

# PHASE EQUILIBRIA IN La-Ni-M, M=(Al, In, Sn) TERNARY SYSTEMS WITH HYDROGEN

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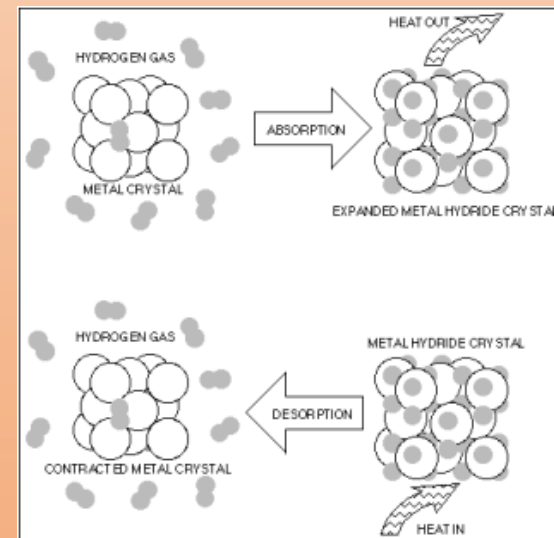
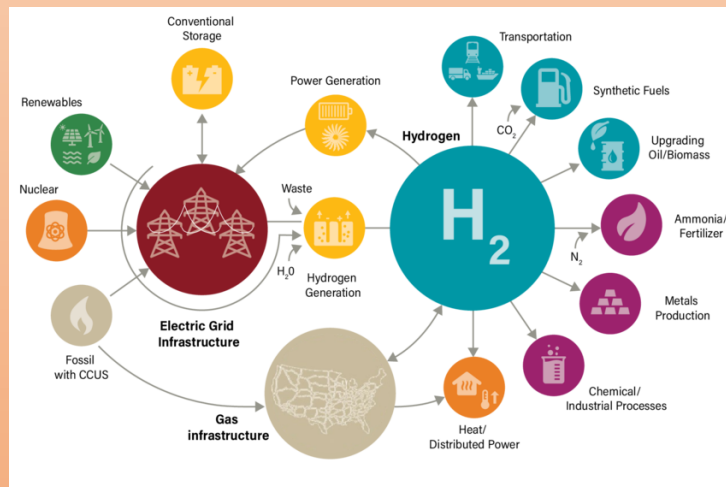


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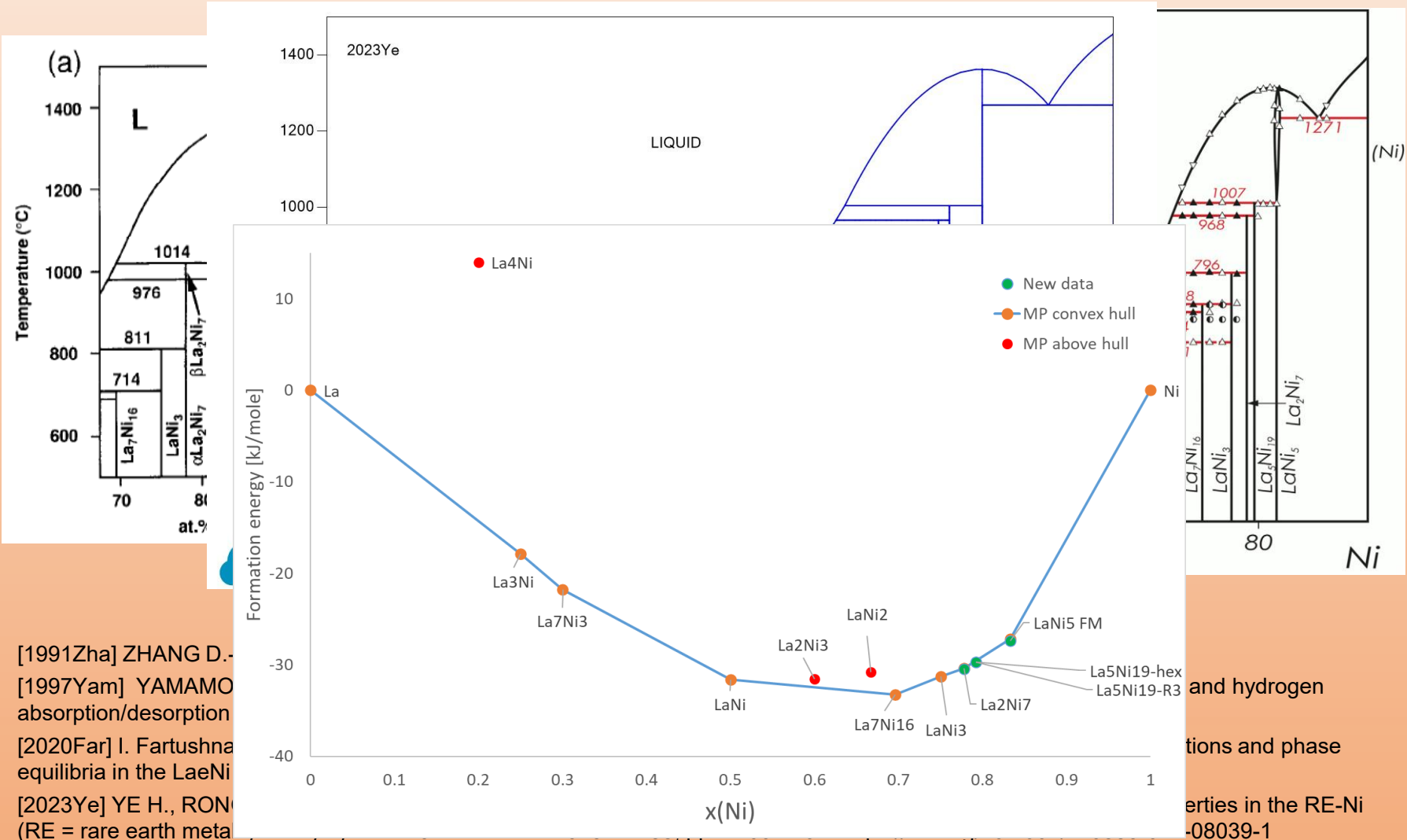
# Hydrogen storage materials

- **hydrogen** may play a key role in energy storage in the future
- green hydrogen: minimal environmental footprint
- **complication**: explosiveness in mixture with oxygen and the problems of transport
- **solution**: store hydrogen in the form of powdered hydrides from which hydrogen gas could be released by changing the temperature or pressure
- $\text{LaNi}_5$  is known as a hydrogen storage material, form relatively stable  $\text{LaNi}_5\text{H}_x$  hydrides
- presence of other phases can affect the thermodynamic and kinetic properties of (de)hydrogenation
- the structures of two types of hydrides  $\text{La}(\text{Ni},\text{M})_5\text{H}_{n-7}$  and  $\text{H}_x\text{T}_y$  are generally known



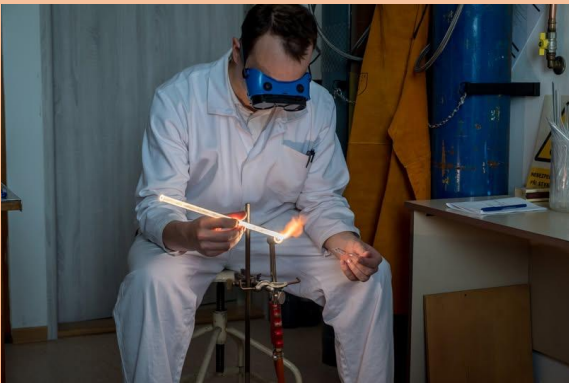
# Binary subsystem La-Ni

a) 1991Zhang; b) 1997Yamamoto; c) 2020Far+2023Ye



# Experimental phase diagram-sample preparation

- the overall composition -  $\text{LaNi}_5$  containing alloys
- prepared from pure metals in arc-melting furnace under the inert atmosphere
- sample mass was 800-1200 mg
- remelted and flipped several times for homogenization
- long term annealing was performed in evacuated quartz glass ampoules employing alumina or tantalum crucibles
- quenched into the liquid nitrogen

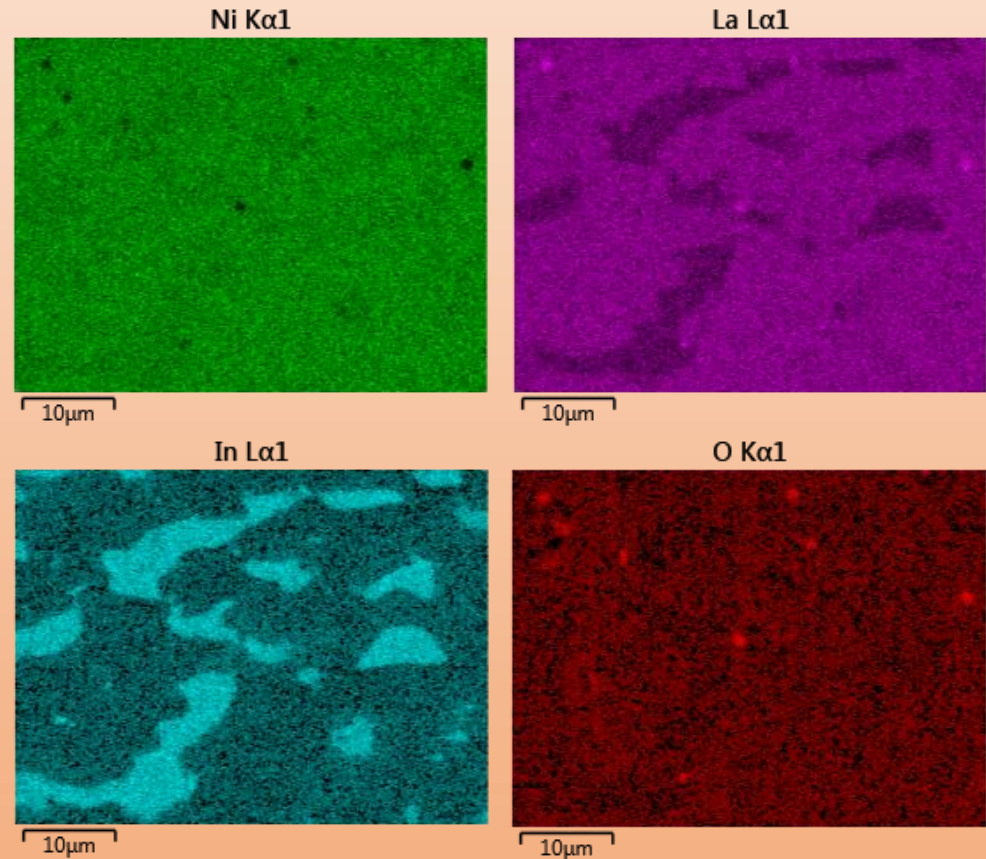


# Phase analysis

- alloyed samples were metallographically prepared (isopropanol as a coolant)
- overall and phase chemical composition was measured by SEM-EDX
- structure was studied by powder XRD



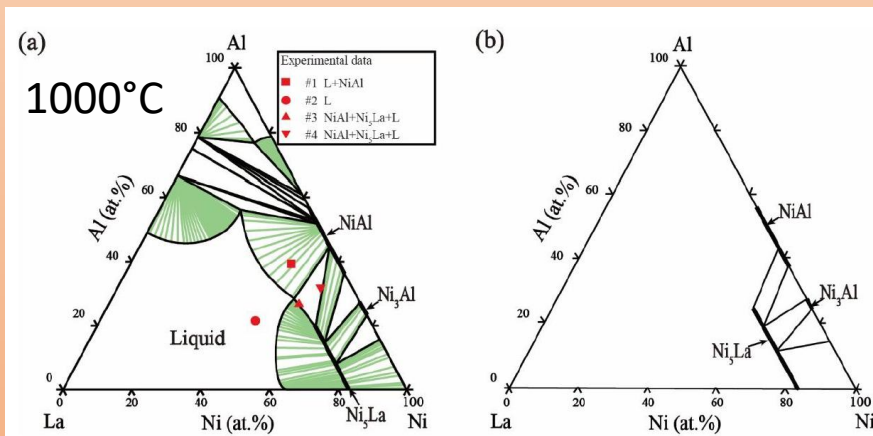
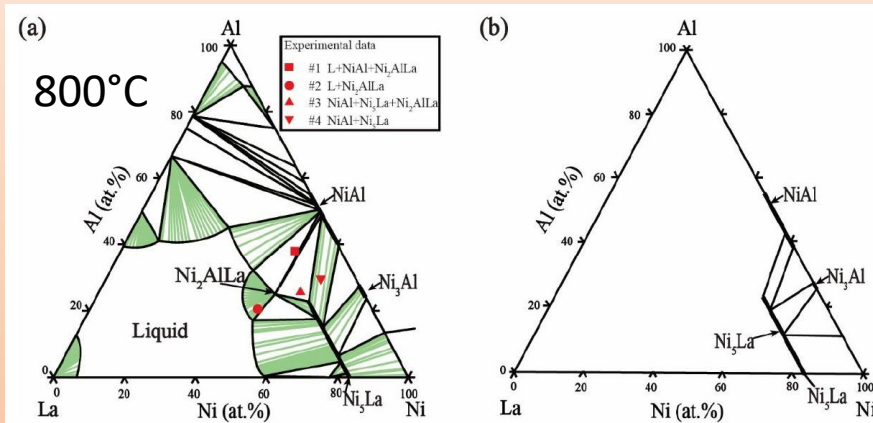
TESCAN LYRA 3 equipped  
by EDX, EBSD, FIB



Sample consisting of phases  $\text{LaNi}_5$  +  $\text{In}_2\text{LaNi}_9$

# Ternary system Al-La-Ni

- ternary system is quite complex
- 17 ternary phases described in literature

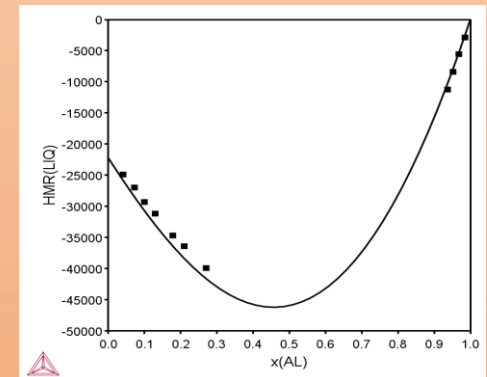
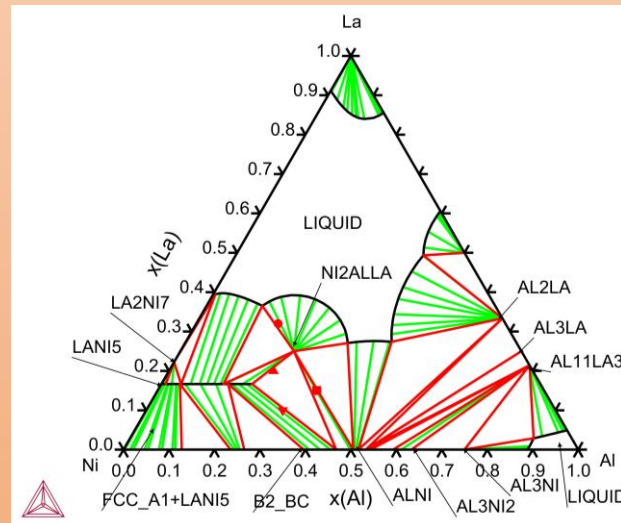
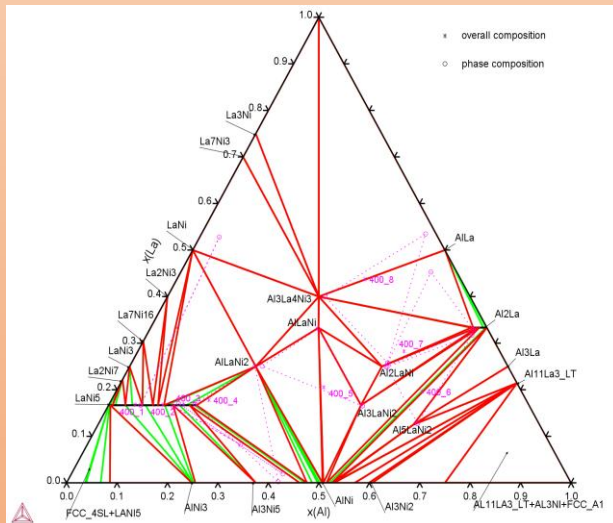
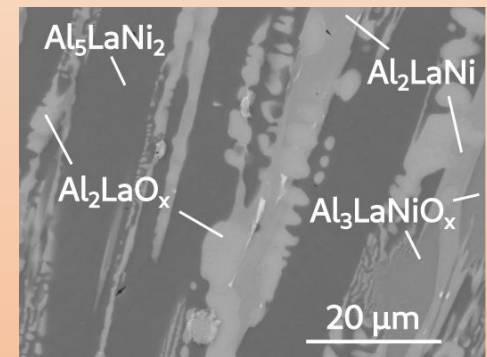
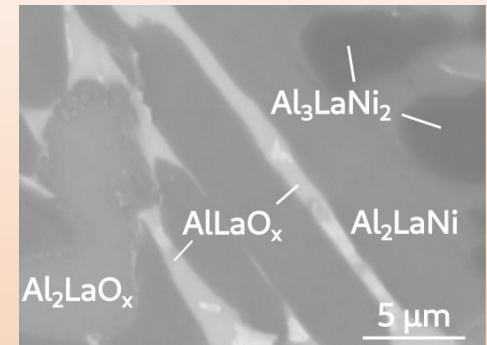


J. Liao, H. Wang, T.-Y. Chen, Experimental Investigation and Thermodynamic Calculation of Ni–Al–La Ternary System in Nickel-Rich Region: A New Intermetallic Compound Ni<sub>2</sub>AlLa Materials, 2018, 11, 2396.

| Phase name                                            | Space group | Lattice parameters |       |        |
|-------------------------------------------------------|-------------|--------------------|-------|--------|
|                                                       |             | a [pm]             | b[pm] | c[pm]  |
| La(Ni <sub>1-x</sub> Al <sub>x</sub> ) <sub>13</sub>  | cF122       | 1172               |       |        |
| LaNi <sub>2</sub> Al <sub>5</sub>                     | oI16        | 703.3              | 967.7 | 402.1  |
| LaNi <sub>2</sub> Al <sub>3</sub>                     | oC*         | 1012.2             | 781.2 | 514.2  |
| LaNiAl <sub>2</sub>                                   | oC16        | 719.9              | 420.3 | 1608.5 |
| La(Ni <sub>1-x</sub> Al <sub>x</sub> ) <sub>2</sub>   |             |                    |       |        |
| La <sub>2</sub> Ni <sub>2.25</sub> Al <sub>0.75</sub> | oP*         | 562.0              | 858.5 | 437.8  |
| La <sub>8</sub> Ni <sub>26</sub> Al <sub>81</sub>     | C2/m        | 310.7              | 41.1  | 165.2  |
| La <sub>31</sub> Ni <sub>54</sub> Al <sub>53</sub>    | P6/m        | 264.3              |       | 41.0   |
| La <sub>2</sub> NiAl <sub>7</sub>                     |             |                    |       |        |
| LaNi <sub>1.44</sub> Al <sub>5.56</sub>               |             |                    |       |        |
| LaNiAl <sub>4</sub>                                   |             |                    |       |        |
| LaNiAl                                                |             |                    |       |        |
| La <sub>4</sub> Ni <sub>3</sub> Al <sub>3</sub>       |             |                    |       |        |
| La <sub>2</sub> Ni <sub>2</sub> Al <sub>1</sub>       |             |                    |       |        |
| *                                                     |             |                    |       |        |
| *                                                     |             |                    |       |        |

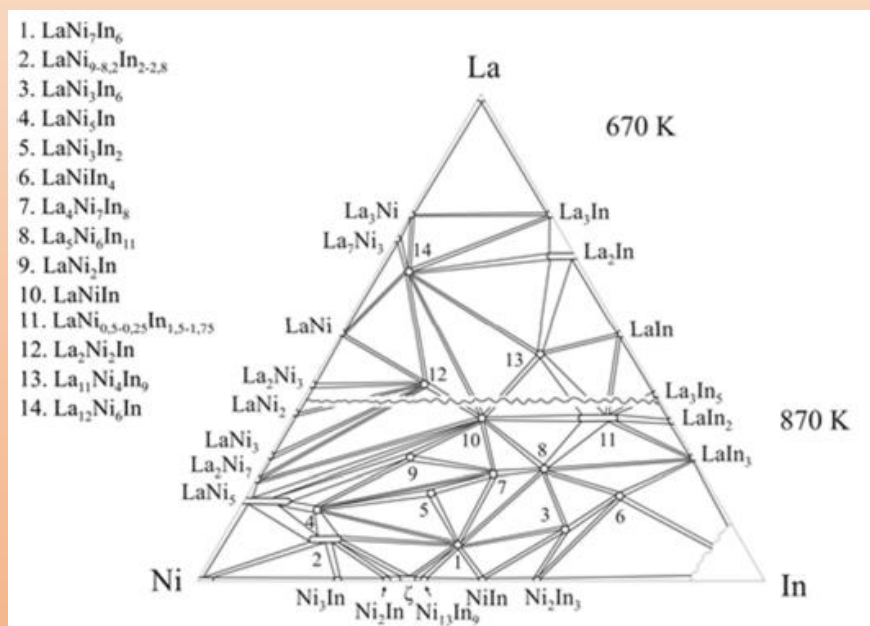
# Ternary phase diagram: Al-La-Ni

- predicted phase diagram at 400 and 800°C with superimposed experimental data
- samples were partly oxidized
- work will continue by new set of samples



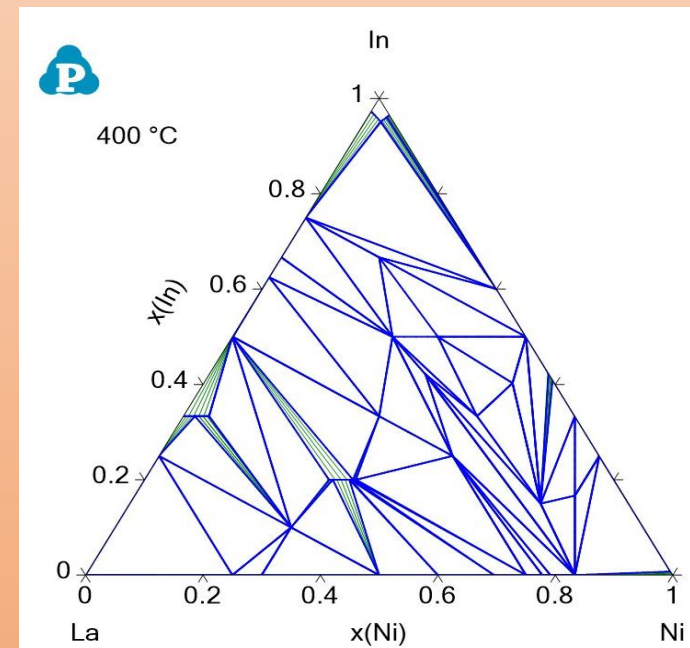
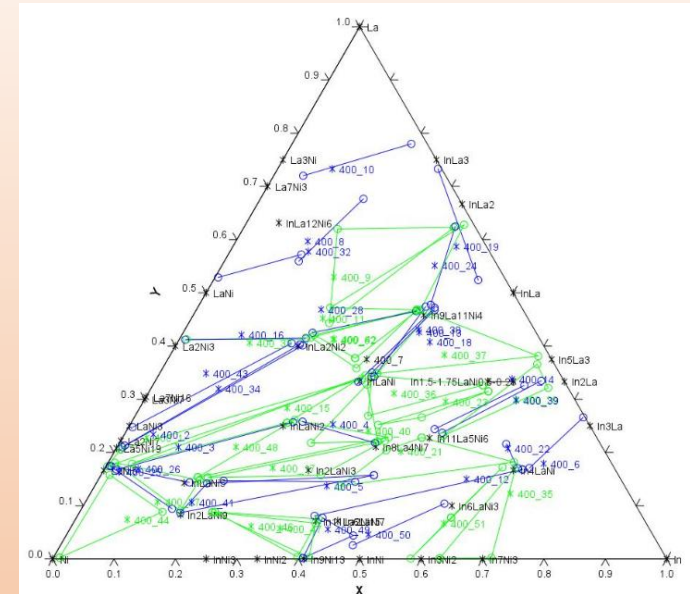
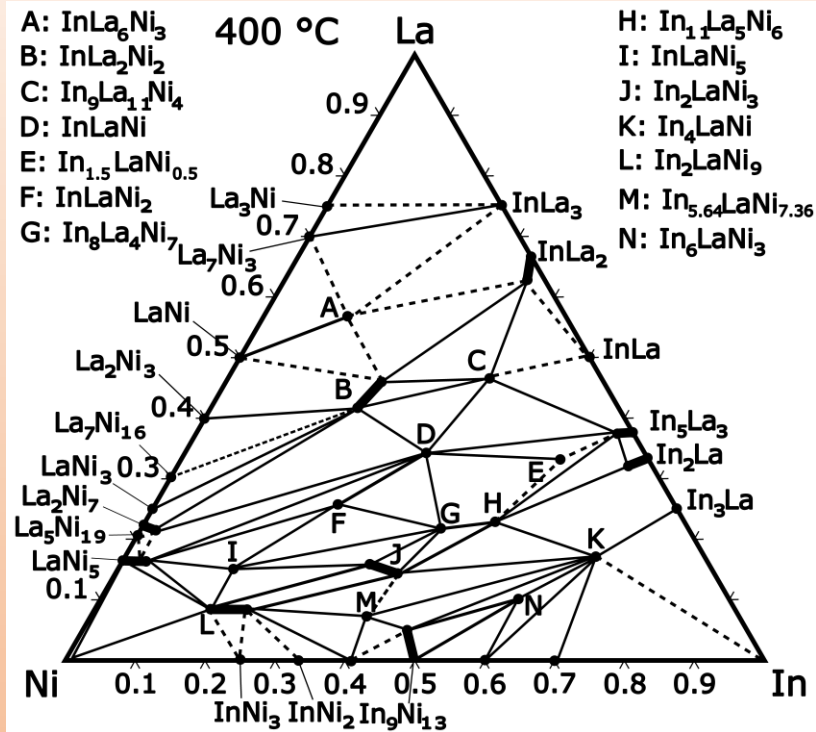
# Ternary system In-La-Ni

- ternary system is quite complex
- experimental PD at 400/600°C
- 14 ternary phases was found



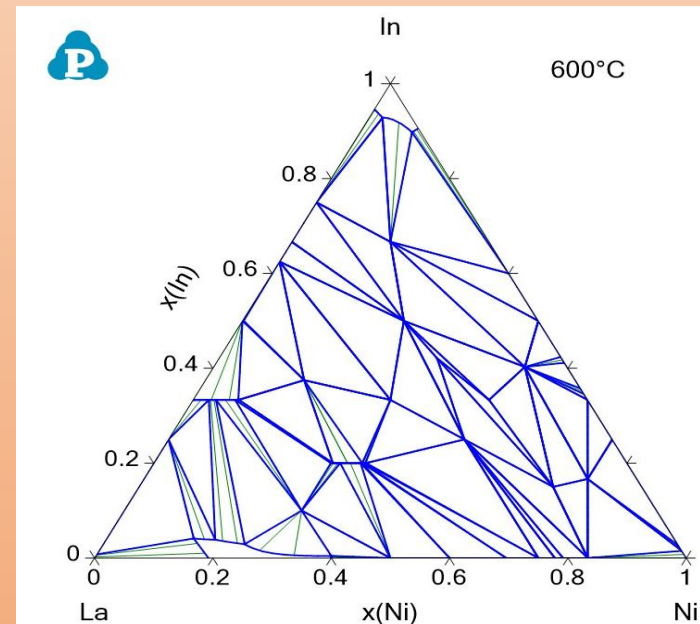
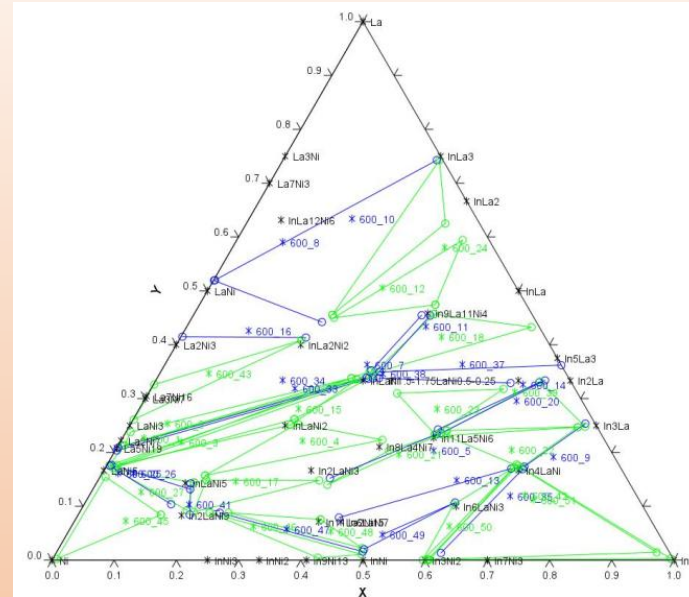
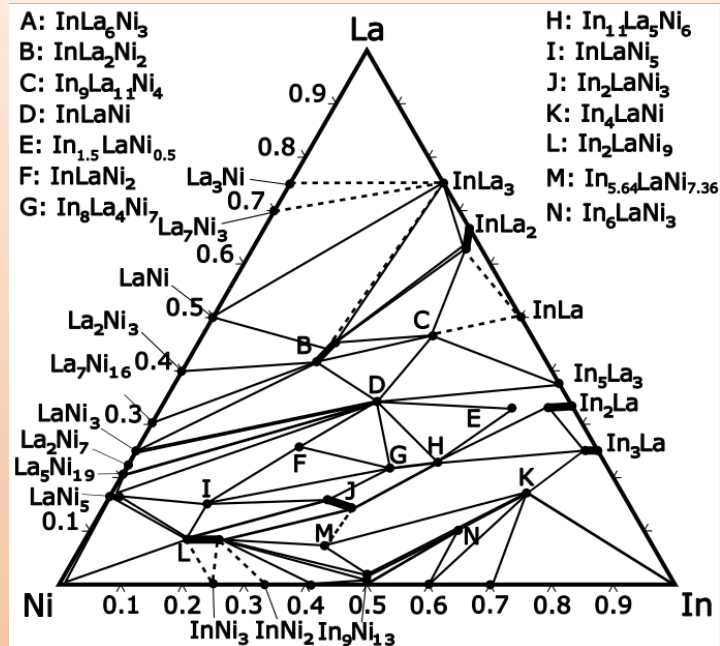
| Phase name                             | Space group     | Lattice parameters [Å] |        |        |
|----------------------------------------|-----------------|------------------------|--------|--------|
|                                        |                 | a                      | b      | c      |
| $\text{La}_{11}\text{In}_9\text{Ni}_4$ | <i>Cmmm</i>     | 15.08                  | 22.54  | 3.85   |
| $\text{La}_2\text{InNi}_2$             | <i>Pbam</i>     | 3.89                   | 7.53   | 15.40  |
| $\text{La}_5\text{In}_{11}\text{Ni}_6$ | <i>Cmmm</i>     | 14.74                  | 14.83  | 4.49   |
| $\text{LaIn}_2\text{Ni}_9^*$           | <i>P4/mbm</i>   | 8.31                   | 8.31   | 4.86   |
| $\text{LaNiIn}_4$                      | <i>Cmcm</i>     | 4.51                   | 16.94  | 7.23   |
| $\text{InLaNi}$                        | <i>P62m</i>     | 7.53                   | 7.53   | 4.10   |
| $\text{LaInNi}_2$                      | <i>Pmma</i>     | 4.12                   | 5.26   | 7.15   |
| $\text{La}_2\text{InNi}_2$             | <i>P4/mbm</i>   | 7.59                   | 7.59   | 3.85   |
| $\text{LaIn}_6\text{Ni}_7$             | <i>Ibam</i>     | 0.8066                 | 0.9248 | 1.2465 |
| $\text{LaIn}_6\text{Ni}_3$             | <i>Pmmn</i>     | 0.4388                 | 0.7574 | 1.2110 |
| $\text{LaInNi}_5$                      | <i>P6_3/mmc</i> | 0.4957                 | -      | 19969  |
| $\text{La}_4\text{In}_8\text{Ni}_7$    | <i>Cmmm</i>     | 1.4640                 | 1.4674 | 0.4439 |
| $\text{LaIn}_{1.5}\text{Ni}_{0.5}$     | <i>P6/mmm</i>   | 1.5017                 | 2.2515 | 0.3838 |
| $\text{LaIn}_{1.75}\text{Ni}_{0.25}$   |                 | 1.5006                 | 2.2503 | 0.3835 |
| $\text{La}_{12}\text{InNi}_6$          | <i>Im-3</i>     | 1.0209                 | -      | -      |
| $\text{LaIn}_2\text{Ni}_3$             | <i>P6/mmm</i>   | 0.9334                 | -      | 0.4356 |

# In-La-Ni at 400°C



- experimental ternary phase diagram
- raw experimental data-13 ternary phases
- preliminarily modelled phase diagram

# In-La-Ni at 600°C

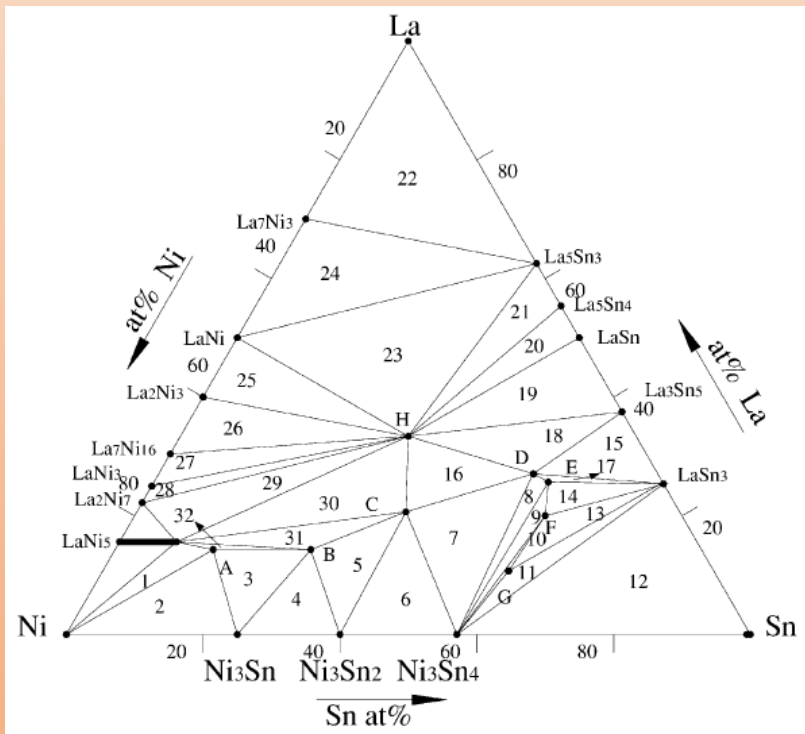


- experimental ternary phase diagram In-La-Ni
- raw experimental data
- preliminarily modelled phase diagram

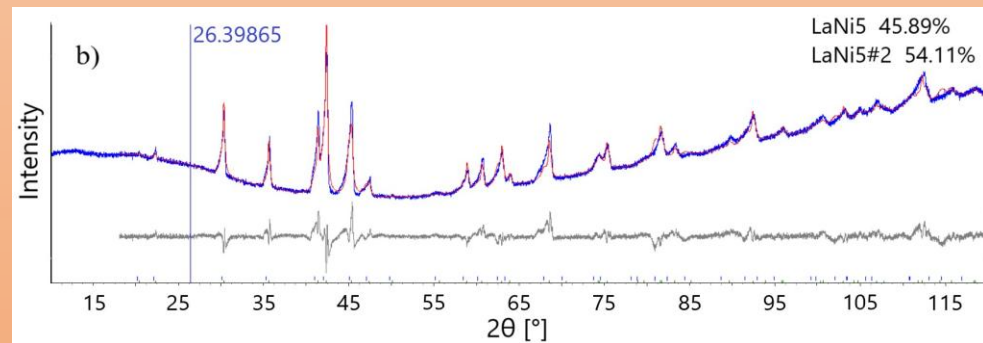
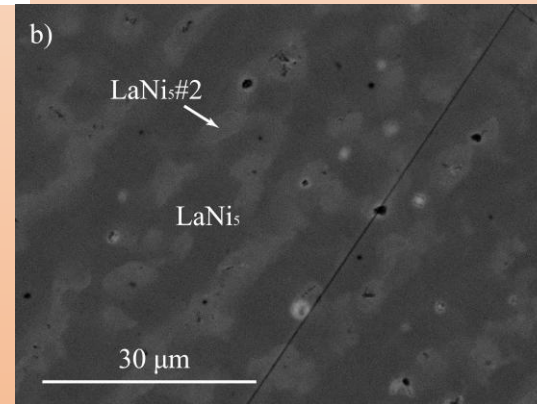
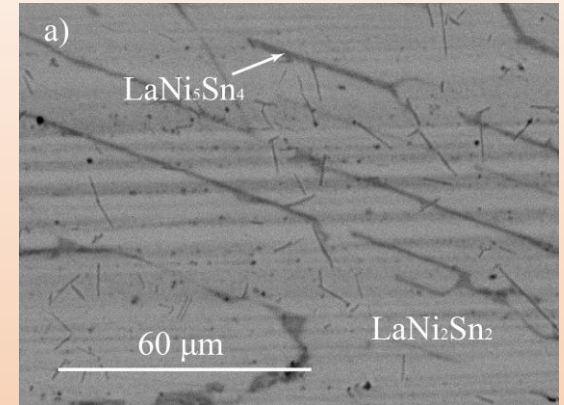
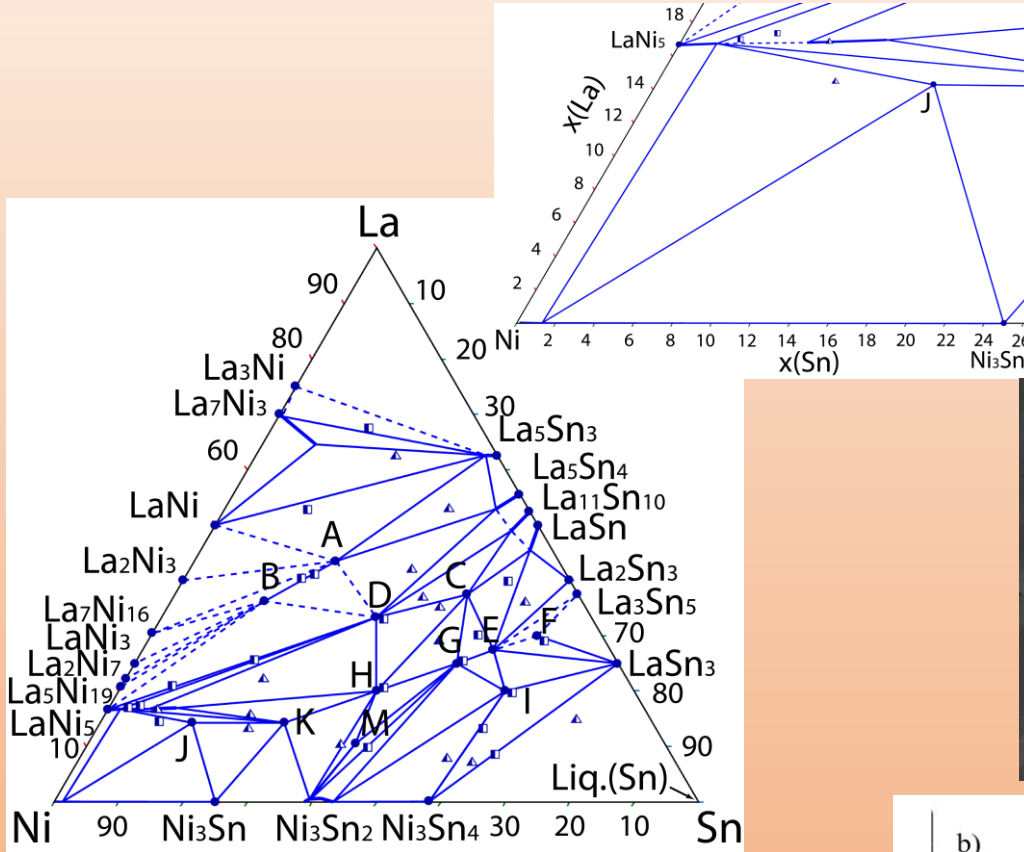
# Ternary system La-Ni-Sn

- ternary system is quite complex
- experimental PD at 210 / 400°C
- 8 ternary phases was found

| Phase name                                       | Space group    | Lattice parameters |        |        |
|--------------------------------------------------|----------------|--------------------|--------|--------|
|                                                  |                | a                  | b      | c      |
| LaNi <sub>5</sub> Sn                             | <i>P63/mmc</i> | 4.958              | 4.958  | 19.943 |
| LaNi <sub>4</sub> Sn <sub>2</sub>                | <i>I-4c2</i>   | 7.766              | 7.766  | 7.851  |
| LaNi <sub>2</sub> Sn <sub>2</sub>                | <i>I4/mmm</i>  | 4.459              | 4.459  | 10.30  |
| La <sub>3</sub> Ni <sub>2</sub> Sn <sub>6</sub>  | <i>Cmcm</i>    | 4.526              | 17.790 | 4.510  |
| La <sub>3</sub> Ni <sub>2</sub> Sn <sub>7</sub>  | <i>Cmmm</i>    | 4.579              | 26.511 | 4.579  |
| LaNiSn <sub>3</sub>                              | n.a.           | n.a.               | n.a.   | n.a.   |
| La <sub>3</sub> Ni <sub>8</sub> Sn <sub>16</sub> | <i>I m -3</i>  | 11.965             | 11.965 | 11.965 |
| LaNiSn                                           | <i>Pnma</i>    | 7.671              | 4.652  | 7.592  |
| LaNi <sub>0.33</sub> Sn <sub>2</sub>             | <i>Cmcm</i>    | 4.57               | 17.35  | 4.484  |

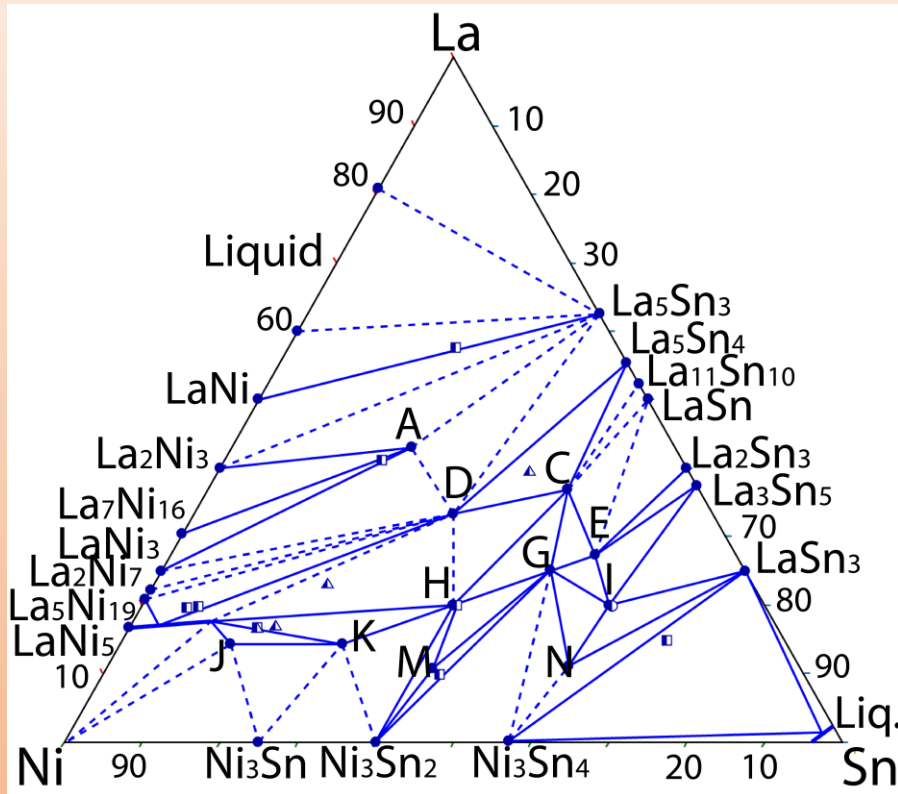


# Ternary phase diagram: La-Ni-Sn

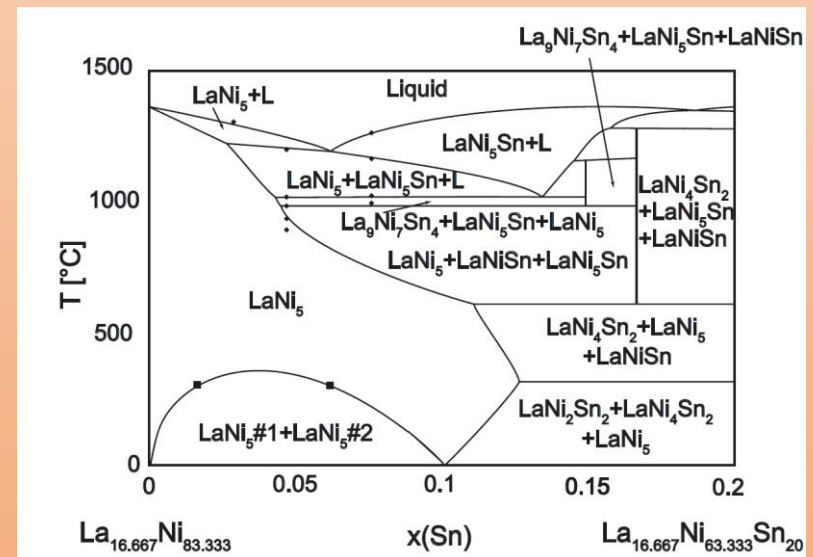
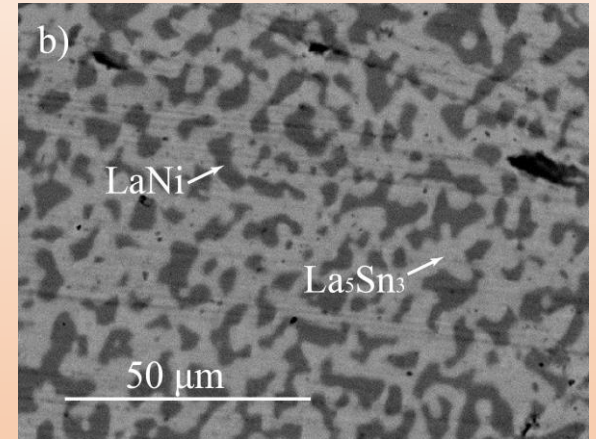


- phase diagram at 300°C
- miscibility gap of  $\text{LaNi}_5 + \text{LaNi}_5\text{H}_2$  phase

# Ternary phase diagram: La-Ni-Sn



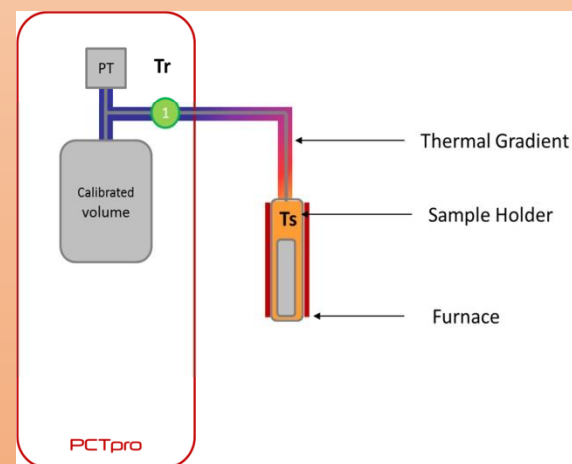
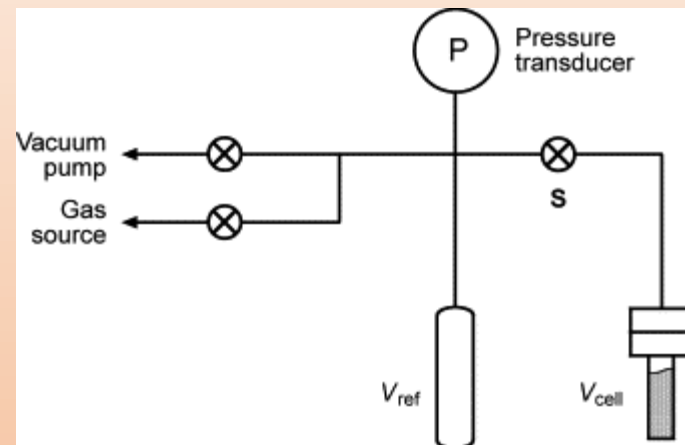
- phase diagram at 600°C



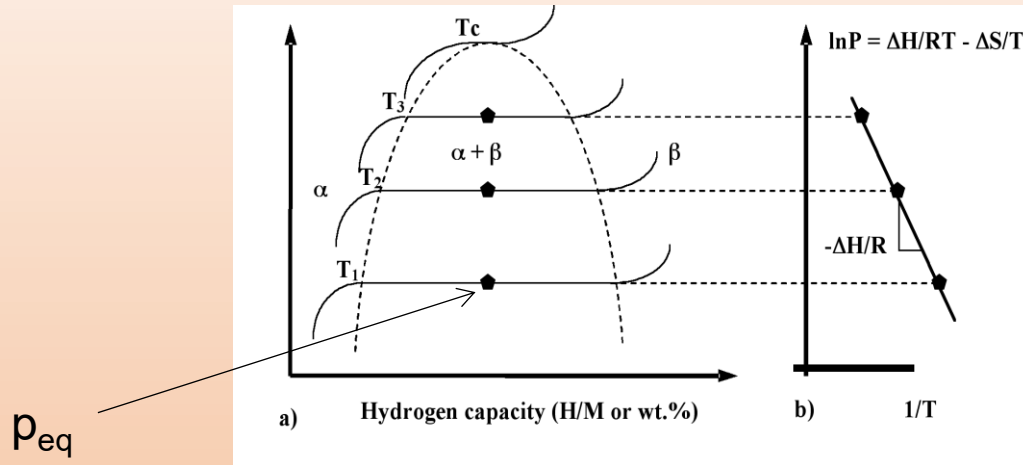
# Sorption properties measurement

## Setaram PCT PRO equipment

- principle - Sievert apparatus - measurement of absorption/desorption at given  $T$  and  $V$  and known sample mass
- Parameters:
  - $T$ : (liq.  $N_2$ , dry ice  $20^\circ\text{C}$  to  $400^\circ\text{C}$ )
  - $P$ :  $10^{-4}$  to  $20\text{ MPa}$
  - 5 reference volumes
  - Accuracy:
    - version EVO – 1%
    - version E&E – 0,12% to 0,5MPa; 0,025% to 20 MPa
  - $H_2$ ,  $CO_2$ ,  $CH_4$ ,  $N_2$ , Ar, He
  - solid samples, foils, powders
  - *two sample cells:*
    - $\varnothing 22 \times 180\text{ mm}$ , max  $400^\circ\text{C}$ , 10 MPa
    - $\varnothing 7,9 \times 150\text{ mm}$ , max.  $400^\circ\text{C}$ , 20 MPa

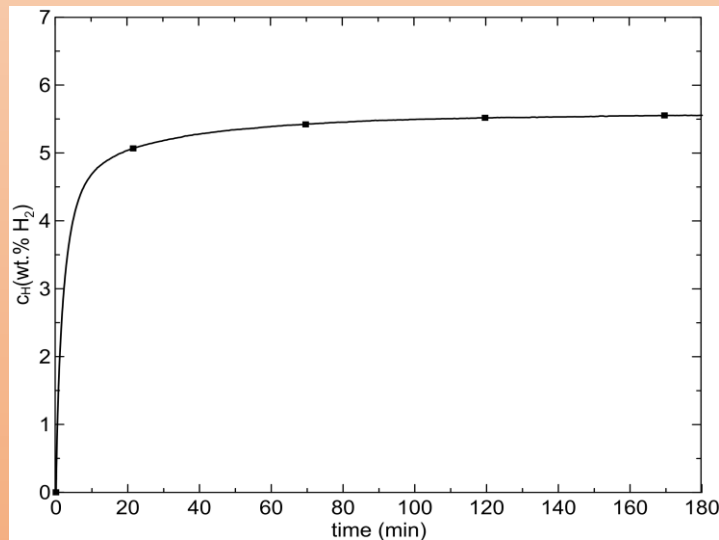


- automatic measurement of isotherms (PCT, PCI) in a given temperature interval, including cyclic measurement.

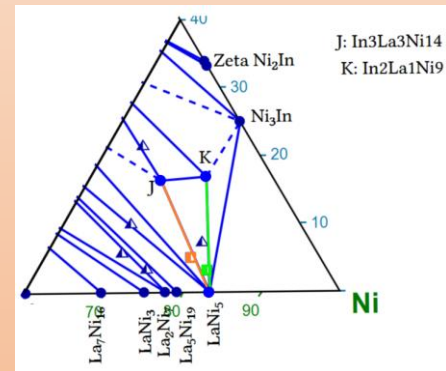
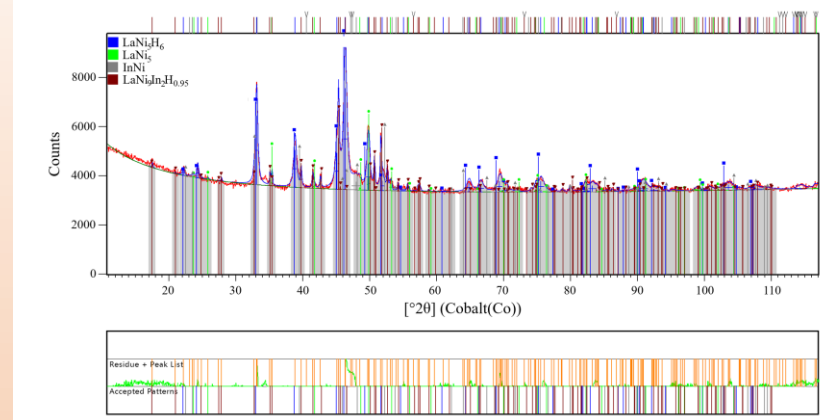
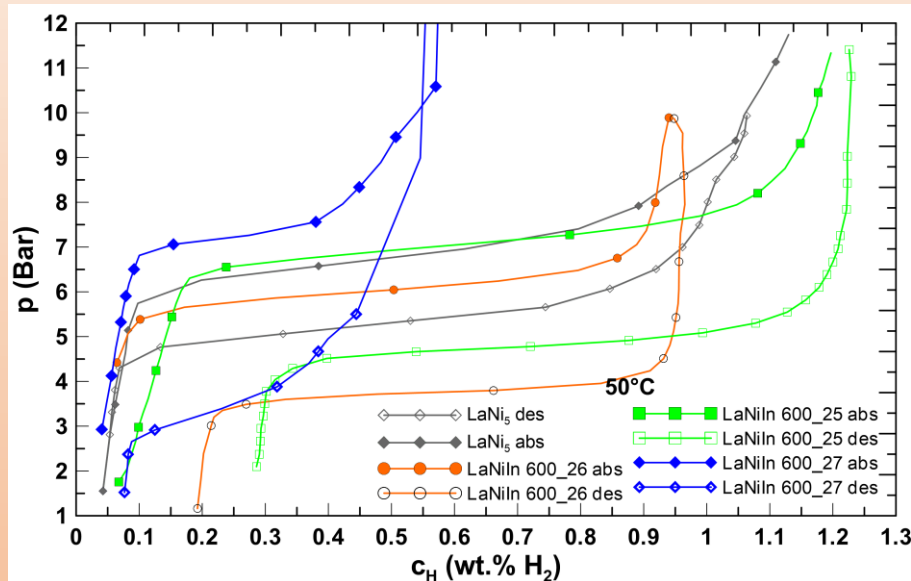


- a) PCT diagram
- b) Van-Hoff diagram

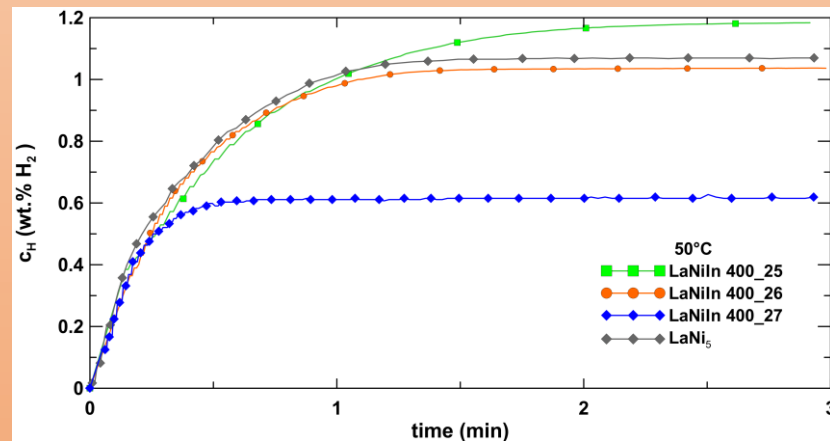
- automatic measurement of kinetic curves, including cyclic measurement



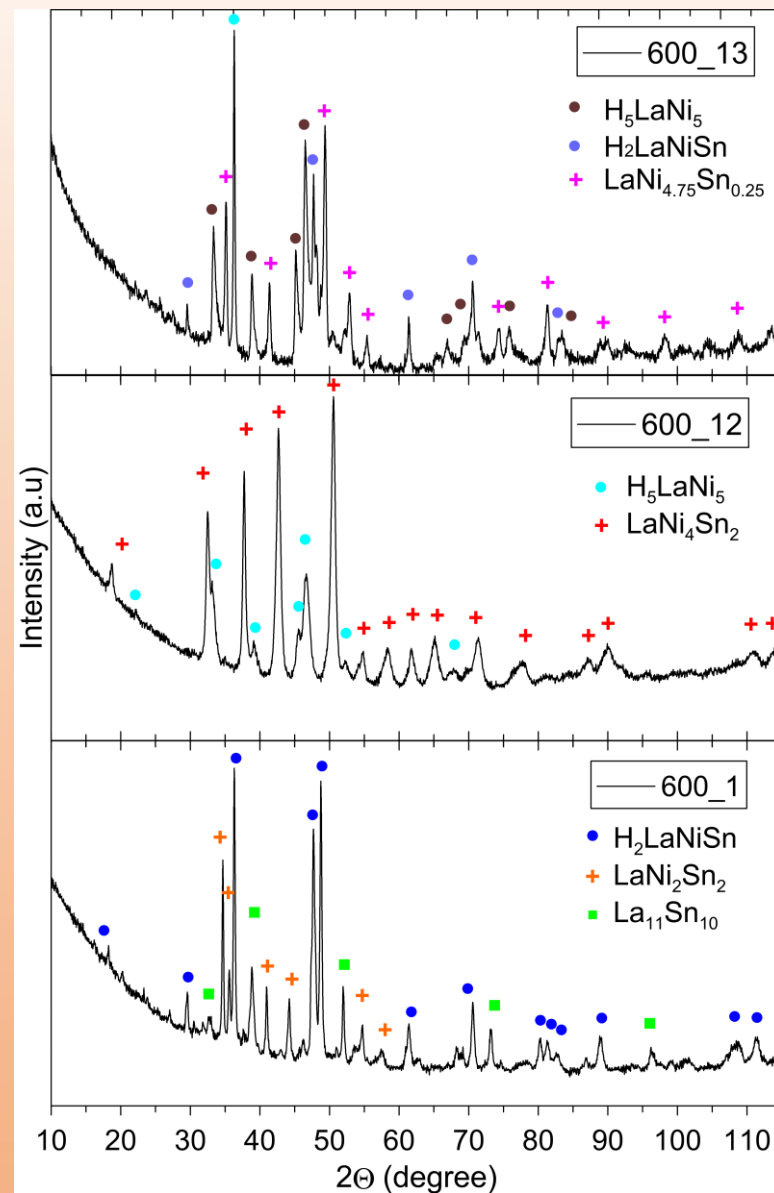
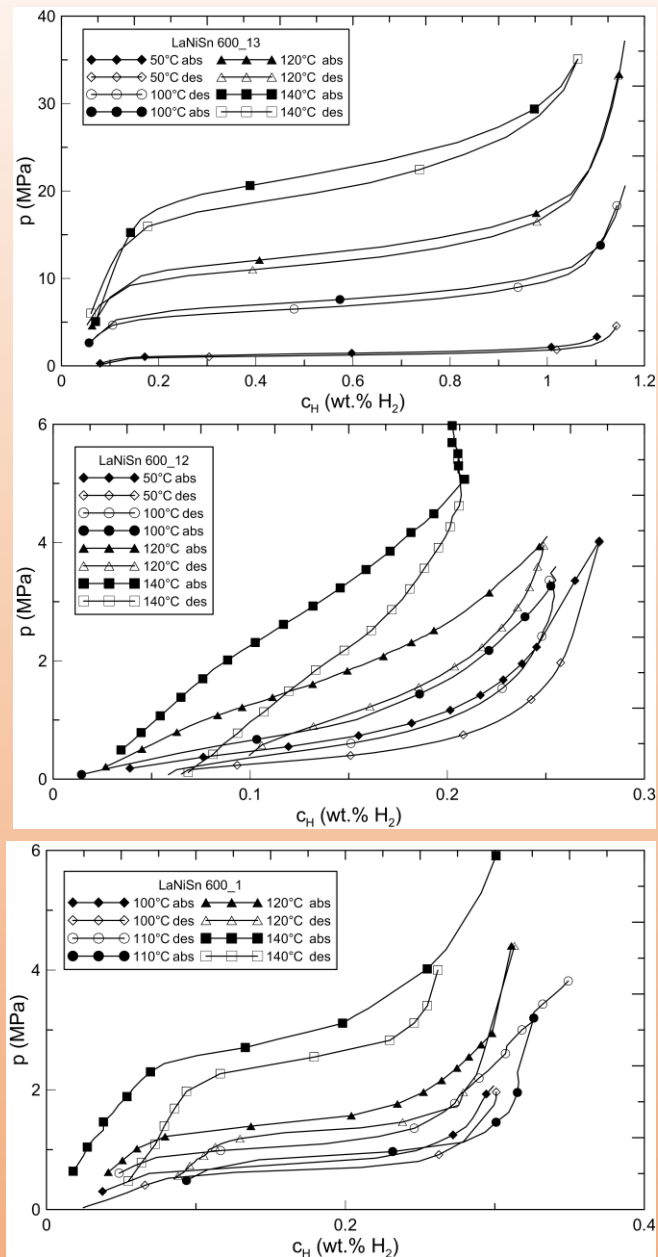
# p-c-T analysis of In-La-Ni



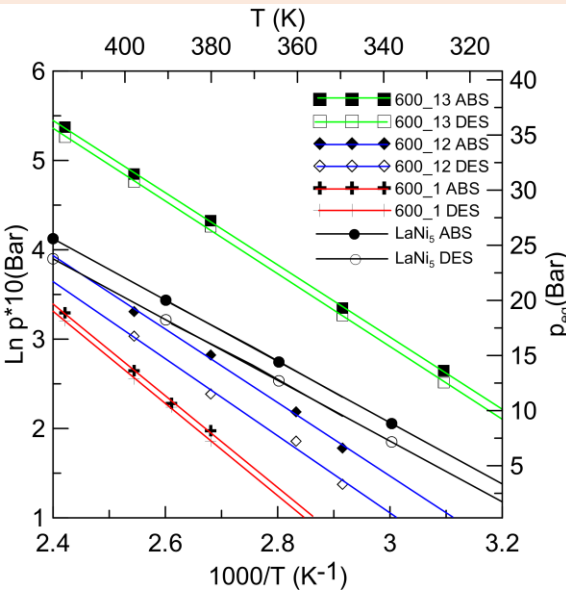
- p-c-T curves
- kinetic measurements



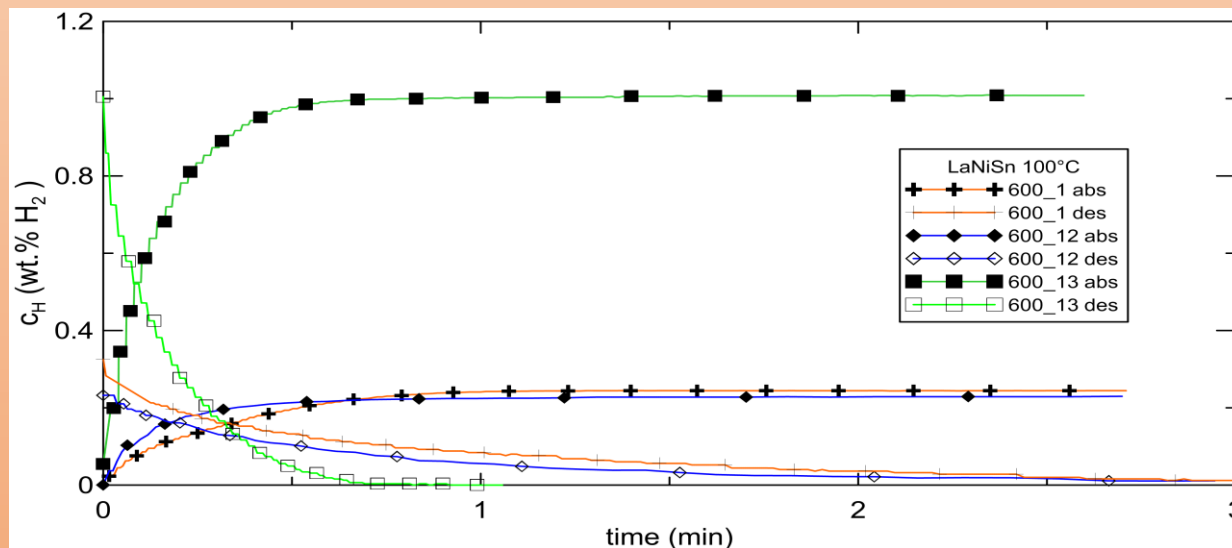
# p-c-T analysis of La-Ni-Sn



# Thermodynamic and kinetic aspects of hydrides reaction



| Sample                   | $\Delta H$ (kJ/mol) |      | $\Delta S$ (J/molK) |       |
|--------------------------|---------------------|------|---------------------|-------|
|                          | ABS                 | DES  | ABS                 | DES   |
| <b>600_1</b>             | -42.7               | 42.9 | -130.8              | 130.4 |
| <b>600_12</b>            | -34.2               | 35.8 | -114.7              | 116.3 |
| <b>600_13</b>            | -33.6               | 33.8 | -125.9              | 125.8 |
| <b>LaNi<sub>5</sub>*</b> | -28.7               | 30.8 | -113.1              | 114.7 |

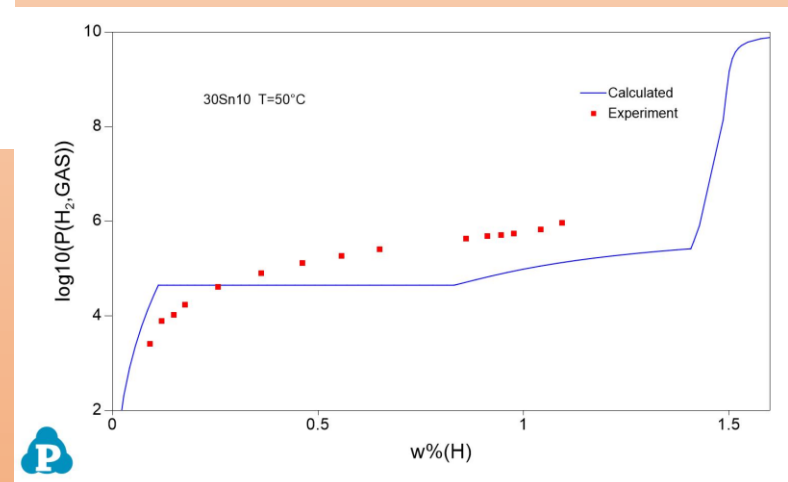
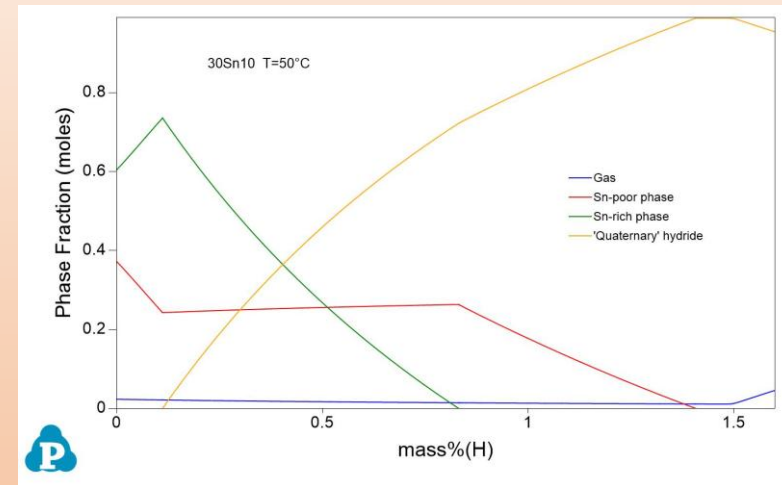
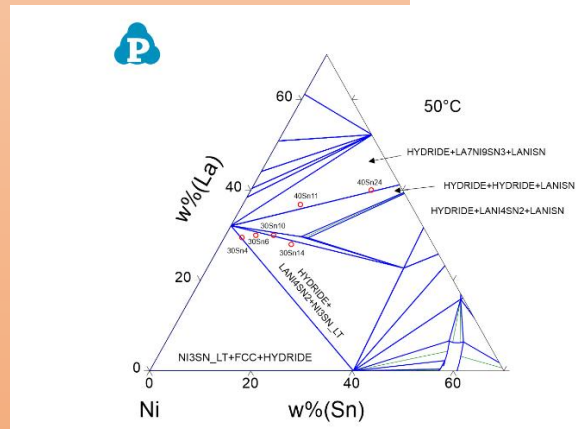
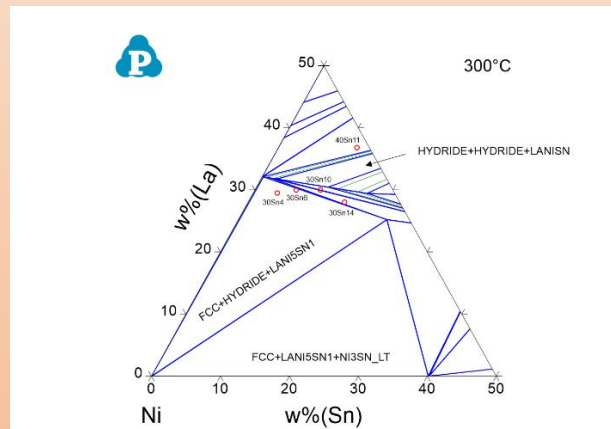


# Results-CALPHAD modelling

binary compound with hydrogen solubility

H atoms in interstitial positions

SL model:  $(\text{La})_1:(\text{Ni},\text{Sn})_5:(\text{H},\text{Va})_7$



# Summary

- La-Ni based ternary systems are quite complex, consists of number ternary phases
- preliminary CALPHAD modelling was done
- addition of In to the  $\text{LaNi}_5$  change the thermodynamic and kinetic aspects of hydrogenation
- in comparison to  $\text{LaNi}_5$  difference between equilibrium pressure of absorption and desorption is bigger for In - contrast to addition of Sn

# Thank you for your attention



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