Design and synthesis of novel p-type TCOs: From computational screening towards film deposition

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Overview

- Introduction
  - → Fundamental problem of p-type TCOs
  - → Overview of p-type research
  - → Research goal

- Case study I: Li-doped Cr_2MnO_4

- Case study II: Doped Ln_2O_2Se

- Outlook

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Introduction

Transparent → Visible light (380 nm / 3,2 eV)
→ Typically: at least > 80%

Conductive → Despite high E_g
→ Typically: ρ around 10^{-3} – 10^{-4} Ω*cm

Oxide → Metal oxide

Why study p-type TCOs?

- Gaining fundamental understanding of hole-conduction mechanisms
- Bringing research field up to date with n-type research

→ Practical: Enables the use of transparent p-n junctions!

Fundamental problem of p-type TCOs

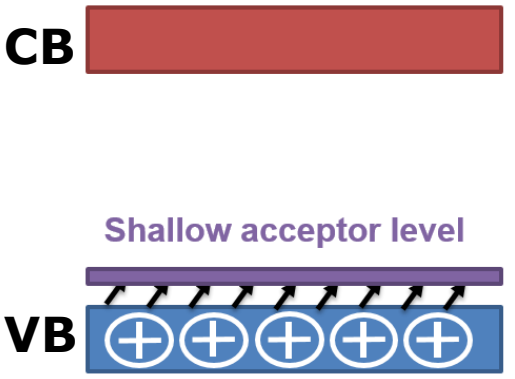
- N-type TCOs:

- Conduction via CBM
- Localized on metal s-orbitals

- P-type TCOs:

- Conduction via VBM
- Localized on oxygen 2p-orbitals

  → **low dispersion, high m'**



Fundamental problem of p-type TCOs

- Computational screening of oxides:

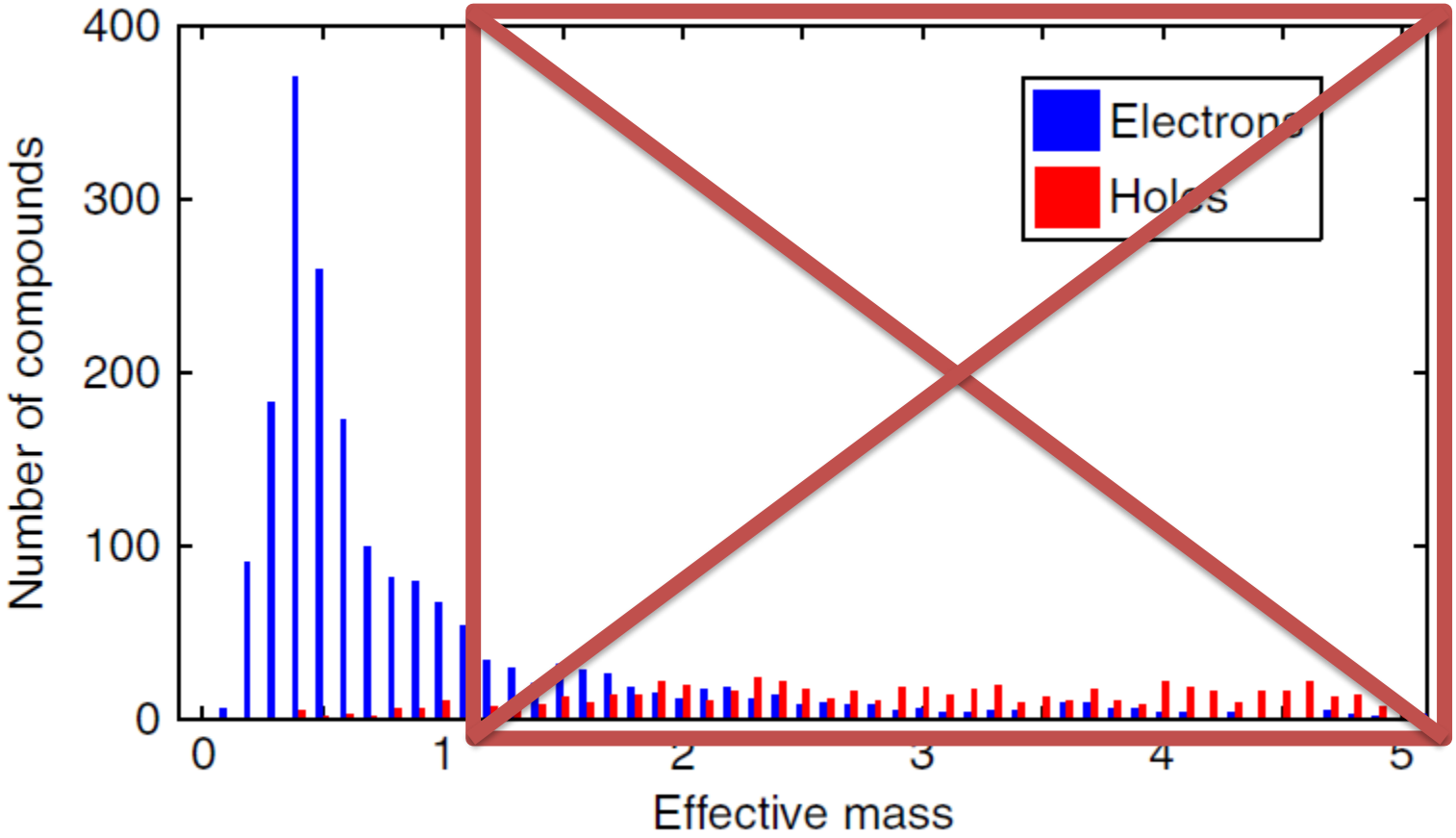


Figure 1 | Effective mass distribution for electrons and holes in oxides.

Reference: Hautier et al. (2013)

Overview of p-type research

Typical strategy:

"Chemical modulation of the valence band" (CMVB)

- Hybridisation between O 2p and metal d-orbitals:
  - → Closed shell d-orbitals: d^{10} s^{0} (ABO_2)
  - → Zn^{2+} + group 9 metal M^{3+}: d^{6} (ZnM_2O_4)
  - → Mn^{2+} spinels: d^{5} (MnM_2O_4) → **Case study I**

- Mixing of O 2p and other anionic p-orbitals:
  - → Oxypnictides: group 15 element (P, As)
  - → Oxychalcogenides : group 16 element (S, Se, Te)

→ **Case study II**

Reference: Kawazoe et al. (2000), Mizoguchi et al. (2002), Hautier et al. (2013)

Research goal

Finding and developing a versatile and efficient method to synthesize "designer oxides"

→ Chemical solution deposition (CSD)

- **Advantages:**
  - Works under ambient conditions
  - Good control of stoichiometry
  - Molecular level mixing: convenient for multimetal oxides and doping
  - Relatively inexpensive (products + operation)

- **Possible disadvantages:**
  - Requires post-deposition anneal: high temperatures are often needed
  - Film quality optimization can be more difficult

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I. Case overview

- Database screening by Peng et al.

  (National Renewable Energy Laboratory, 2013)

- P-type ternary Mn-oxides

- Candidate from computational screening using:

  - Thermodynamic stability
  - Wide band gap (> 3 eV)
  - Light hole effective mass
  - No hole self-trapping
  - No formed hole-killer defects
  - Presence of formed hole-producer defects

Reference: Peng et al. (2013)

I. Case overview

- Mn: High-spin d^5 configuration (tetrahedral coordination)

With relatively large E_g (3,3 eV) + spin-forbidden d-d transitions

→ Good visible light transparency

- p-d coupling between oxygen p and Mn d

→ Higher VB dispersion

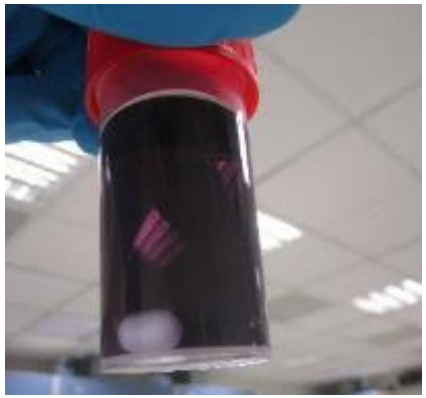
- Cr_2MnO_4 is p-type dopable, but requires extrinsic dopants

→ Best options: $\mathbf{Li_{Mn}}$ and Mg_{Cr}

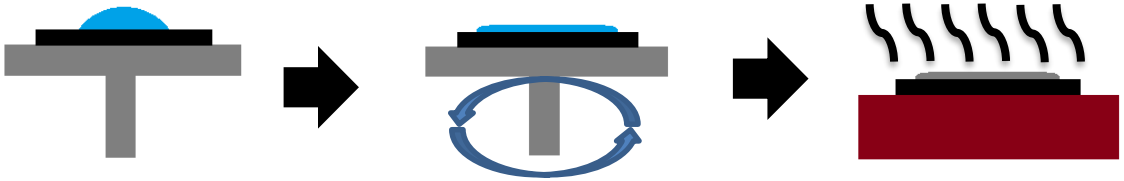
Reference: Peng et al. (2013)

I. Experimental outline

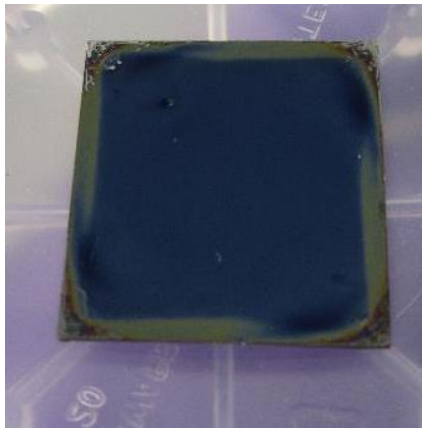
Precursor synthesis



Film deposition
(spin-coating)

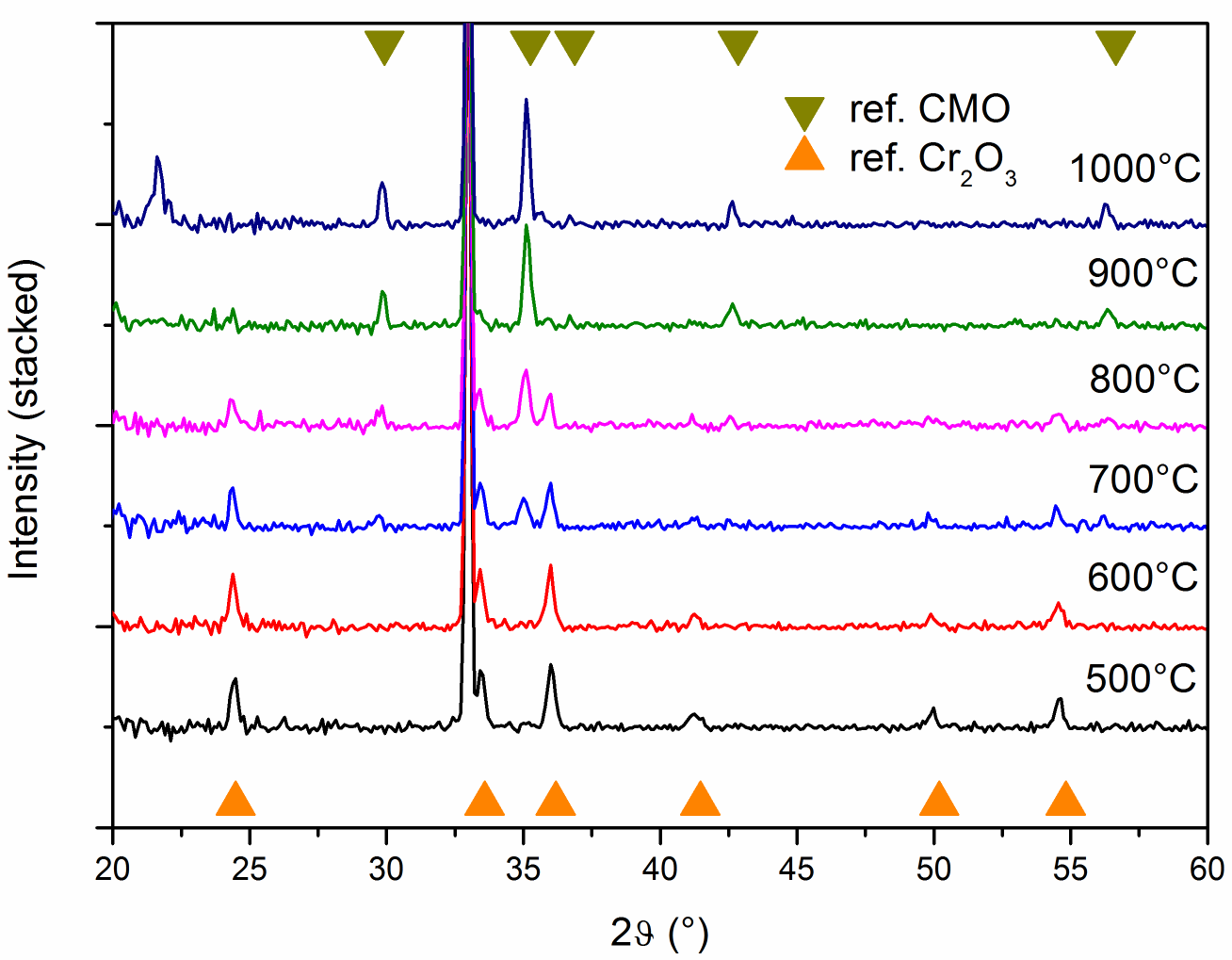


Thermal processing towards
crystalline films



I. Sample characteristics

Phase formation a.f.o. temperature (XRD):



I. Adding the dopant

- Already achieved in powder form by Nagaraja et al. (2014)
- < 10 at.% Li was seen as optimal
- Own observations:
  - x < 5 at%: No change in phase comp.
  - 5 < x < 10 at%: Phase separation
  - x > 10 at%: Li-containing secondary phases

  → Successful at low doping levels or Li-loss?

Reference: Nagaraja et al. (2014)

Case study I: Conclusions

- Development of a stable, aqueous Cr-Mn multimetal precursor
- Synthesis of the Cr_2MnO_4 host material was successful, thin film deposition via spin-coating
- Dopant addition was straightforward, but heavily disturbs the system at higher doping levels
  → Secondary phase formations

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II. Case overview

- Database screening by Sarmadian et al.

  (Antwerp University, 2016)

- Synthesis and characterization of (doped) lanthanide oxyselenides

- Ln_2O_2Se with Ln: La^{3+}, Nd^{3+}, Gd^{3+}, Pr^{3+}

- Candidate from computational screening using:

  - $E_g > 2,5$ eV
  - $m'_{hole} < 1$
  - p-type dopable (shallow acceptor level)
  - thermodynamic stability
  - Favorable band energies vs. BPE

Reference: Sarmadian et al. (2016)

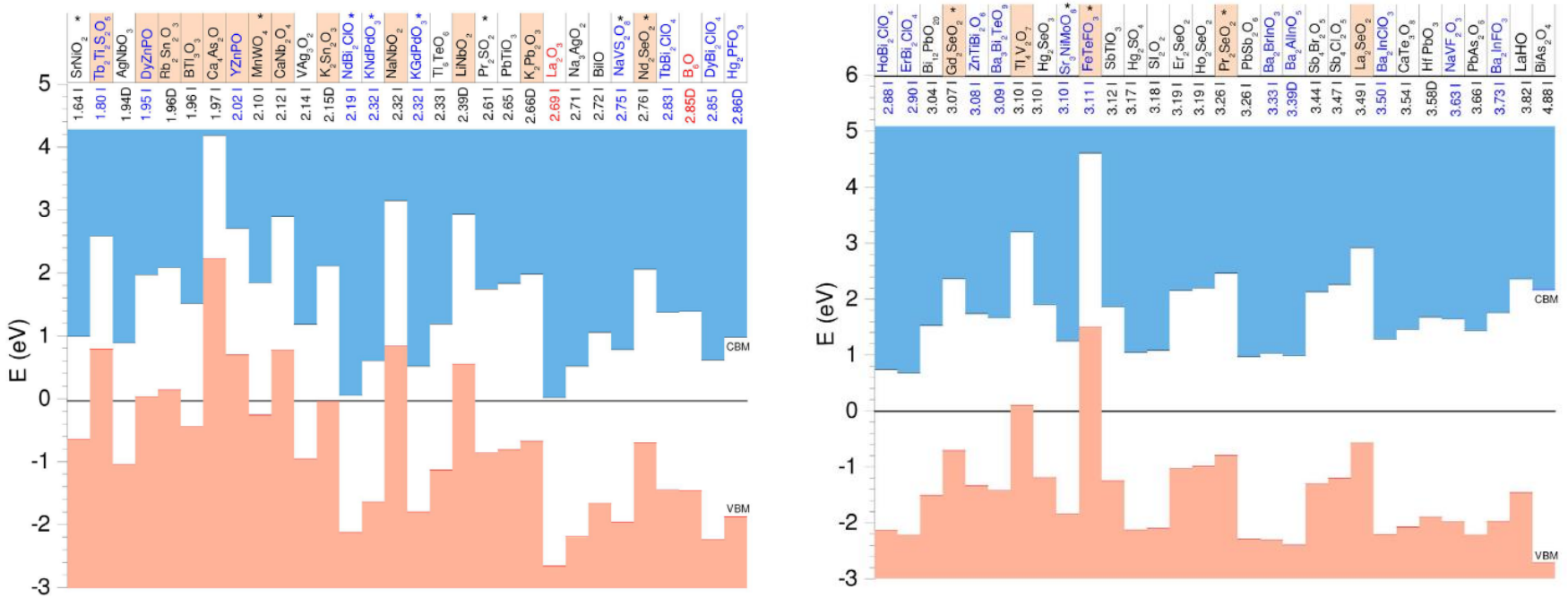
II. Case overview

- Metal oxychalcogenides:
- Using S or Se: larger p-orbitals + lower E
  → Lowers VBM
- M: highly electropositive (group 1+2, REEs)
  → Increases CBM
- Combination leads to increased E_g

Reference: Ueda et al. (2000), Banerjee et al. (2005)

II. P-type dopability screening

VB and CB energies vs. BPE



Reference: Sarmadian et al. (2016)

II. Experimental outline

- **Workplan:**

Synthesis of (aqueous) Ln^{3+}-precursor

↓

Deposition of Ln_2O_3 films

↓

Thermal treatment towards crystalline films

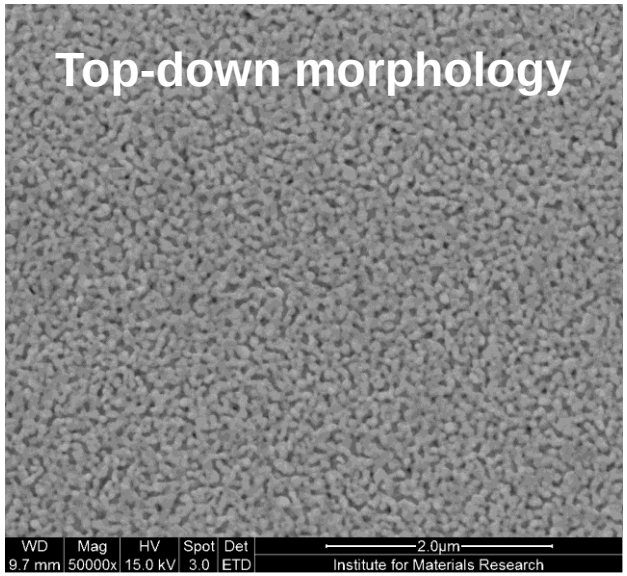
↓

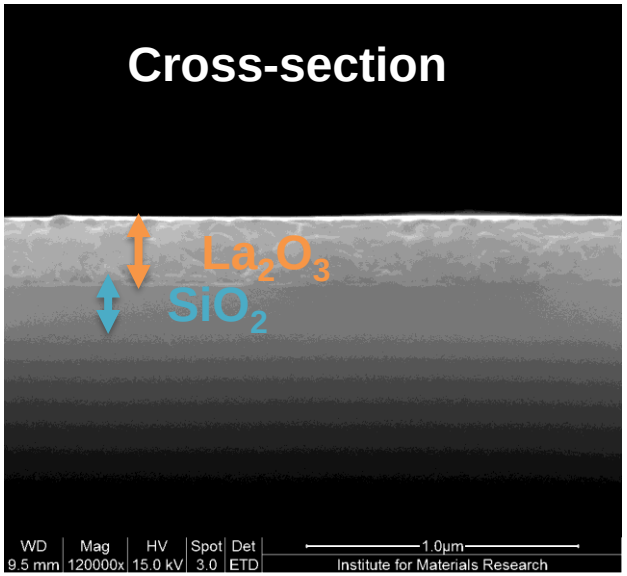
Selenization using dedicated setup

II. Sample characteristics (**Pre**-Selenization)

- 250 nm La_2O_3 films
- Substrate: Thermal SiO_2 on top of Si
- Stored under inert atmosphere / water-free environment

SEM-analysis:

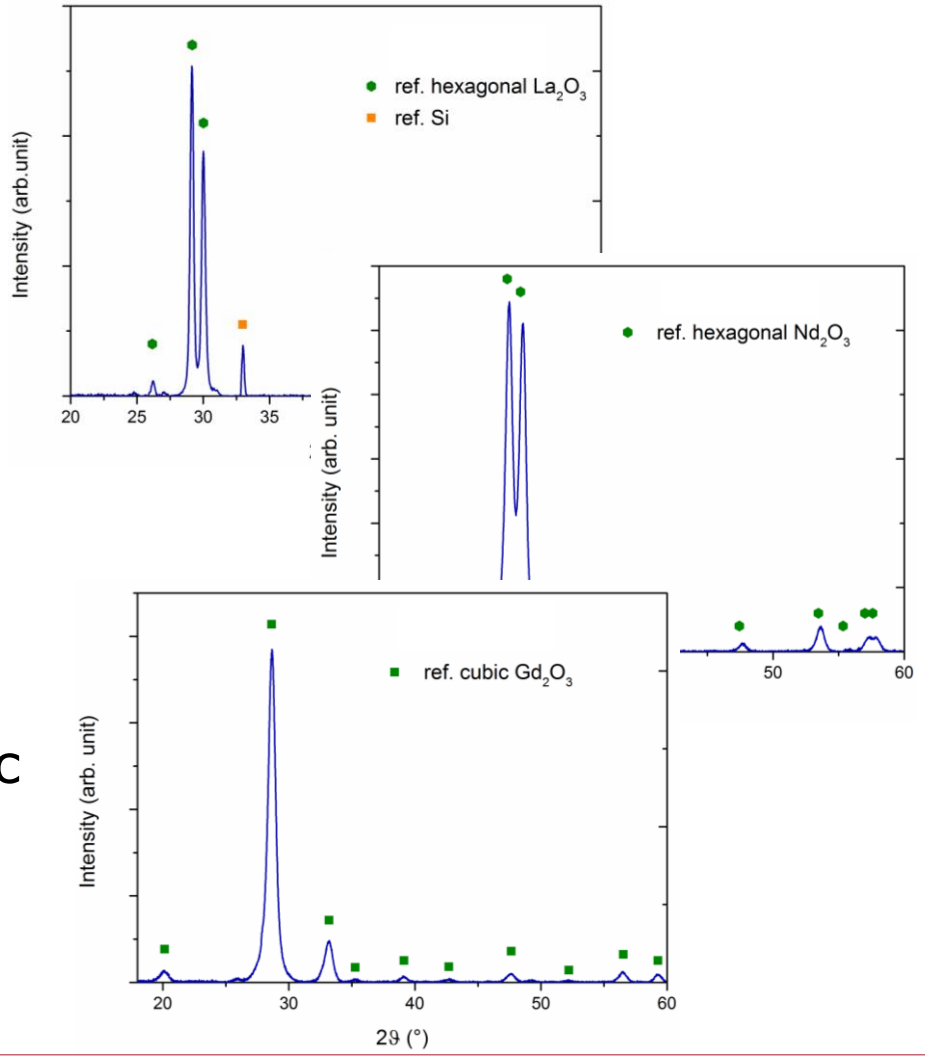




II. Sample characteristics (**Pre**-Selenization)

XRDs of starting phases:

- La_2O_3: hexagonal
- Nd_2O_3: hexagonal
- Gd_2O_3: body-centered cubic



II. Selenization step

	Se-vapor	**H_2Se**
Se-source:		
Reactivity:	Low	High
Temperature range:	High *(500-900°C)*	Low *(300-600°C)*
Processing requirements:	Mediocre	High
Controllability:	Low	High

II. Selenization step

- Selenization trends a.f.o. time and temp
  - → Short t / low T: Oxide dominant
  - → Long t / high T: Selenide dominant

- Secondary phase $Ln_4O_4Se_3$
  - → Very dominant for La-series

- Possible reaction mechanisms:

$$2\ Ln_2O_3 + 3/8\ Se_8 \rightarrow 2\ Ln_2O_2Se + SeO_2$$

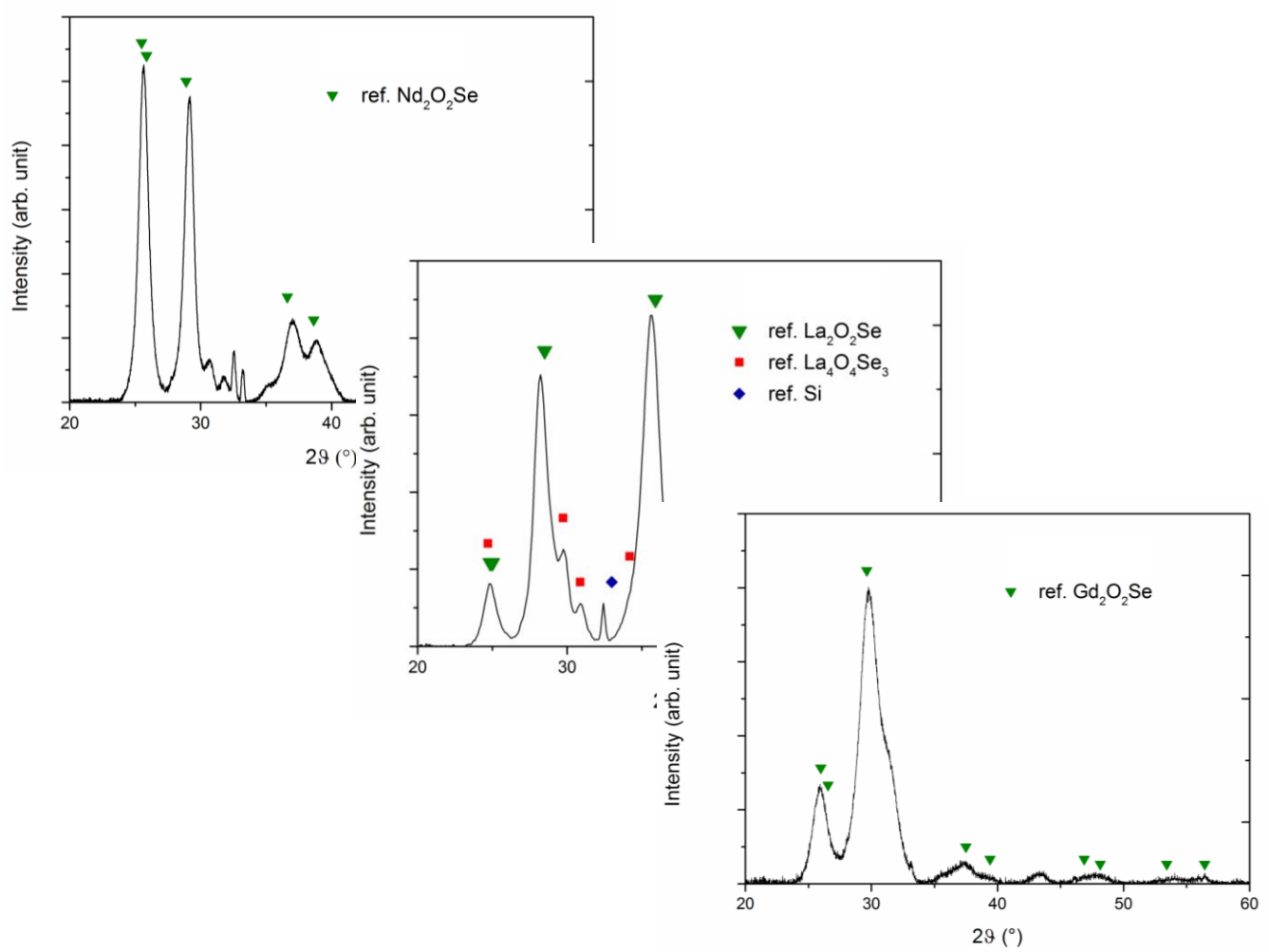
$$Ln_2O_3 + H_2Se \rightarrow Ln_2O_2Se + H_2O$$

Possible Se-dimerisation? 2 La_2O_2Se + "Se" → $La_4O_4Se_3$

II. Sample characteristics (**Post**-Selenization)

Resulting phase after selenization step:

- Nd_2O_3:
- La_2O_3:
- Gd_2O_3:



Case study II: Conclusions

- Crystalline Ln_2O_3 (Ln: La, Nd, Gd,…) thin films were succesfully deposited starting from an aqueous precursor system

- A partial anion-substitution (O → Se) was made via selenization of the Ln_2O_3 oxide films, leading to a class of novel p-TCO host materials

- Some selenization trends were observed, depending on the Se-source and processing time/temperature

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Outlook

- Having a better understanding of the influence of doping on the final phase formation of the host material
- Check the effect of the substrate type on the final film composition and properties
- Investigating the primary opto-electronic properties of the processed films

Acknowledgements

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Thank you for your attention!

Questions or suggestions?

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