Up- and Down Conversion of Functional (M-A-Ch) Materials -

a strategy combining solid state synthesis of functional materials, resource efficiency and computational modeling

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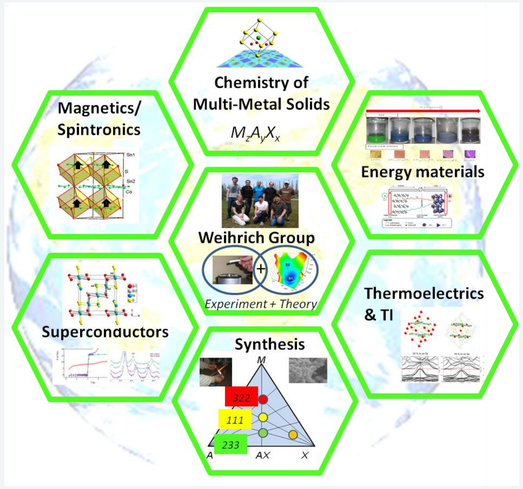
Sustainable Synthesis of Materials by: Conversion Chemistry

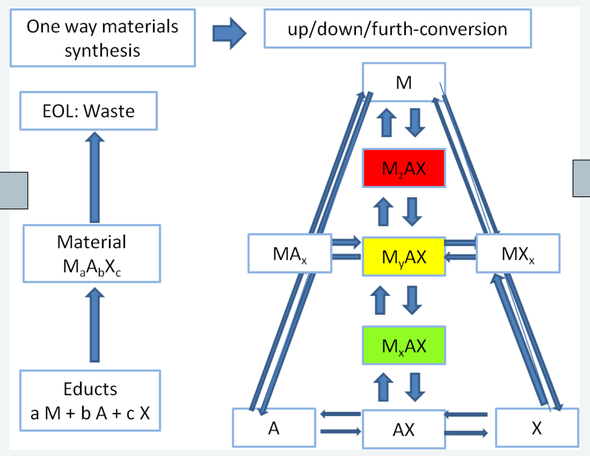
Concept

- From one-way- to multi-conversion reactions
  - up-, down-, forth-conversion
  - Sustainable chemical processes:
  - Dissolution
  - Control of product formation
- Sustainability and resource efficiency:
  - Resource efficient processes
  - Recovery/Substitution of critical elements
  - Close reaction cycles
- Sol-Gel and Liquids reaction media:
  - Mild conditions
  - Green approach
- Multinary M-A-X-Functional Materials
  - known and novel compositions and structures
  - Metastable compounds
- Green IT:
  - DFT prediction on stability
  - Prediction of targets

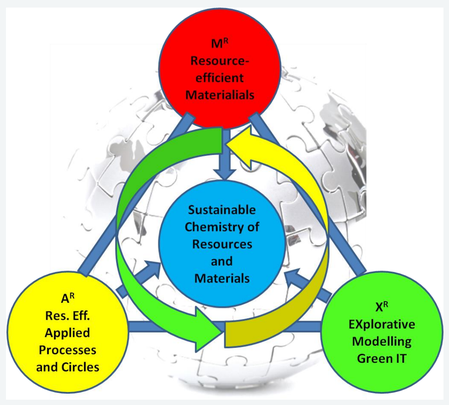
Synthesis of Functional M-A-X-Materials



Functional M-A-X-Materials by conversion processes

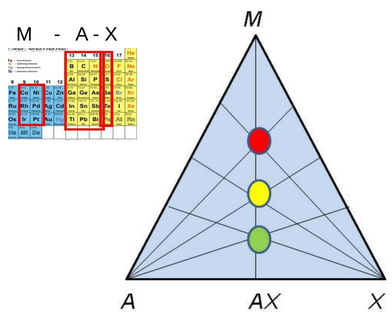


Sustainability and Resource Efficiency

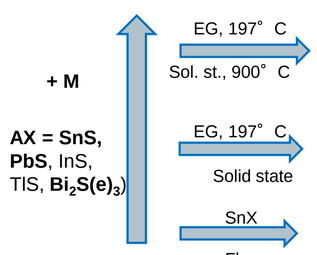


M-A-X-Phase diagram: Materials and Conversions in Liquids and Melts

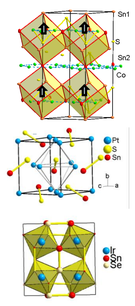
Phase diagram: of M-A-X chalcogenides



Conversion of AX:



Compositional & structure design:

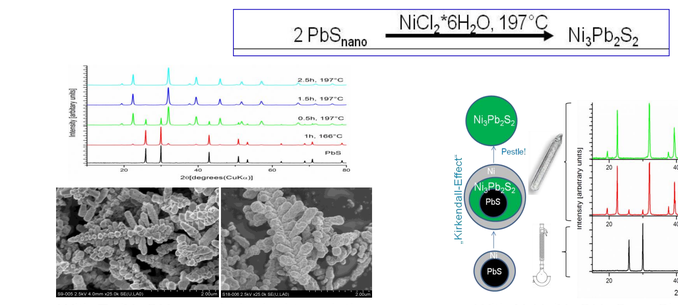


Electronic design:

Goals

- Low temperature conversions
- Solved reaction mechanisms and paths
- Conversion of SnX, Bi_2X_3, InS to M_xAX_y compounds
- Dissolution of SnS and Bi_2S_3:
- Muliple conversions, different paths
- Directed reactions and control of product formation
- Electronic design of materials properties
- Morphological templating
- Formation of spintronic ($Co_3Sn_2S_2$), thermoelectric (Co_3InSnX_2, $Ir_2Sn_3X_3$, $Ni_3Sn_2S_2$, PtSnX), superconducting ($Ni_3Bi_2X_2$) materials

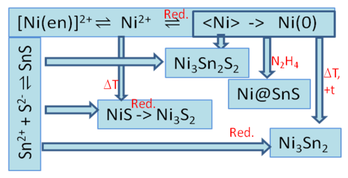
Control of product formation from AX + M reactions



With En/NaOH: morphological templating

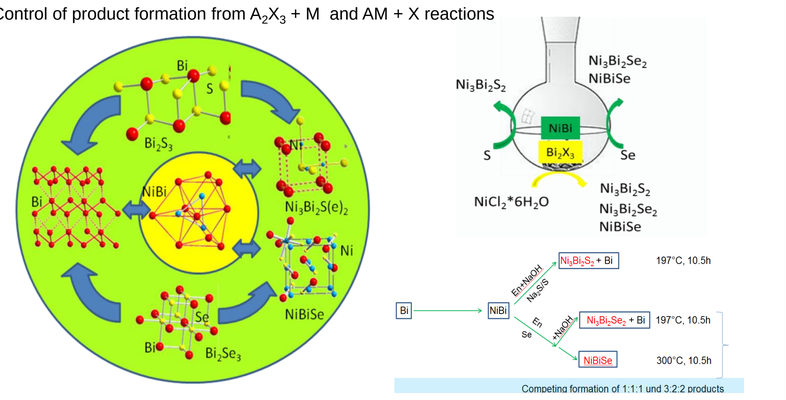
N_2H_4/NaOH;

With N_2H_4/NaOH: Core-Shell particles



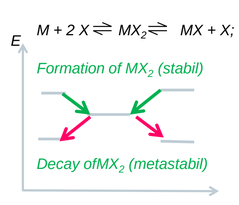
Multiple conversions of SnS + M

Control of product formation from A_2X_3 + M and AM + X reactions

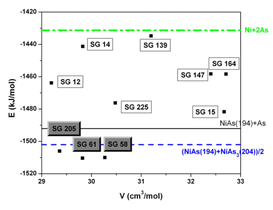


Green IT: Prediction of Targets, Structures, Properties, Stability

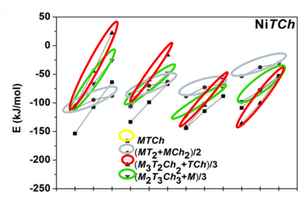
Predictions on structures and stability for MX_2, $M_3A_2X_2$



Stability diagram for MX_2: formation and decay



Energy diagram for competing MX_2 structures

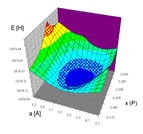


Energy diagram for competing M_xAX structures and compositions

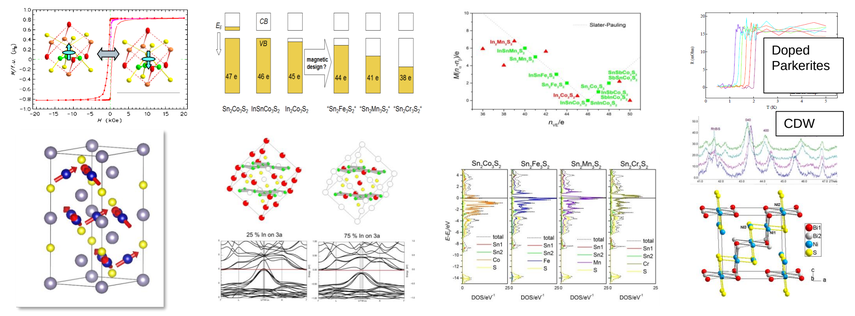
DFT Modeling

⇒ Sustainable and resource efficient:
- ⇒Saving raw materials
- ⇒Saving time and energy

⇒ Predictive Power
- ⇒ Structures
- ⇒ (Meta-) Stability
- ⇒ Functional targets



Electronic Desing along $M_3A_2X_2$



Half metal $Co_3Sn_2S_2$ | Thermoelectric Co_3SnInS_2 | Magnetci design $M_3A_2S_2$ | Superconduting $M_3Bi_2S_2$

Target Compositions and Green Reaction Paths

Step 1:

M + SnX	M = Ni, Co,

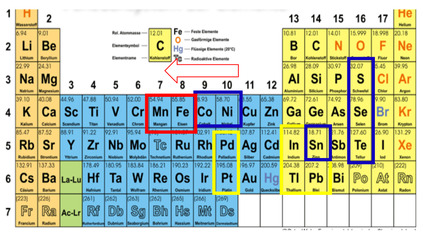
Step 2:

M + SnX	M = Fe, Mn

Step 3:

M + AX_x	A = In, Bi, Sm
MSnX	M = Pd, Pt

Investigated compounds and compostions for conversion reations in ionic liquids



Known and unknown compostions in the M-A-X-Phase diagram: investigationstep one (blue), step 2 (red) step 3 (yellow)

X	M = Mn	Fe	Co	Ni	Rh	Ir	Pd	Pt
S	Mn_2SnS_4 *Cmmm, C2/m*	Fe_2SnS_4 *I41/a*	$Co_3Sn_2S_2$	$Ni_3Sn_2S_2$, Ni_6SnS_2, Ni_9SnS_2	$Rh_3Sn_2S_2$	$Ir_2Sn_3S_3$		PtSnS
Se	Mn_2SnSe_4 *Pnma*	-	$Co_2Sn_3Se_3$	$Ni_{5.62}Se_2Sn$	-	$Ir_2Sn_3Se_3$	$Pd_7Se_{9.9}Sn_2$	PtSnSe
Te	Mn_2SnTe_4 *Pnma* (Mn,Sn)Te	-	$Co_2Sn_3Te_3$;	$Ni_{0.33}Sn_{3.67}Te_4$, $Ni_{2.86}SnTe_2$ $Ni_{5.76}SnTe_2$;	$Rh_2Sn_3Te_3$	$Ir_2Sn_3Te_3$	PdSnTe Pd_5SnTe $Pd_{6+x}SnTe_2$	PtSnTe

Sol-Gel and hydrothermal synthesis:
⇒ low temperatures
⇒ kinetic control of product formation
⇒ study of reaction mechanism
⇒ direction of reactions
⇒ Microwave assistance

Cooperation with Prof. Dr. Kunz, Univ. Regensburg

Goals

- Directed synthesis routes
- Novel Products and polymorphs
- Study of Reaction Paths
- Back and furth conversion
- DFT modeling – Green IT
- Green Chemistry and reaction paths

Methods:
- Solid state synthesis
- In situ high- and low temperature and high pressure X-ray diffraction
- DFT modelling on various levels and codes CRYSTAL17, vasp, FPLO – energy diagrams, structure-property-relations, bond formation

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