FRH$_2$ La Réunion - May 23rd 2023

Synthesis of silicon-based complex hydrides for solid hydrogen storage

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PhD started on January 9th, 2023

Supervised by Raphaël Janot (LRCS) and Fermin Cuevas (ICMPE)

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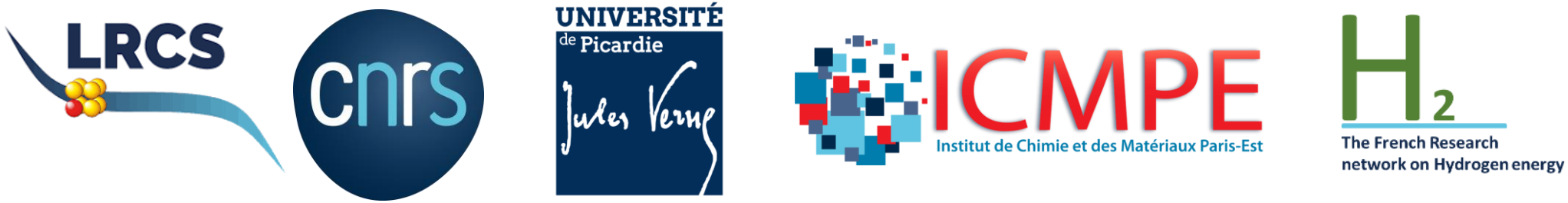


Cursus

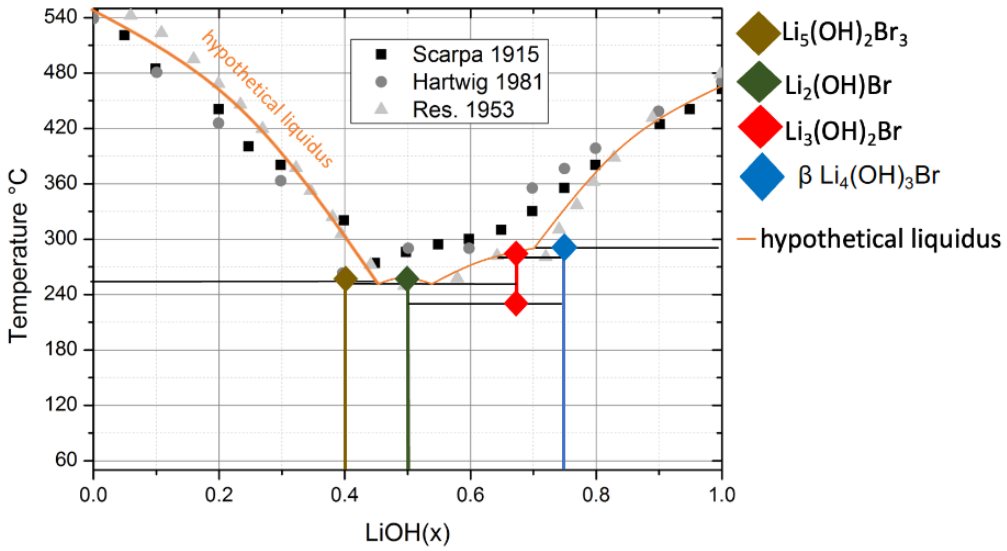
Master Chimie du Solide et des Matériaux at Université de Rennes 1

Internship at Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB)

Supervised by Matthew Suchomel, Eric Lebraud and Nicolas Penin

<u>Subject:</u> Revisiting the $LiBr_x$ -$LiOH_{1-x}$ phase diagram for energy storage applications

New phase diagram proposed



Master internship defense on June 28th, 2022

Introduction

$M^+ [SiH_3]^-$ for hydrogen storage (M = Na, K, Rb, Cs)

$KSiH_3$ reported in 1961 by Ring:

Synthesis conditions: $K_{(s)}$ + $SiH_{4(g)}$ in monoglyme at -78°C

$MSiH_3$ (M= Na, Rb, Cs) reported in 1968 by Amberger:

Synthesis conditions: M(s) + $SiH_{4(g)}$ in monoglyme at 20 °C

$$\frac{2}{3} MSi + H_2 \rightleftharpoons \frac{2}{3} MSiH_3$$

DFT calculations on KSi/$KSiH_3$ predict interesting properties

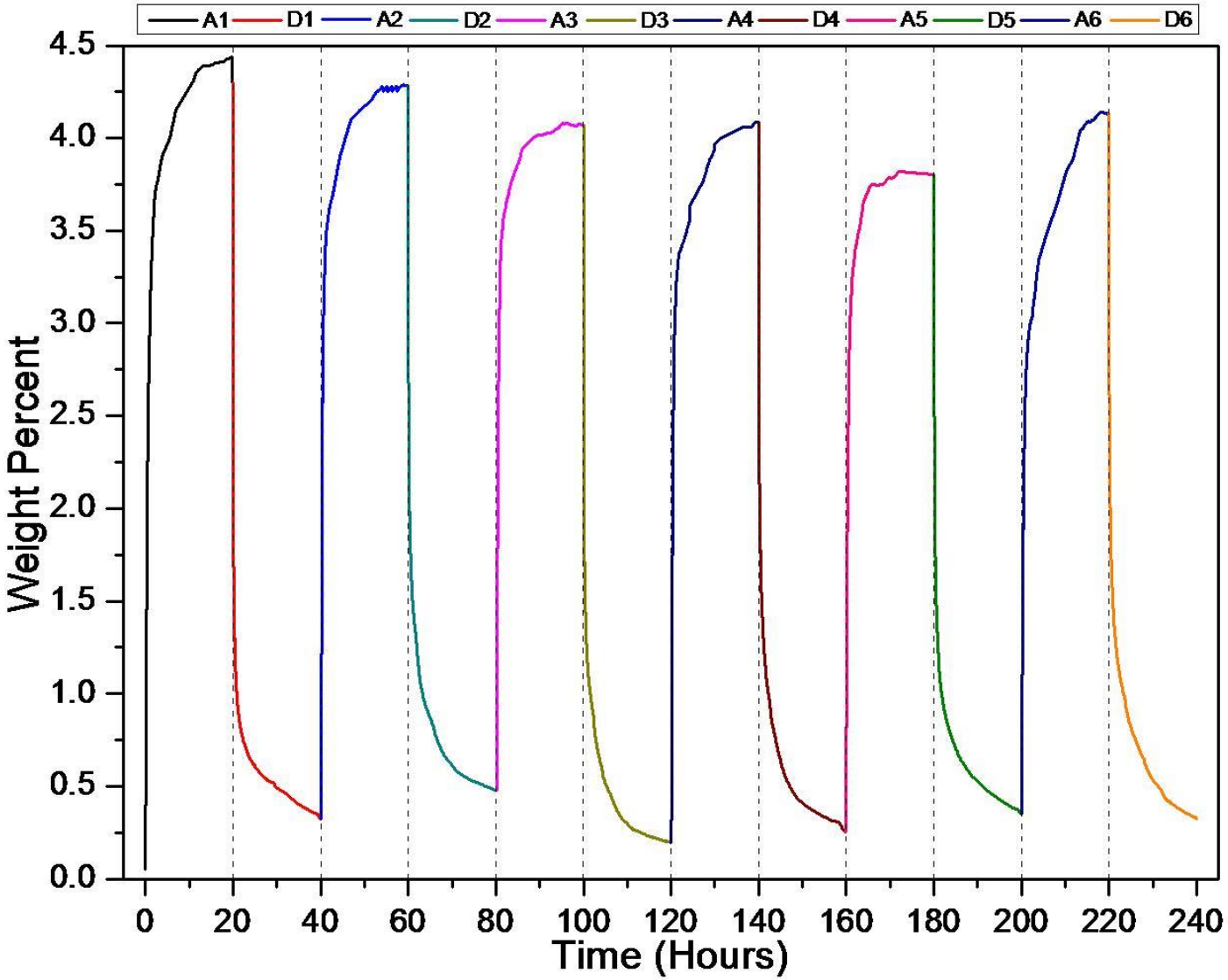
Introduction

Synthetized KSi in sealed steel tubes
Annealed for 48h at 500°C

KSi/α-$KSiH_3$:
Reversible storage of 4.3 wt. %

Abs: T=100°C, P = 50 bar
Des: T=200°C, P < 1 bar

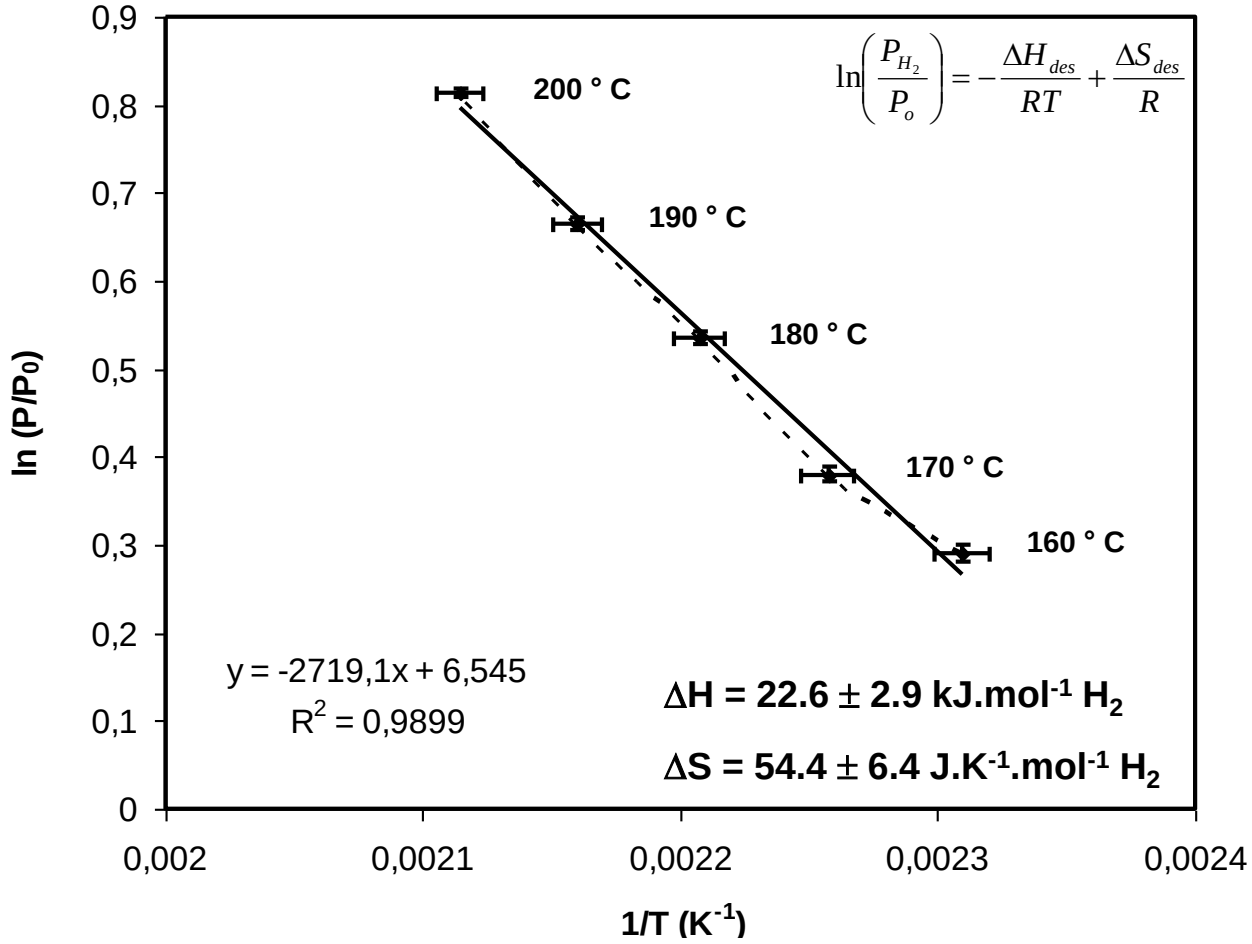
Cycling: KSi +3/2 H_2 ⇔ α-$KSiH_3$



Introduction

Experimental Van't Hoff Plot

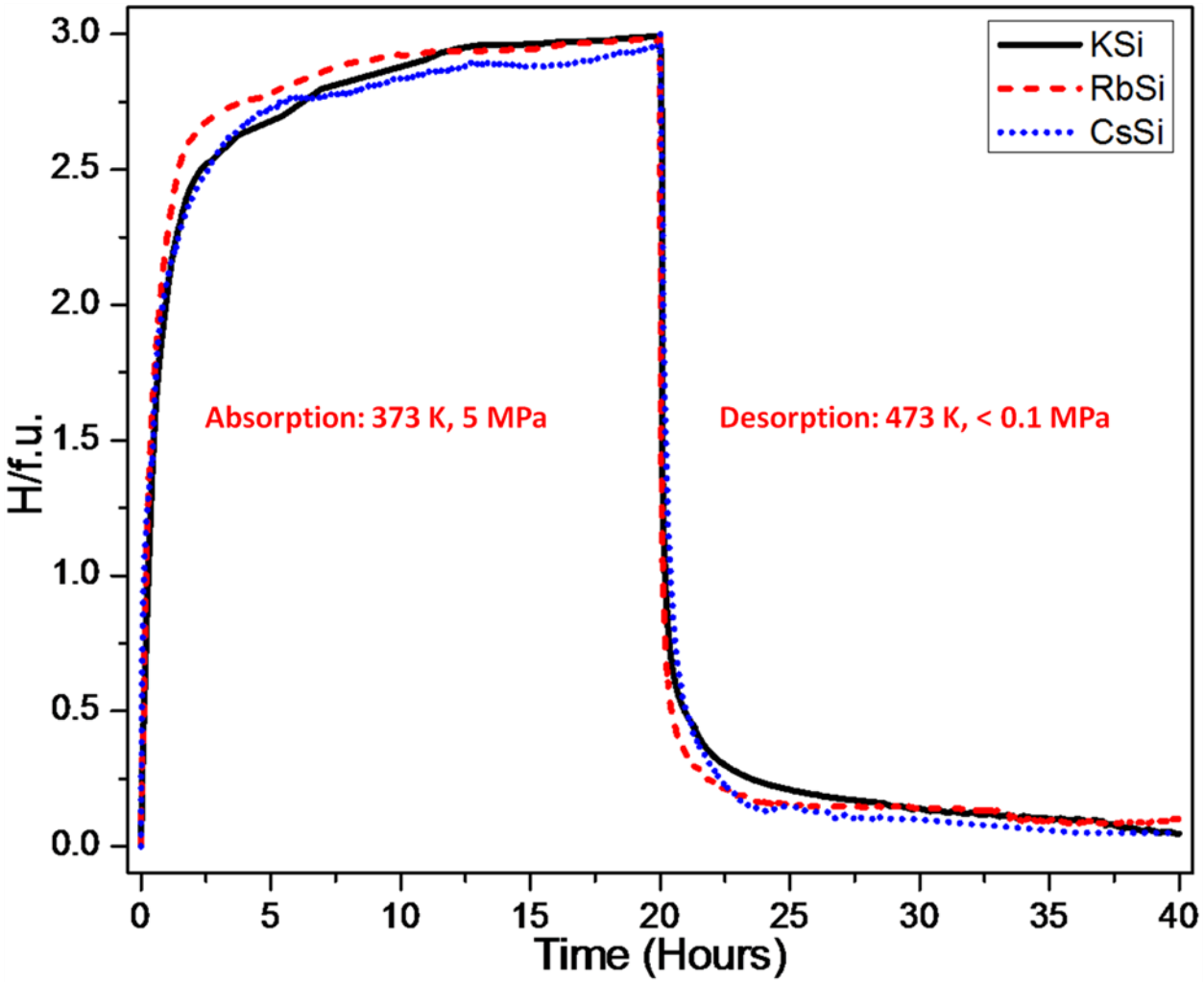
$KSi + 3/2\ H_2 \Leftrightarrow \alpha\text{-}KSiH_3$



	ΔH_{des} (kJ/mol H_2)	ΔS_{des} (Jmol^{-1}K^{-1} H_2)	T@1 bar (°C)
Experimental	23	54	142
Predicted	28	63	170

Introduction

Absorption/desorption kinetics of MSi



Same kinetics whatever is the alkali cation

Direct hydrogenation of NaSi :

Disproportionation:

$$46NaSi + 19H_2 \rightarrow 38NaH + Na_8Si_{46}$$

Same for KSi if reaction is too fast:

$$KSi \xrightarrow{\text{slow hydrogenation}} KSiH_3$$

$$KSi \xrightarrow{\text{fast hydrogenation}} KH$$

$$46KSi + 19H_2 \rightarrow 38KH + K_8Si_{46}$$

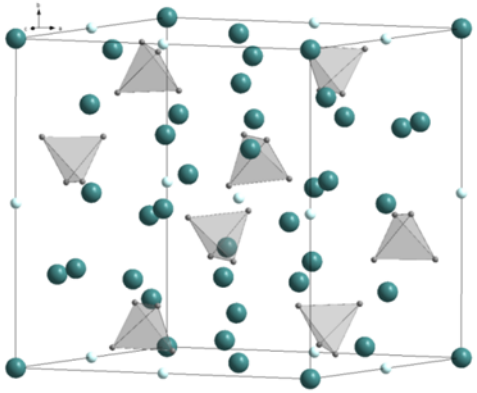
ΔH_{DFT} = -28 kJ/mol H_2

ΔH_{DFT} = -68 kJ/mol H_2

Introduction

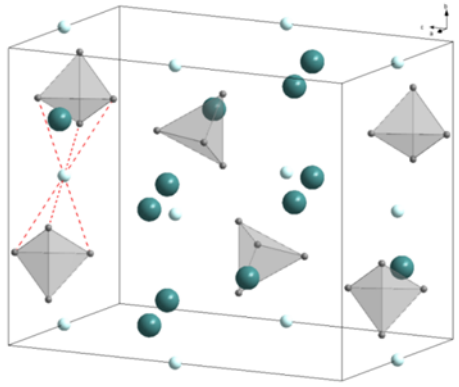
1986: report of K_7LiSi_8 and K_3LiSi_4 by a german team

K_7LiSi_8



Pa-3

K_3LiSi_4



Pnma

K_7LiSi_8 powder (burgundy red color)

Hydrogen properties have never been studied

$K_{8-x}Li_XSi$ as hydrogen storage material ?

Von Schnering, H. G., Schwarz, M., & Nesper, R., *Angew. Chem. Int. Ed. Engl.* **25** (1986) 556.

Synthesis of $K_{8-x}Li_xSi_8$

Precursors:

- crystalline Si powder (40 µm)

- Potassium metal preserved in mineral oil

- Lithium granules

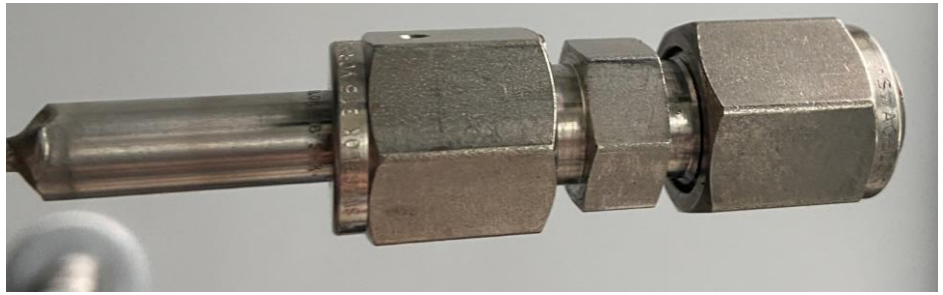
Synthesis conditions:

First tests by direct synthesis in sealed steel tube: unsuccessful, very sticky, sample non homogeneous

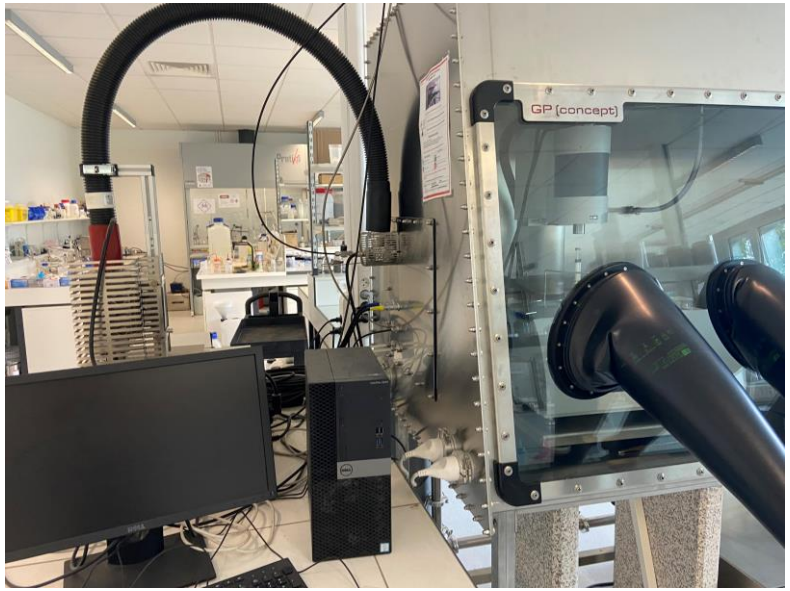
Need a first ball-milling (BM) step, then annealing

- BM: 48 cycles of 15 min at 600 rpm (5 min break)
- Annealing: 48h at 500°C in sealed steel tubes

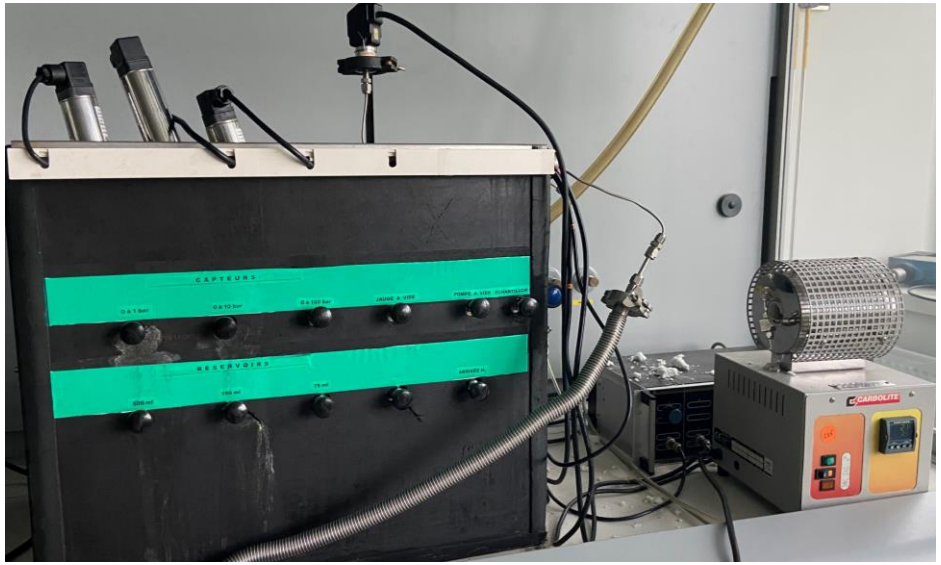
Characterization tools and methods



Sample holder for hydrogenation



TGA and mass spectrometry inside glovebox

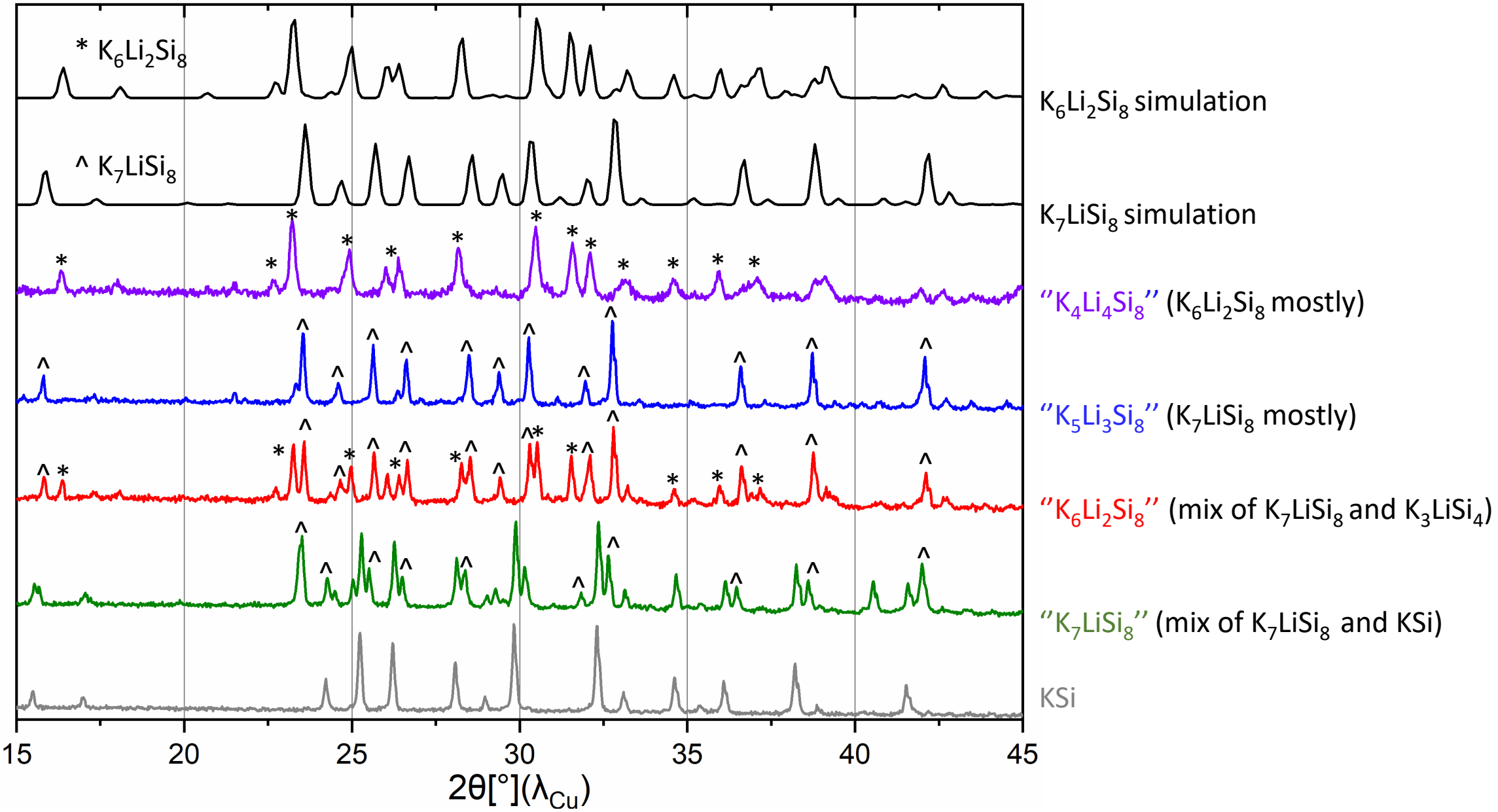


Manual hydrogenation bench

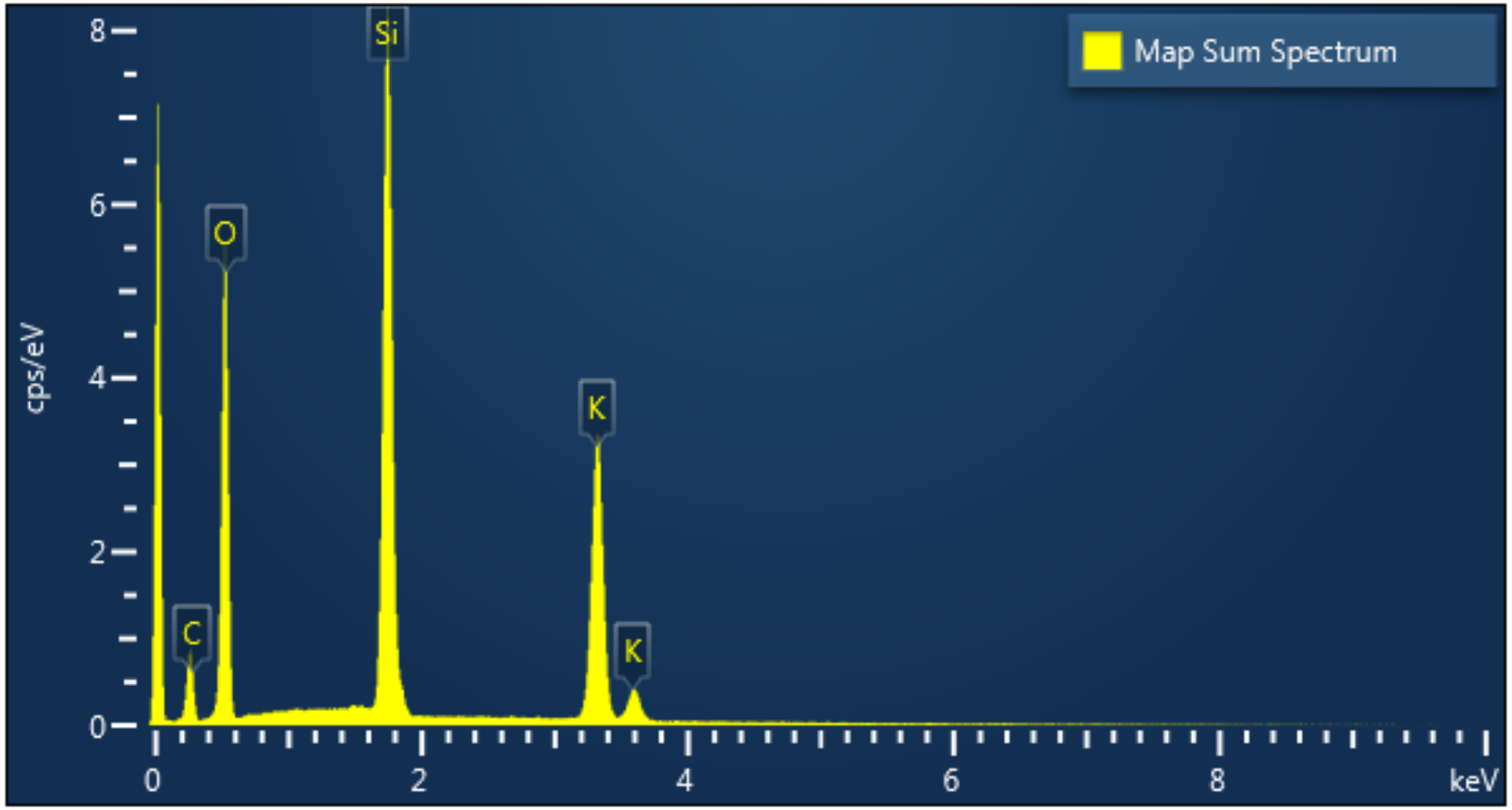
XRD cell with beryllium window

Synthesis of $K_{8-x}Li_xSi_8$ with x=0,1,2,3 or 4

X-ray powder diffraction of samples synthetized at 500°C



Energy dispersive X-ray analysis with scanning electron microscopy

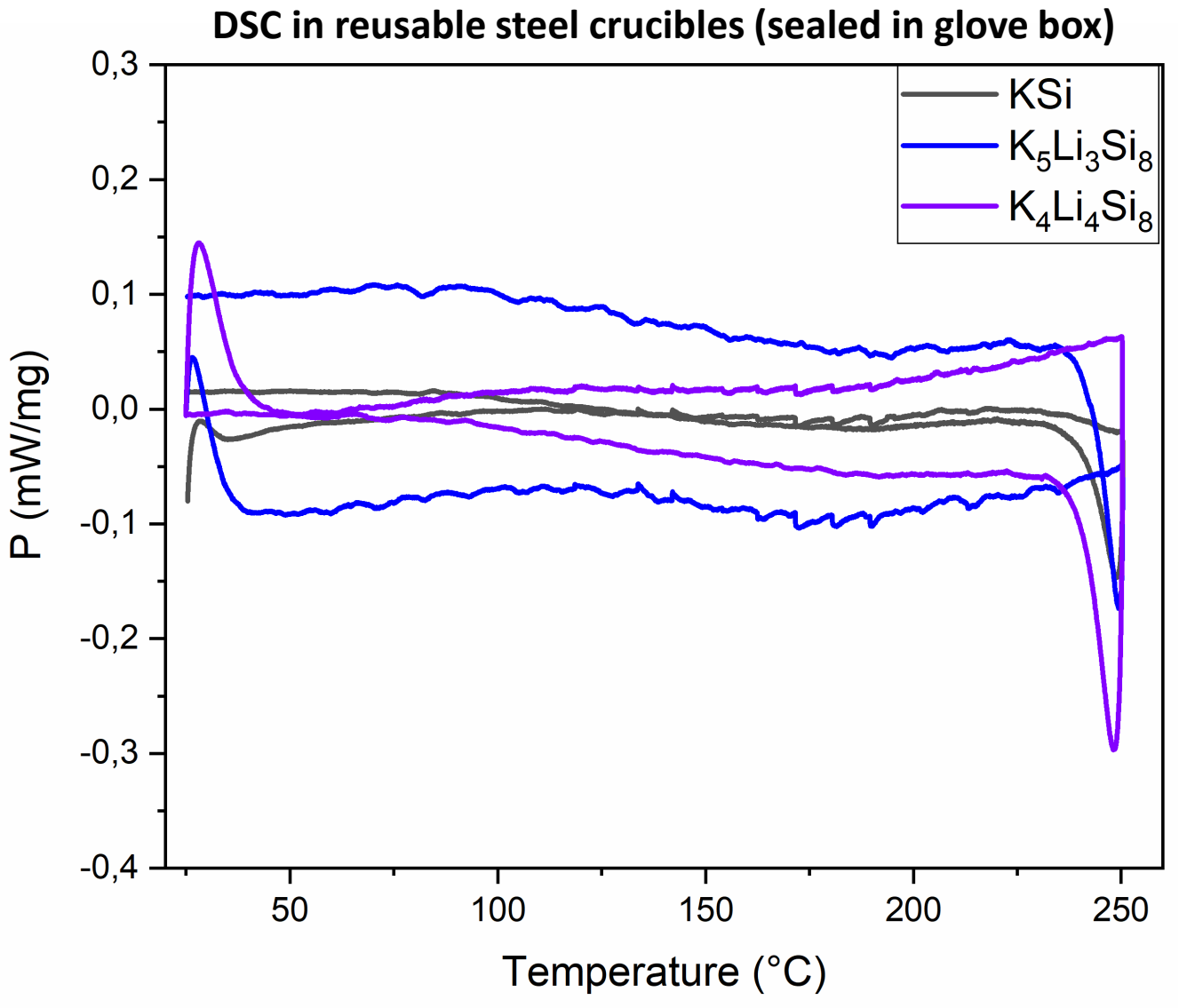


Element	%mol
C	6,8
O	48,4
Si	23,5
K	21,3
Total:	100.00

EDX analysis of KSi

No trace of Fe in our sample → no contamination

Differential Scanning Calorimetry under Ar



Conditions:

5°C/min
25 to 250 °C under Ar flow

Observation:

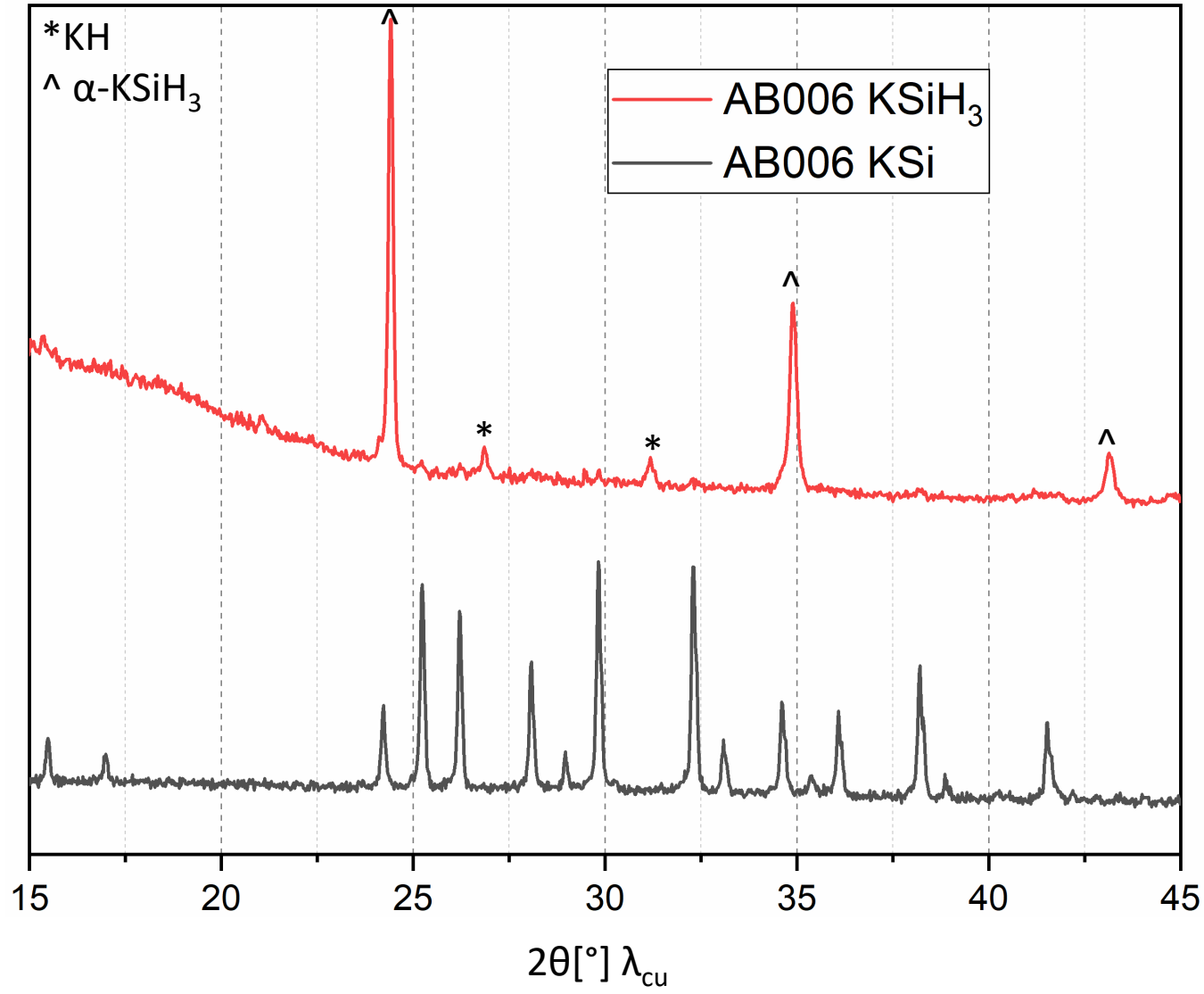
No exo/endothermic peak, no trace of unreacted Li

Conclusion:

No melting peaks of unreacted K or Li

Hydrogenation of KSi

X-ray powder diffraction of KSi and hydrogenated KSi (α-$KSiH_3$)



Conditions of hydrogenation:

150°C during 48h under 40 bar of H_2

Little formation of K_8Si_{46} and KH:

$KSi + \frac{3}{2} H_2 <-> KSiH_3$

$46\ KSi + 19\ H_2 \rightarrow K_8Si_{46} + 38\ KH$

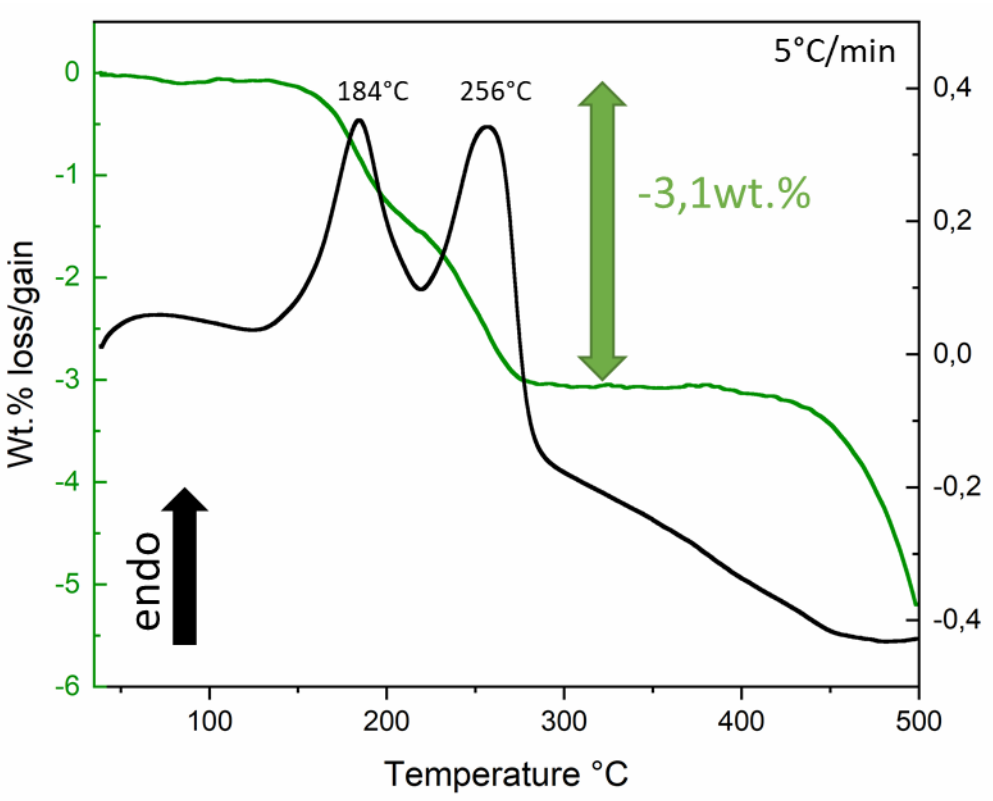
Thermal analysis of α-$KSiH_3$

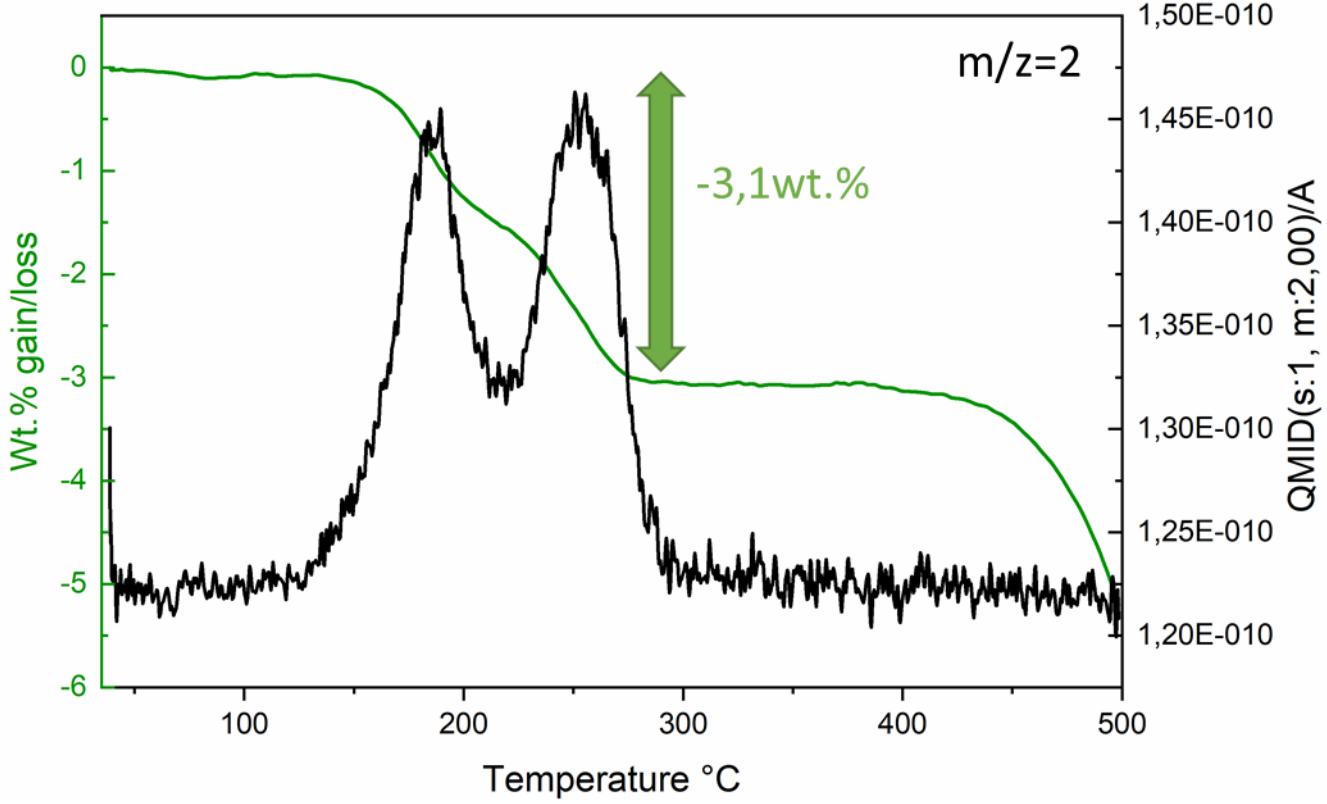
TGA and DTA:

- 3,1 wt.% mass loss
- 2 endothermic peaks (184°C/256°C)

TGA and mass spectrometry:

- 3,1 wt.% mass loss
- H_2 desorption only

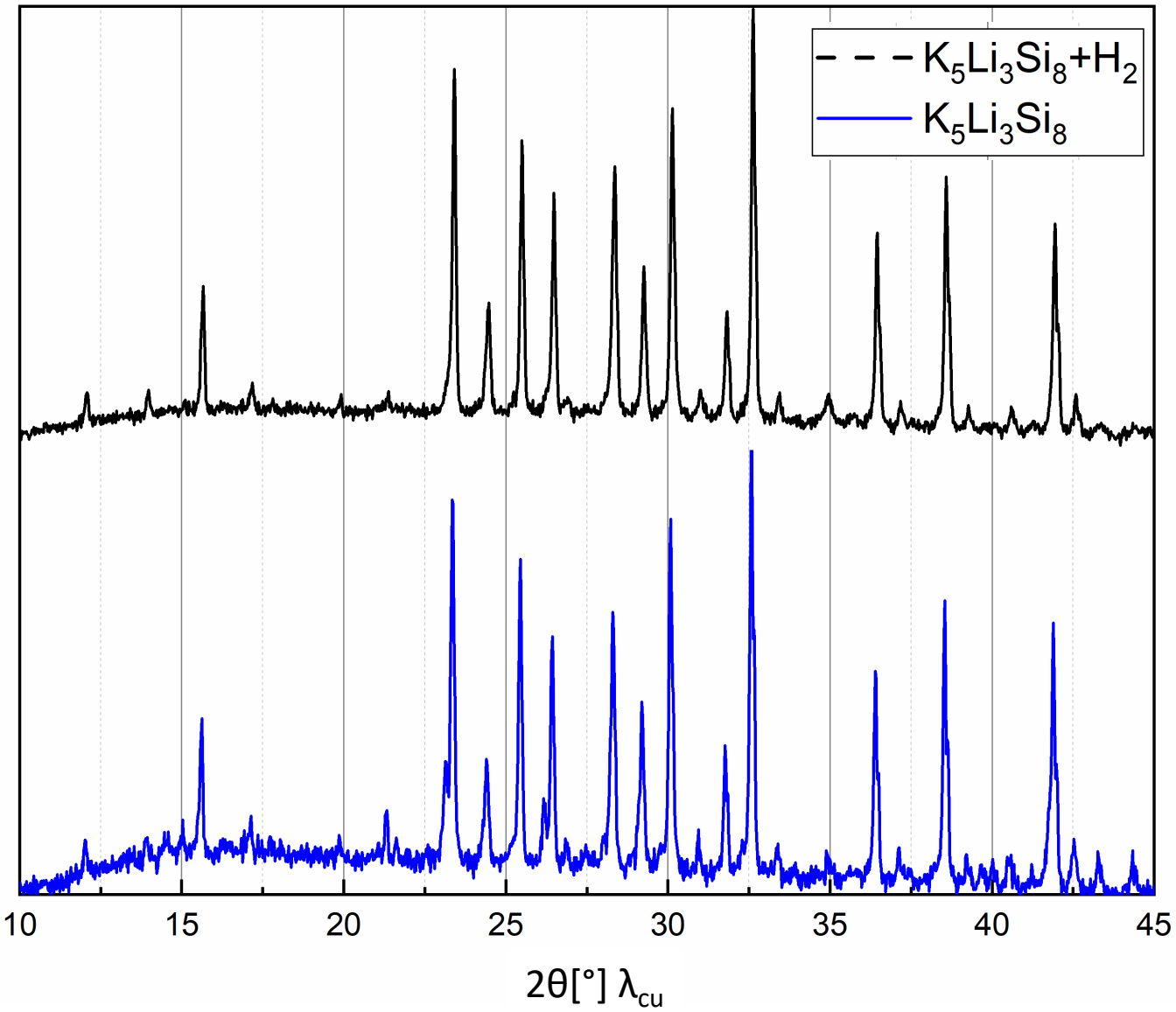




Thermal analysis by TGA, DTA and MS (in glove box)

Hydrogenation of « $K_5Li_2Si_8$ »

Sample = mainly K_7LiSi_8 from XRD



Conditions of hydrogenation:

180°C during 48h under 40 bar of H_2

No changes after hydrogenation

Thermal analysis of « $K_5Li_2Si_8$ » after hydrogenation

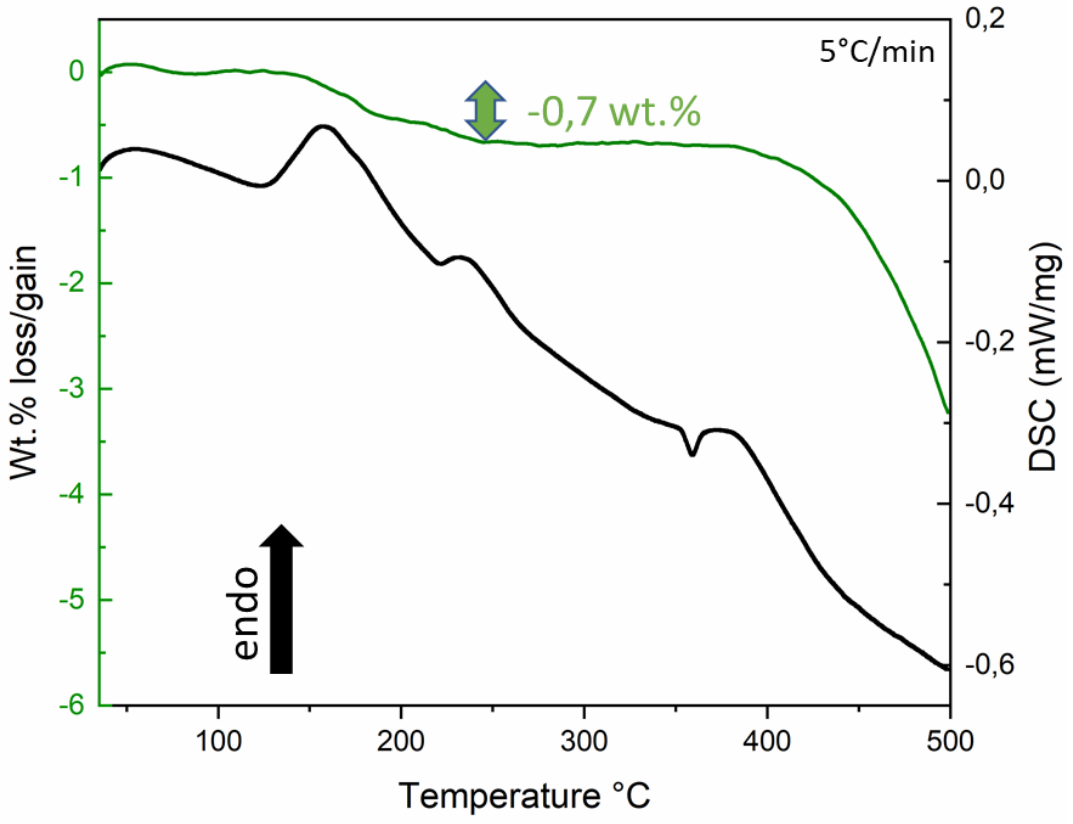
Thermal analysis by TGA, DTA and MS (in glove box)

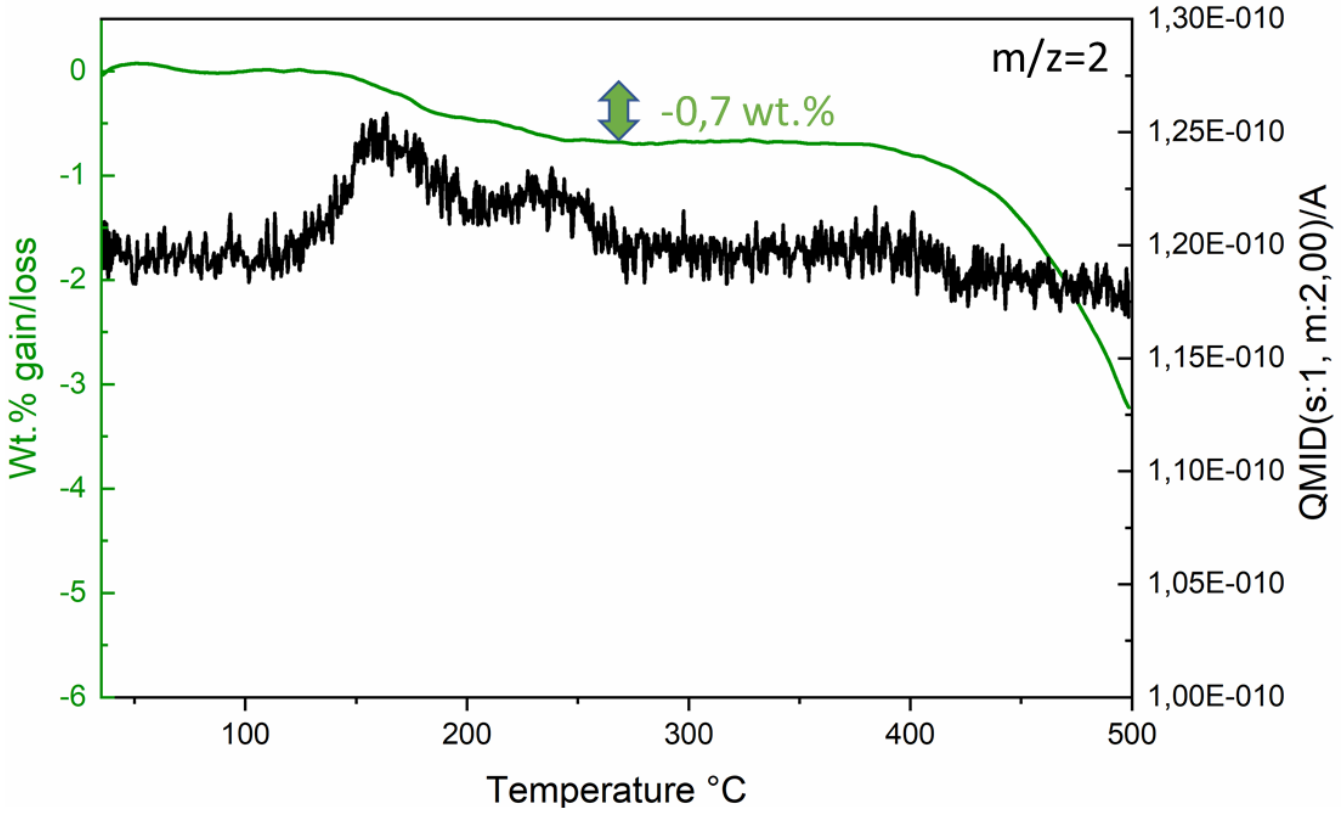
TGA and DTA:

- 0,7 wt.% mass loss
- 2 endothermic peaks

TGA and mass spectrometry:

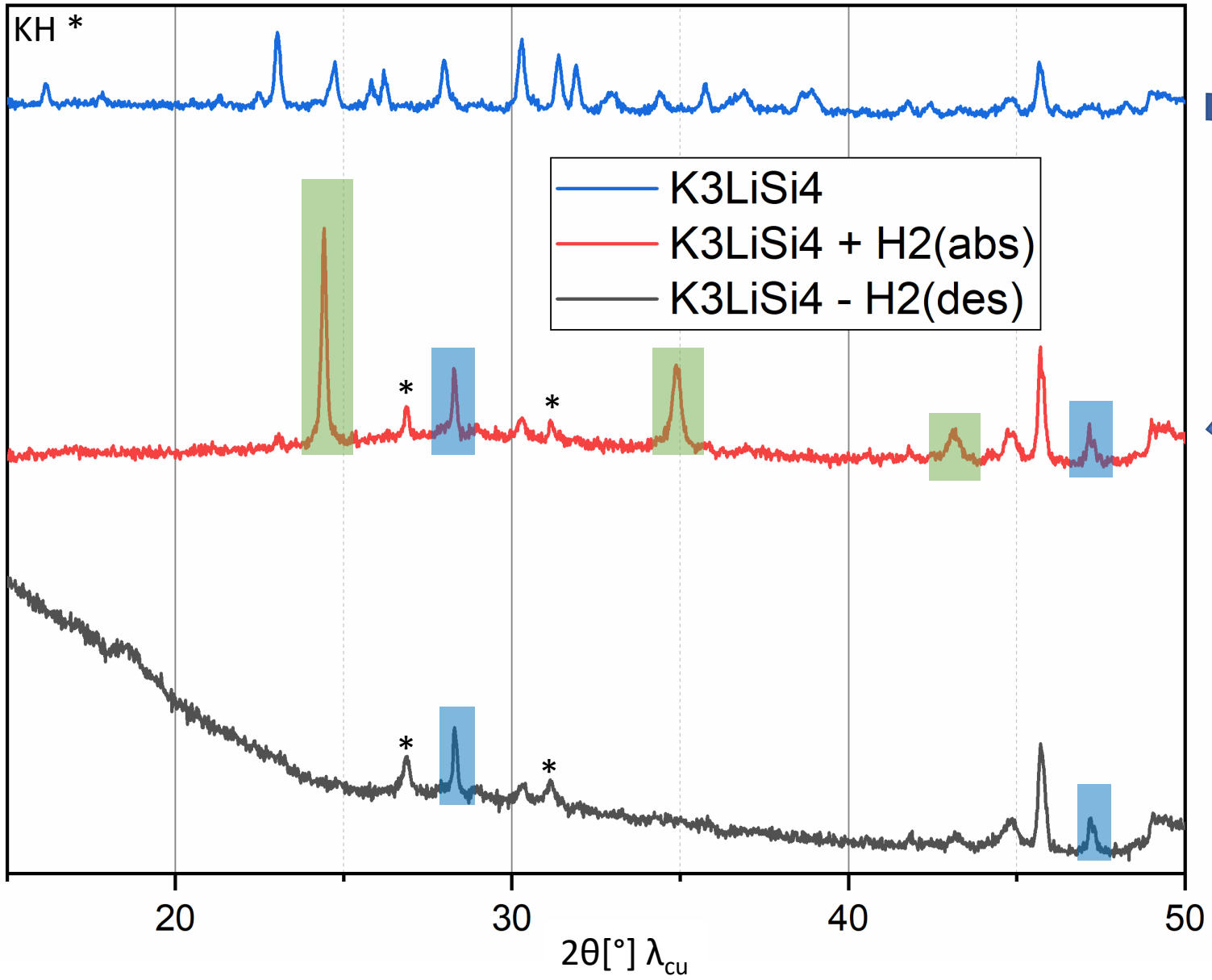
- 0,7 wt.% mass loss
- H_2 desorption only





Hydrogenation of « $K_4Li_4Si_8$ »

Sample = mainly K_3LiSi_4 from XRD



α-$KSiH_3$

Si

$K_3LiSi_4 + 3/2H_2$ <-> α-$KSiH_3$ + « LiSi »

« LiSi » = $Li_{12}Si_7 + Si$

α-$KSiH_3$ = ?

The LiAlSi intermetallic and its possible hydride ?

Introduction LiAlSi

In 1960, Nowotny et al. prepared LiAlSi by a melting reaction of the elements

In 1993, Dahl et al. studied the hydrogenation properties of LiAlSi:

$$\mathbf{LiAlSi + 0{,}45\ H_2 <-> LiAlSiH_{0,9}}$$

80 bar, T=535°C during 30 hours

In 2015, Kunkel et al. reported however the following :

No difference before and after exposing LiAlSi samples to 80 bar during 4 days at 550°C

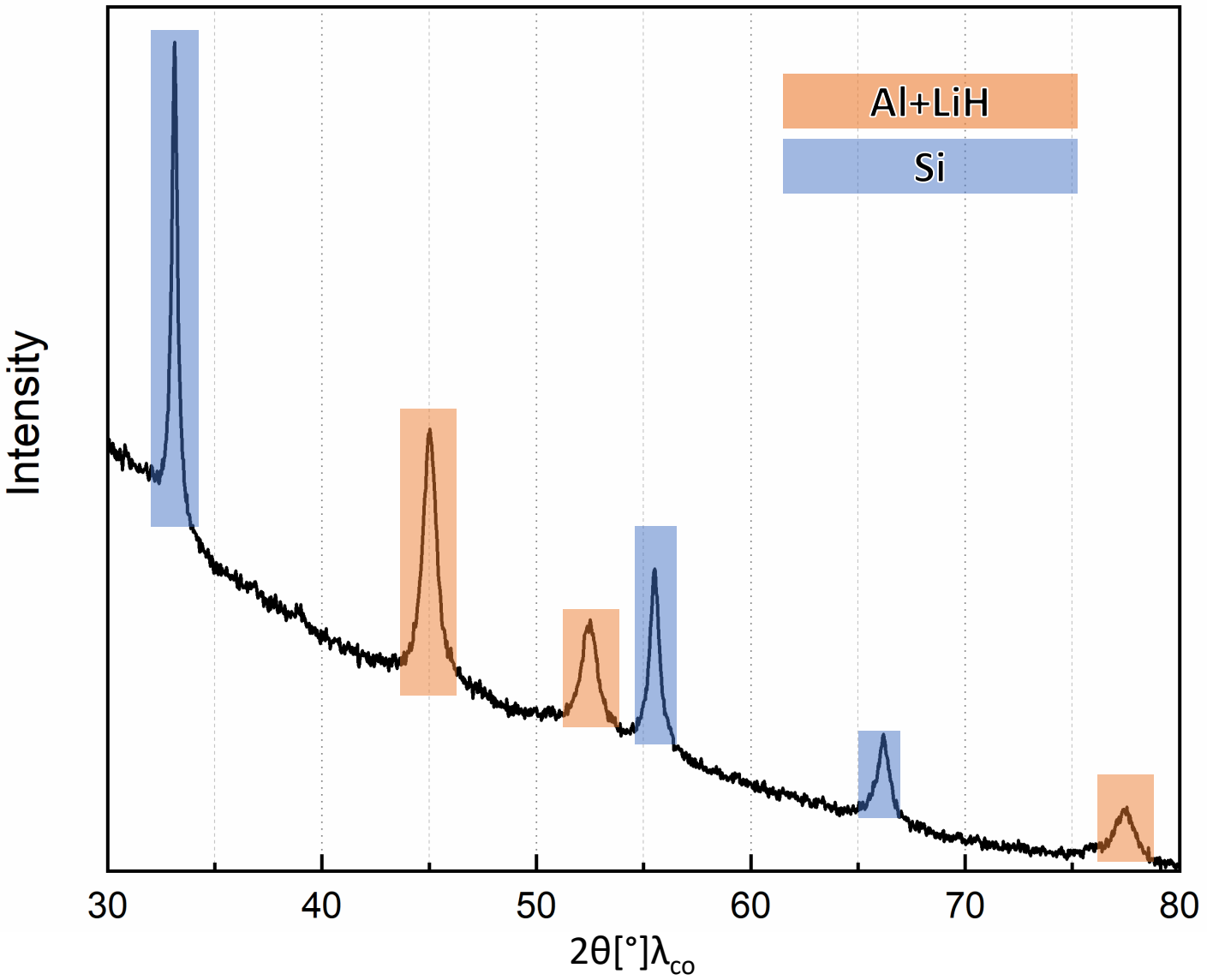
But they found a slow decomposition reaction:

$$\mathbf{LiAlSi + \tfrac{1}{2}\ H_2 -> LiH + Al + Si}$$

H. Nowotny, F. Holub, *Monatsh. Chem.,* **91** (1960), pp. 878-887
C. Dahl, H.-U. Schuster, *Z. Anorg. Allg. Chem.,* **619** (1993), pp. 1629-1632
N. Kunkel, C. Reichert, M. Springborg, D. Wallacher, H. Kohlmann, J. Solid State Chem., **221** (2015), pp. 318-324

Synthesis of $LiAlSiH_x$ by reactive ball-milling

Powder X-Ray Diffraction of $LiAlSiH_x$



<u>$LiAlSiH_x$ synthesis conditions:</u>

Reactive Ball-Milling under H_2

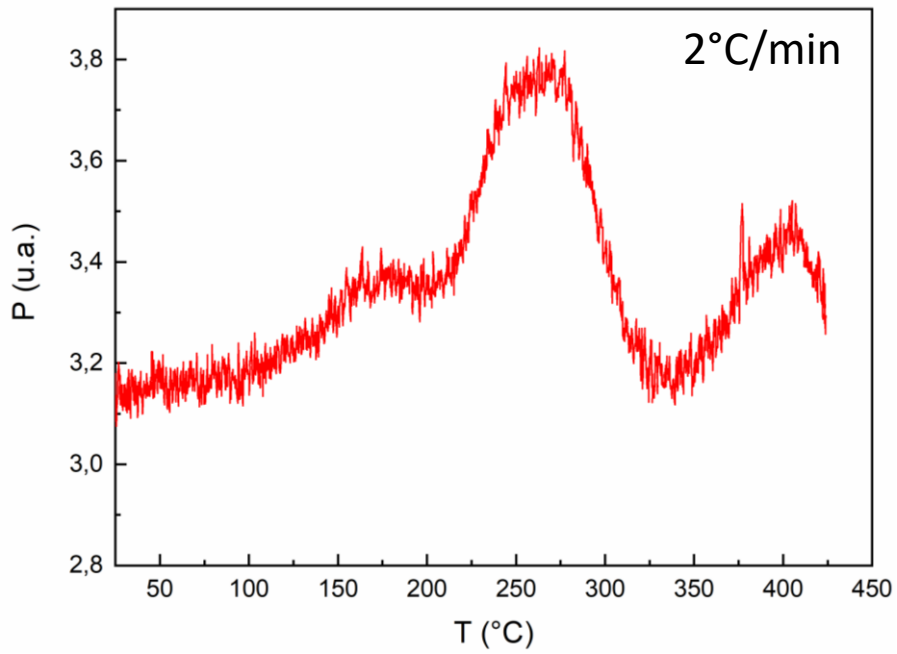
P_{H2} = 80 Bar

Speed: 800 rpm

3 cycles of 3 hours of milling with 3 hours of breaks

$LiAlSiH_x$ Desorption

Pressure variation during heating under vacuum

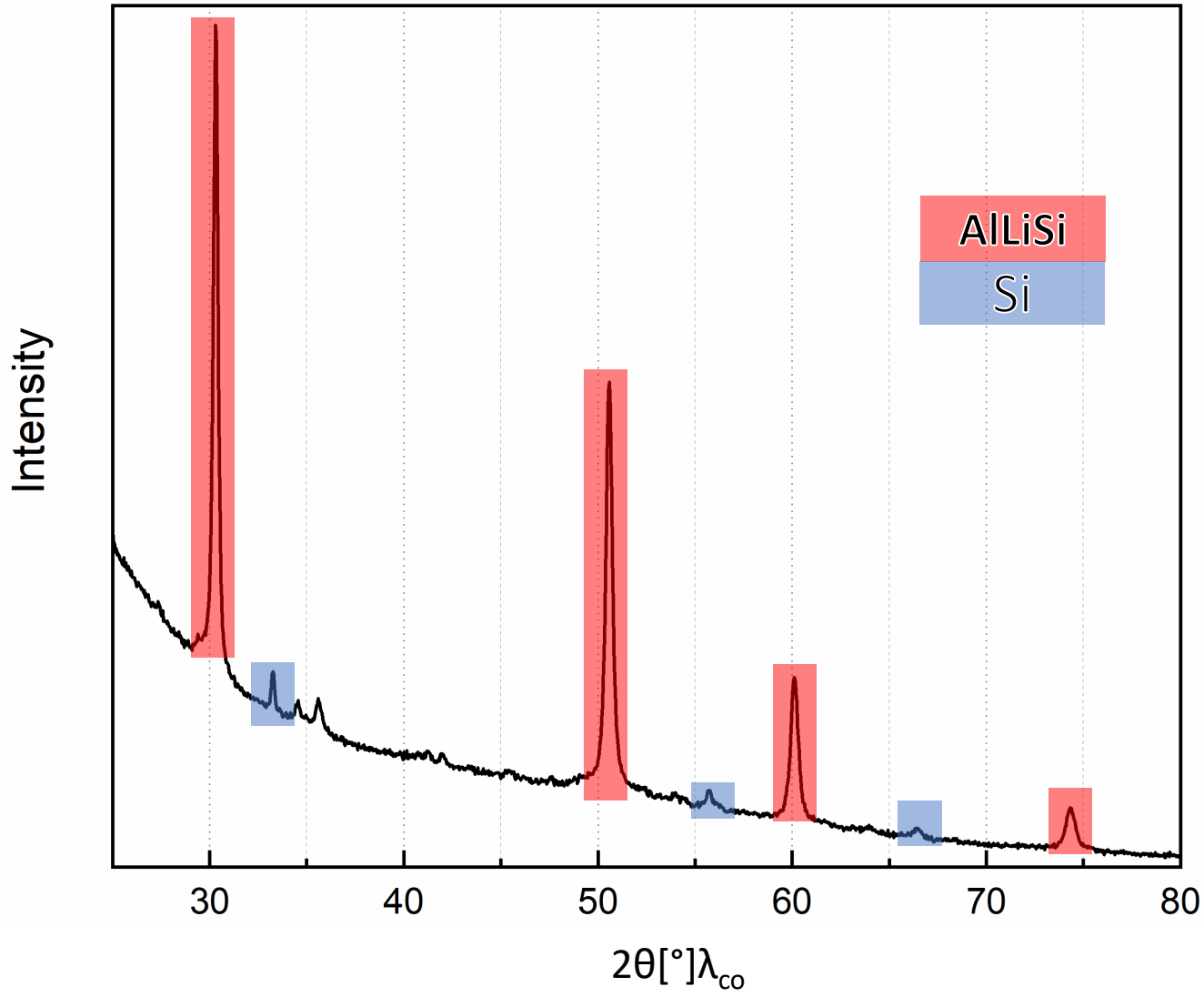


After desorption we obtain our material of interest:

LiAlSi intermetallic with traces of Si

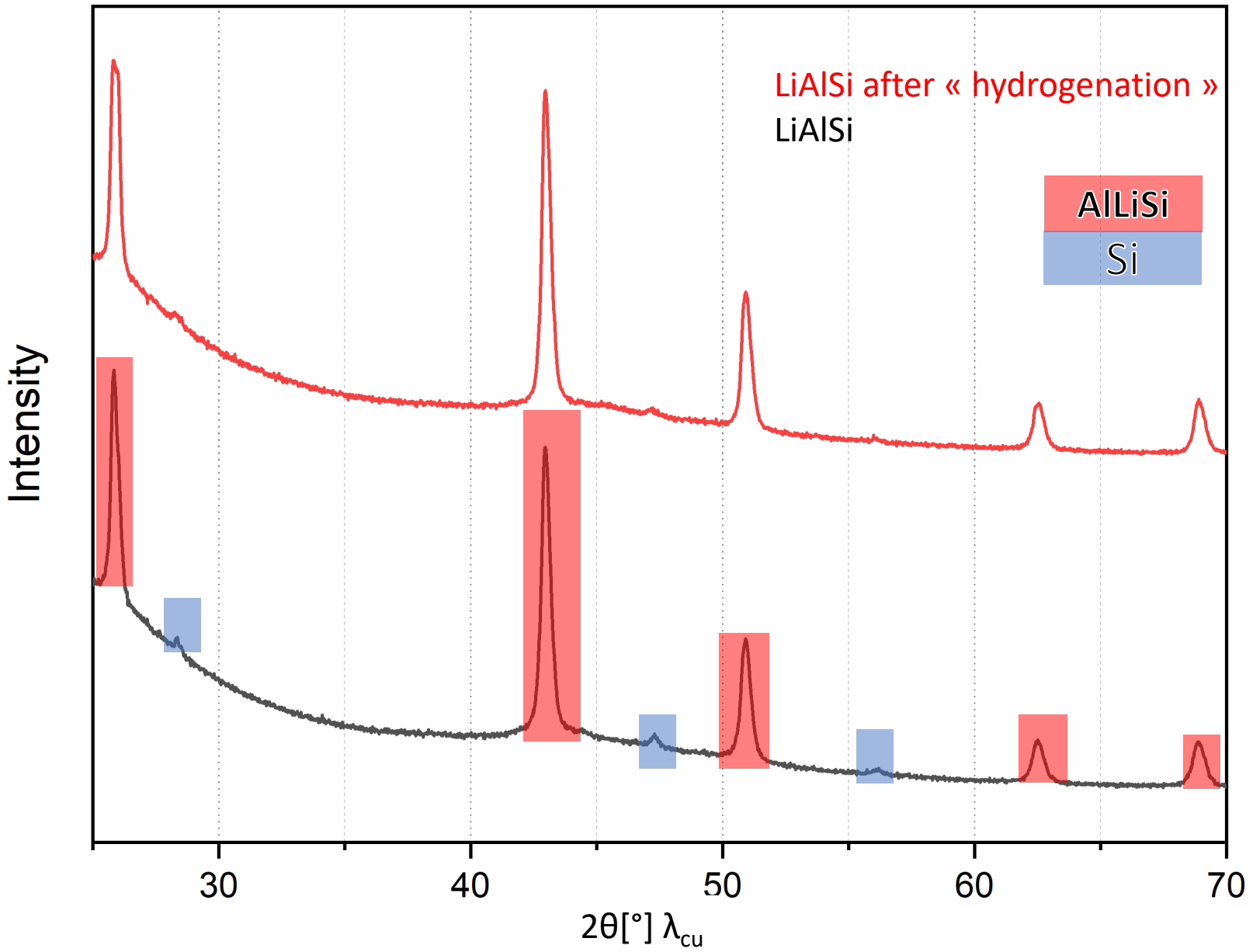
Can LiAlSi store hydrogen reversibly ?

Powder X-Ray Diffraction of $LiAlSiH_x$ after desorption



Can LiAlSi absorb hydrogen ?

X-Ray Diffraction of LiAlSi before and after hydrogenation



Conditions of hydrogenation:

48 hours under 80 Bar at 450°C

Conclusion:

For now:

$LiAlSi + xH_2$ ✗ $LiAlSiH_x$

In this condition (80 bar at 450°C)

Perspectives

- Further investigation of hydrogenation properties of K_7LiSi_8 and $K_6Li_2Si_8$
- Study mixed $M_{1-x}M'_xSi$ phases (M=Rb, Cs, K)
- Substitute Lithium by Strontium ($Li_xSr_{1-x}AlSi$) or Calcium ($Li_xCa_{1-x}AlSi$)

Acknowledgments

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