# Mechanochemistry an old technique appearing in a new light – A contribution to more sustainable processes

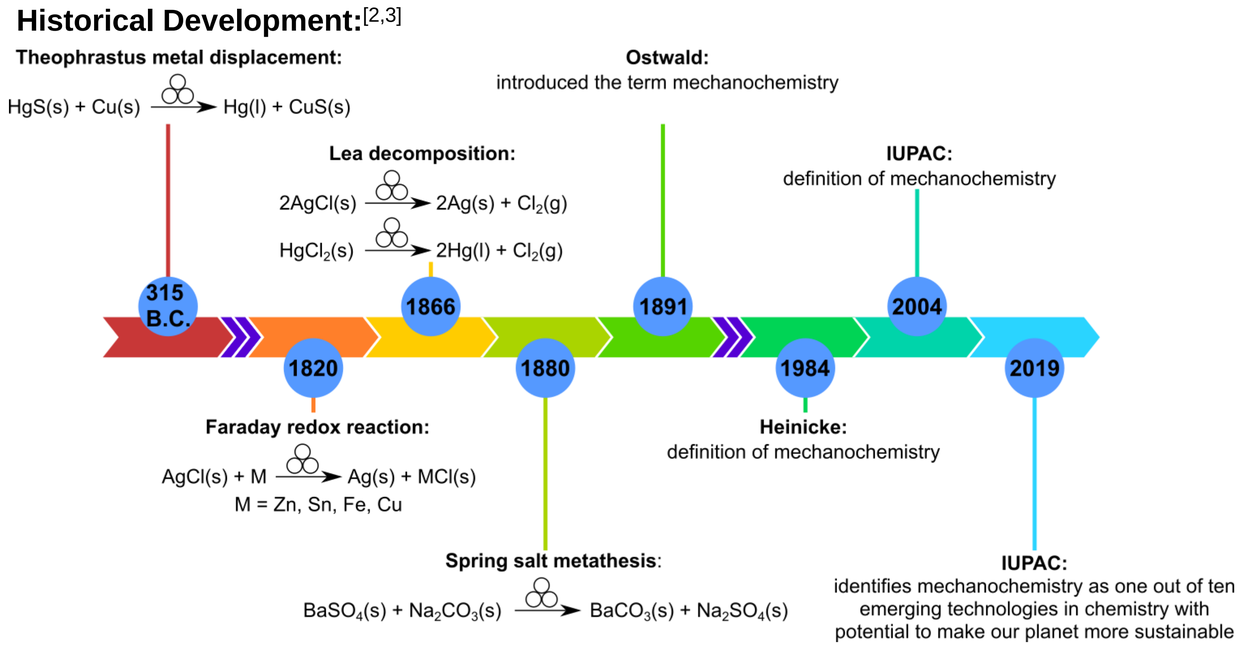
**Tobias Benjamin Straub, Annika Betke, Dennis Becker, Guido Kickelbick***

Saarland University, Inorganic Solid State Chemistry, Saarbrücken, Germany

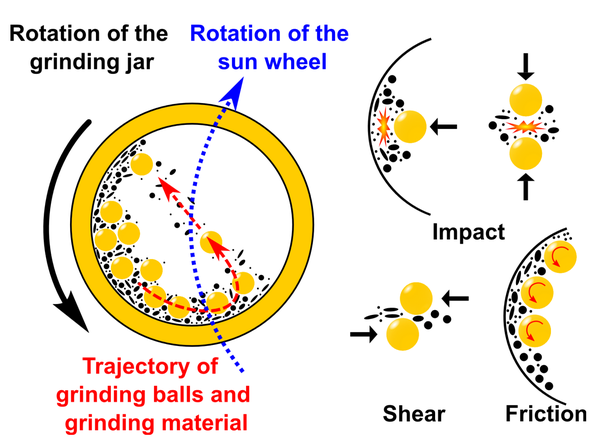
## Introduction

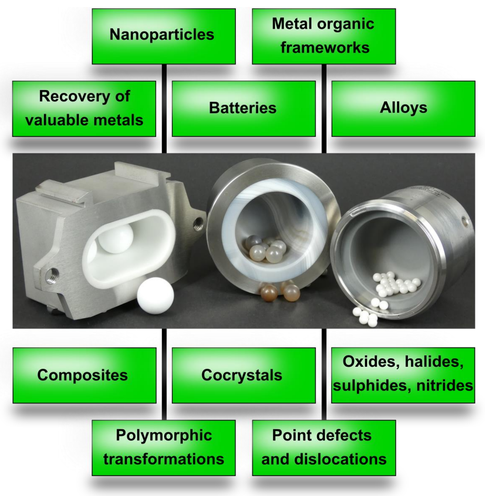
Mechanochemistry: “Chemical reaction that is induced by the direct absorption of mechanical energy.” IUPAC[1]

**Historical Development:**[2,3]




## Principle and Applications



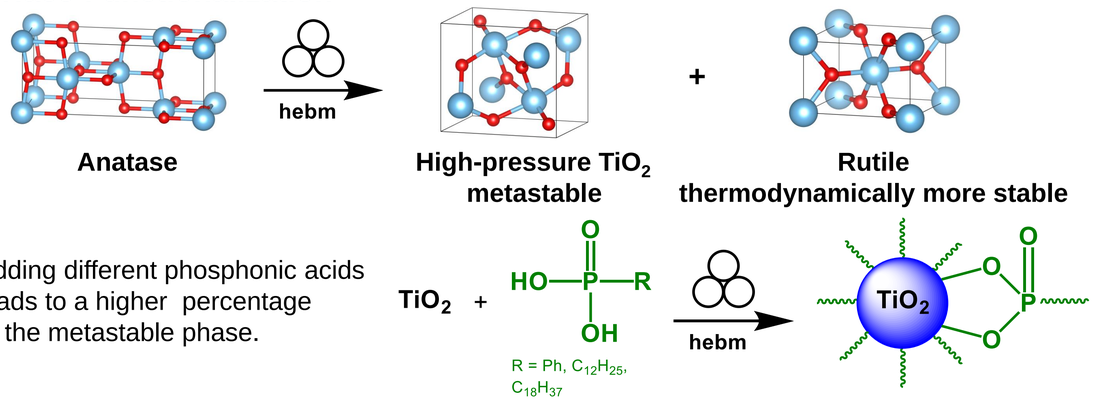

**Advantages:**

- absence of solvents, reduction of by-products
- lower reaction temperatures, shorter reaction times
- metastable phases can be obtained
- increased defect formation
- new synthetic pathways are realized[5-9]

Symbol for a mechanochemical transformation: ; hebm: **h**igh **e**nergy **b**all **m**illing, ssr: **s**olid-**s**tate **r**eaction[4]

## Results

### Example 1: Stabilization of Metastable Phases by Nanocrystallite Surface-Functionalization[10-12]




Adding different phosphonic acids leads to a higher percentage of the metastable phase.




### Example 2: Li-Intercalation Chemistry in Lithium Titanate[7]

**LiOH and $TiO_2$ (anatase or rutile)**

**or**

**monoclinic $Li_2TiO_3$**

**or**

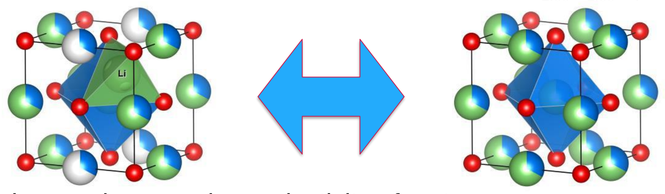
**spinel $Li_4Ti_5O_{12}$**

***hebm***

**cubic $Li_2TiO_3$ with partial tetrahedral instead of octahedral site occupation**

**ideal cubic $Li_2TiO_3$**

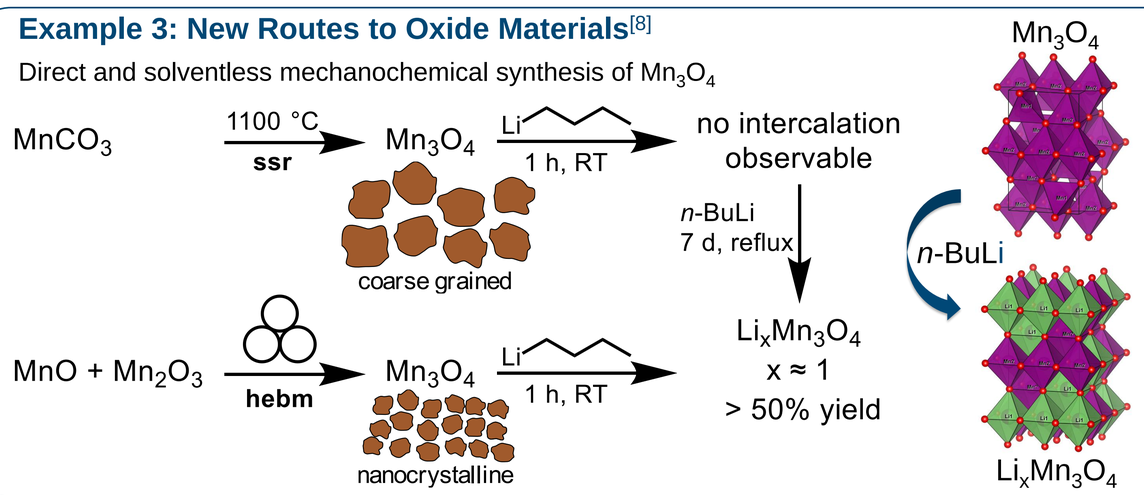
- High temperature phase: typically formed at T > 1150 °C
- NaCl structure type with statistical distribution of $Li^+$ and $Ti^{4+}$ on *4a* site ($Li_{2.66}Ti_{1.33}O_4$)




Impedance spectroscopy measurements show an increase in conductivity of up to three orders of magnitude this may be due to the displacement of Li ions.

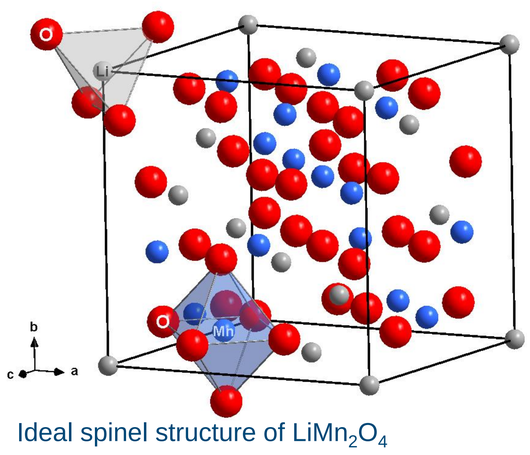
### Example 3: New Routes to Oxide Materials[8]

Direct and solventless mechanochemical synthesis of $Mn_3O_4$




### Example 4: Surface Functionalized Oxidic Nanoparticles and their Application for the Intercalation of Lithium[9]

Lithium Containing Precursors e.g. $Li_2CO_3$, LiOH, $Li_2O$ + Manganese Oxides e.g. $MnO_2$, $Mn_2O_3$ + $HO—P(=O)(OH)—R$ (R = Ph, alky-chain, ethylen oxide derivatives) —hebm→ $Li_xMn_yO_z$ Surface-functionalized Nanoparticles




Ideal spinel structure of $LiMn_2O_4$

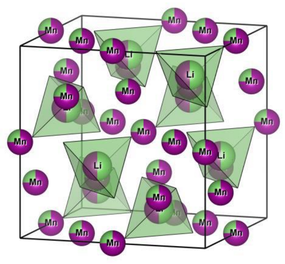
Deintercalation ⇌ Intercalation

$Li^+$

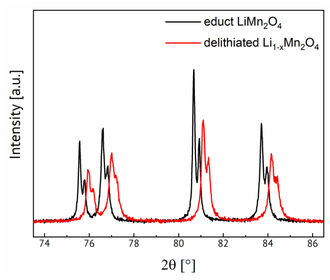
$Li_2CO_3 + Mn_2O_3 \xrightarrow[ssr]{800\ °C} LiMn_2O_4 +$ $HO—P(=O)(OH)—R$ —hebm→ surface functionalized $LiMn_2O_4$

coarse grained → nanocrystalline

Milling $LiMn_2O_4$ with phenylphosphonic acid leads to diminution of the particle size, a distribution of lattice parameters, cation disorder and formation of phases with orthorhombic, tetragonal and cubic symmetry. But in contrast to the unfunctionalized $LiMn_2O_4$, the de- and lithiation are strongly inhibited.




Disordered spinel structure of $LiMn_2O_4$




Section from a powder X-ray diffraction Pattern of partially delitiated $LiMn_2O_4$

## Conclusions

Mechanochemistry provides an opportunity for the synthesis of products by an energy input different from thermo-, photo-, or electrochemistry. Applying this technique in inorganic chemistry new synthetic pathways are realized or metastable phases can be obtained. Inorganic materials can be obtained in simpler synthetic processes (e.g. $Mn_3O_4$) simultaneous with the reduction of by-products, the absence of solvents, shorter reaction times and lower reaction temperatures. Because of the advantages shown above, mechanochemistry was identified by IUPAC in 2019 as one of the ten technologies with the potential to make our planet more sustainable.

## References

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