

# Laser-induced sintering of Titanium niobate films from powders of $\text{TiO}_2$ and $\text{Nb}_2\text{O}_5$ for energy applications.

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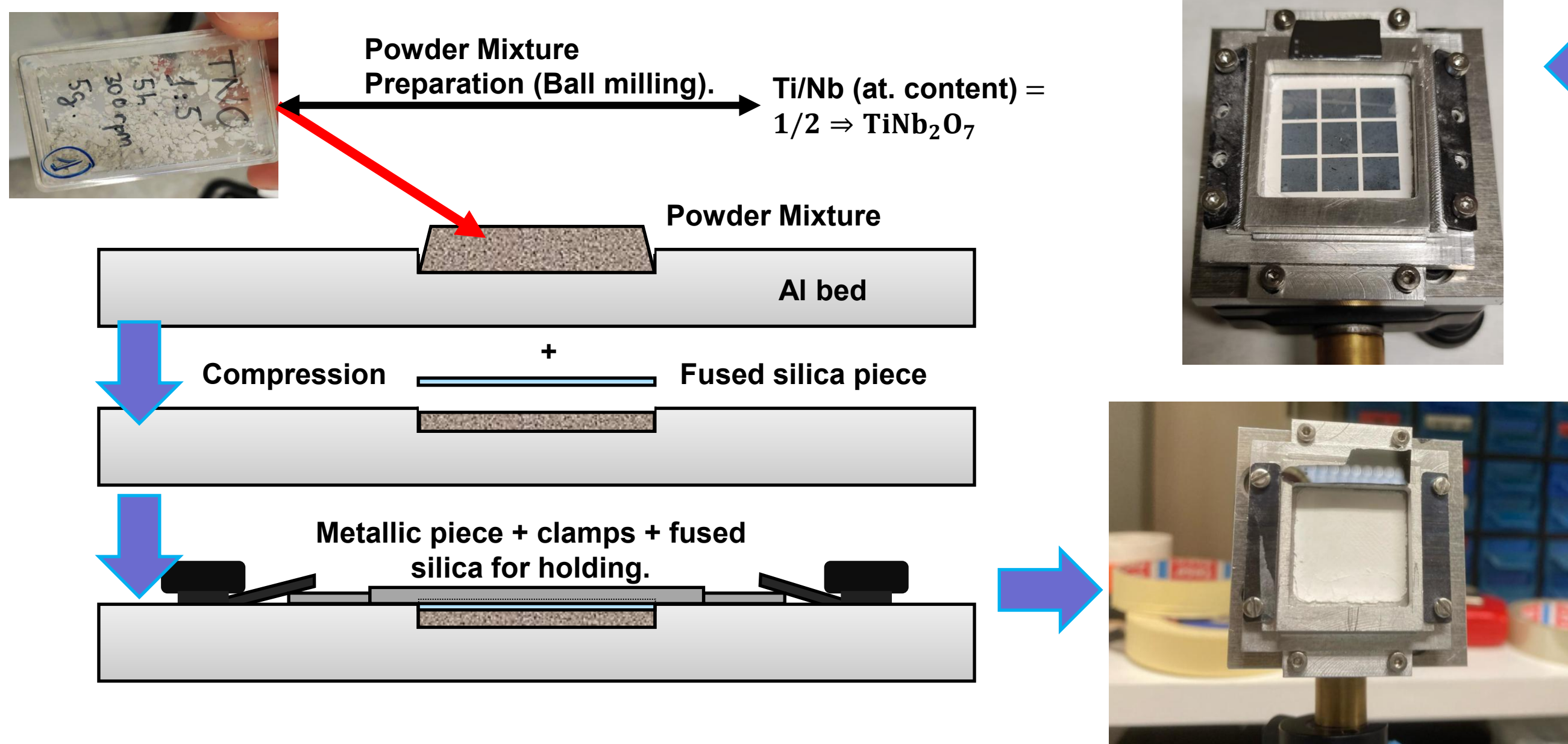
## Introduction

Titanium niobates (TNOs) are a family of materials with diverse stoichiometries and crystalline structures, which turn them into a complex-system that requires highly controlled treatments in order to achieve a proper production. The most stable TNO-structure is  $\text{TiNb}_2\text{O}_7$ , which is an oxide that have already proven its excellent performance in emergent applications, specifically for energy storage in Li-ion batteries [1,2].

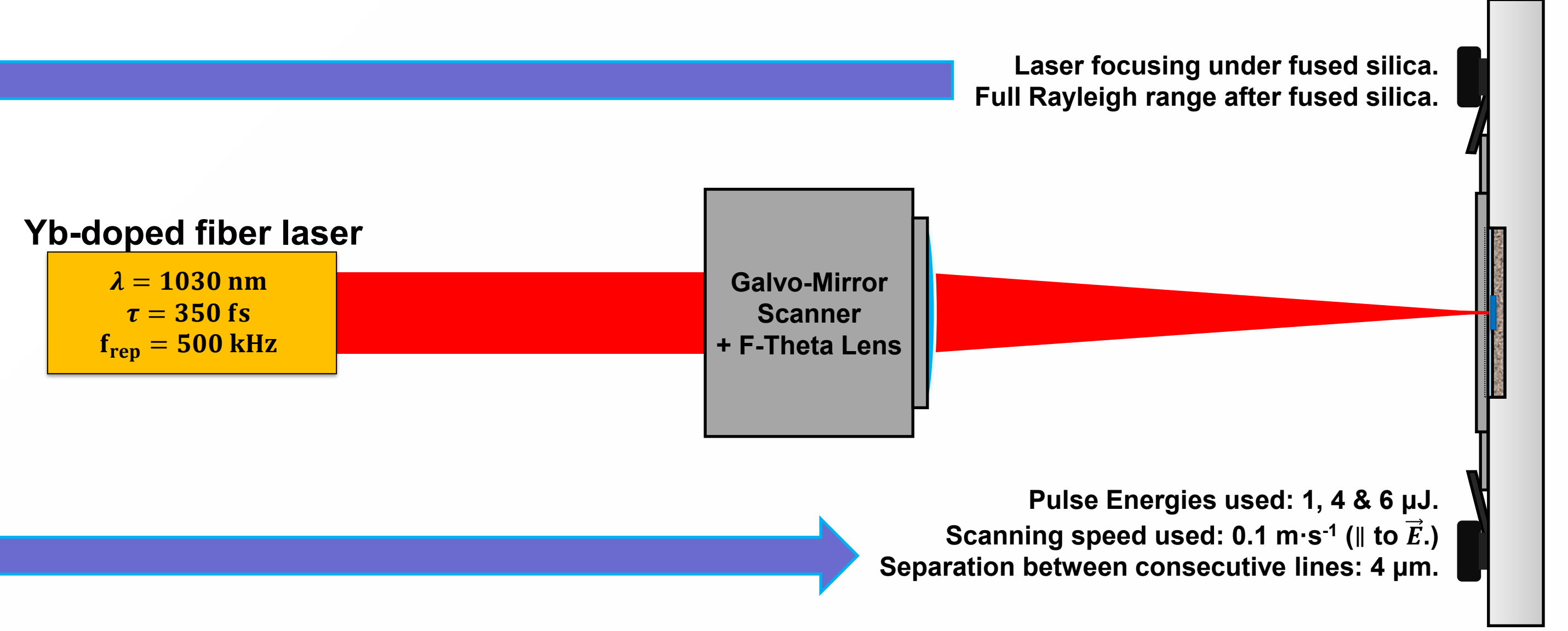
Recently, the feasibility of inducing the sintering of compact  $\text{Nb}_2\text{O}_5$  films by fs-laser powder bed fusion while improving their electrical conductivity several orders of magnitude has been demonstrated [3]. For the case of  $\text{Nb}_2\text{O}_5$ , microstructure and anisotropy of the layers were controlled with fs-laser conditions, triggering the stabilisation of a monoclinic oxygen-deficient phase (thus, much more conductive and better for energy storage than stoichiometric niobium oxide). In this work, a similar approach has been followed in order to induce the sintering of compact TNO films starting from a mixture of  $\text{TiO}_2$  and  $\text{Nb}_2\text{O}_5$  powders. A characterization of the sintered films has been performed in order to understand which phases have been induced by fs-laser irradiation of the powders, leading to different scenarios depending on how do we change the laser pulse energy.

[1] Y. Zhang, et al., *Electrochim. Acta* **330**, 135299 (2020). [2] X. Wu, et al., *Electrochem. Commun.* **25**, 39-42 (2012). [3] B. Sotillo, et al., *Mater. Des.* **224**, 111346 (2022).

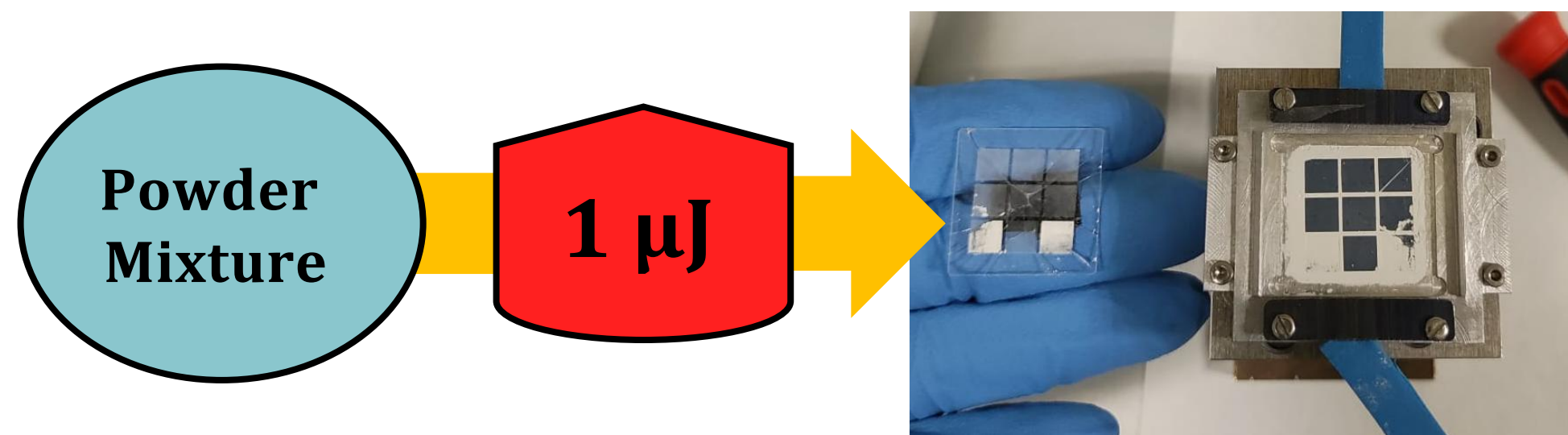
## Powder Preparation



## Experimental Irradiation Setup



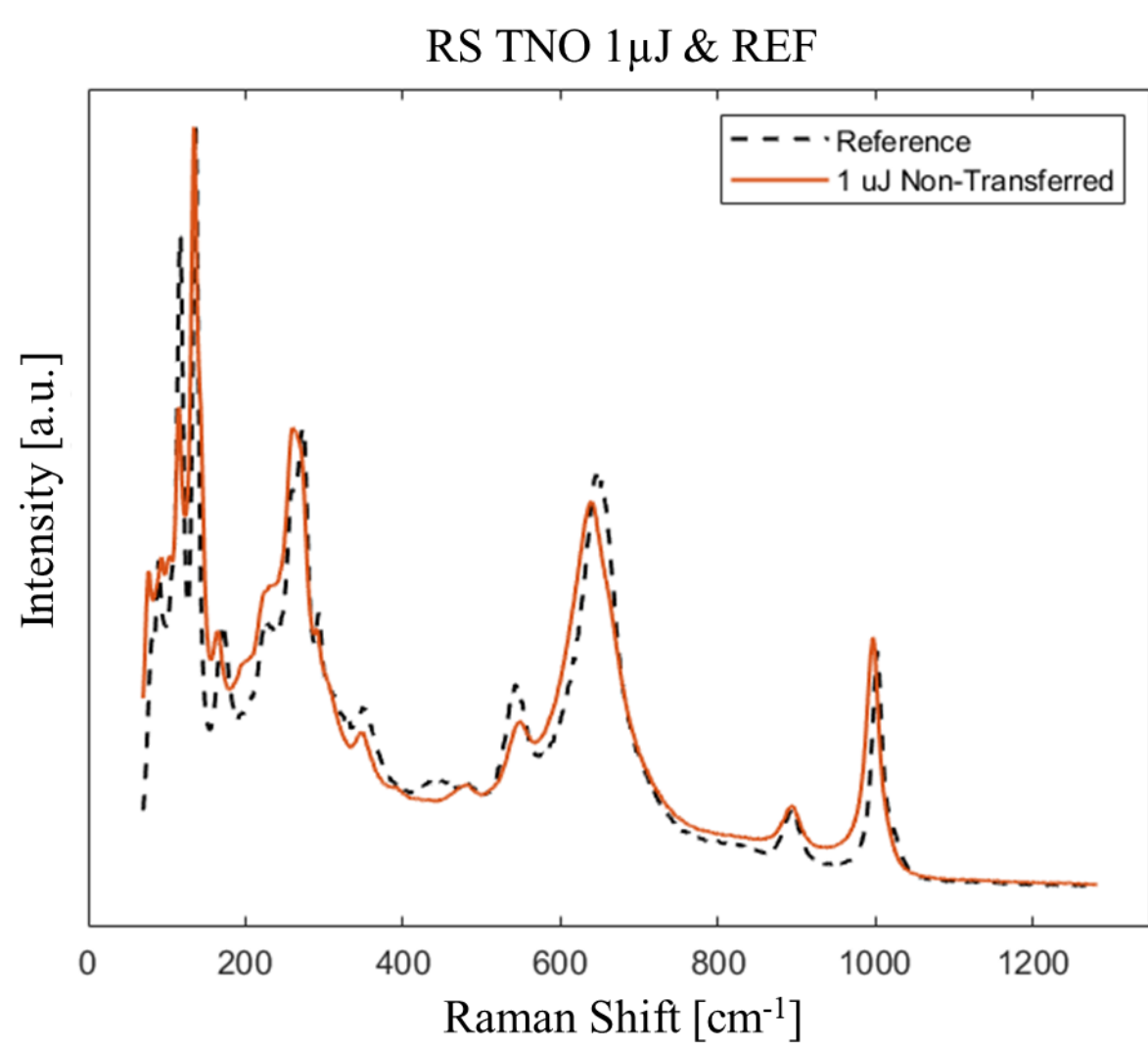
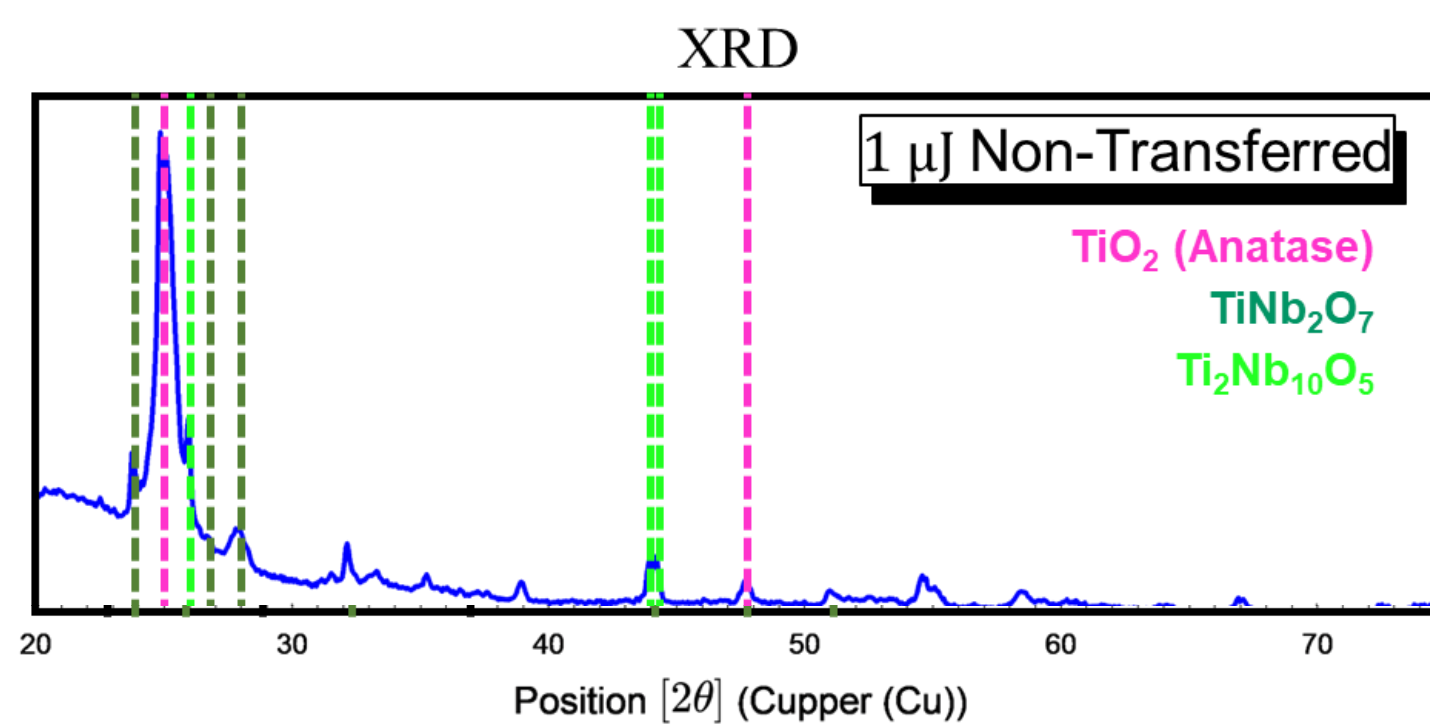
### NON FILM TRANSFER SCENARIO



- Sintered material remains on the top of the powder mixture after removing the fused silica glass.
- Samples can be recovered from the powder easily, but they are fragile and difficult to handle.
  - Excess powder sticks to the films and cannot be completely cleaned.

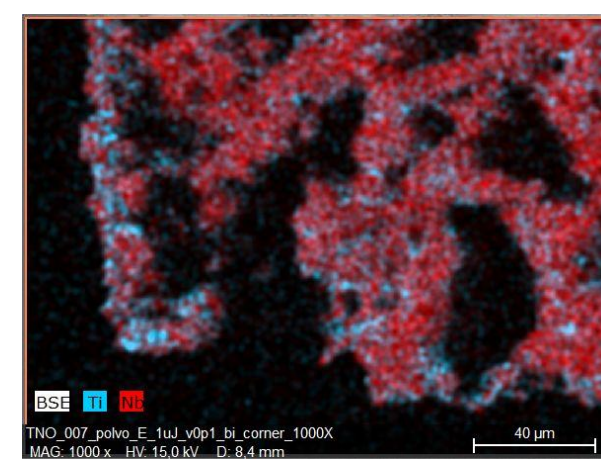
### X-Ray Diffraction

- XRD of non-transferred film show several TNO reflections:  $\text{TiNb}_2\text{O}_7$  (1:2 ratio) and  $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$  (1:5 ratio).
- The intense (101)  $\text{TiO}_2$  reflection is due to the non-transformed  $\text{TiO}_2$ , which segregates.

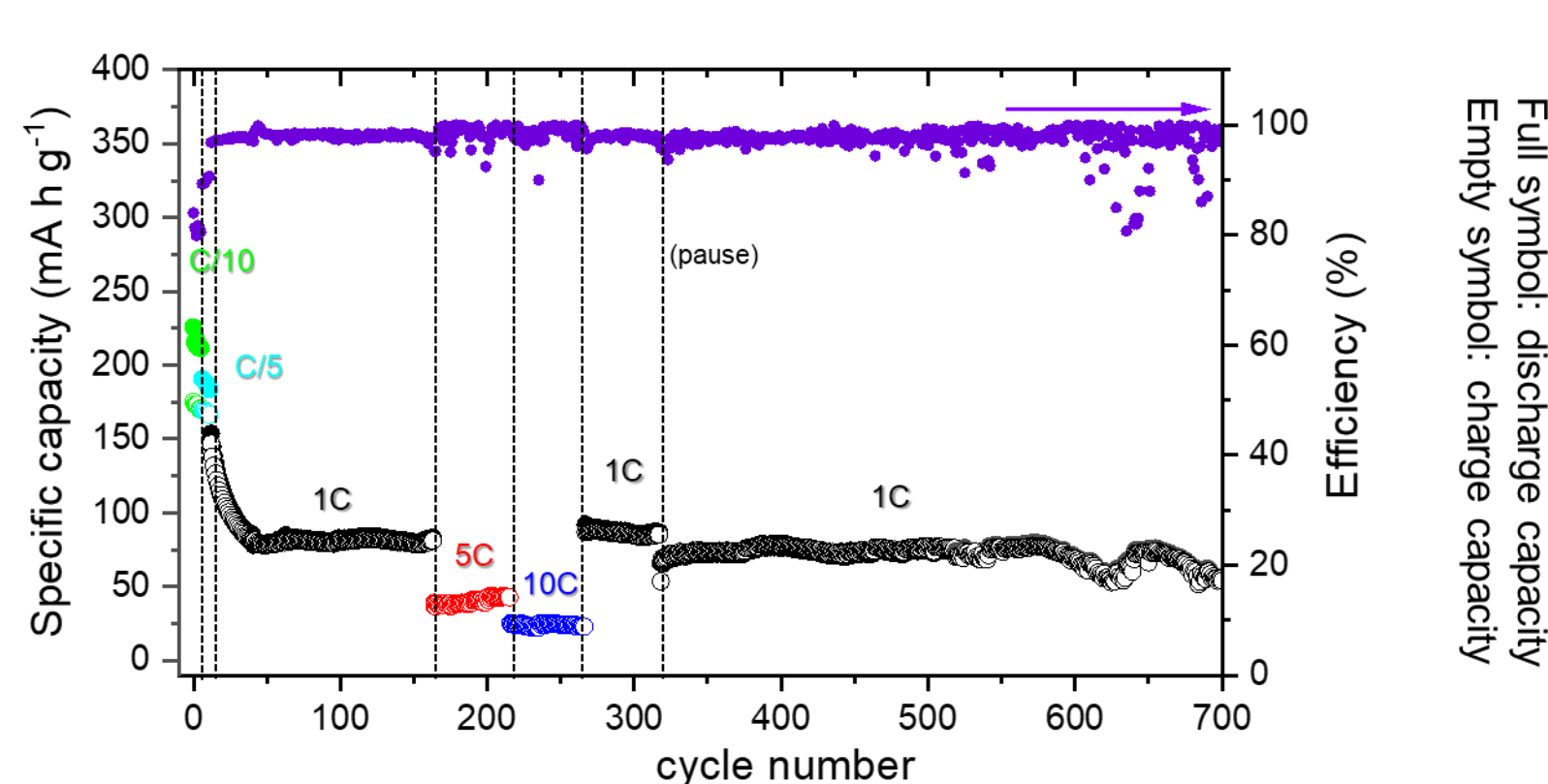
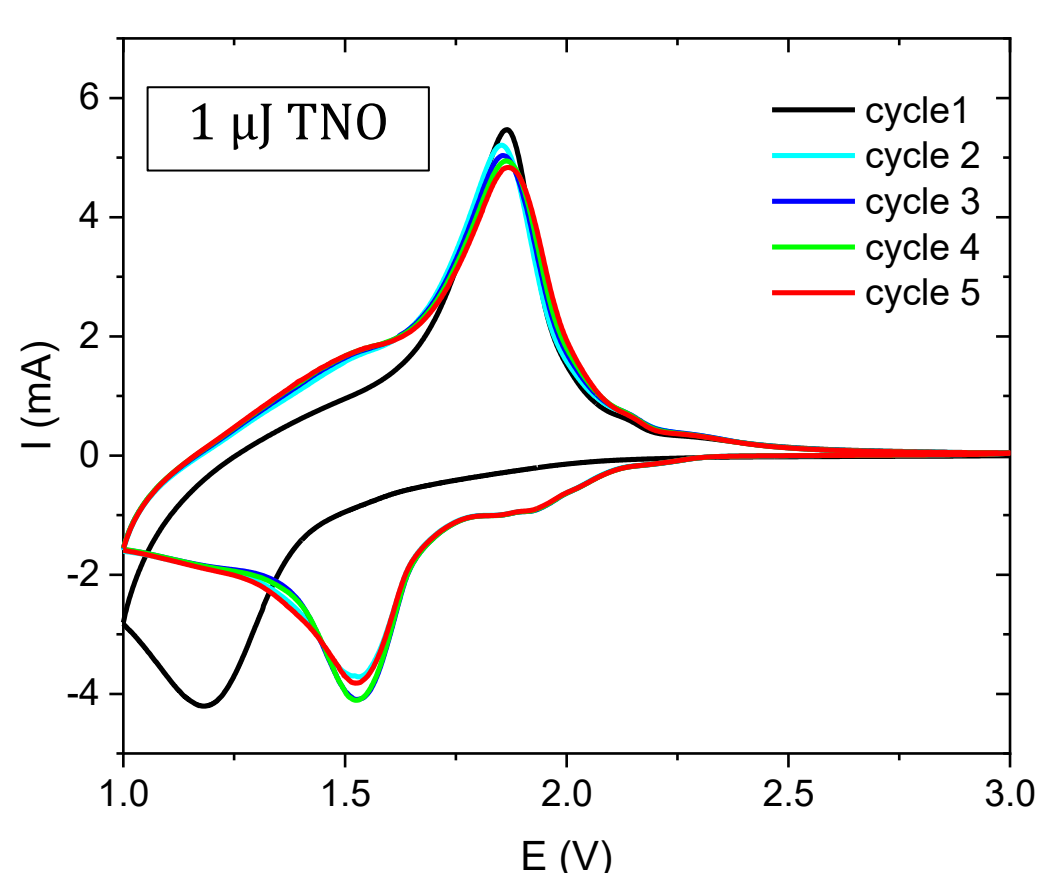


### Raman Spectroscopy

- Top-view RS of non-transferred 1 μJ films show an intense TNO12 behaviour.
- The presence of  $\text{TiO}_2$  is not obvious in the spectrum because it is not homogeneously segregated.



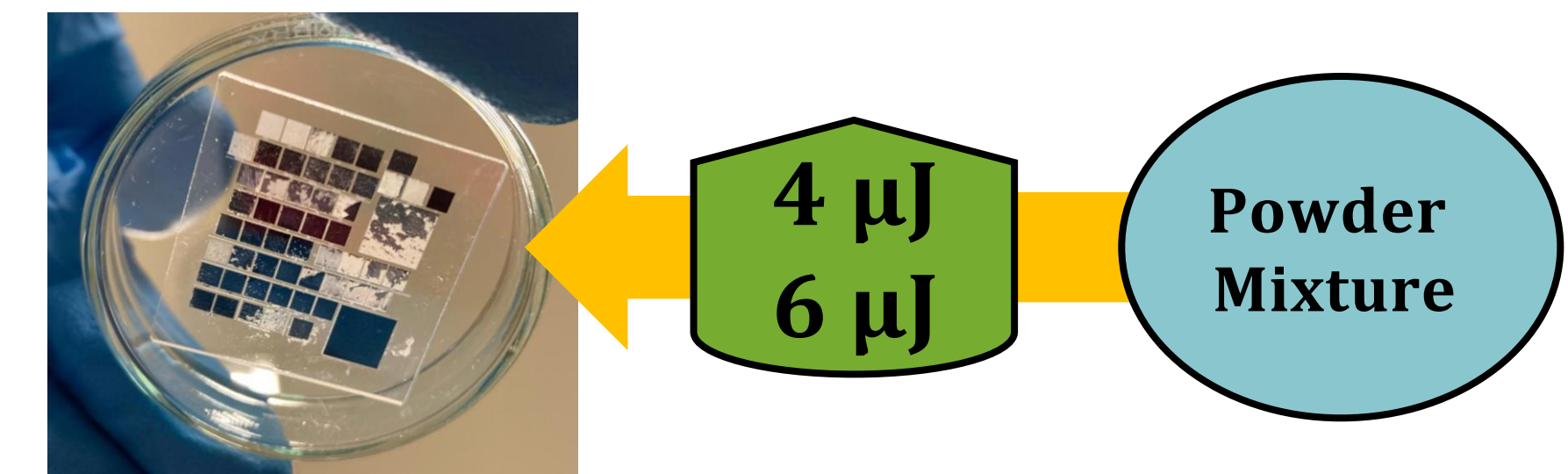
### Sintered films in LIBs



- The material is working.
- Usual redox-V for Nb and Ti are displaced with respect to the measured voltametric cycles.
- Presence of possible  $\text{TiO}_2$ -TNO composite.

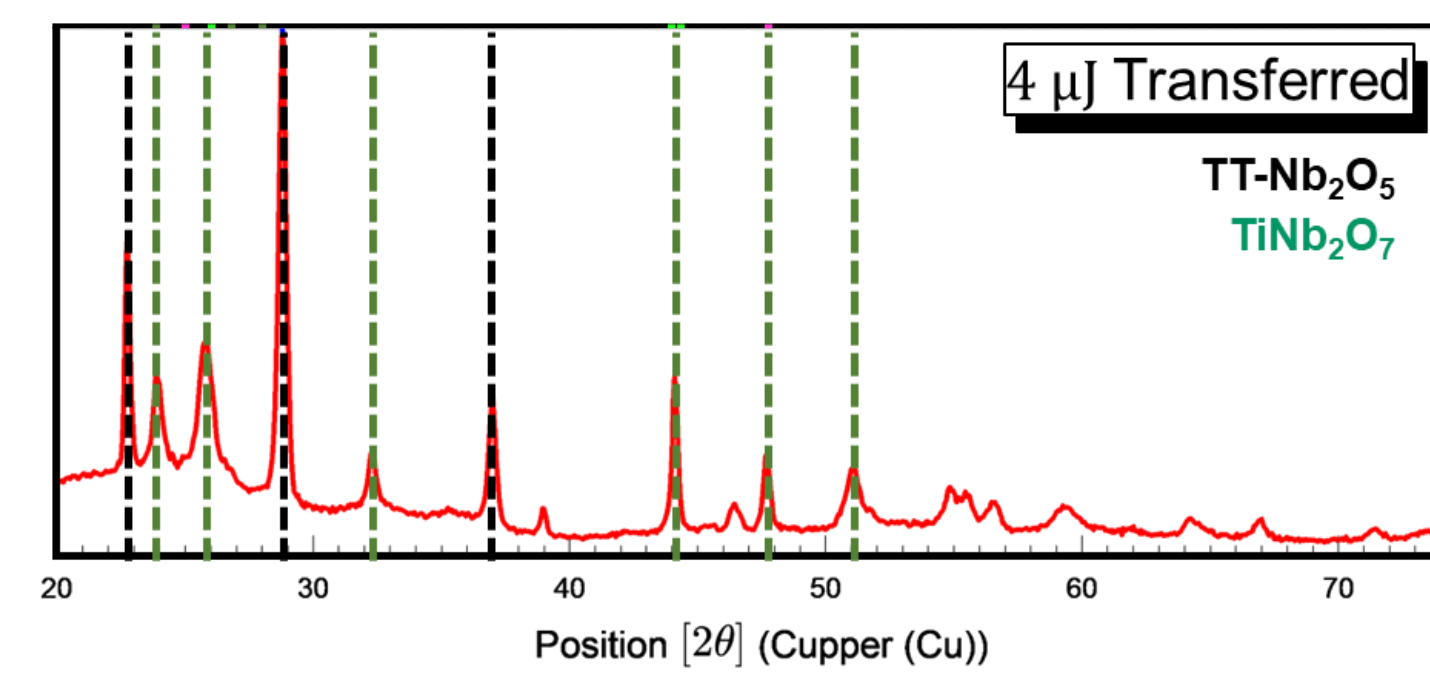
- Cyclability assured up to 1000 cycles.
- Good efficiency (even for fast cycling).
- Low specific capacity (<100 mA h g⁻¹).
- More TNO without  $\text{TiO}_2$  must be tested.

### FILM TRANSFER SCENARIO



- Sintered material appears completely stuck on the fused silica glass.
- After ultrasonication cleaning the sintered films remain stuck on the fused silica.
  - Blue Coloration  $\Rightarrow$   $\text{Nb}^{5+}$  is reduced to  $\text{Nb}^{4+}$ .

### XRD

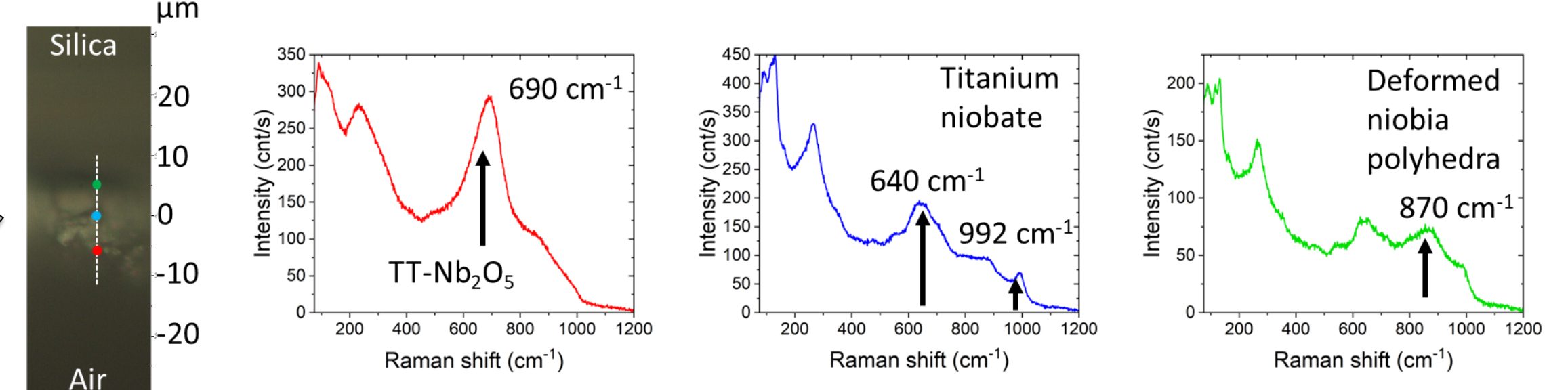


### X-Ray Diffraction

- XRD of transferred film at 4 μJ shows the (001) and (100) reflections of TT- $\text{Nb}_2\text{O}_5$ .
- Only the films processed at 4 μJ show intense enough reflections of TNO12.

### Raman Spectroscopy

- Cross-RS of 4 μJ transferred films show a gradient in depth of different TNO and  $\text{Nb}_2\text{O}_5$  phases.



### Electrical performance

$$\frac{\sigma_{\text{Transferred}}}{\sigma_{\text{Nb}_2\text{O}_5}} = 10^7$$

## Conclusions

- Energy-efficient TNO film formation has been induced by fs-laser sintering starting from powders.
- By adjusting the laser pulse energy, two scenarios can be achieved: transferred and non-transferred materials.
- For 1 μJ, the films are a mixture or composite of TNO and non-modified  $\text{TiO}_2$ . The samples are easy to recover and can be used to prepare a slurry.
- For 4 μJ, a gradient in depth of  $\text{Nb}_2\text{O}_5$  and TNO phases can be observed. The conductivity of these samples has been improved seven orders of magnitude compared to pure  $\text{Nb}_2\text{O}_5$ .
- The 1 μJ samples have proven their performance in a LIB, reaching 1000 cycles, but they must be improved for competitive results.

## Acknowledgements

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