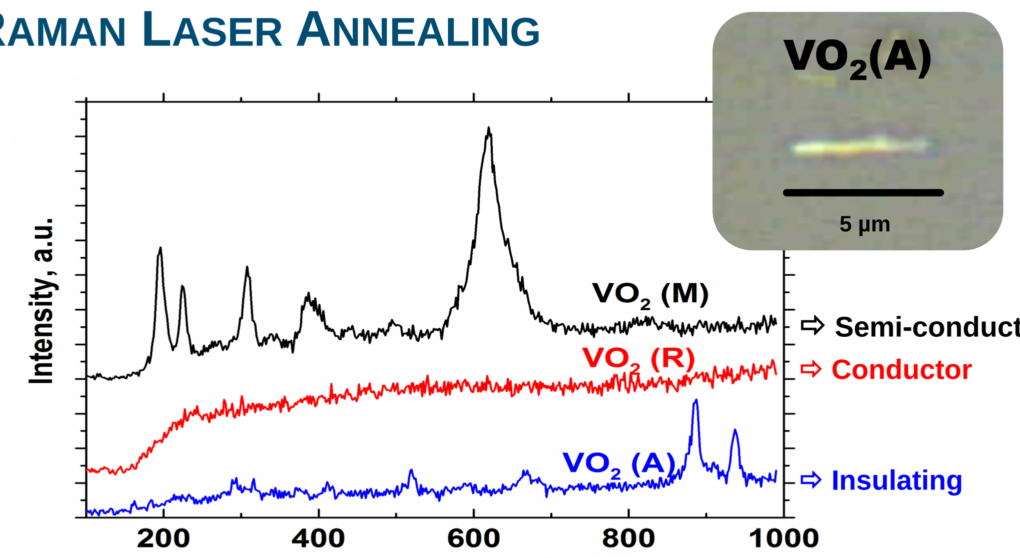
- Incomplete conversion of $VO_2(B)$ ⇨ $VO_2(M)$

IN SITU Ar FLOW XRD ⑤



⑤ S. R. Popuri, M. Miclau, A. Artemenko, C. Labrugere, A. Villesuzanne, and M. Pollet, *Inorg. Chem* **52(9)**, 4780–4785 (2013)

RAMAN LASER ANNEALING



- Phase transition sequence:

$VO_2(A)$
⇩
$VO_2(R)$
⇳
$VO_2(M)$

CONCLUSION & OUTLOOK

- Influence of hydrothermal synthesis parameters was evaluated:

NON-ASSISTED:
- The lower temperature to form $VO_2(B)$ is 180°C
- Time has a very important role on the formation of $VO_2(A)$: t > 72h
- Appropriate morphology for integration in electronic device

MICROWAVE-ASSISTED:
- Faster way to form VO_2 nanostructures: t < 8h
- Possibility to produce $VO_2(M)$
- Incompatible $VO_2(M)$ morphology with integration in electronic devices

- Investigation was supported by vibrational calculations: theory allows to assign vibrational modes of different VO_2 phases and LCAO-DFT calculations match with experimental spectra. This work should be optimized
- Further work should be conducted to form $VO_2(M)$ from $VO_2(B)$ and $VO_2(A)$ using this new versatile route

UMR 8182

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