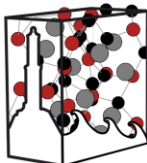




TOFA

20th DISCUSSION MEETING ON THERMODYNAMICS OF ALLOYS
20 - 24 September 2026
BLED - SLOVENIA

Synthetic, structural, thermodynamic and theoretical investigation of alkali metal selenides

Inorganic MAterials GrOup
IMAGO 

Sara Guerrucci

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Introduction

My PhD project is part of a broader project:
LEGACY - Healing wide-gap chalcopyrite



The project involves:

- ▶ University of Genova
- ▶ CNR IMEM Parma
- ▶ University of Parma



Università
di **Genova**



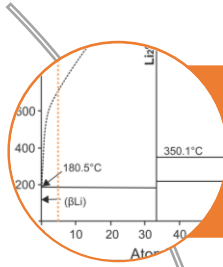
UNIVERSITÀ
DI PARMA

Aim:

Synthesis and investigation of the chemical and physical properties of alkali selenides as dopants in CIGS thin-film solar cells



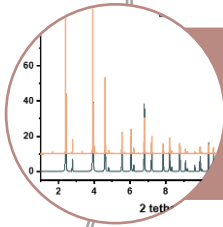
Overview



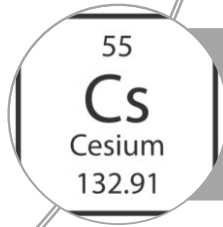
State of the Art



Synthesis: Reactive Flux Method



Results

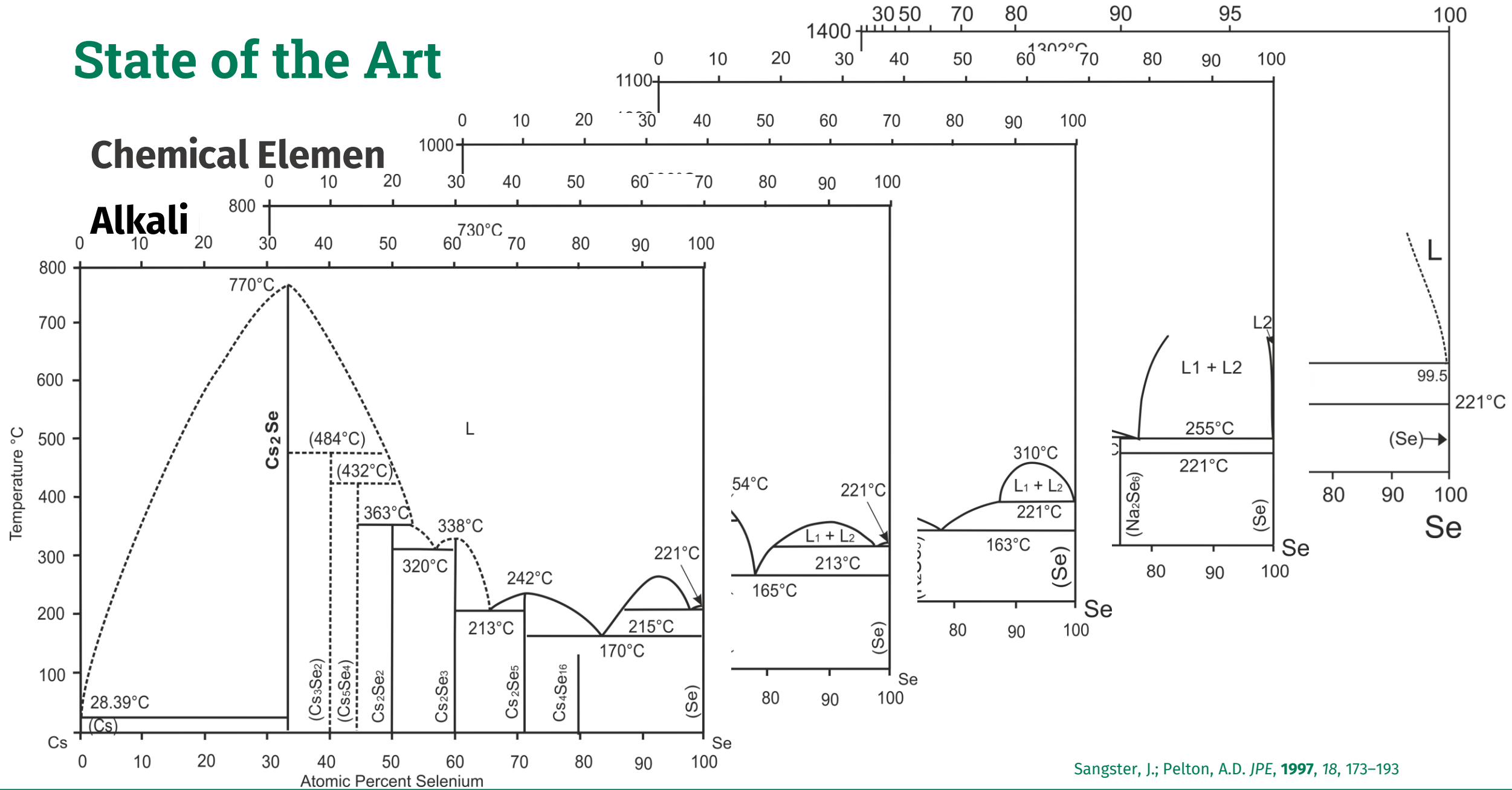


Conclusion and Ongoing work

State of the Art

Chemical Elements

Alkali



Sangster, J.; Pelton, A.D. *JPE*, **1997**, 18, 173–193

Synthesis: Reactive flux method

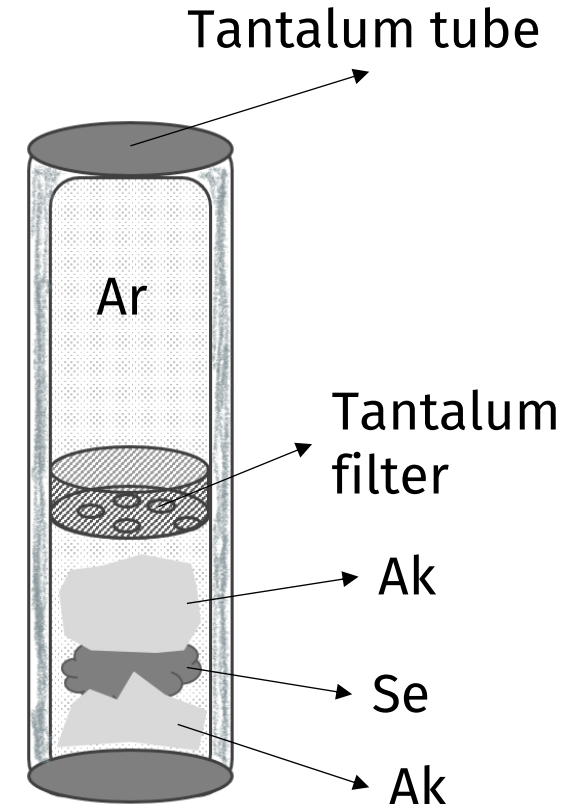
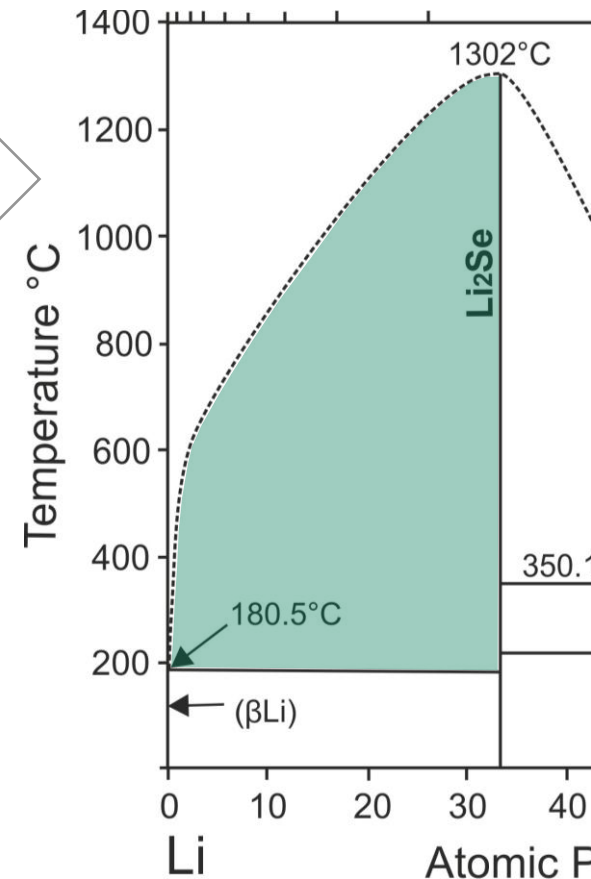
- Ar glovebox
- Tantalum tube
- Tantalum filter

Strong excess of
Ak with respect
to the Ak_2Se
composition

Crystallization
of Ak_2Se
crystals in "L+
 Ak_2Se " region

Composition:

- **95** at. % of Li or Na and **5** at.% of Se
- **90** at. % of K and **10** at.% of Se
- **85** at. % of Rb or Cs and **15** at.% of Se



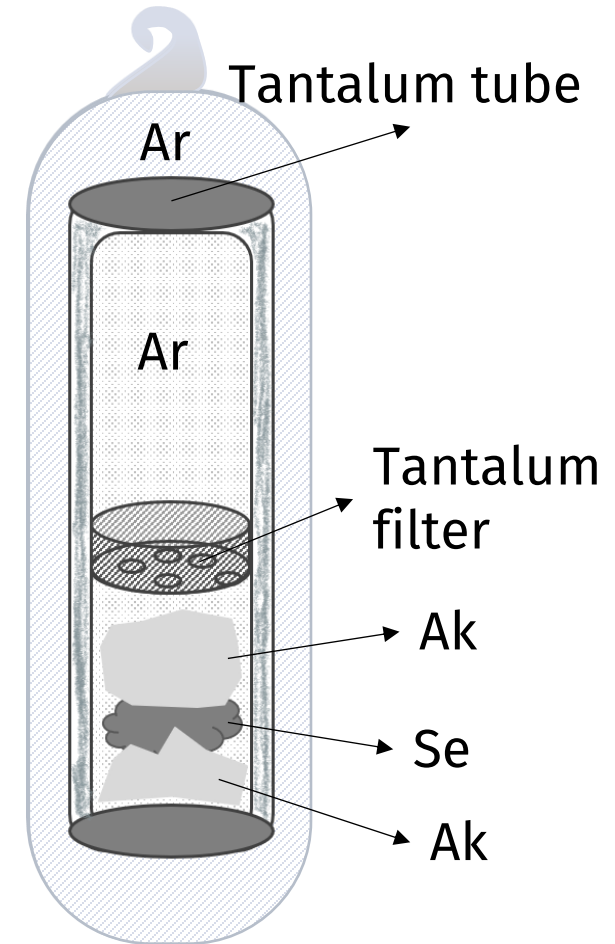
Synthesis: Reactive flux method

Thermal cycle used for the synthesis

Temperature	Time or rate
From 25°C to L region	10°C/min
L region °C	8 hours
From T (L) to 300- 200°C	0.1°C/min
Centrifuge T	2 days

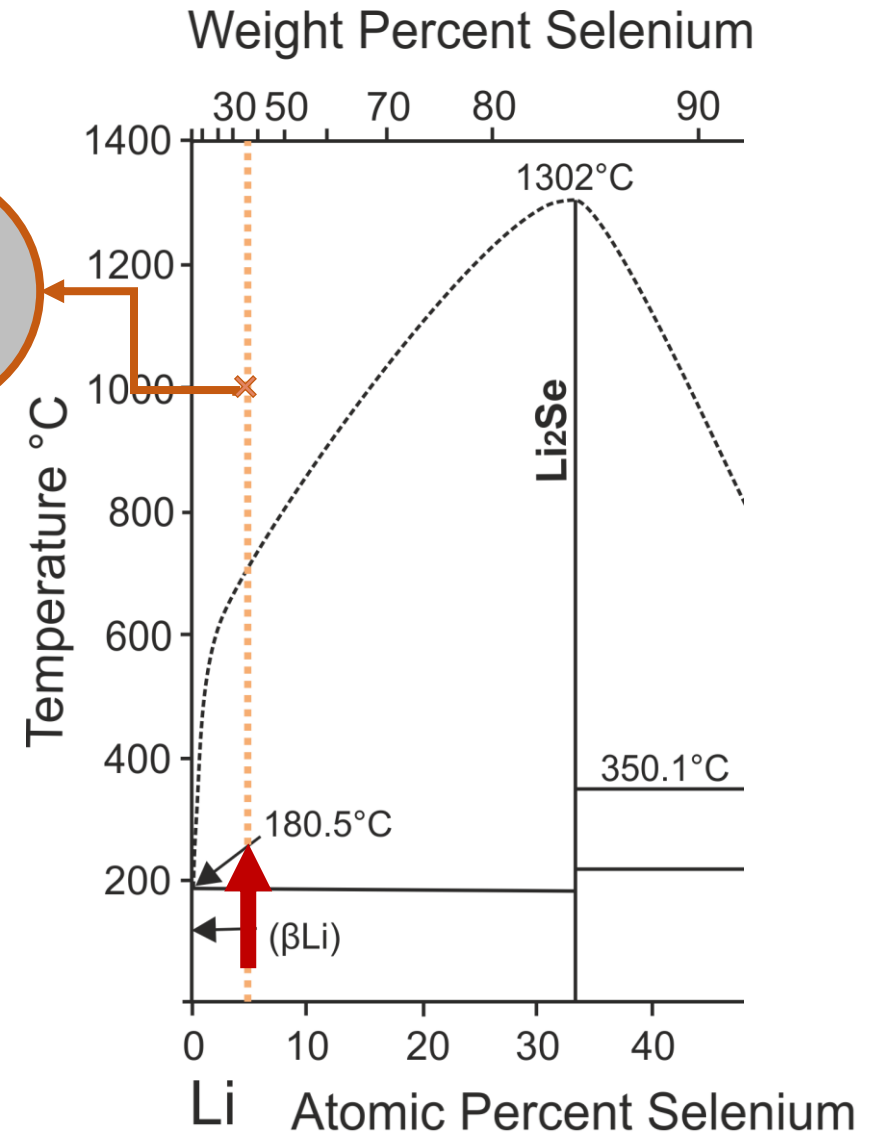
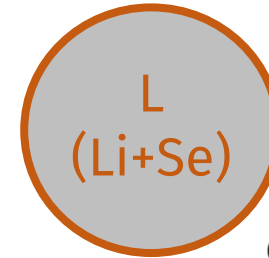
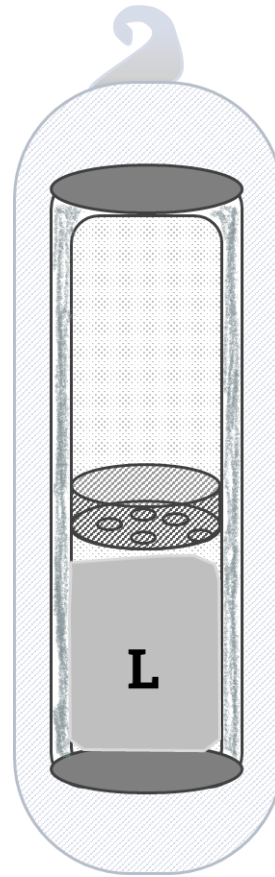
L Region = Li: 1000 – Na: 800 – K: 700 – Rb: 600 – Cs: 550 °C

- Prevent oxidation of Ta
- Quartz vial



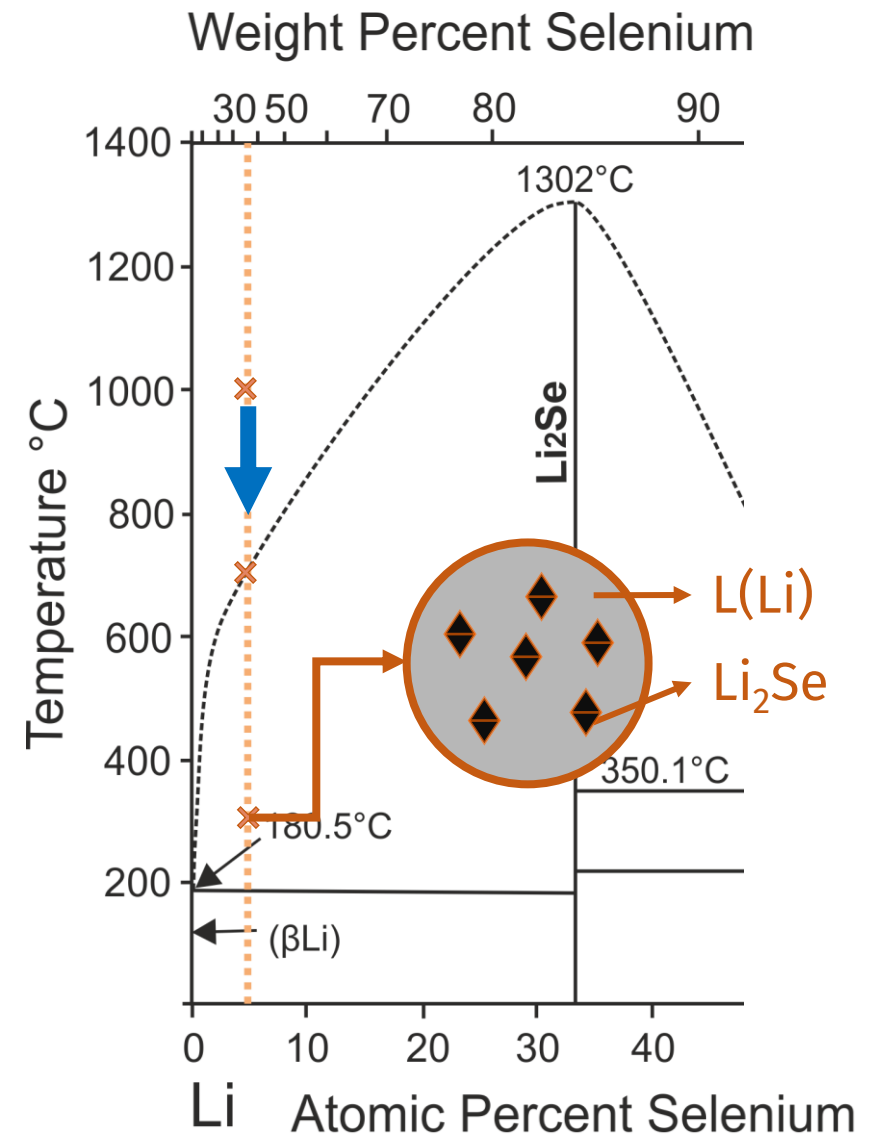
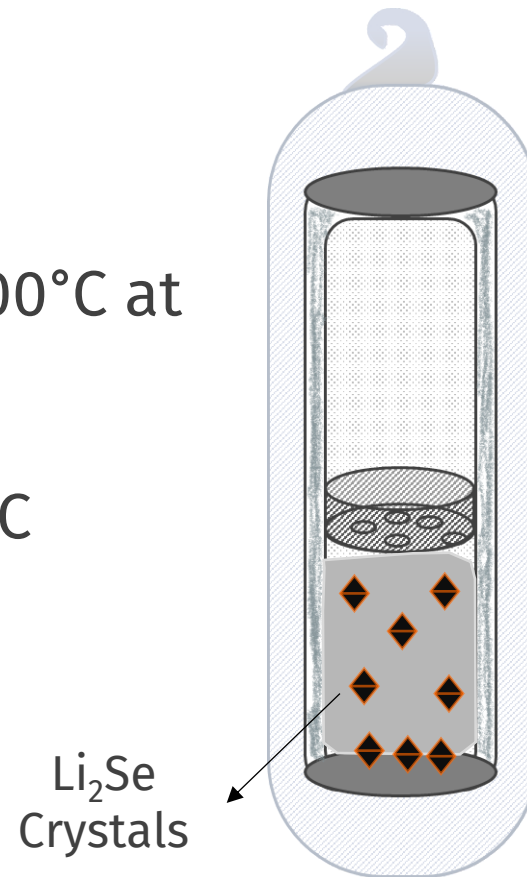
Synthesis: Reactive flux method

- ▶ From 25°C to 1000°C at 10°C/min
- ▶ At 1000°C for 8 hours



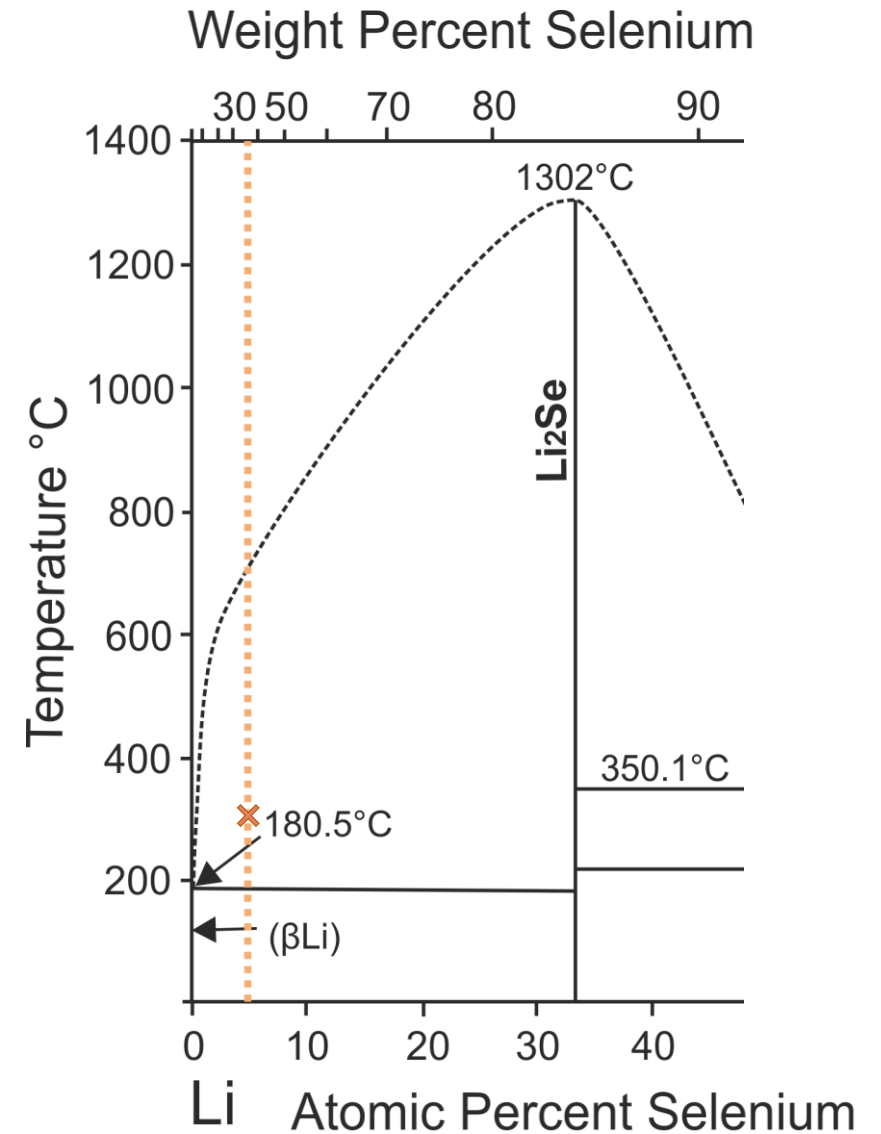
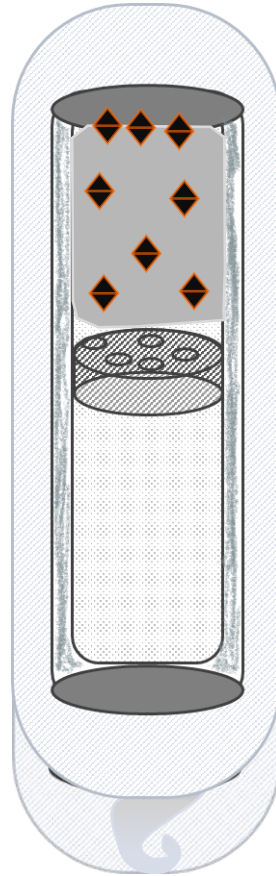
Synthesis: Reactive flux method

- ▶ From 1000°C to 300°C at 0.1°C/min
- ▶ Stabilized at 300°C



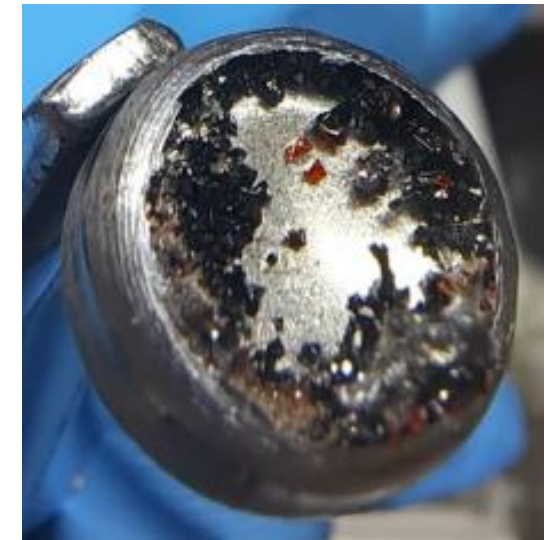
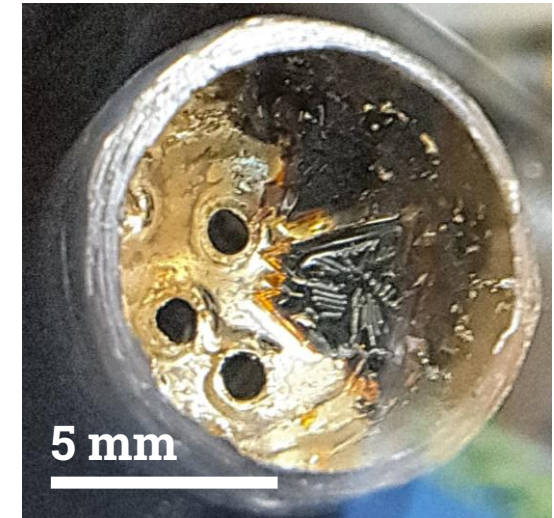
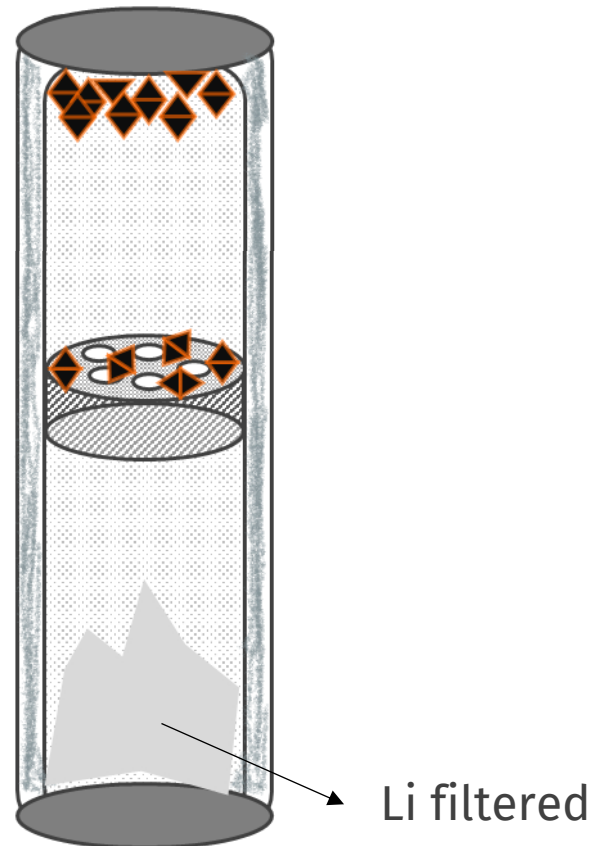
Synthesis: Reactive flux method

- ▶ Stabilized at 300°C
- ▶ Sample is rotated
- ▶ Centrifuge: 3000 rpm, 5 times at 300°C

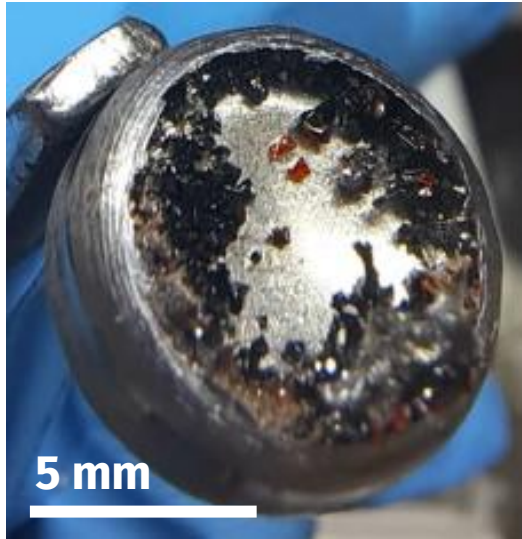


Synthesis: Reactive flux method

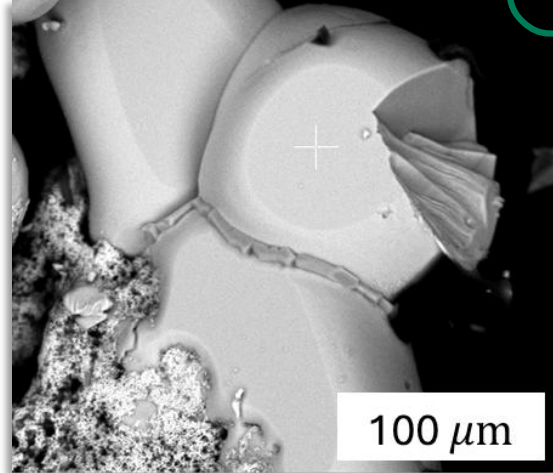
- ▶ Ar Glovebox
- ▶ Tube cut to collect the sample



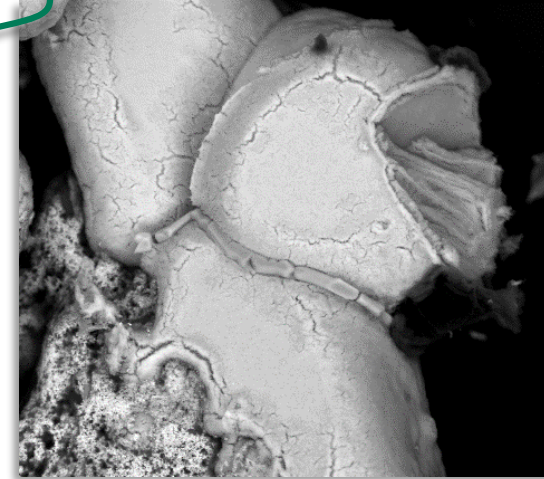
Results: Li_2Se



High-resolution synchrotron X-ray diffraction were performed at beamline ID31 at the European Synchrotron Radiation Facility (ESRF)



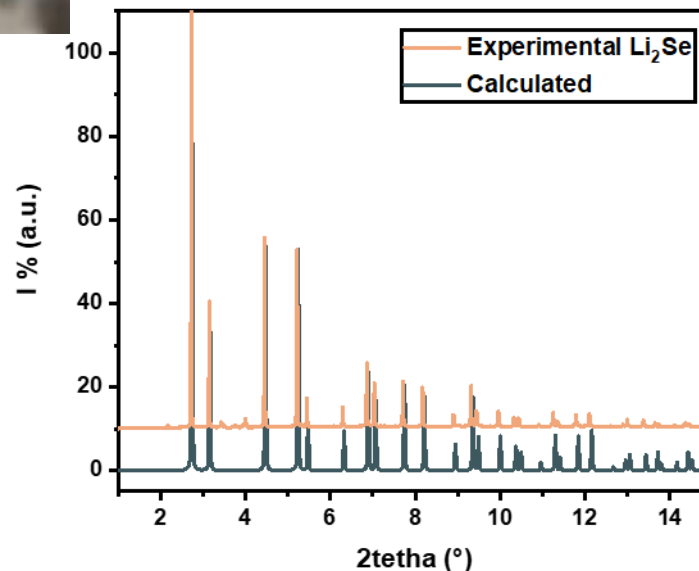
Before air exposure



After 5 min

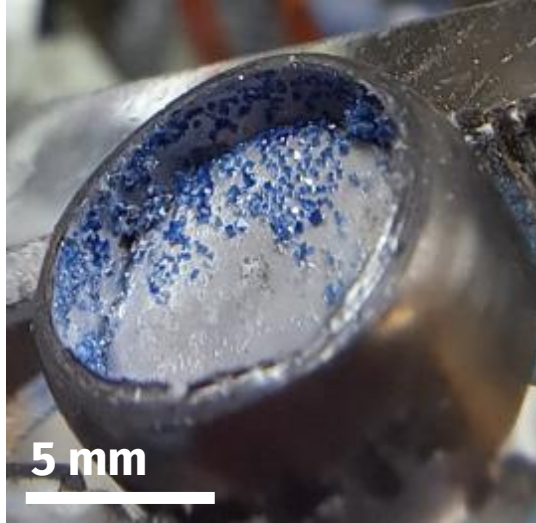


After 5 + 10 min

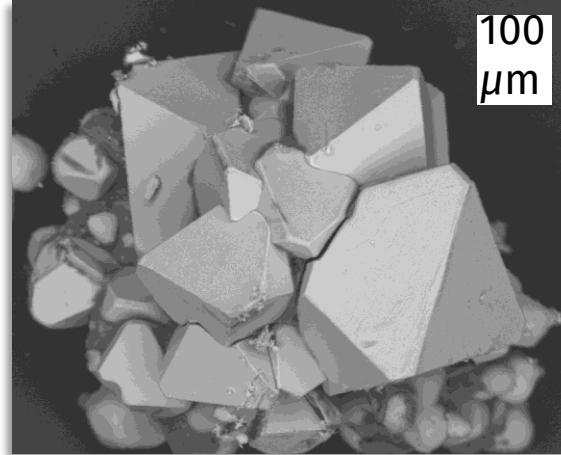


- ▶ Li cannot be detected by SEM due to its low atomic number
- ▶ Excellent match with the XRD pattern of the phase

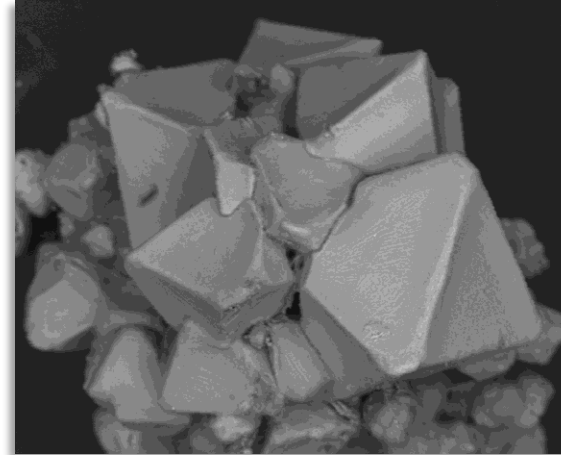
Results: Na₂Se



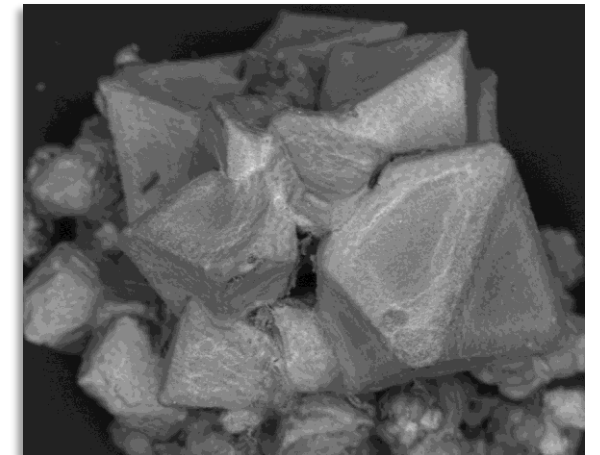
High-resolution synchrotron X-ray diffraction were performed at beamline ID31 at the European Synchrotron Radiation Facility (ESRF)



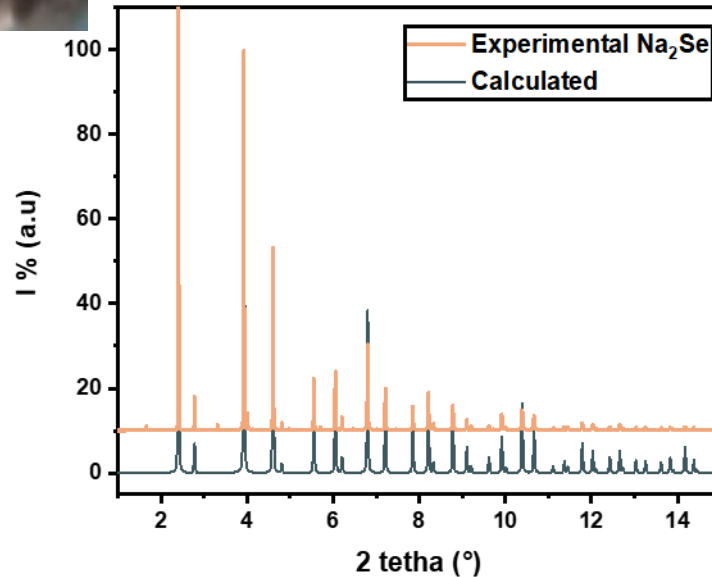
Before air exposure



After 5 min

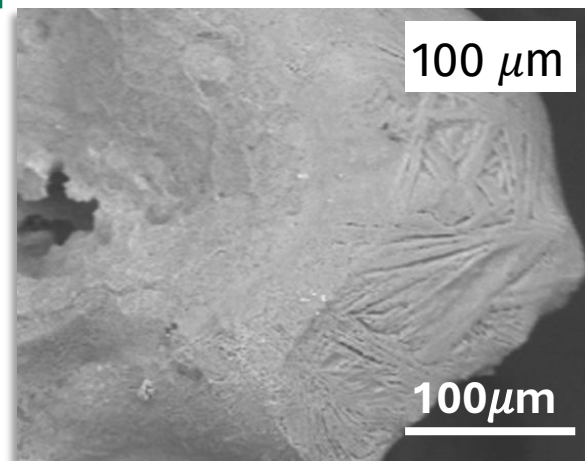


After 5 + 10 min

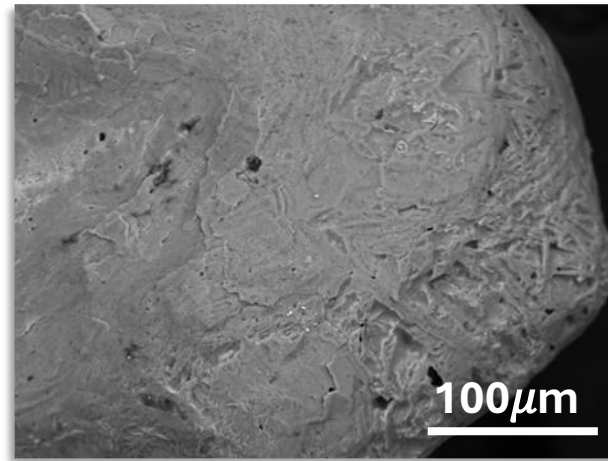


Analysis	Na	Se	O
Before	64.2 (8)	31.8 (6)	4 (1)
After 5'	49 (2)	18 (4)	33 (6)
5' + 10'	42 (1)	14 (2)	44 (2)

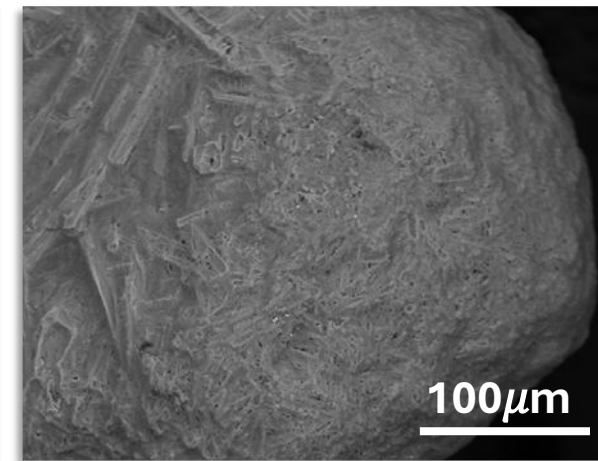
Results: K₂Se



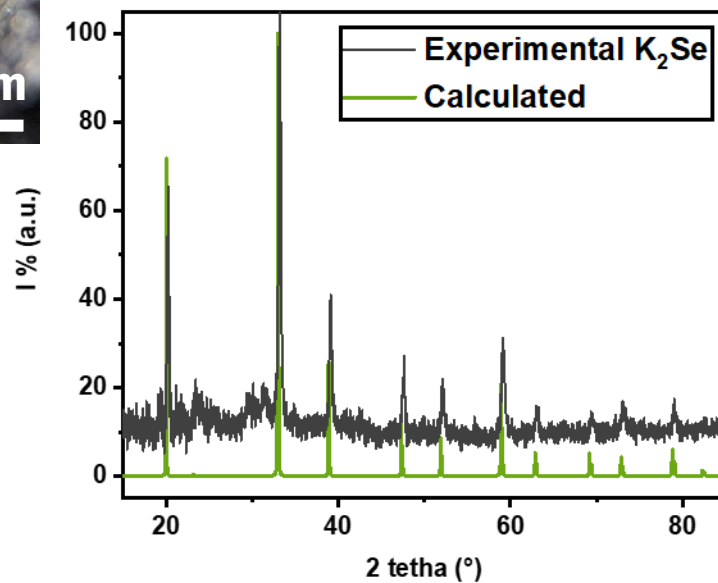
Before air exposure



After 5 min



After 5 + 10 min



Analysis	K	Se	O
Before	38 (7)	20 (2)	42 (9)
After 5'	29 (3)	19 (3)	52 (5)
5' + 10'	36 (1)	30 (2)	34 (6)

Results: K_2Se

The crystals are intensely colored, but why?



Measurements are challenging due to air sensitivity of the compounds



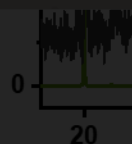
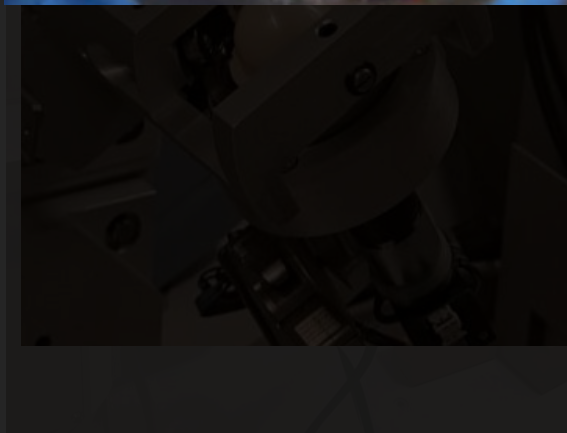
► Samples loaded

► Sample holders:
ray polymer do



+ semi-transparent X-

Rb_2Se Crystals



Results

The crystals are intensely colored, but why?



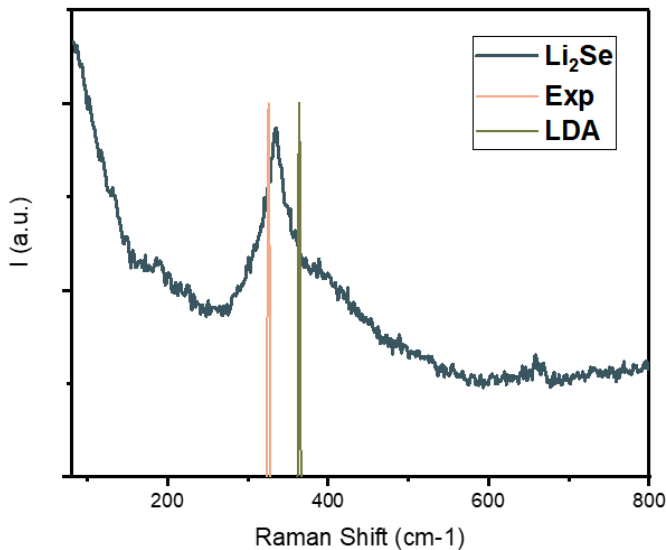
Mechanical representation

$$M = T_{2g} + 2T_{1u}$$

Acoustic and Optic modes:

$$\Gamma_{\text{acoustic}} = T_{1u}$$

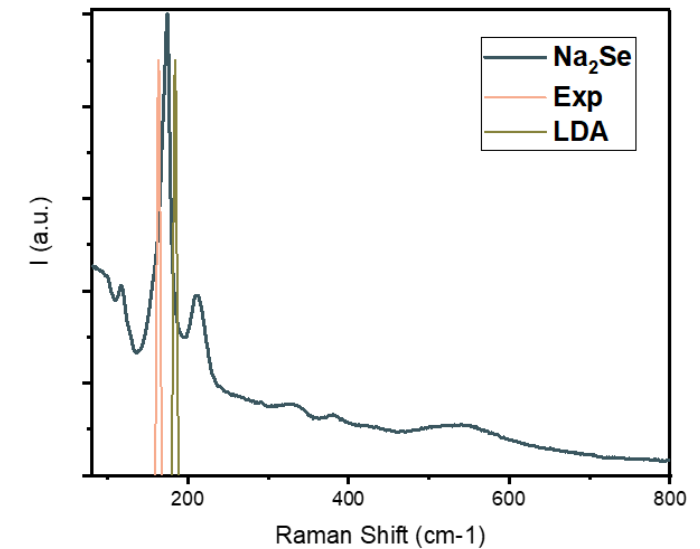
$$\Gamma_{\text{optic}} = T_{2g} + T_{1u}$$



Raman Active Modes

WP	A _{1g}	A _{1u}	A _{2g}	A _{2u}	E _u	E _g	T _{2u}	T _{2g}	T _{1u}	T _{1g}
8c	.	.	.	.	.	.	.	1	.	.
4a	.	.	.	.	.	.	.	.	.	.

Raman active modes: T_{2g}

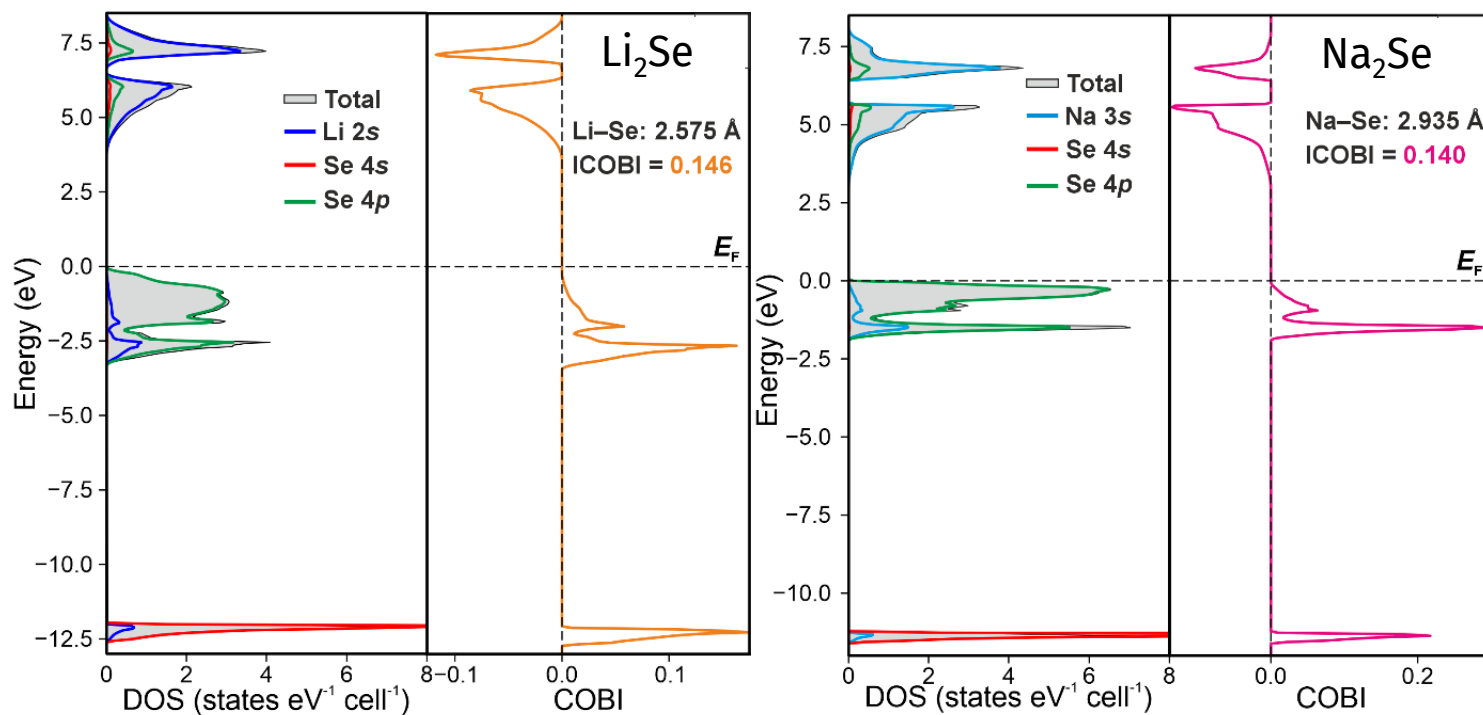


Kroumova et. al. Phase Transitions (2003), 76, Nos. 1-2, 155-170.

Theoretical investigation

3 energy region:

- below -10 eV: Se 4s
- from about -3 eV to E_F : Se 4p
- above E_F : mainly contributed by the Ak states



VASP HSE06

Reference ICOBI values:
C-C bond in diamond = 0.95
Na-Cl in rock-salt = 0.09

$$\text{ICOBI}_{\text{Li-Se}}^{\text{HSE06}} = 0.146 \quad \text{ICOBI}_{\text{Na-Se}}^{\text{HSE06}} = 0.140$$

Compound	Atom (X)	HSE06	
		q_i	E_M (kJ mol ⁻¹)
Li ₂ Se	Li	+0.55	-826
	Se	-1.10	
Na ₂ Se	Na	+0.60	-862
	Se	-1.20	

band gaps

- Li₂Se: indirect ≈ 3 eV
- Na₂Se: direct ≈ 2 eV



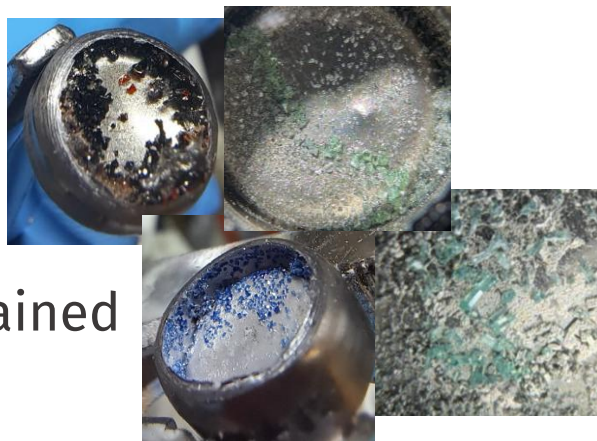
Li-Se interactions are slightly more covalent than Na-Se ones

Conclusion

&

Ongoing work

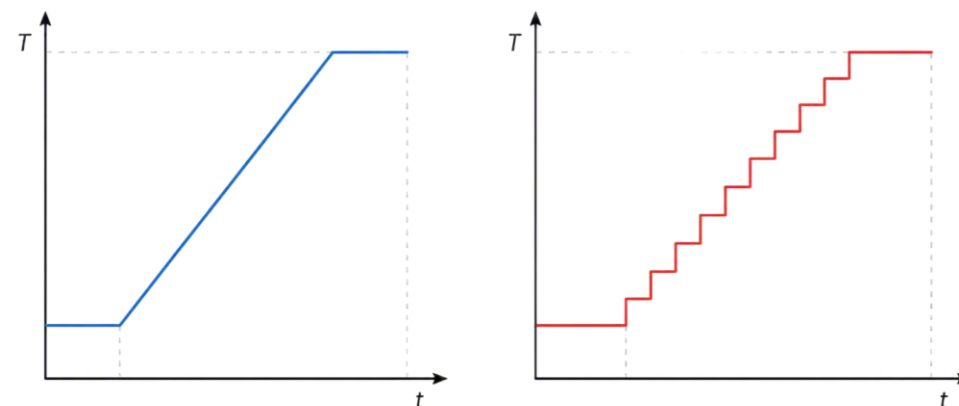
- ▶ Crystals obtained



- ▶ Phase confirmation achieved
- ▶ High-quality XRPD performed

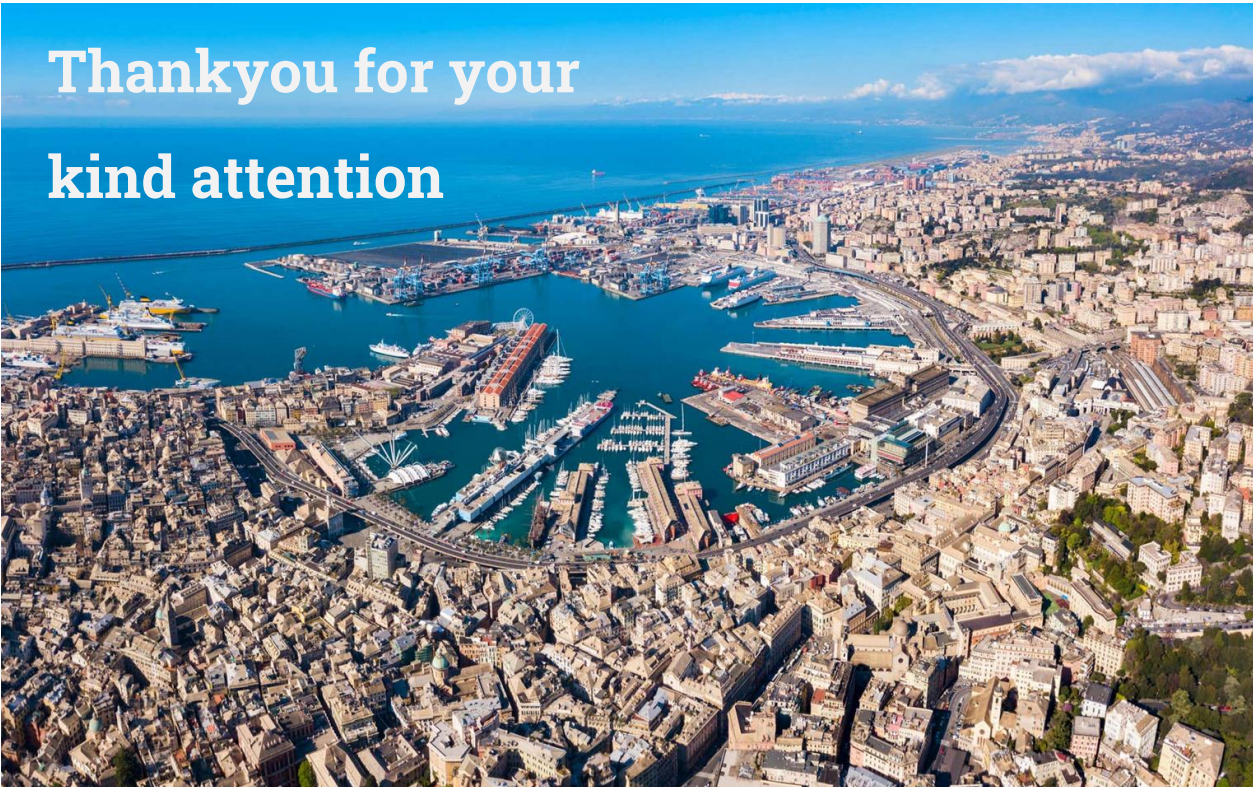
- ▶ Rietveld refinement and investigation of the origin of structural defects (and possibly the color)
- ▶ Characterization of Rb_2Se and Synthesis of Cs_2Se (waiting the winter)
- ▶ Thermodynamic studies: Heat capacity investigation

Both by continuous and Step by step methods





Thankyou for your
kind attention



I would like to thank

- ▶ **My Supervisors:**
Simona Delsante and Riccardo Freccero
- ▶ **PI of the LEGACY project:**
Diego Colombara
- ▶ **My colleagues and collaborator**
Mohammad Mohammadizadeh
Boghrabad and Giulia Spaggiari

