Skoltech
LOMONOSOV MOSCOW STATE UNIVERSITY
Russian Science Foundation

Crystallography and Crystal Chemistry
IX International School-Conference of Young Scientists ICYS-2024

Hydrothermal synthesis

Dr. **Stanislav** S. **Fedotov**

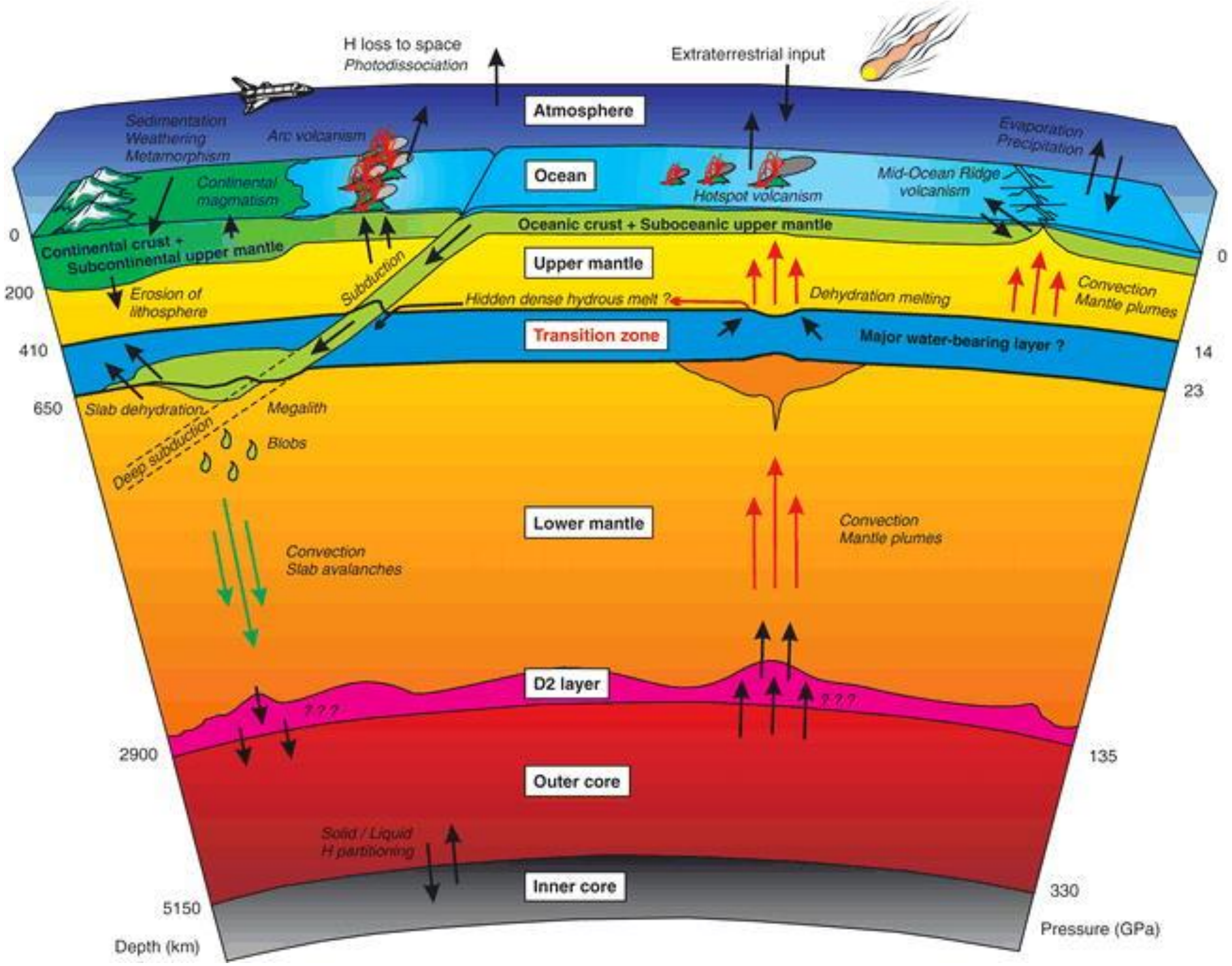
PhD in **Chemistry, Associate Professor**

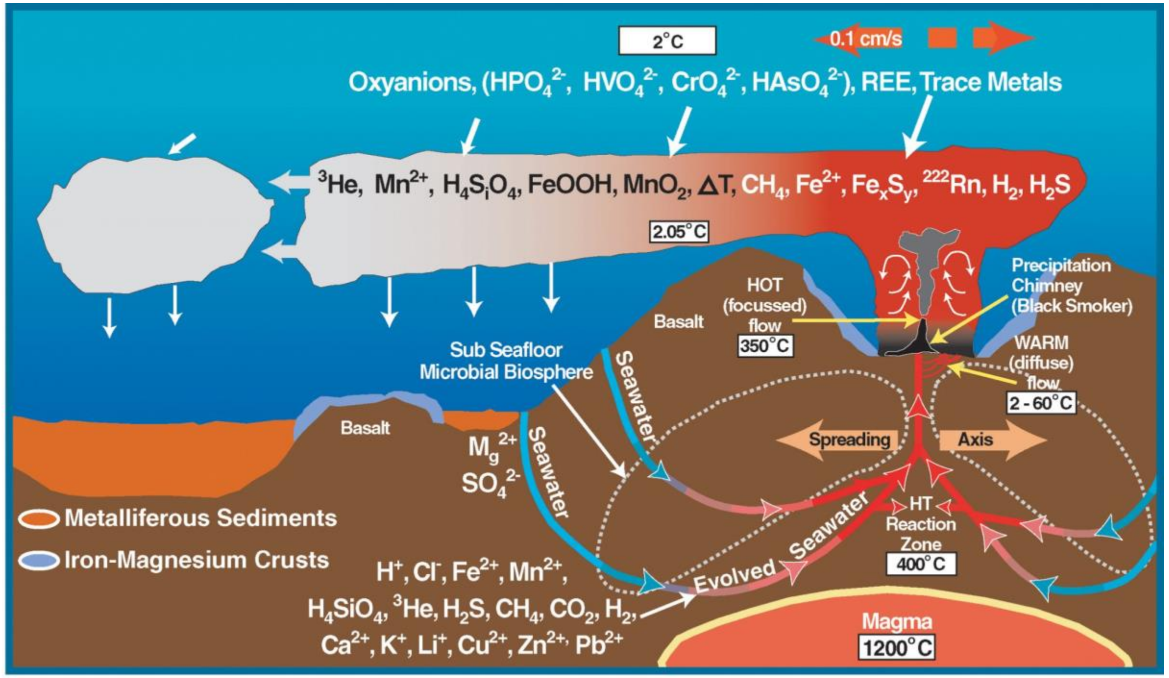
Center for **Energy Science** and **Technology**

Skoltech, Moscow, Russian Federation

November 18th, 2024

Hydrothermal synthesis in Nature

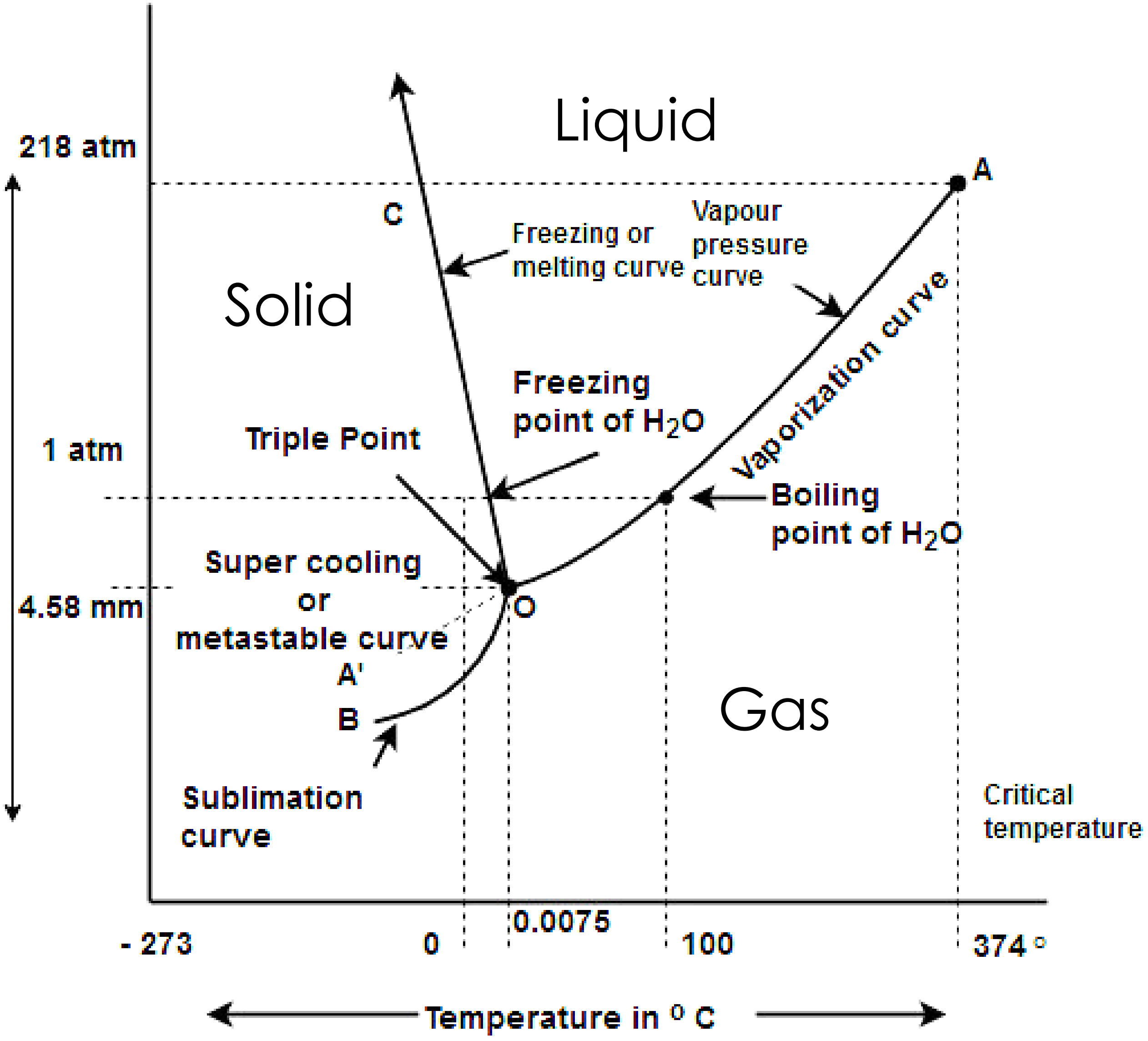




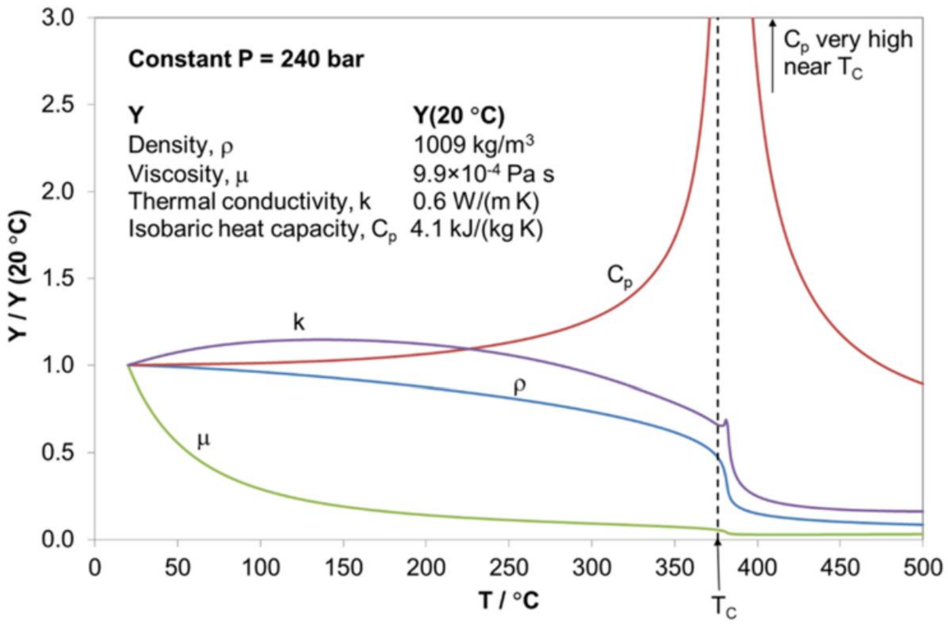
Genesis of various rocks, minerals and ore deposits through laboratory simulations of the conditions existing in the Earth's crust.

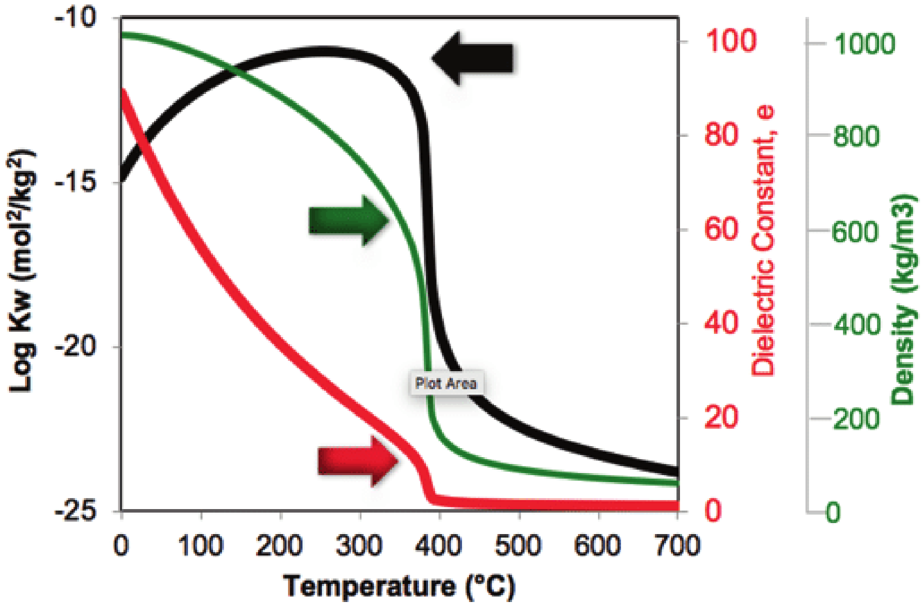
https://sureshemre.wordpress.com/2014/05/04/huge-amount-of-water-in-earths-mantle/

Water transformations



https://www.ques10.com/p/29668





Chem. Rev. 1–141 (2017)

Definitions

Sir **Roderick Murchison** (1792–1871)

- heterogeneous reactions in aqueous media above 100°C and 1 bar

- a group of methods in which crystallization is carried out from superheated aqueous solutions at high pressures

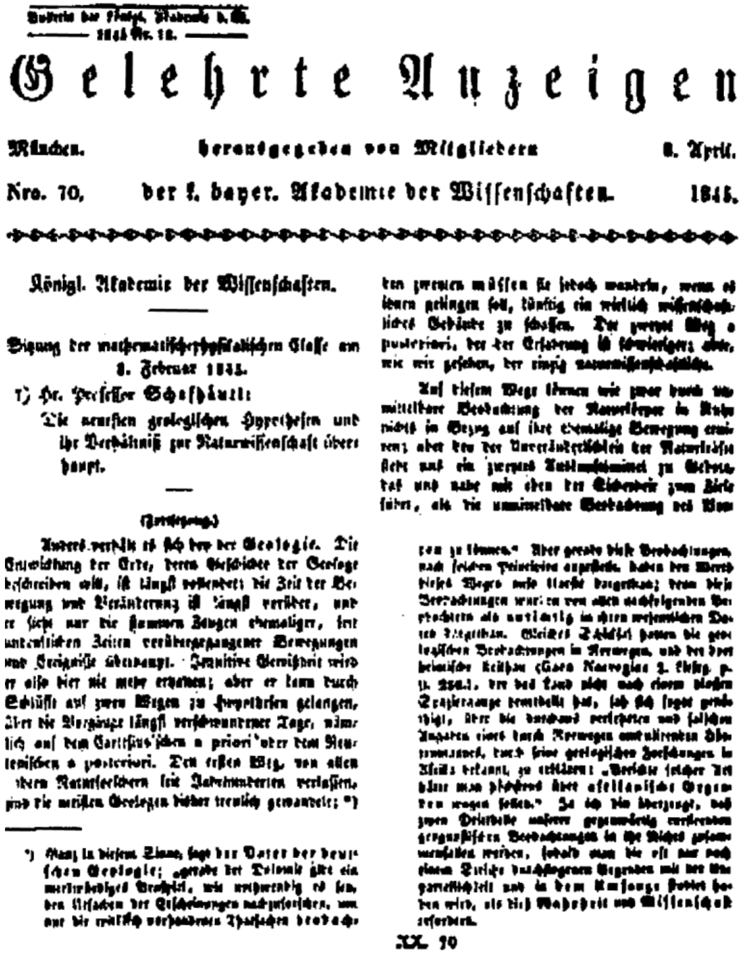
- hydrothermal synthesis involves water as a catalyst and occasionally as a component of solid phases in the synthesis at elevated temperature (>100°C) and pressure (greater than a few atmospheres)

- reactions occurring under the conditions of high-temperature–high-pressure (>100°C, >1 atm) in aqueous solutions in a closed system

✓ **any heterogenous chemical reaction in the presence of a solvent (whether aqueous or nonaqueous) above room temperature and at pressure greater than 1 atm in a closed system**

The synthesis of a particular mineral or in obtaining compounds similar to natural minerals

The first publication on hydrothermal research in 1845: synthesis of quartz crystals upon transformation of freshly precipitated silicic acid



Gelehrte Anzeigen

München. herausgegeben von Mitgliedern 8. April.

Nro. 70. der k. bayer. Akademie der Wissenschaften. 1845.

Königl. Akademie der Wissenschaften.

Sitzung der mathematisch-physikalischen Classe am 8. Februar 1845.

1) Hr. Professor Schafhäutl:

Die neuesten geologischen Hypothesen und ihr Verhältniß zur Naturwissenschaft überhaupt.

(Fortsetzung.)

Development

1850-1900
Mineral synthesis, imitation of natural conditions
Simple glass reactors

1900-1940
Mineral synthesis, improvement in PT conditions, German domination

1940-1950
Large size and large scale production of quartz, beginning of zeolites, clays, and micas

1950-1960
Phase diagrams for natural systems

1960-1970
Synthesis of technological materials, new inorganic compounds without natural analogues

1970-1980
A variety of new materials synthesis, ceramic processing in a bigger way, advanced materials
Appearance of many hydrothermal labs in several countries

1980-1990
Decline in interest on hydrothermal research.
Importance of the technique in materials science, physical chemistry of hydrothermal solutions

1990-2000
Diversification of hydrothermal technique, physical chemistry of hydrothermal solutions
Russian domination

2000-…
High-tech Era
Age of solvothermal
Entry of organic chemists, environmental scientists

Skoltech

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RSF Russian Science Foundation

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Solvothermal synthesis

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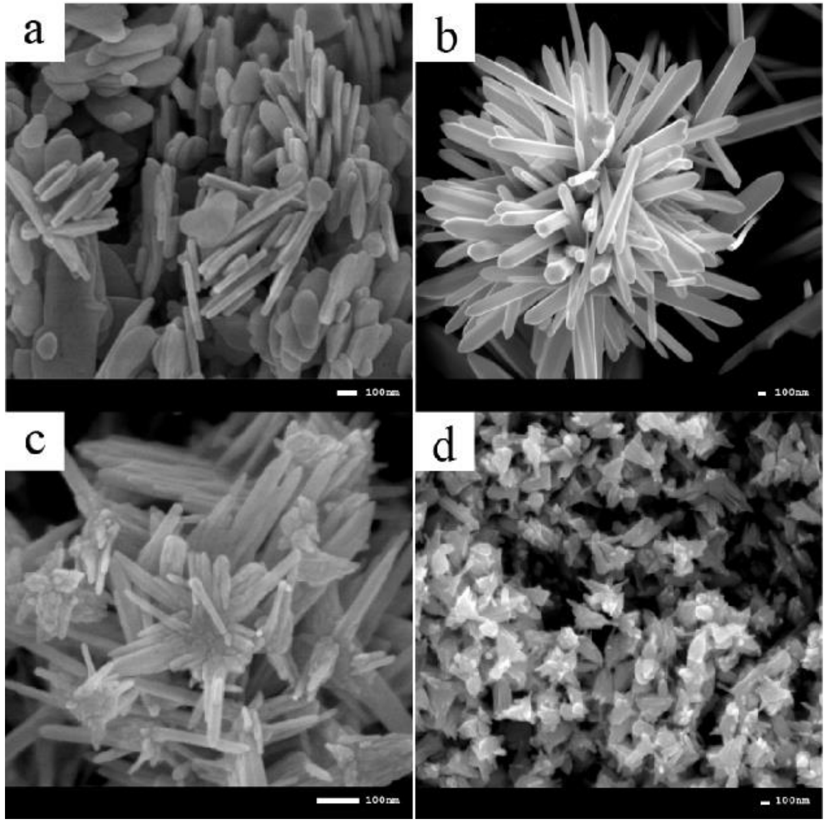
Skoltech, Moscow, Russian Federation

November 18th, 2024

Solvothermal synthesis

PTFE-lined stainless steel autoclave reactor

“Black box”



- **pH** (morphology and phase control)
- **Solvent**: stable at exp. conditions, inert, not hazardous
- **Temperature**: depending on the inner lining (PTFE up to 240°C)
- **Time**: minutes - weeks
- **Agitation**: yes/no

Key parameters

Chemical factors

– chemical nature of the solvent and its physicochemical properties,
– chemical composition, structure and properties of the precursors,
– nature of the additives,
– pH value of the reaction medium.

Solvent

(i) control the concentration of the chemical species in the solution affecting the kinetics of the reaction
(ii) modify the coordination of solvated species and induce specific structures
(iii) participation in the reaction or inert

Thermodynamical factors

– temperature
– pressure.

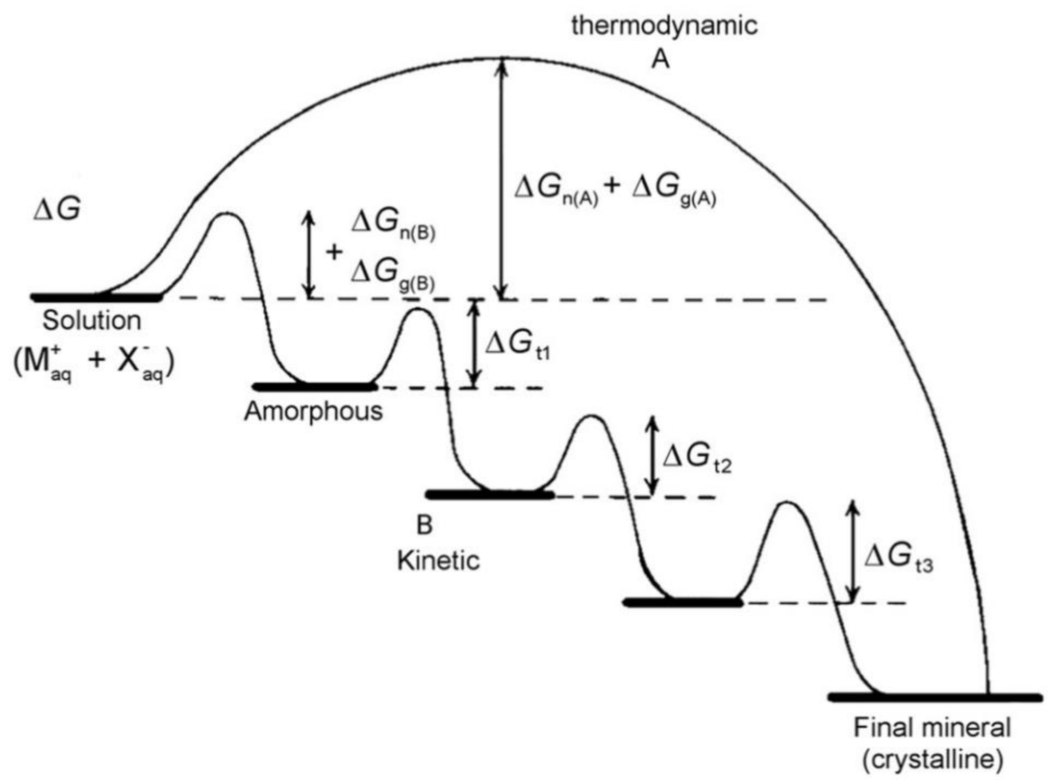
Additives

used for governing the morphology of the obtained crystallites:
– capping agents (polymers, alkylamines, CTAB),
– organics as structure-directing agents due to their ability to interact with chemical groups (in particular COOH−, NH2) through a typical size matching at the nanoscale,
– mineralizer-assisted processes in particular for inducing a specific structural form or for improving the crystal growth
– oxido-reduction syntheses (reductants or oxidants).

pH

– coordination geometry of the transition metal
– coordinating mode of the ligands,
– control the size and the morphology of the crystallites,
– facilitate the elaboration of nanocomposites.

Thermodynamics and kinetics



Thermodynamical factors
– temperature
– pressure

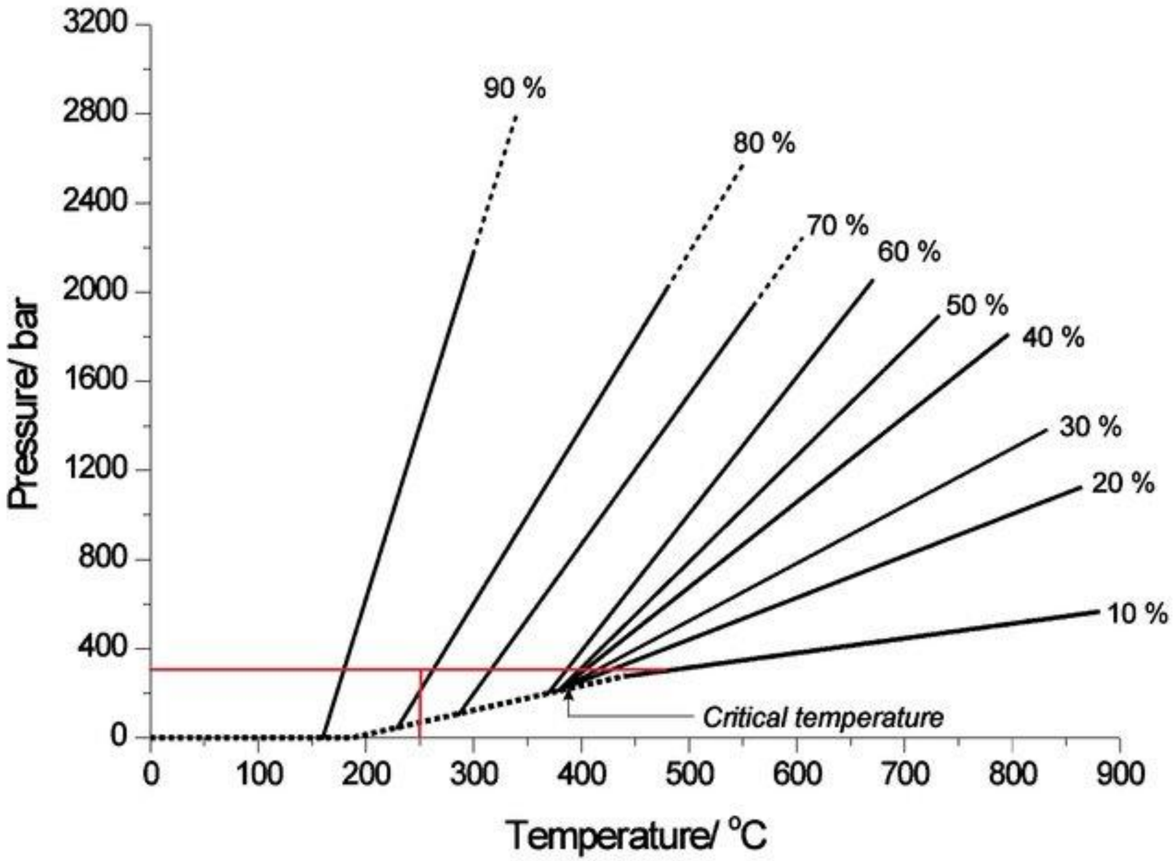
The role of temperature:

- Gibbs energy of the chemical reaction,
- entropic factor
- solubility of the precursors,
- stability of the reactants (through solvothermal decomposition),
- chemical composition of the solvent (through its partial decomposition),
- formal oxidation states of the transition metals *etc*.

Formation of intermediate compounds which are able to modify the kinetics of the reaction

Consequently, the phase evolution to the final crystallites can modify the nucleation and the crystal growth steps and therefore their size and morphology.

Thermodynamics and kinetics: pressure



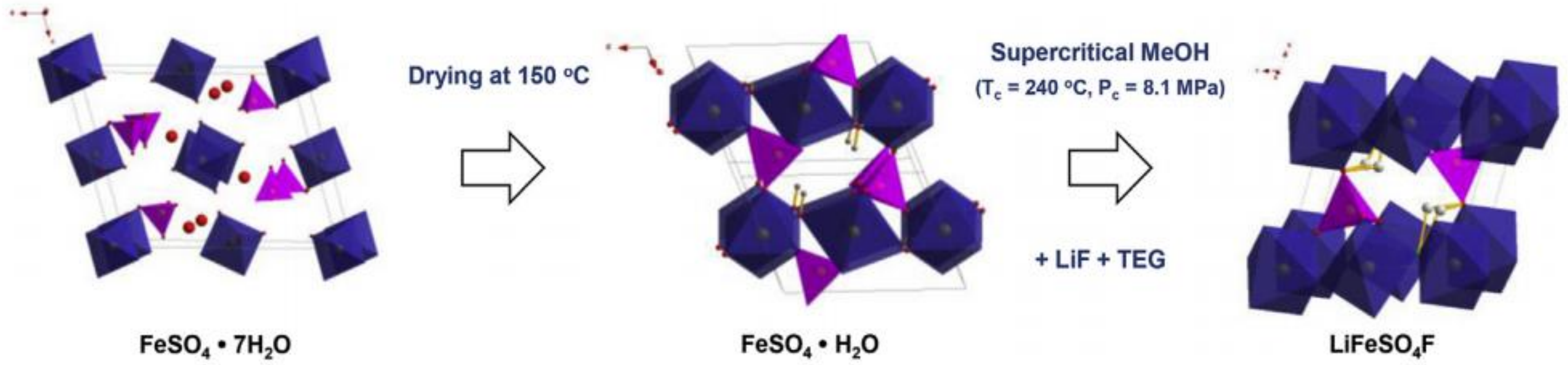
The role of pressure:
i) stabilization of more dense structures, if the pressure range is large enough,
(ii) enlargement of the thermal stability domain of the reactants,
(iii) enhancement of the chemical reactivity and of the kinetics of the involved reactions.

Time: minutes - weeks

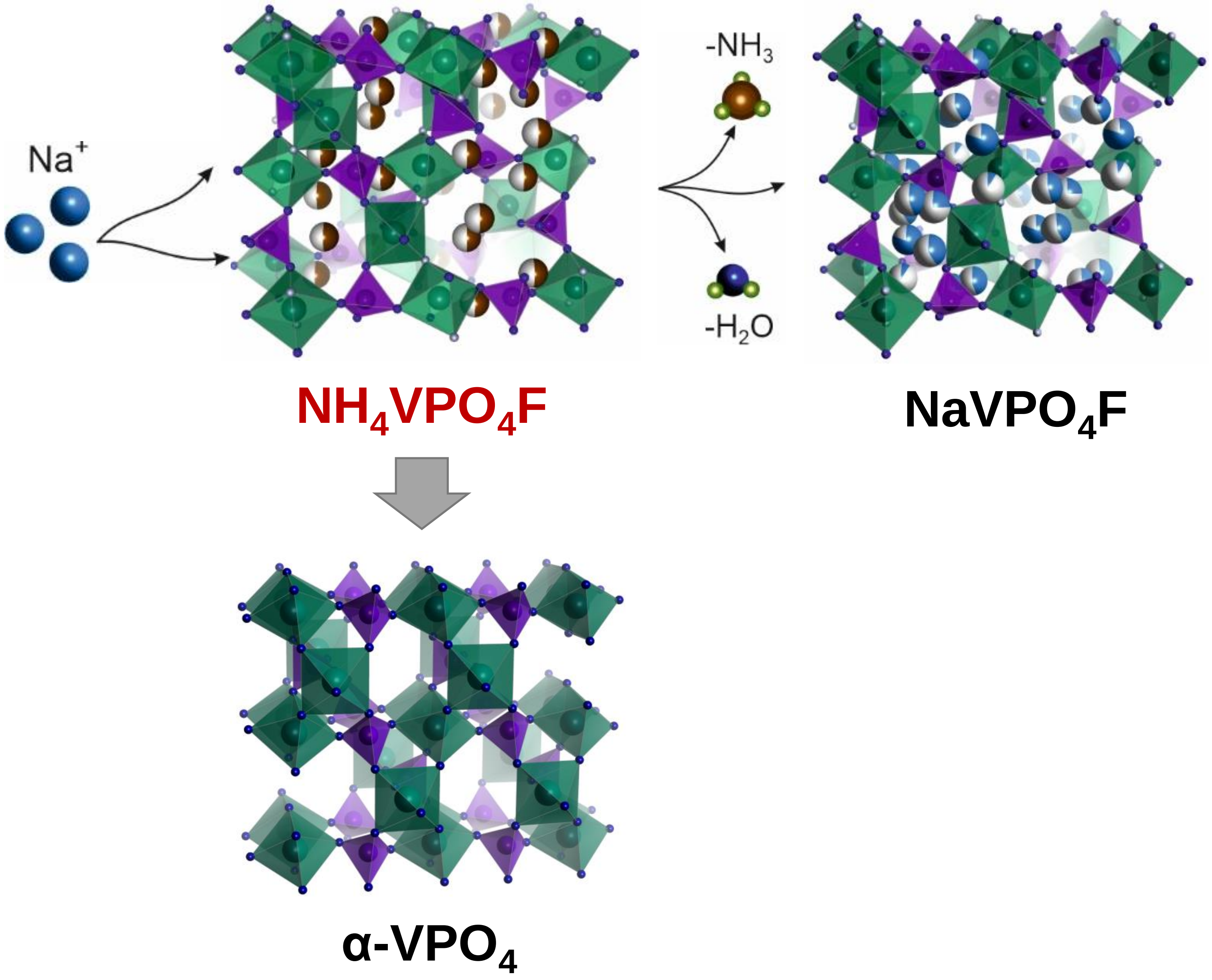
Agitation: temperature and concentration gradients; turbulent and laminar flows

Topochemical reaction

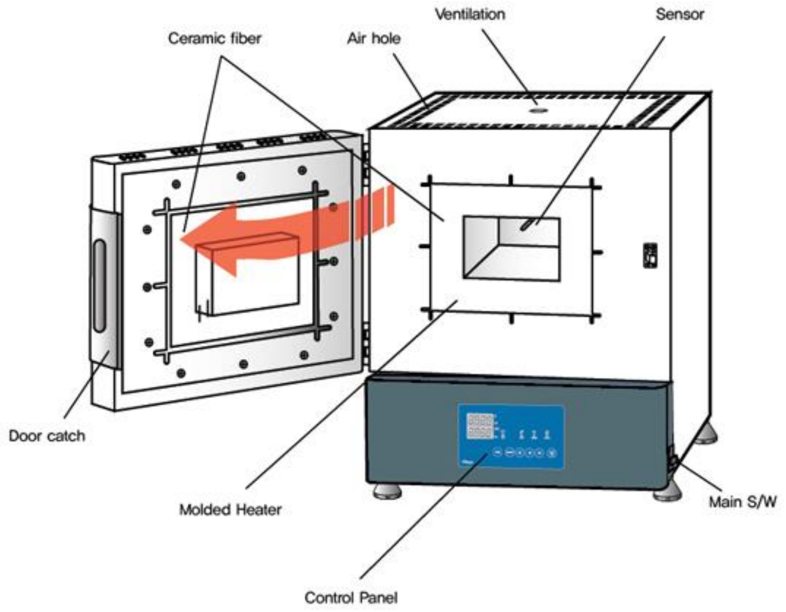
Using reactants/precursors with crystal structures similar to that of the product (topotactic and epitactic reactions).

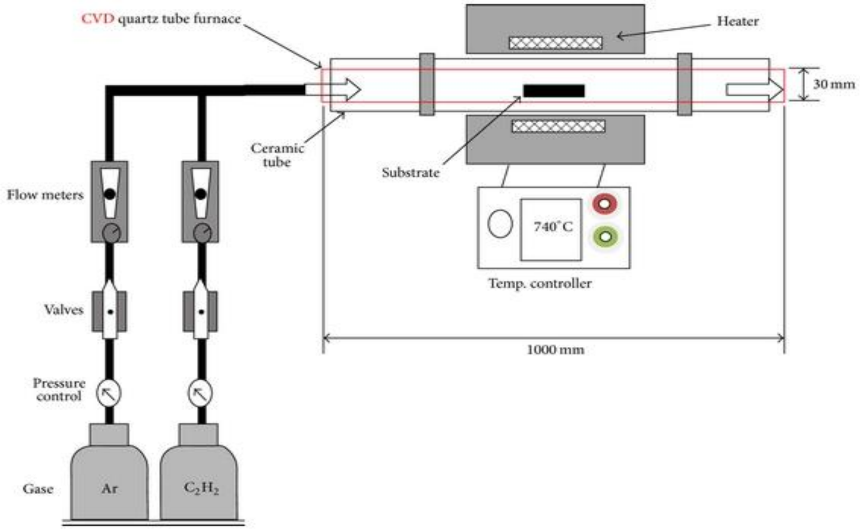


Topochemical reaction



High-temperature annealing after solvothermal





Annealing specifics

Choosing of appropriate atmosphere

- Ar (fully inert)
- N_2 (partly inert)
- O_2 (oxidizing conditions required)
- Air
- Others (NH_3, H_2S, CO or CO_2 etc.)

Choosing of appropriate crucible (container)

- Ceramic (Al_2O_3, Y-doped-ZrO_2)
- (Inert) metals (platinum 1770 °C, gold 1063 °C, molybdenum)
- Quartz (sealed tubes)

Gas	Color system
N_2	Азот
NH_3	Аммиак
Ar (raw)	Аргон сырой
Ar (tech)	Аргон технический
Ar (purified)	Аргон чистый
C_2H_2	Ацетилен
H_2	Водород
He	Гелий
N_2O	Закись азота
O_2	Кислород
H_2S	Сероводород
Air (compressed)	Сжатый воздух
CO_2	Углекислота

Consequences of high reaction temperatures:

- It can be difficult to incorporate ions that readily form volatile species (i.e. Ag^+, Li^+).
- It is not possible to access low temperature, metastable (kinetically stabilized) products.
- High (cation) oxidation states are often unstable at high temperature, due to the thermodynamics of the following reaction:

$$2MO_n\,(s) \rightarrow 2MO_{n-1}(s) + O_2(g)$$

Solvothermal synthesis

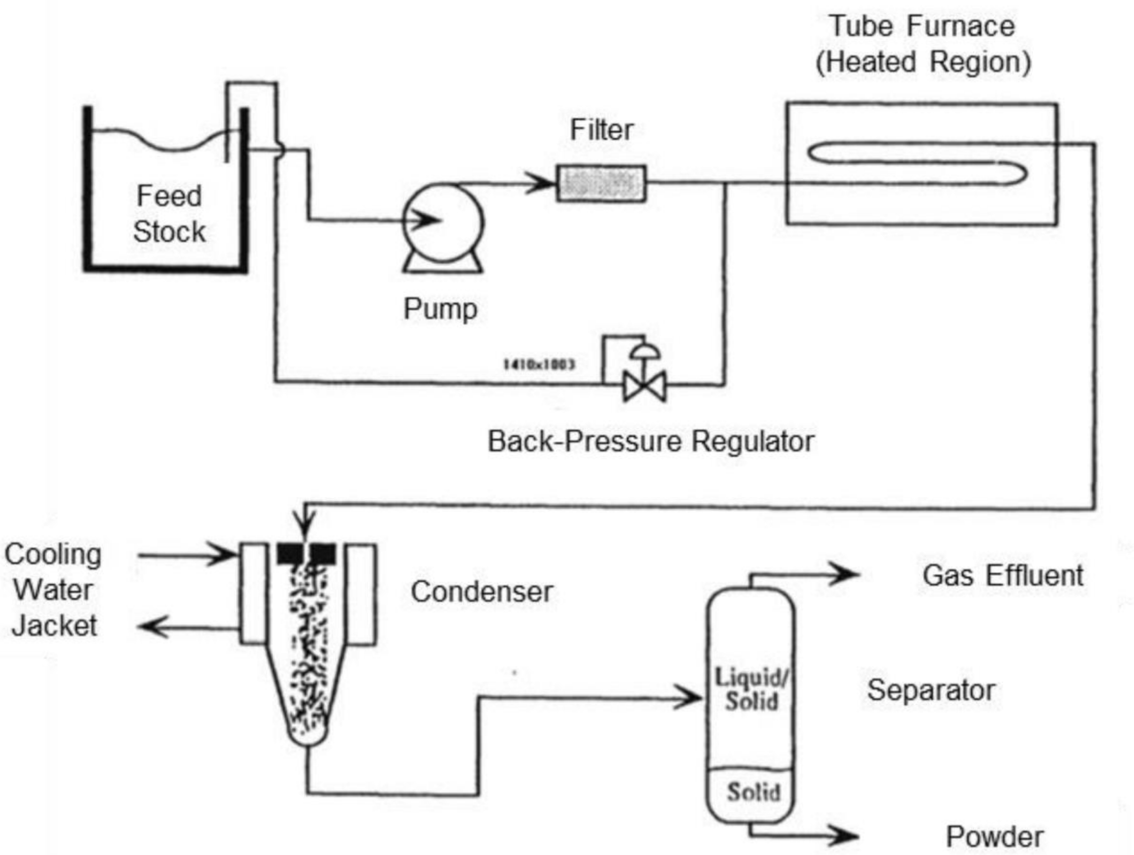
PTFE-lined stainless steel autoclave reactor

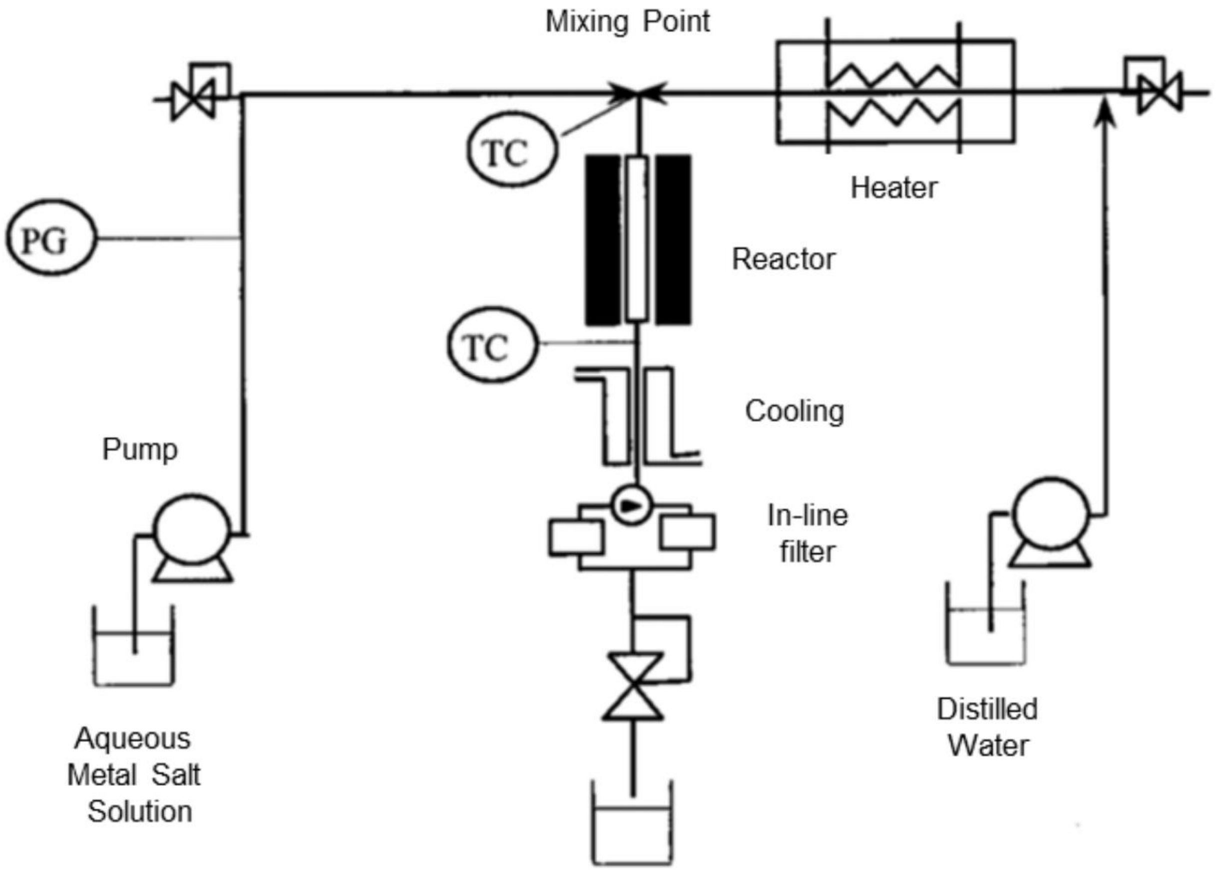
"Black box"

1000 liters

Easy-scalable

Continuous-Flow synthesis





Continuously pumped dissolved metal salts into a heated pipe section in a furnace

Synthesis temperature was not well defined

Pacific Northwest Laboratories, U.S. Technology 2003 Conference (1993)

Continuous combination of preheated supercritical water and ambient precursors at a mixing point

A high-temperature combined stream, from which nanoparticles were produced

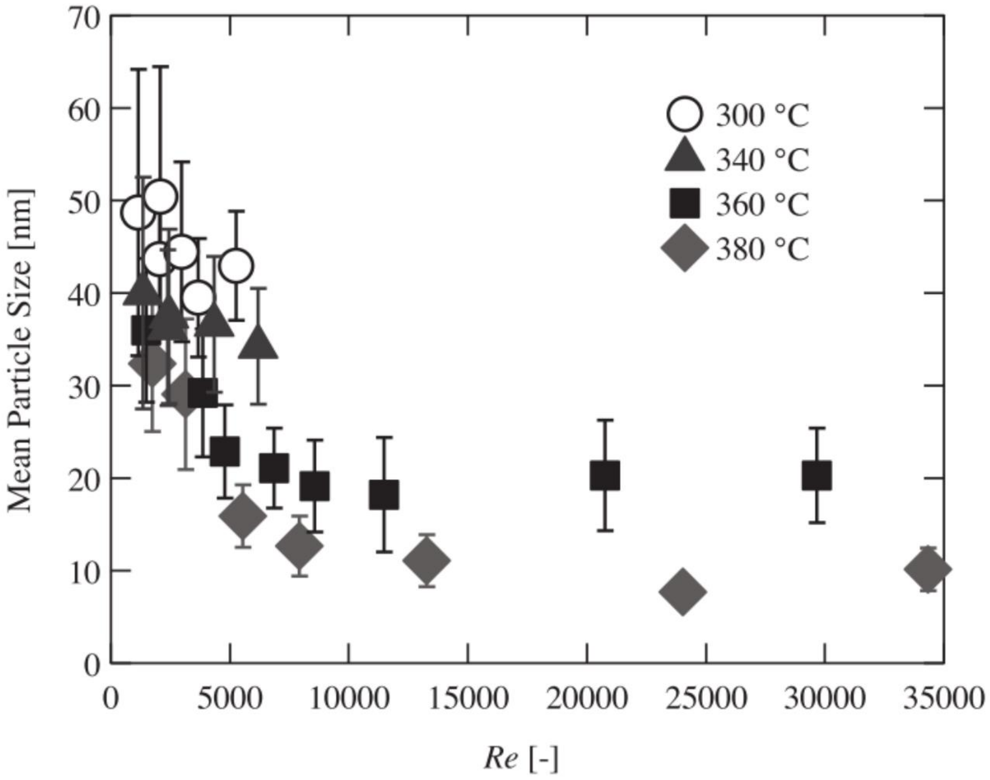
Ind. Eng. Chem. Res. 39, 4901–4907 (2000)

Continuous-Flow synthesis

$$R_e = \frac{\rho d v}{\mu}$$

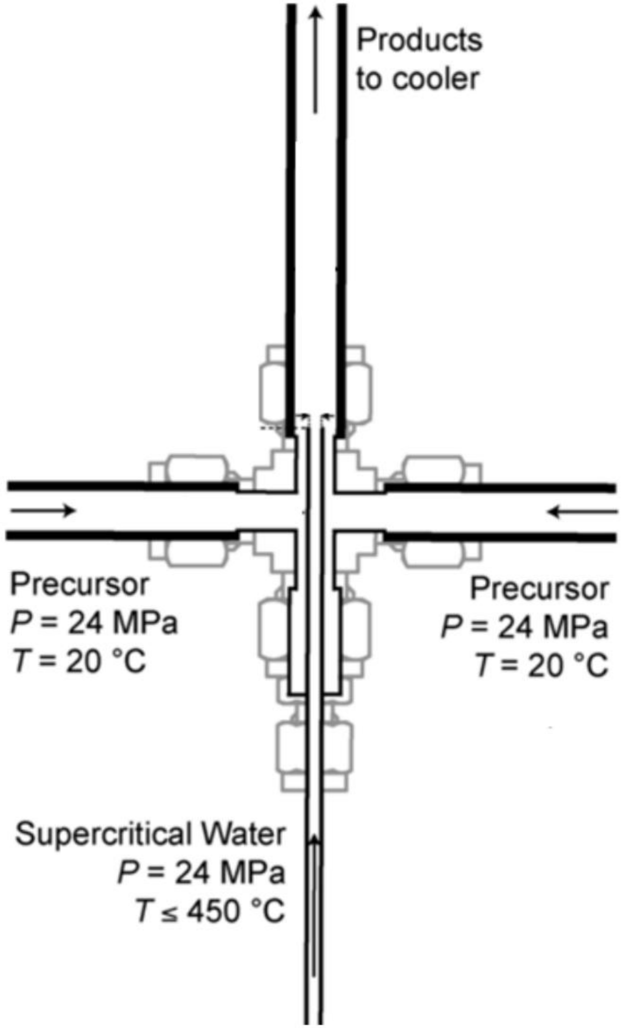
Reynolds number

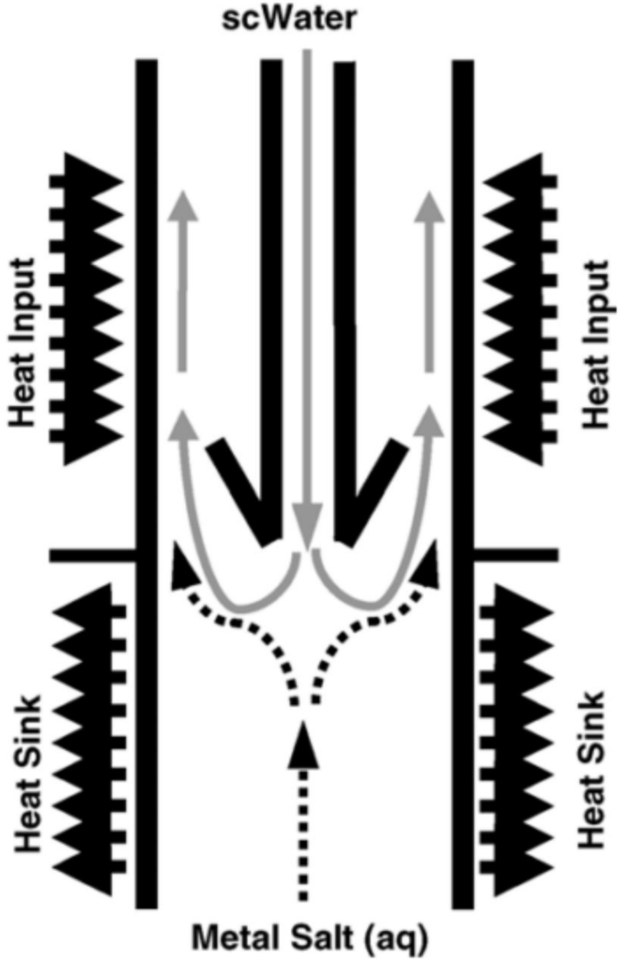
fluid density ρ,
inner pipe diameter d,
fluid velocity v,
fluid viscosity μ



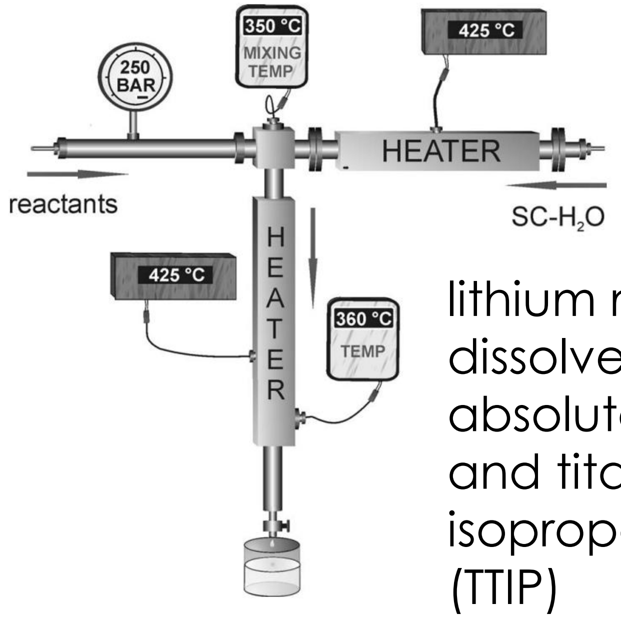
CeO_2 particle size synthesized via CHFS

J. Supercrit. Fluids 110, 161–166 (2016)





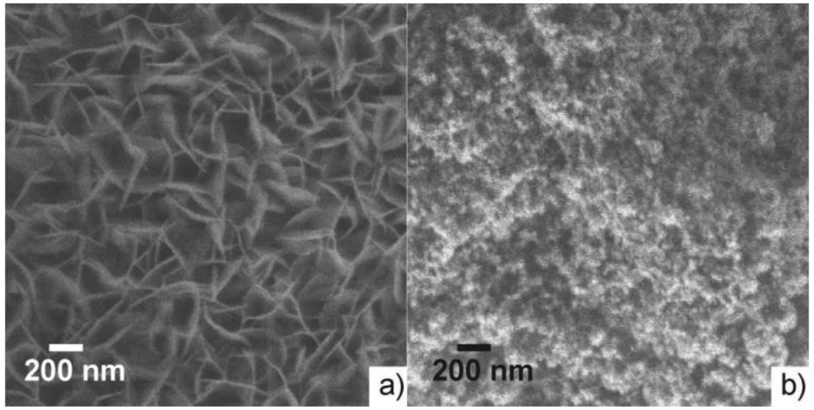
Continuous-Flow LTO synthesis

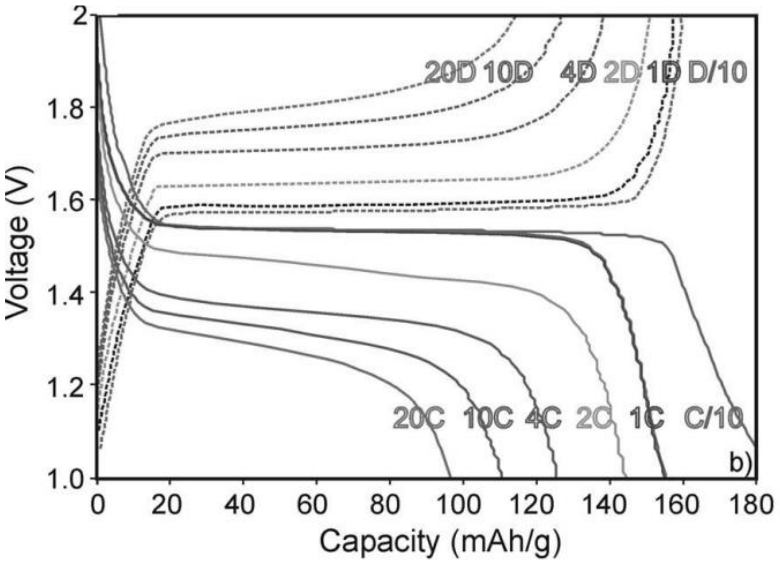


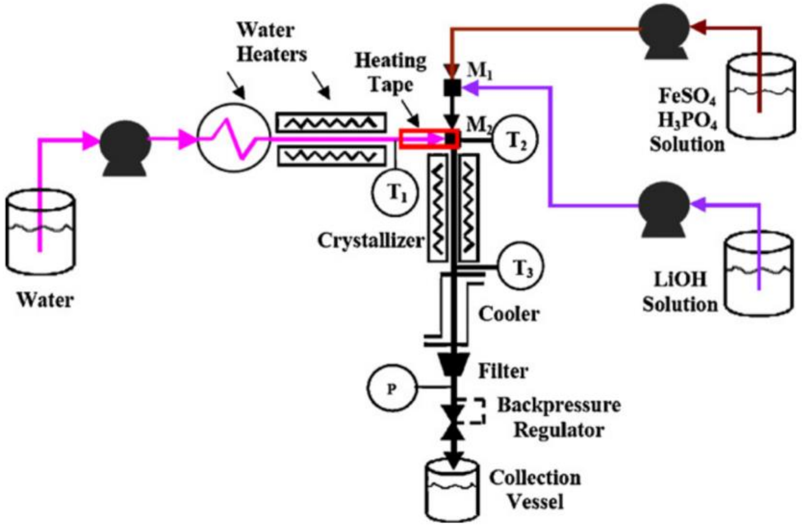
lithium metal dissolved in absolute ethanol and titanium (IV) isopropoxide (TTIP)

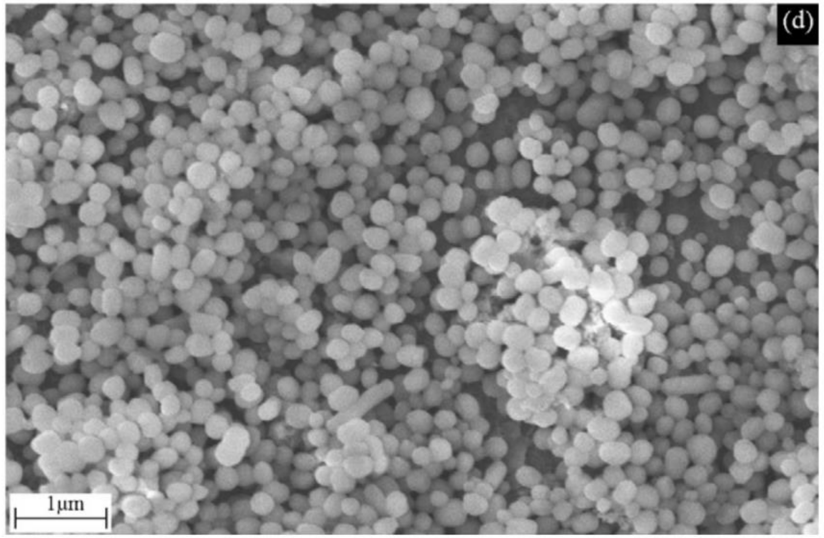
10.1016/j.supflu.2007.09.001

Rapid Green Continuous Flow Supercritical Synthesis of High Performance $Li_4Ti_5O_{12}$ Nanocrystals for Li Ion Battery Applications





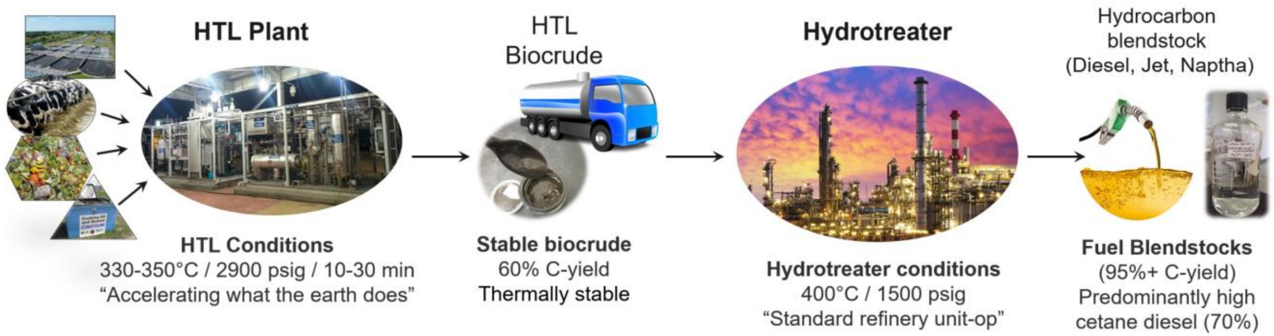


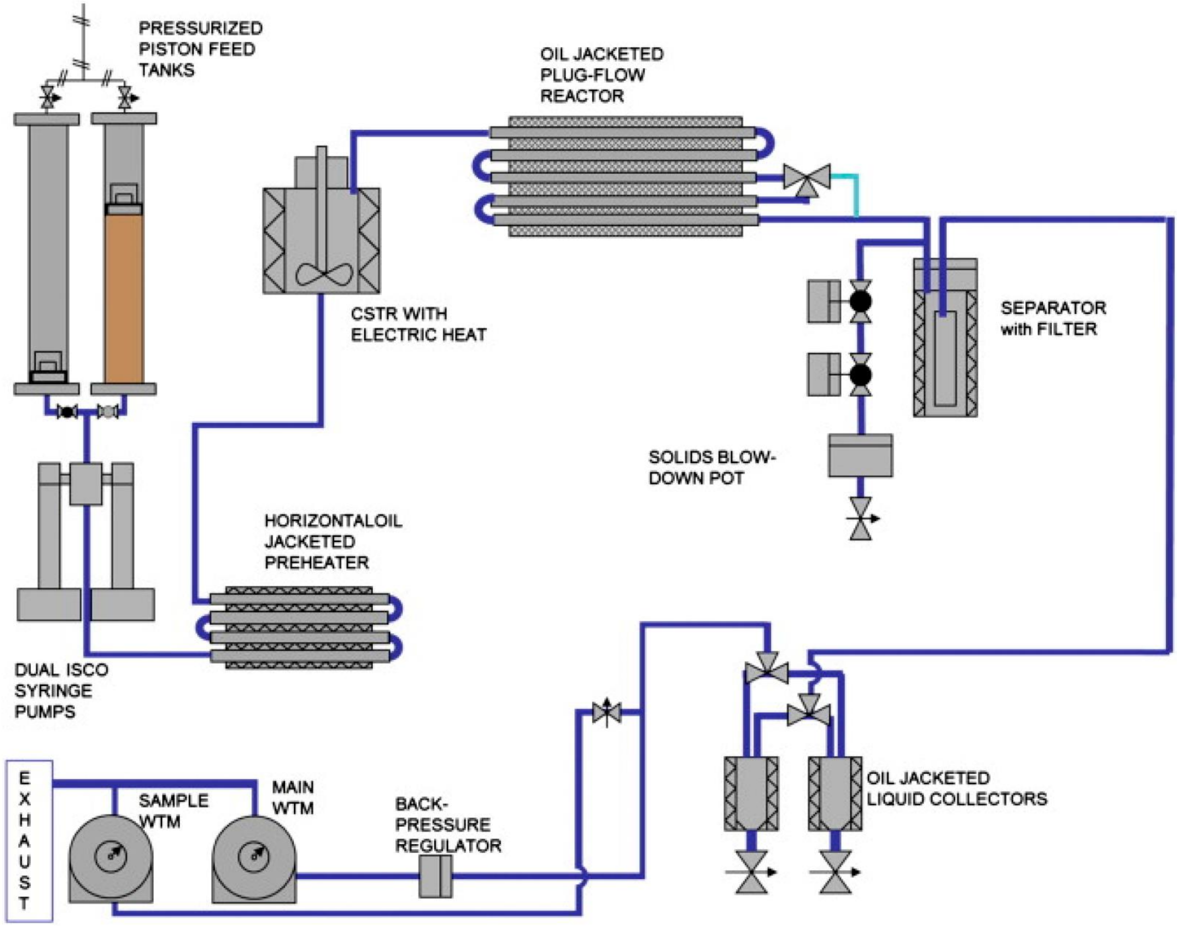


Continuous hydrothermal synthesis of lithium iron phosphate particles in subcritical and supercritical water

DOI: 10.1149/2.084202jes

Continuous-Flow synthesis





Plant in Pacific Northwest National Laboratory

Continuous-Flow commercial systems

THALESNano

SYRRIS

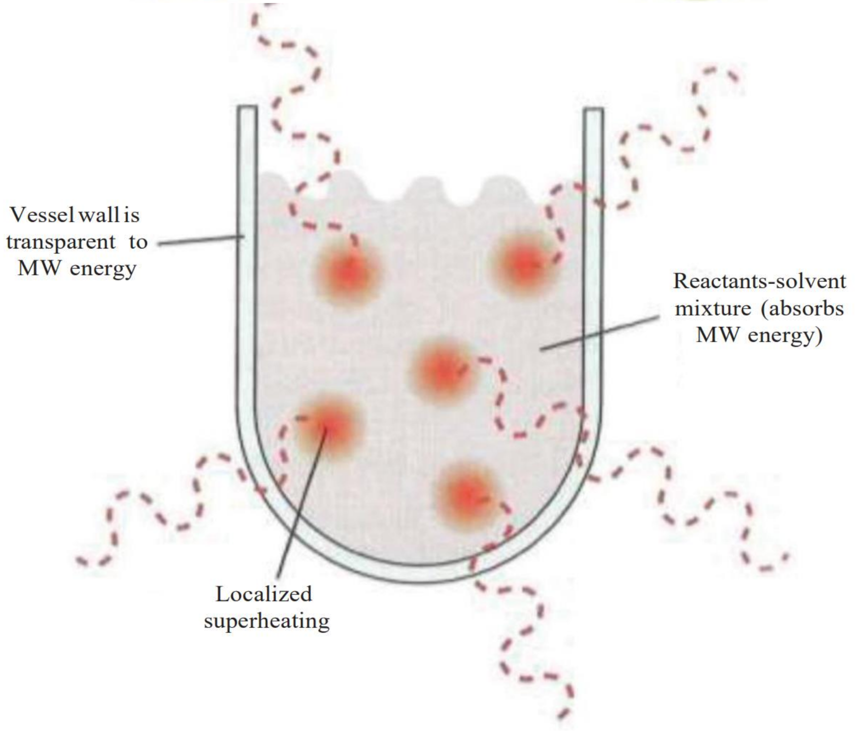
h.e.l

UNIQSIS
Accessible flow chemistry

Microwave-assisted hydro(solvo)thermal synthesis

Rapid volumetric heating without the heat conduction process

Conventional **Microwave**



Microwave Synthesis: Chemistry at the Speed of Light, CEM Pub., Matthews, NC, p. 295, 2002.

Conventional heating - heat conduction along the walls followed by diffusion to the central volume.

In this less efficient process, there is loss of heat energy as well as non-uniform heating of the reaction medium.

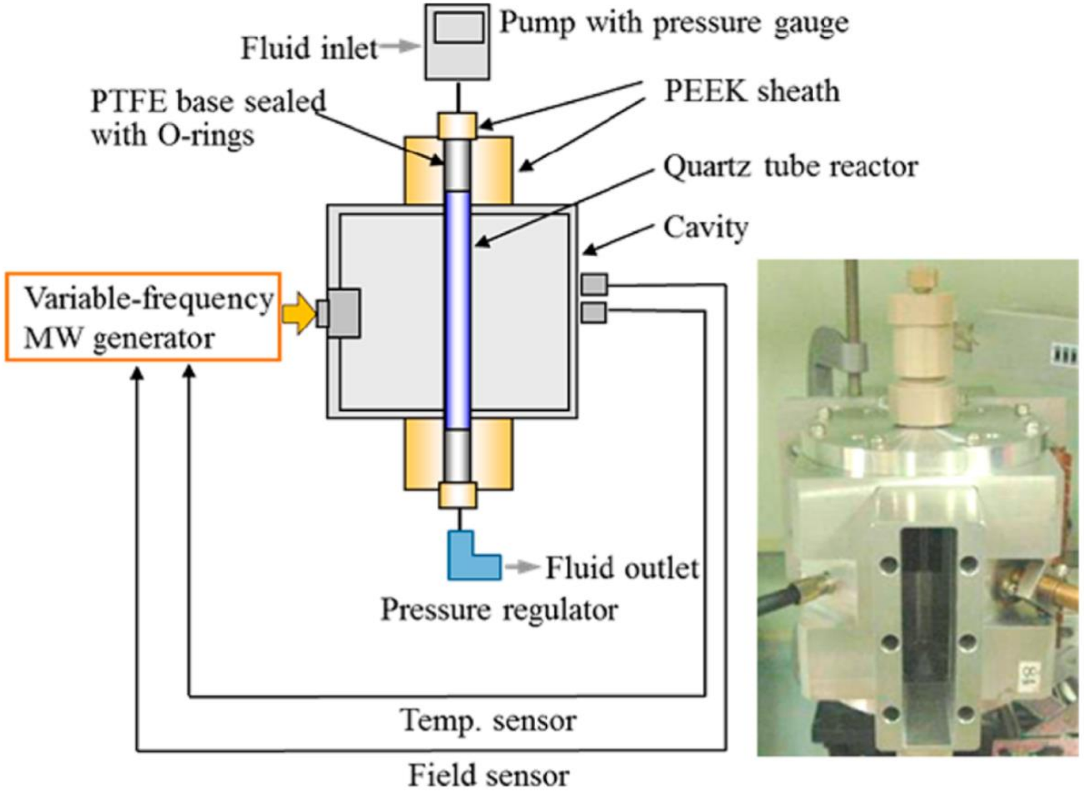
This leads to unequal distribution with some regions more heated than others, which results the need of extra time to obtain the final product.

A broad size distribution.

No clear and unequivocal evidence for the existence of “specific microwave effects” or “nonthermal microwave effects”

The more polar a solvent is, the higher its ability to couple with the microwave energy, leading to a rapid increase in temperature and fast reaction rate

Microwave-assisted hydro(solvo)thermal synthesis

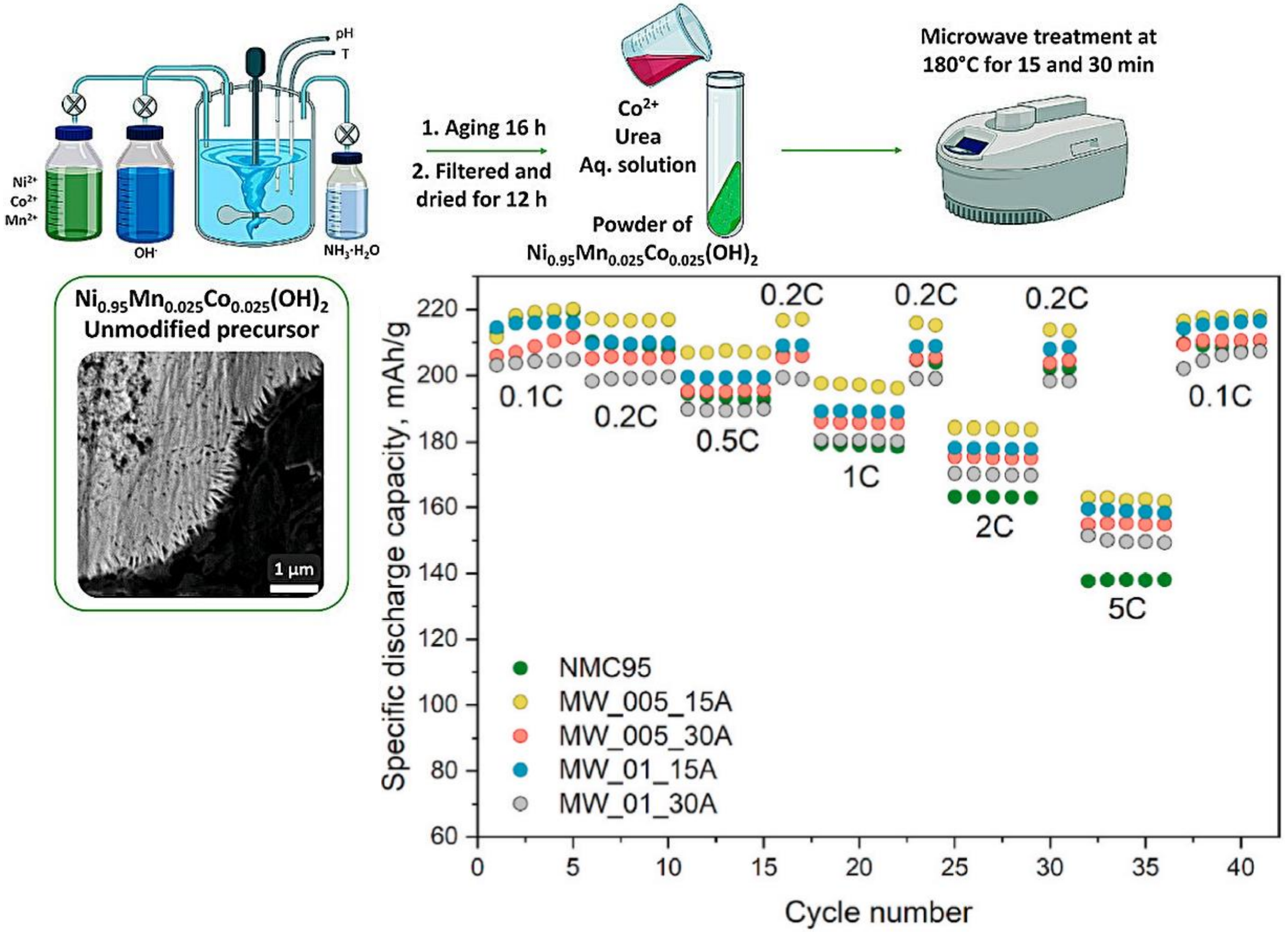


The quartz reactor tube is connected with the PEEK sheath, which is designed to resist up to a pressure of **10 MPa**.

Nishioka, M. et al Ind. Eng. Chem. Res. 2013, 52, 4683.

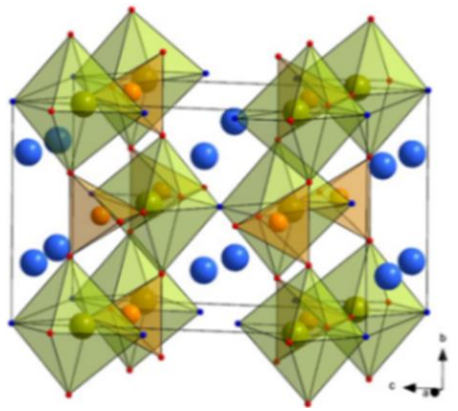
Microwave-assisted hydro(solvo)thermal synthesis

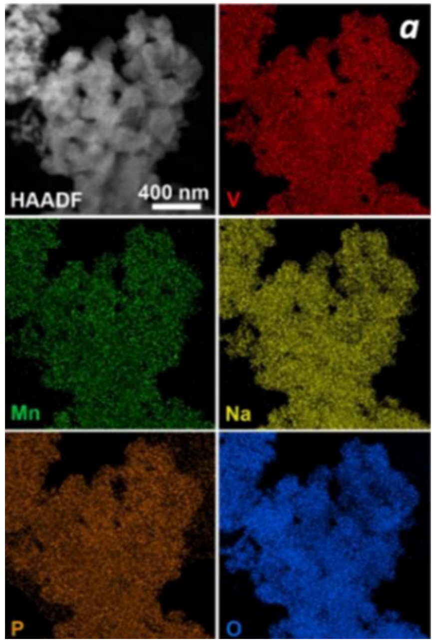
Ni-rich NMC: core-shell modification
$(Ni_{0.95}Mn_{0.025}Co_{0.025})_{1-x}Co_x(OH)_2$

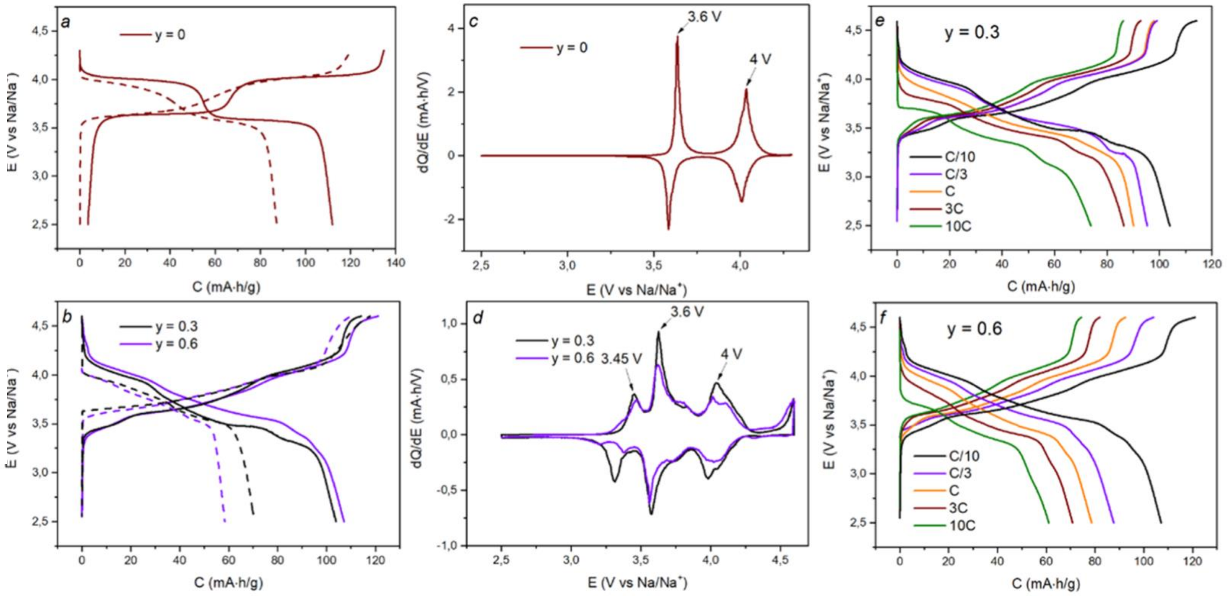


Mn-doped $Na_3V_2(PO_4)_2F_3$

$Na_{3.6}V_{1.4}Mn_{0.6}(PO_4)_2F_3$



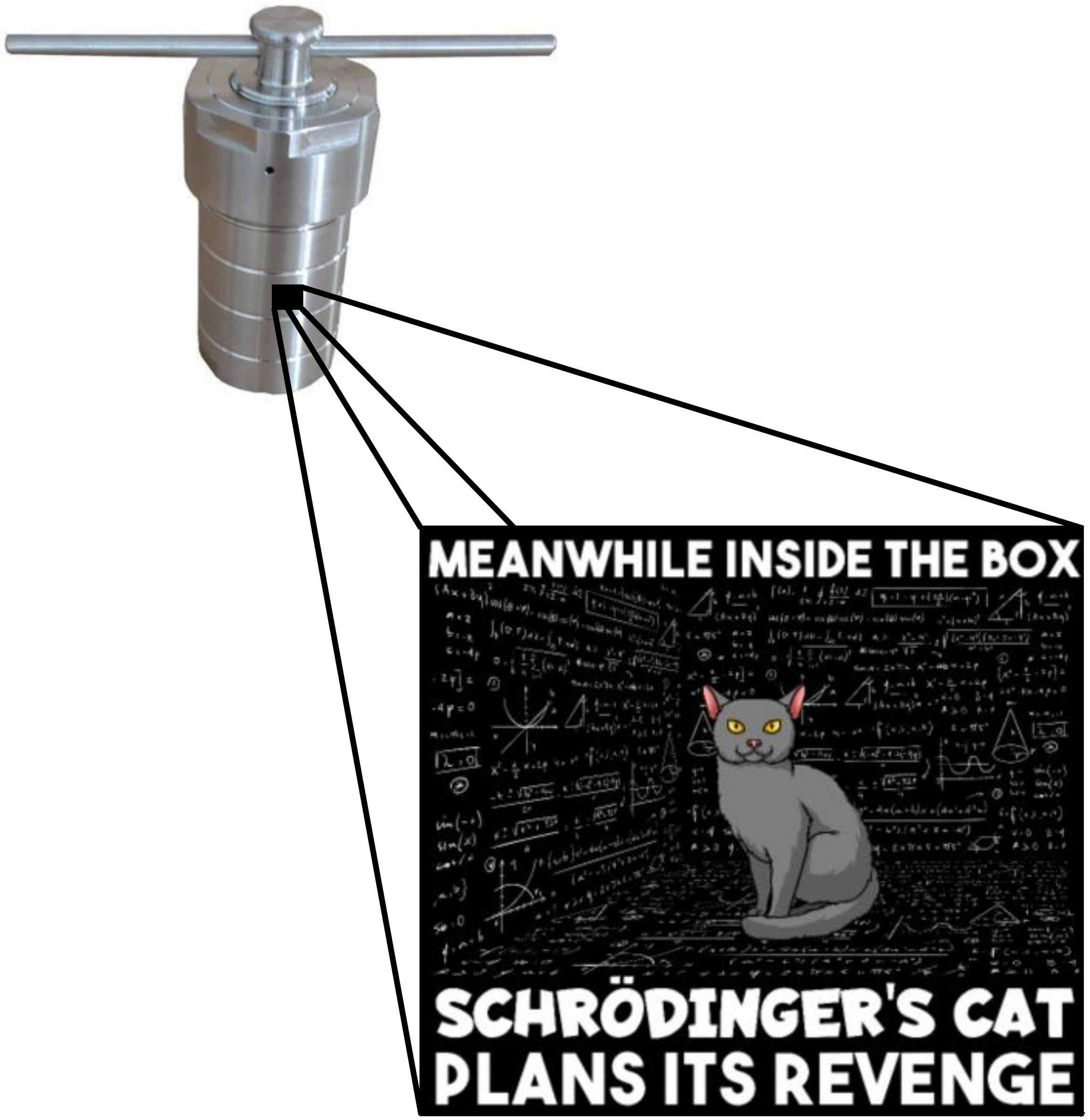




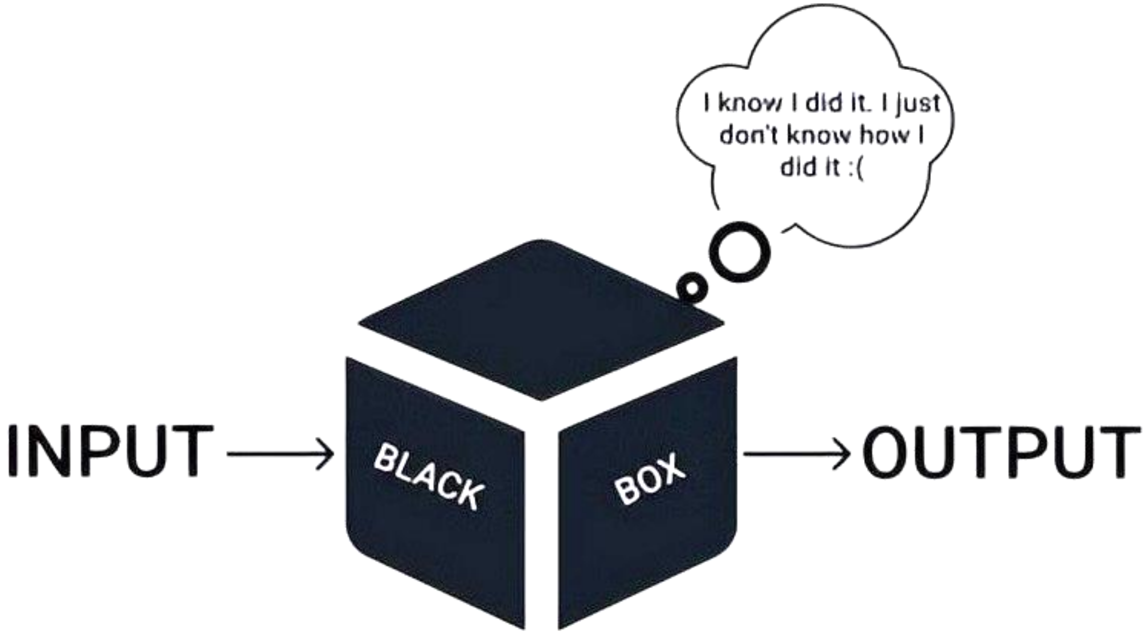
Lyutsia A. Sitnikova et al J. Power Sources 602 (2024) 234302

Anna R. Iarchuk et al ACS Appl. Energy Mater. 2021, 4, 5007−5014

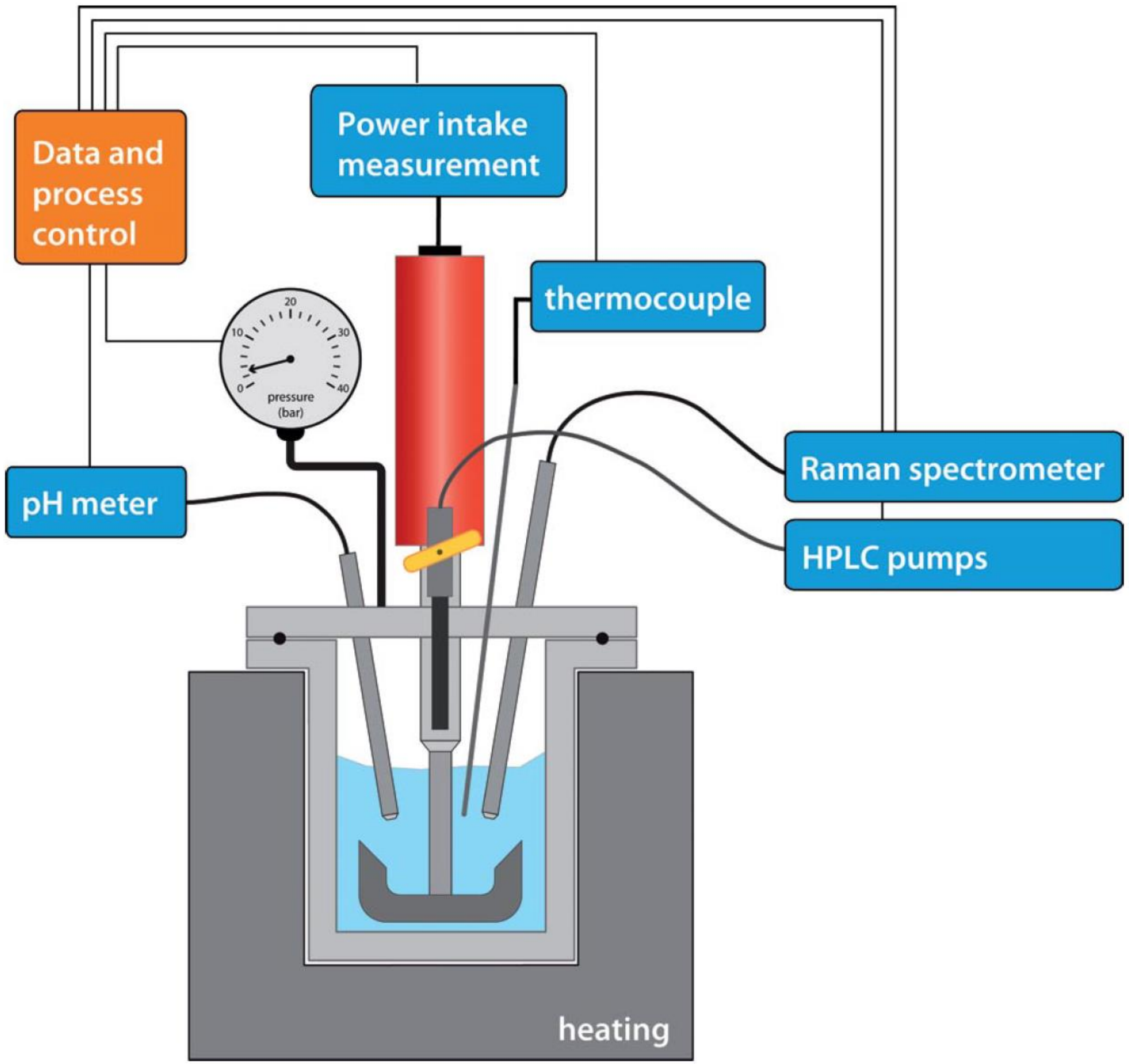
Monitoring of the reaction?

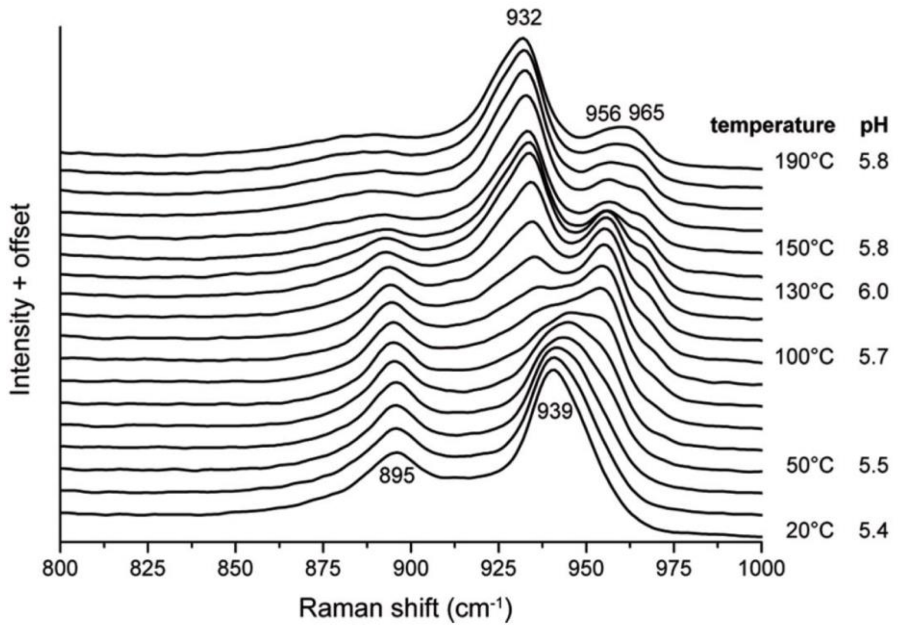


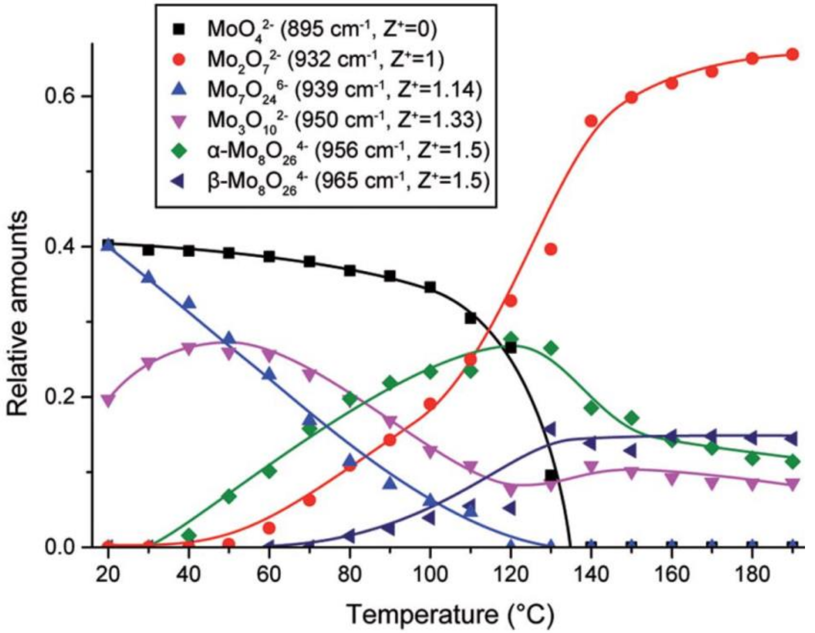
“**Black box**” problem



Monitoring of the reaction: pH, temperature, Raman

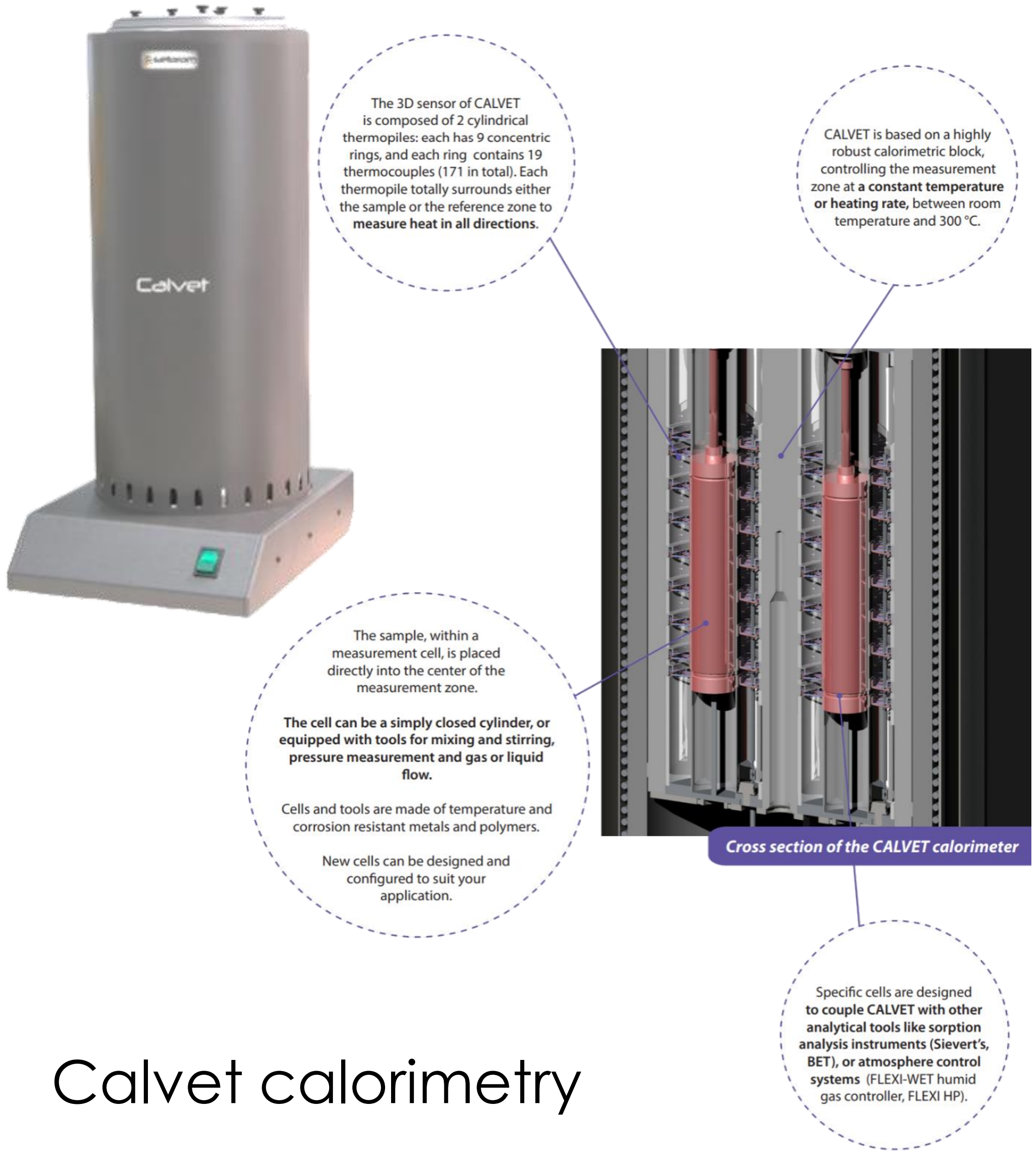




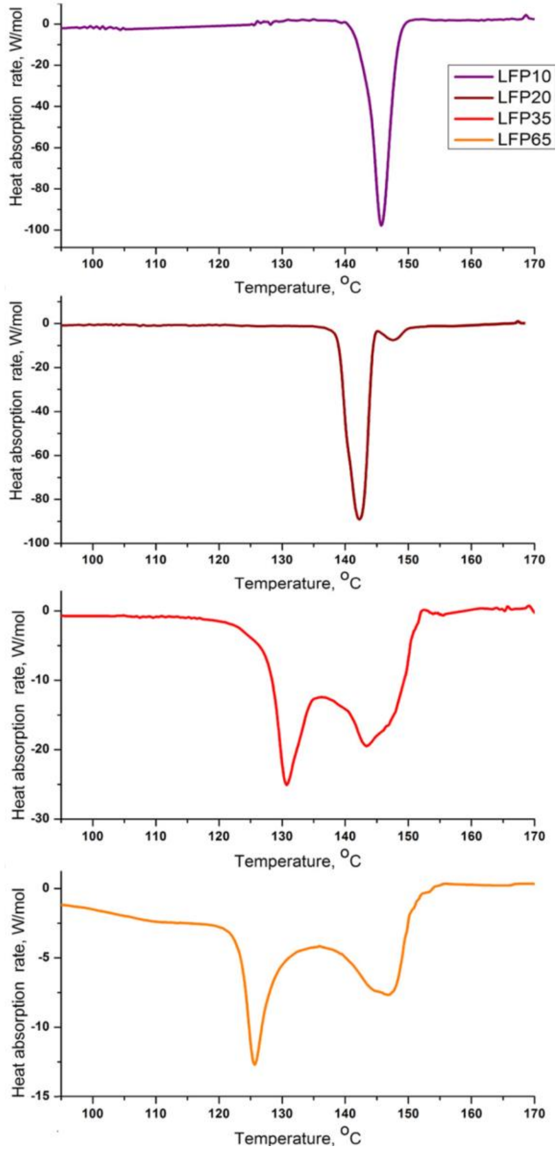


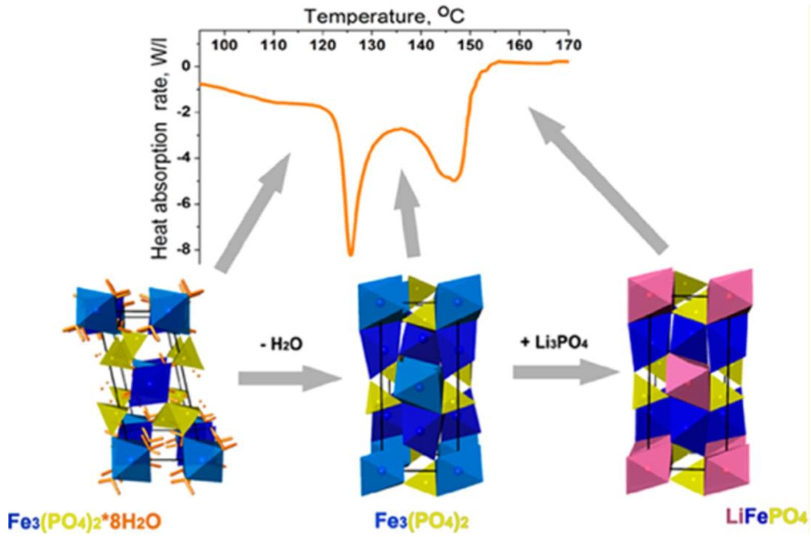
Z. Anorg. Allg. Chem. **2014**, *640, (14),* 2730–2736

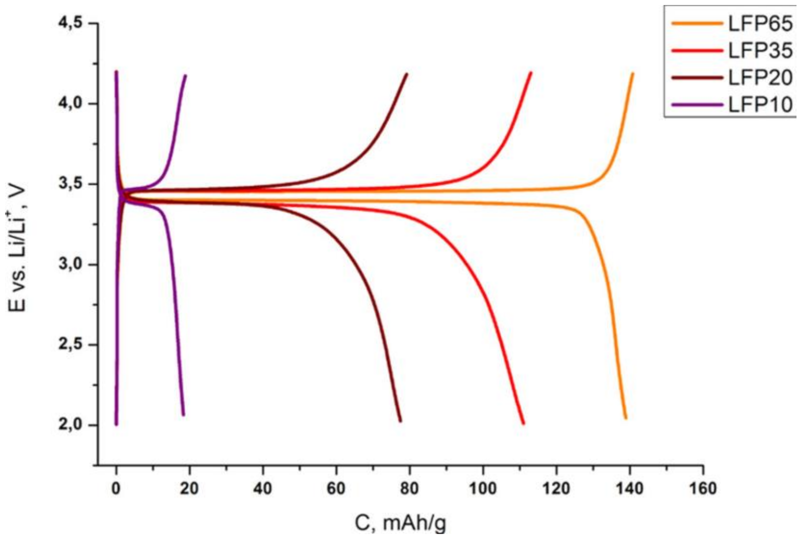
Monitoring of the reaction: calorimetry



Calvet calorimetry

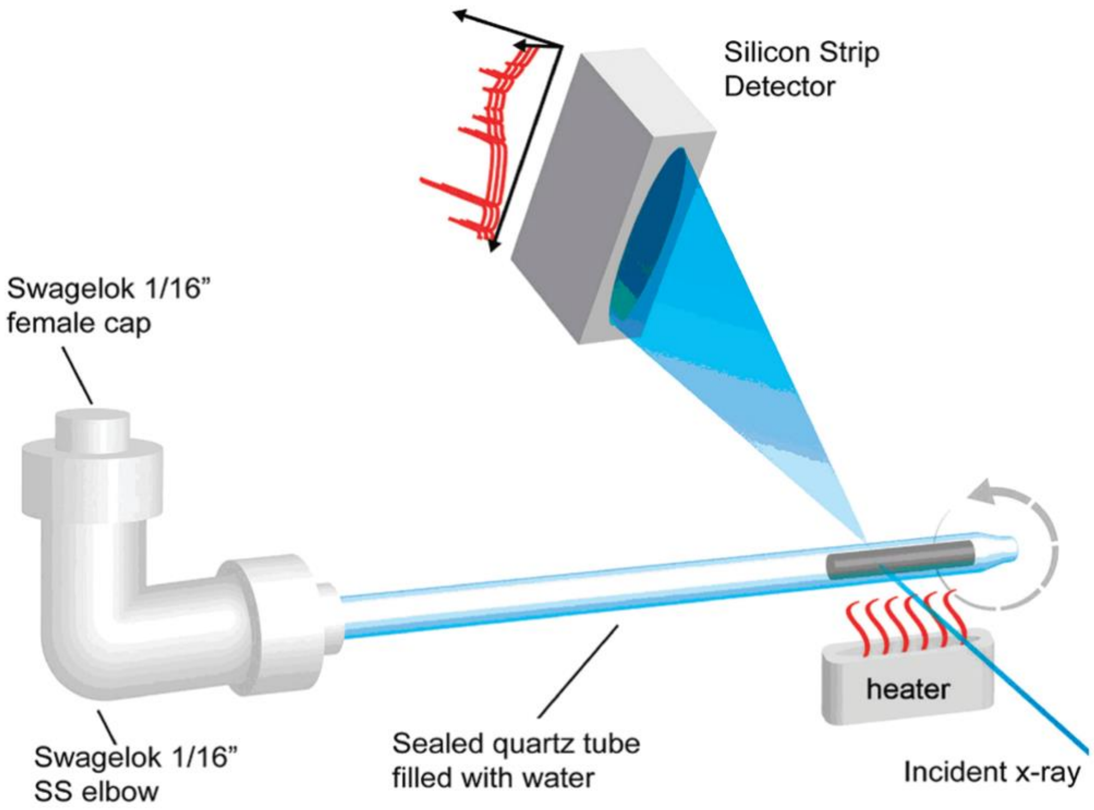


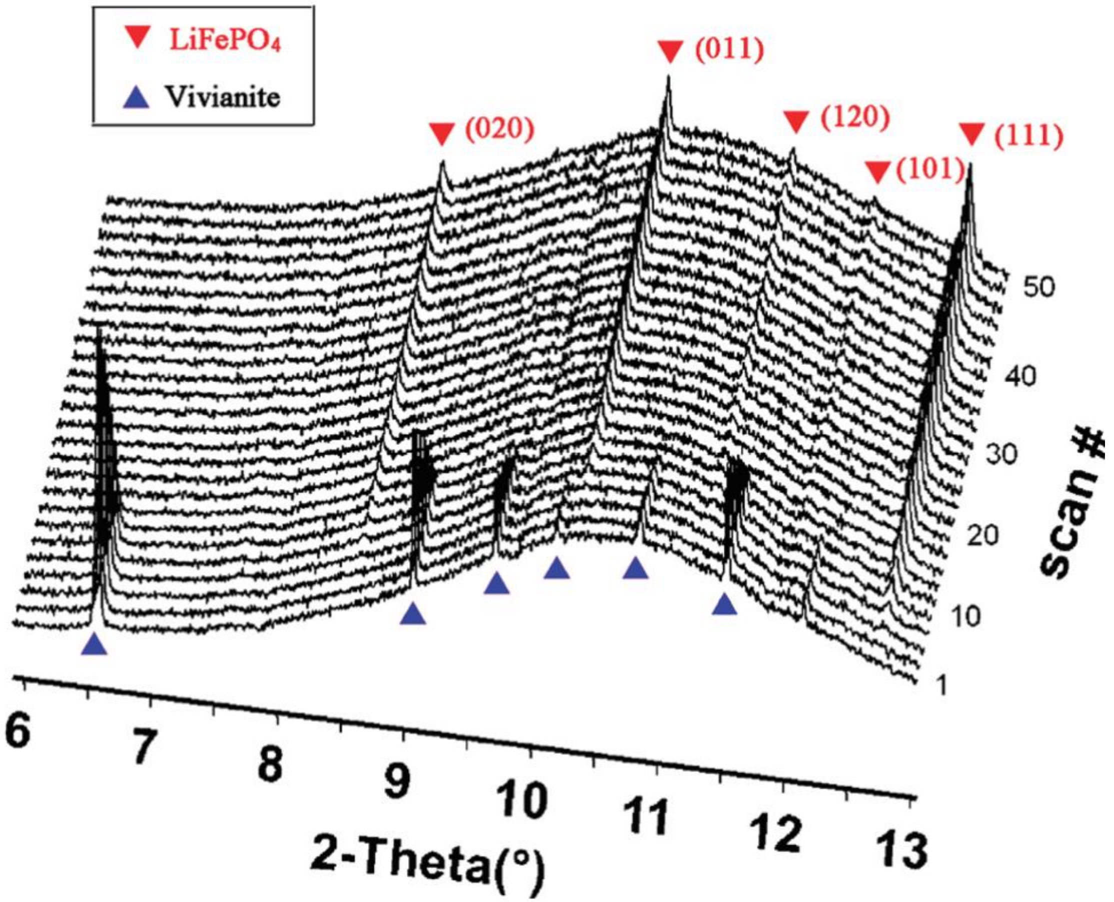




Cryst. Growth Des. 2018, 18, 879−882 DOI: 10.1021/acs.cgd.7b01366

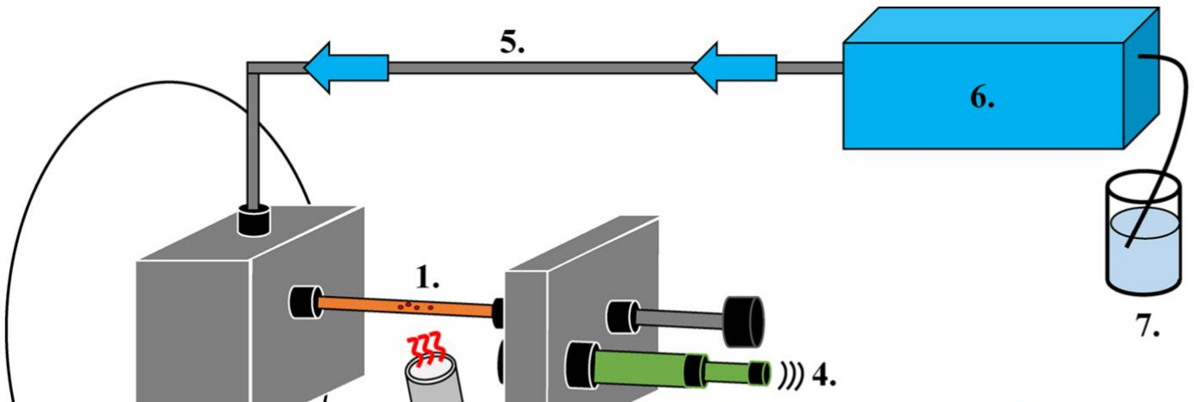
Monitoring of the reaction: SXRD

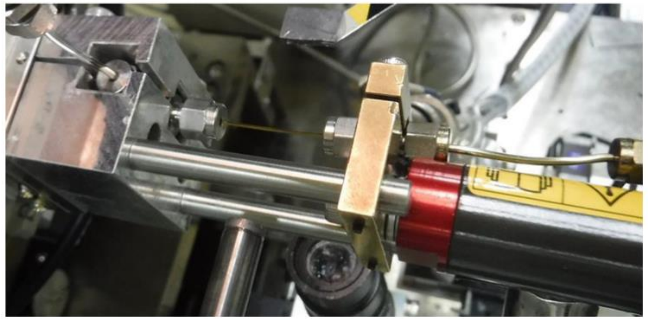




J. Phys. Chem. Lett. 2011, 2, 1874–1878

Monitoring of the reaction: SXRD

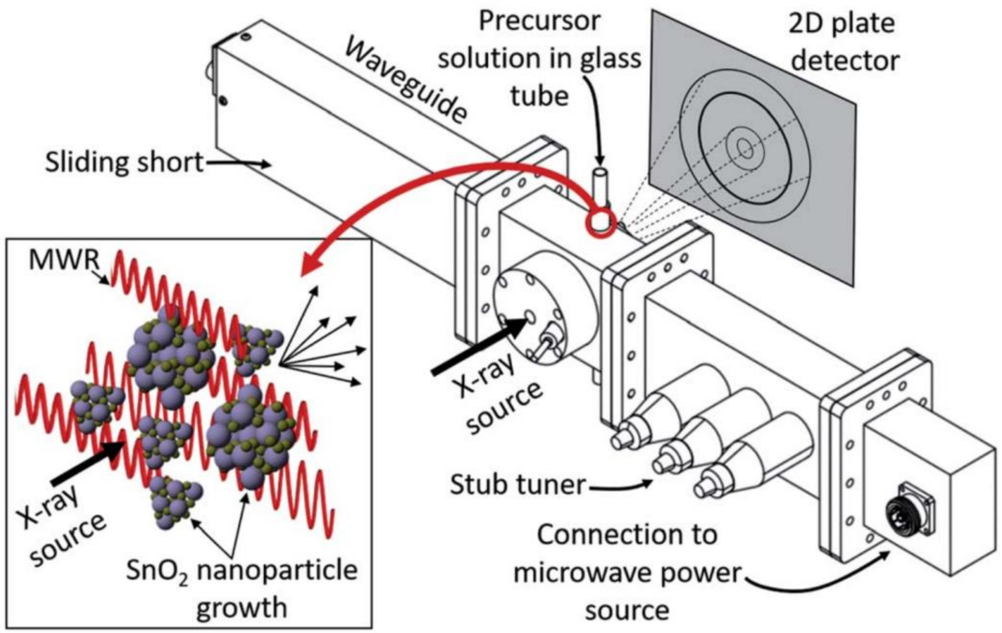




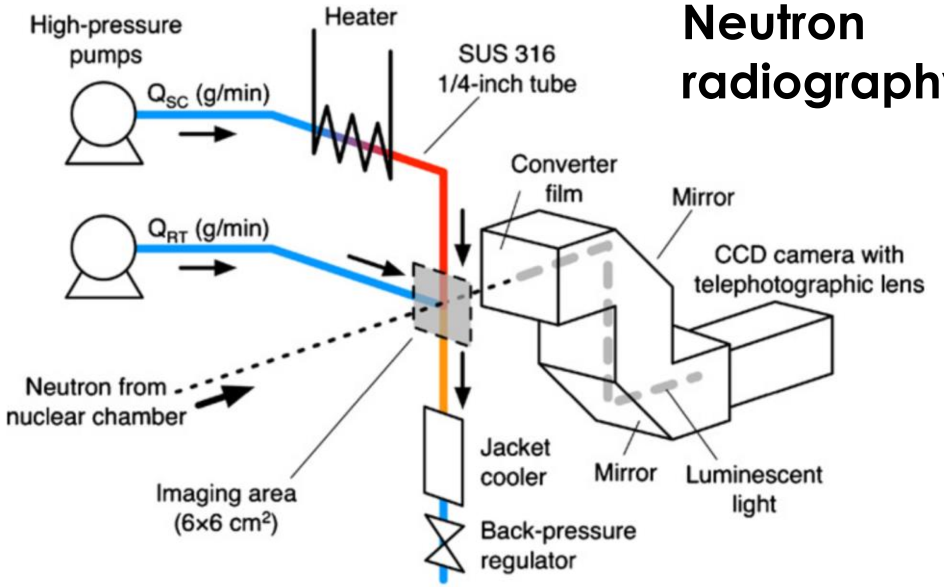
1, fused-silica capillary. 2, heater. 3, oscillation along omega-axis of diffractometer. 4, piston-type vibrator. 5, stainless steel tube. 6, high-pressure pump. 7, sample solution

https://doi.org/10.1016/j.supflu.2018.10.016

MWR-assisted synthesis



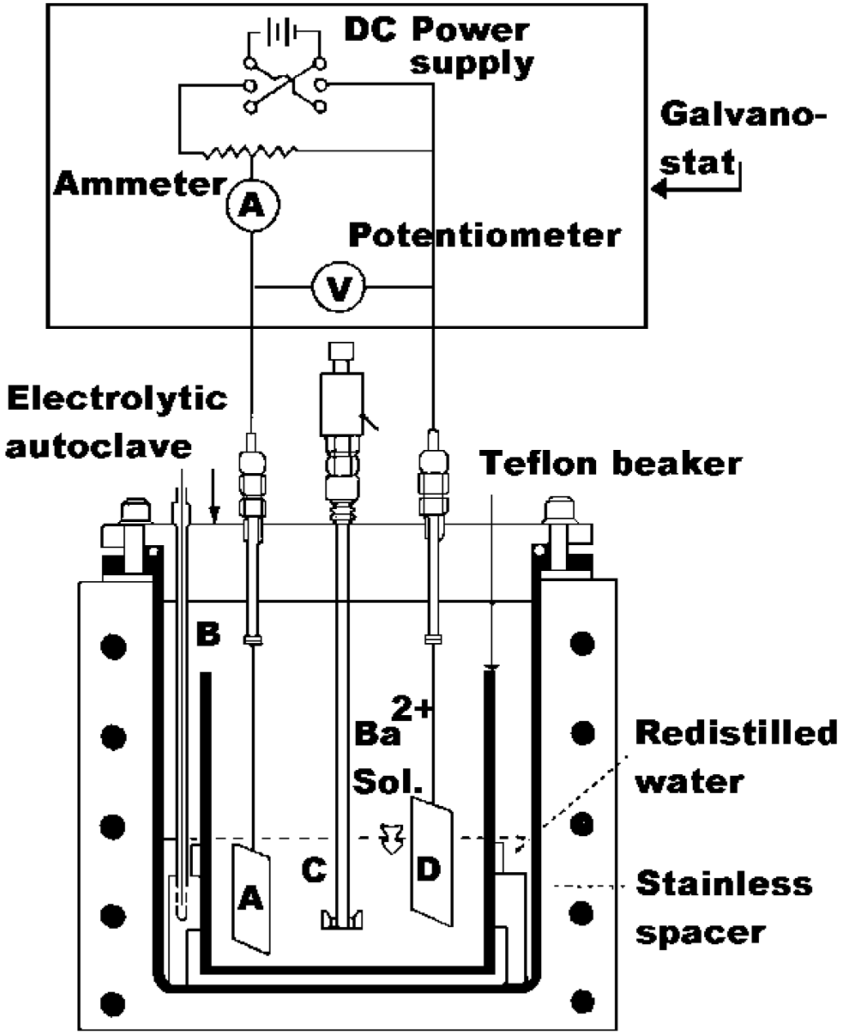
Neutron radiography

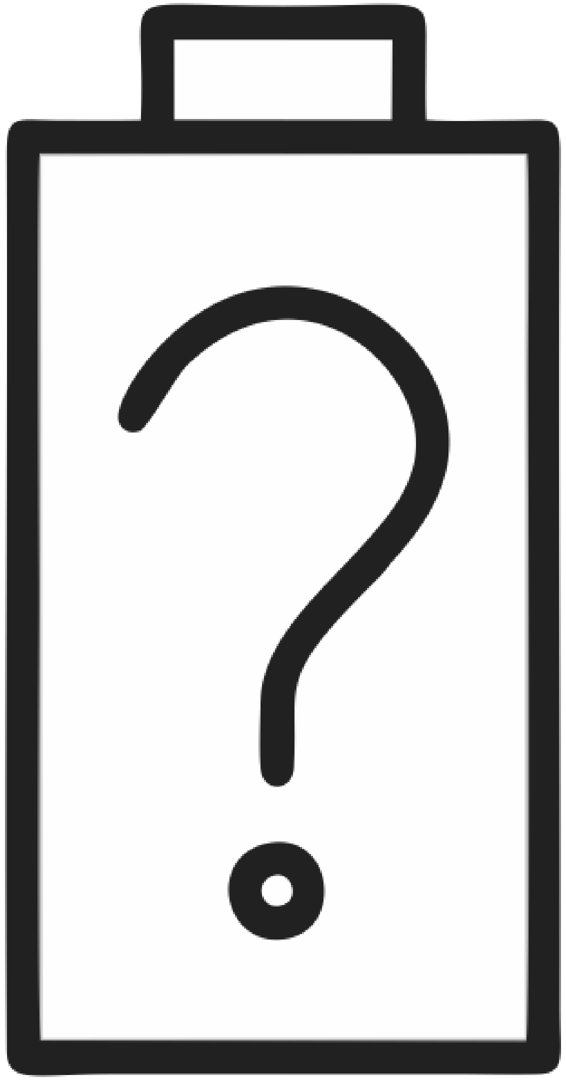


S. Takami et al. / J. of Supercritical Fluids 63 (2012) 46–51

Monitoring of the reaction: electrochemistry

Electrochemical synthesis, the characterization of catalysts, corrosion measurements or basic research on new electroactive species can also be carried out at higher pressures and beyond room temperature





Thanks for your attention

s.fedotov@skoltech.ru

Special thanks to Dr. Anatolii Volkov