Transport properties in layered thermoelectric chalcogenides

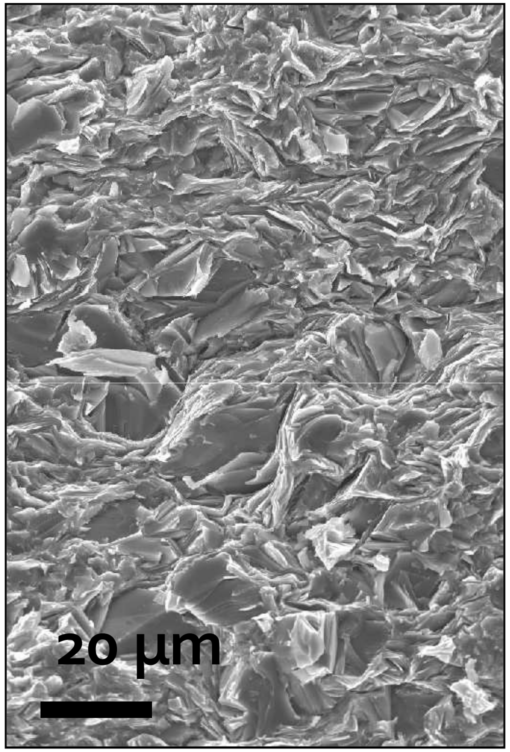
Intercalation, substitution and non stochiometry : three different approaches to increase phonon scattering in TiS_2

-26 February 2014 –

Emmanuel Guilmeau

EPSRC Workshop, Manchester

Summary



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2. Intercalation : the case of copper and silver
3. Heavy metal cations Substitution (Ta, Nb)
4. Non-stochiometry: Tuning of TE properties and structural disordering

MS_2 layered Dichalcogenides

MS_2 Layered Structure

- Trigonal prismatic or octahedral
- Hexagonal packed planes
- Van-der-Waals interaction between layers
- Alkali, Metal intercalation

Electronic Properties

- Insulating-SC-Metal
- Degree of filling of d bands (metal)
- Non stoichiometry

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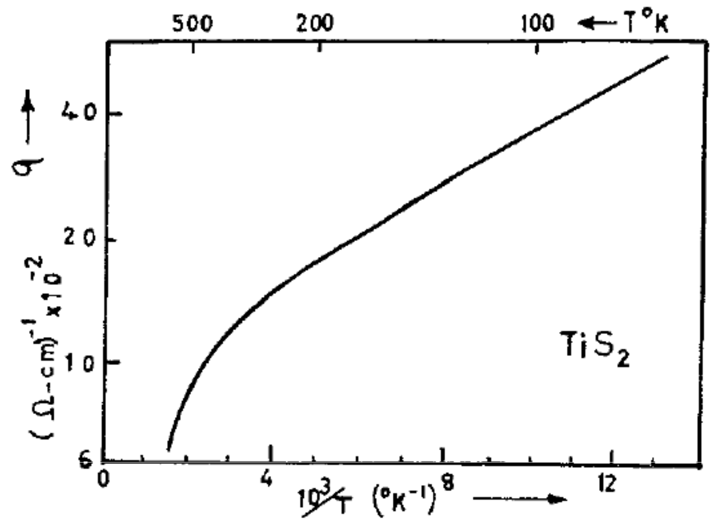
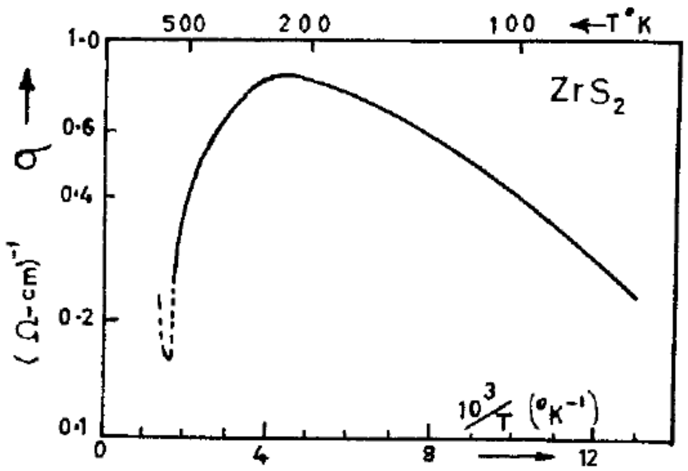




J.A.Wilson and A.D. Yoffe, Adv. Phys (1969)

MS_2 layered Dichalcogenides

MS_2 Layered Structure

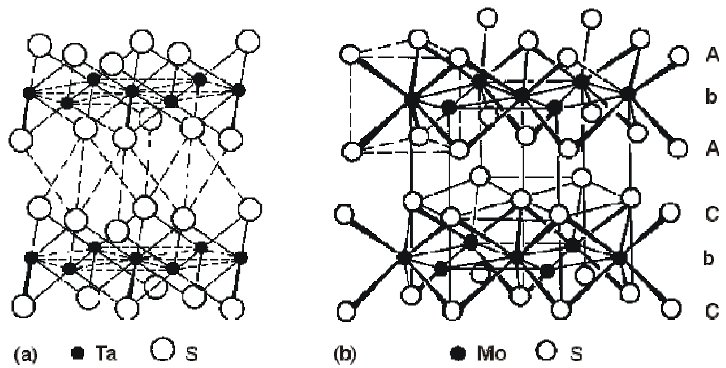
- ❑ Trigonal prismatic or octahedral
- ❑ Hexagonal packed planes
- ❑ Van-der-Waals interaction between layers
- ❑ Alkali, Metal intercalation

Strong Anisotropy

- ❑ Two-dimensional character, e.g. electrical and thermal properties
- ❑ Electron mobility in CdI_2 planes
- ❑ Phonon scattering along *c* direction

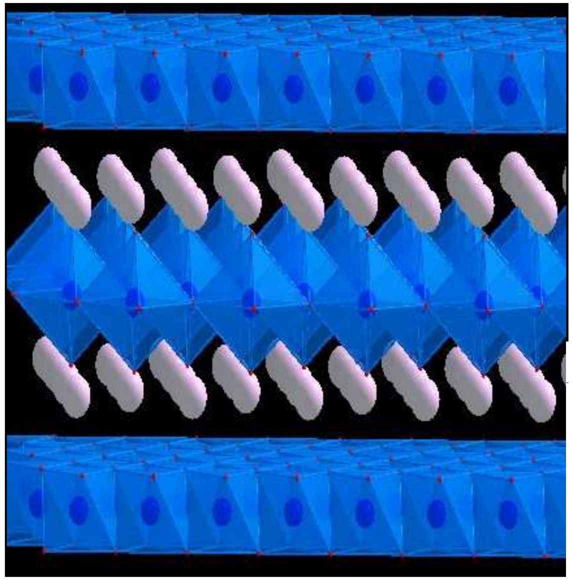
Electronic Properties

- ❑ Insulating-SC-Metal
- ❑ Degree of filling of d bands (metal)
- ❑ Non stoichiometry



MS_2 layered Dichalcogenides

$[Ca_2CoO_3]_{0.62}[CoO_2]$



An Oxide Single Crystal with High Thermoelectric Performance in Air

Ryoji FUNAHASHI*, Ichiro MATSUBARA, Hiroshi IKUTA[1], Tsunehiro TAKEUCHI[2], Uichiro MIZUTANI[2] and Satoshi SODEOKA
Osaka National Research Institute, AIST, Midorigaoka, Ikeda, Osaka 563-8577, Japan
[1]*Center for Integrated Research in Science and Engineering, Nagoya University, Chikusa-ku, Nagoya, Aichi 464-8603, Japan*
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(Received September 27, 2000; accepted for publication October 6, 2000)

Misfit-layered cobaltite with an anisotropic giant magnetoresistance: $Ca_3Co_4O_9$

A. C. Masset, C. Michel,* A. Maignan, M. Hervieu, O. Toulemonde, F. Studer, and B. Raveau
Laboratoire CRISMAT, UMR 6508 associée au CNRS, ISMRA et Université de Caen 6, Boulevard du Maréchal Juin, 14050 CAEN Cedex, France

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Laboratory of Oxidic Materials, Institute of Physics, 162 53 Prague 6, Cukrovarnicka 10, Czech Republic

(Received 1 February 2000)

*A. C. Masset et al., PR B **62**, 166, 2000*
*R. Funahashi et al., JJAP **39**, L1127, 2000*

$\rightarrow S = +120\ \mu V/K$

MS2 compounds | Intercalation | Substitution | Non-stochiometry

Why TiS_2 as a TE element?

Criteria for thermoelectricty

☑ **Narrow band-gap semiconductor**

Low electrical resistivity, high Seebeck coefficient

$n = 10^{20}$ cm^{-3}
High Power factor
1.7 mW/mK^2 @ 300K

☑ **Flexible compositions for tuning transport properties**

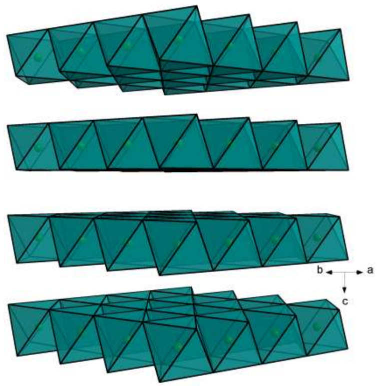
Optimum carrier concentration

Large unit cell, complex structure, disorder

Low thermal conductivity

Heavy elements

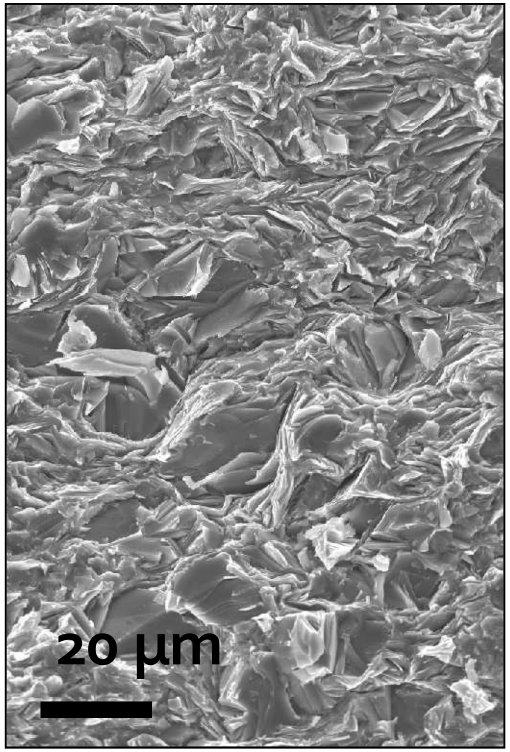
Low thermal conductivity



TARGET:
Decrease thermal conductivity

MS2 compounds | Intercalation | Substitution | Non-stochiometry

Summary



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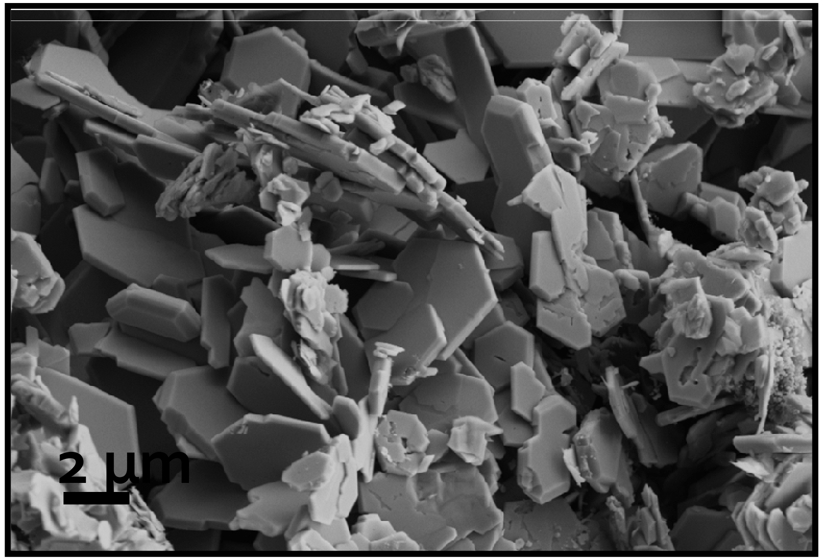
Material Processing

Powder

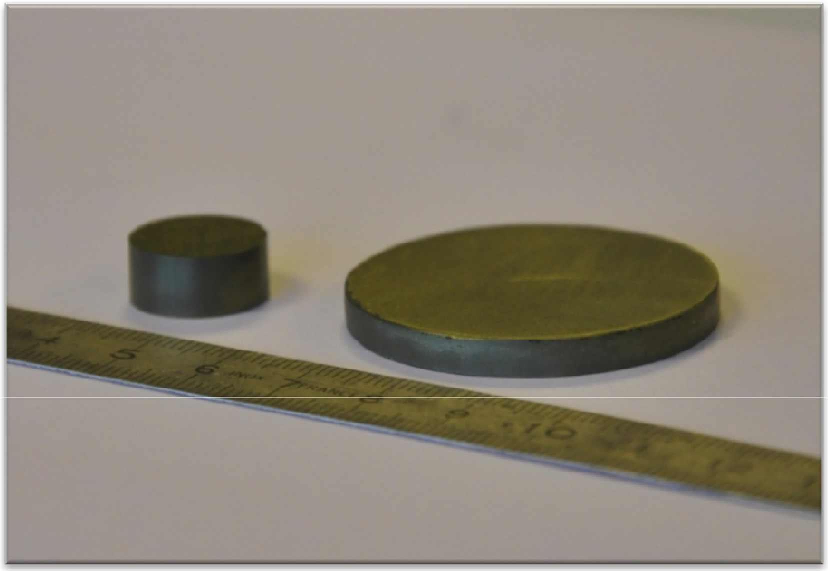
Sealed tube synthesis (650°C/12h)

Grain size
(5 µm)

Traces of TiO_2



Bulk



SPS Sintering 600-900°C 50-300 MPa

Relative Density
> 95%

Grain size
(20 µm)

Slight (001) texture

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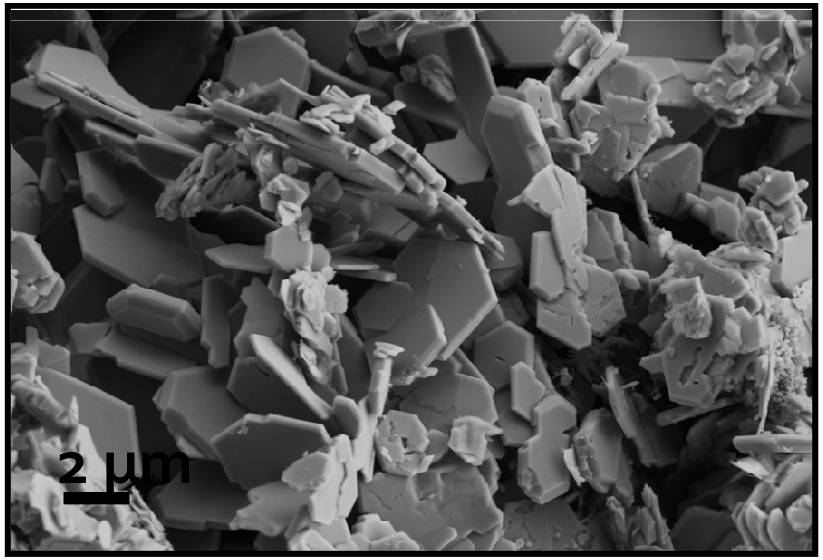

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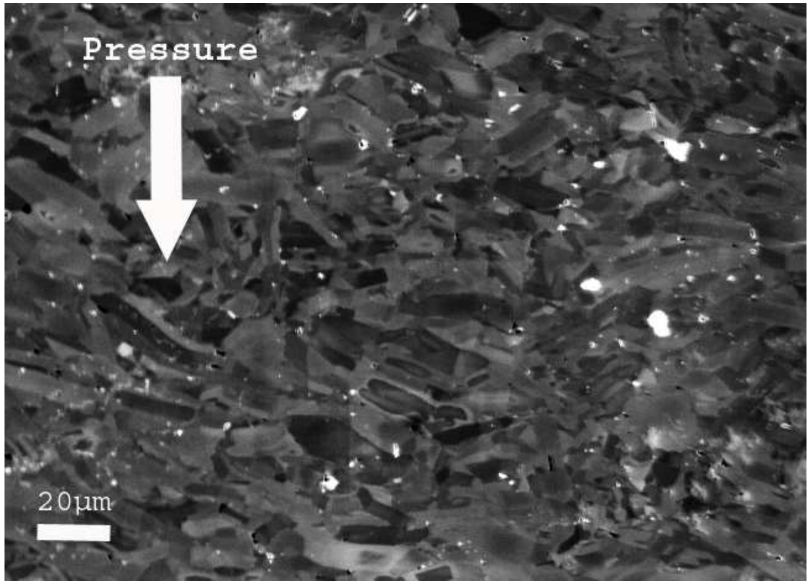

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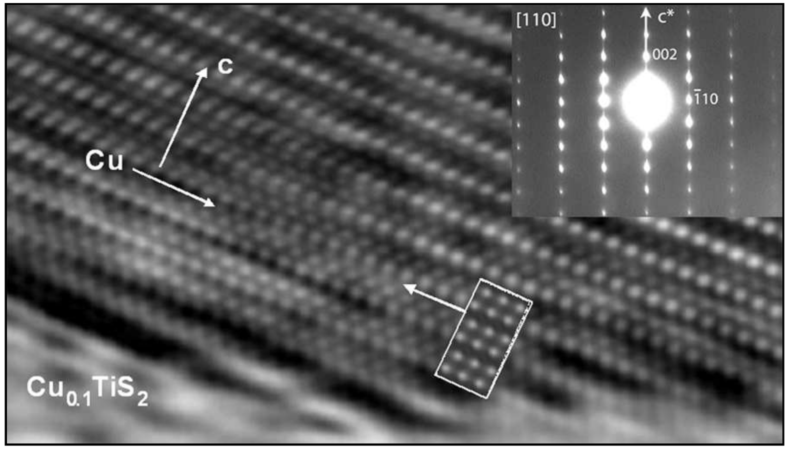
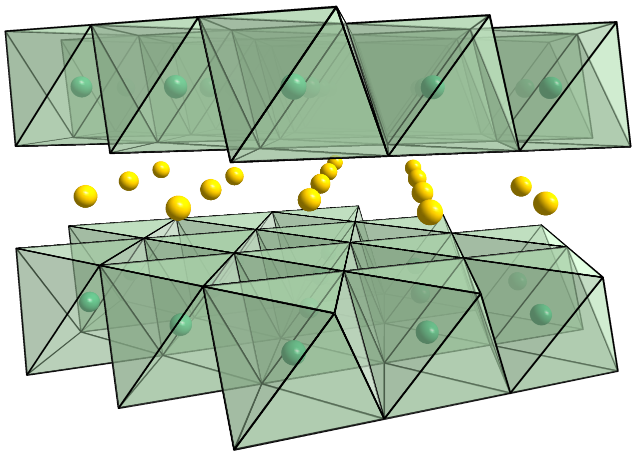
Intercalation in TiS_2

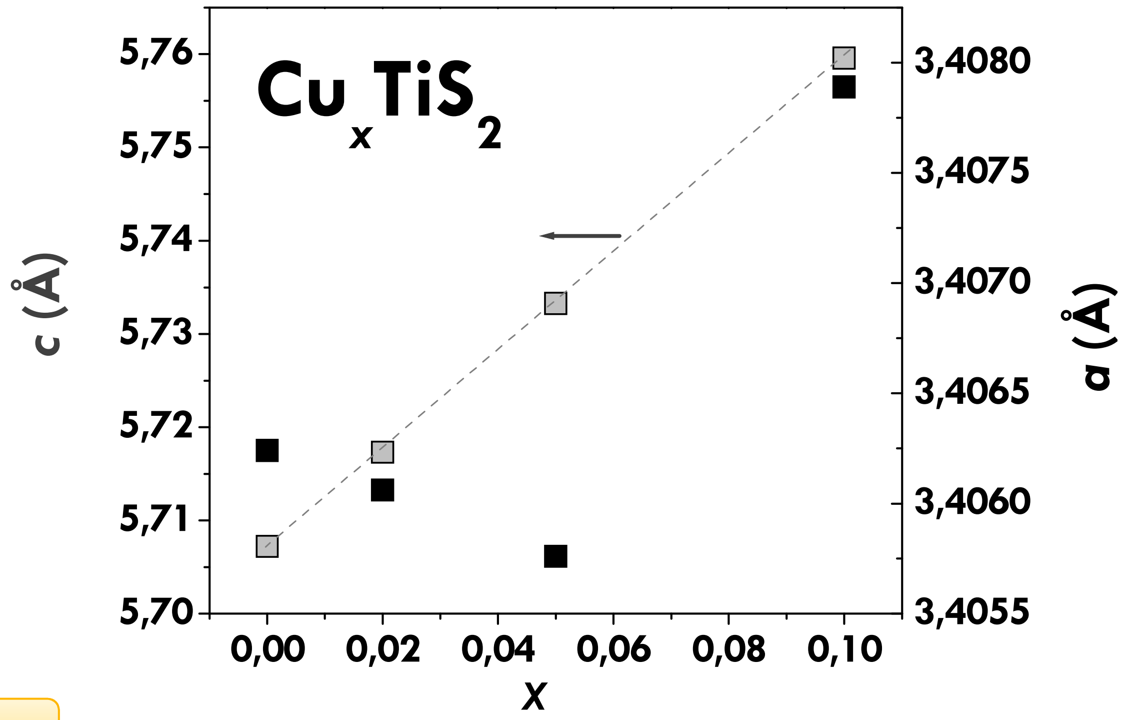
Synthesis and Structure

- ❑ Copper diffusion by In Situ SPS
- ❑ High density (>95%)
- ❑ Slight (001) texture
- ❑ *c* cell parameter increase
- ❑ TEM: Elongated dot reflexion

$\rightarrow$Disorder



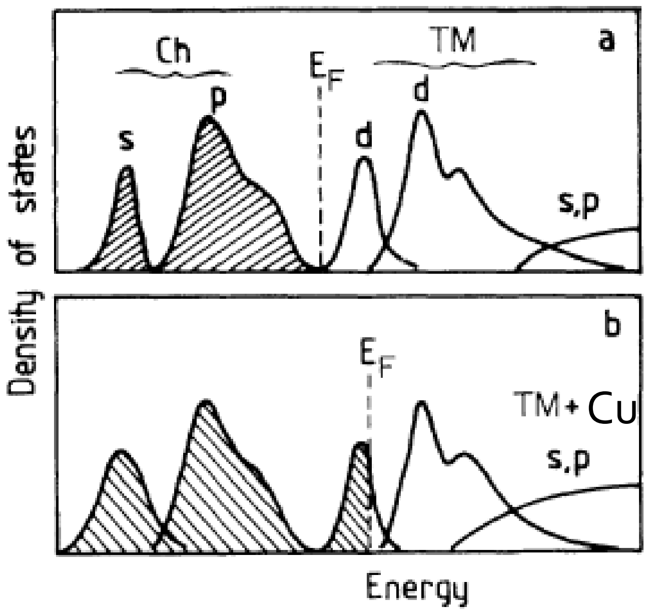




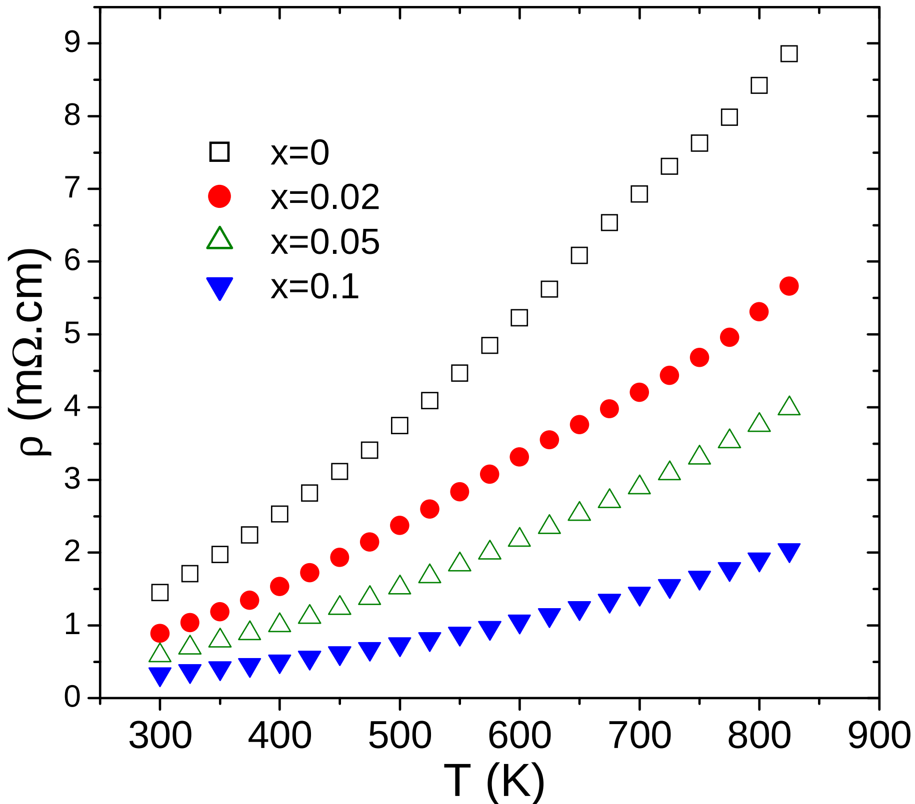
Intercalation in TiS_2

Electrical Properties

- Increase in carrier concentration
- Charge Transfer to conduction band (Ti 3d)
- Decreased electrical resistivity and Seebeck coeff.



E. Guilmeau *et al.* , APL (2011)



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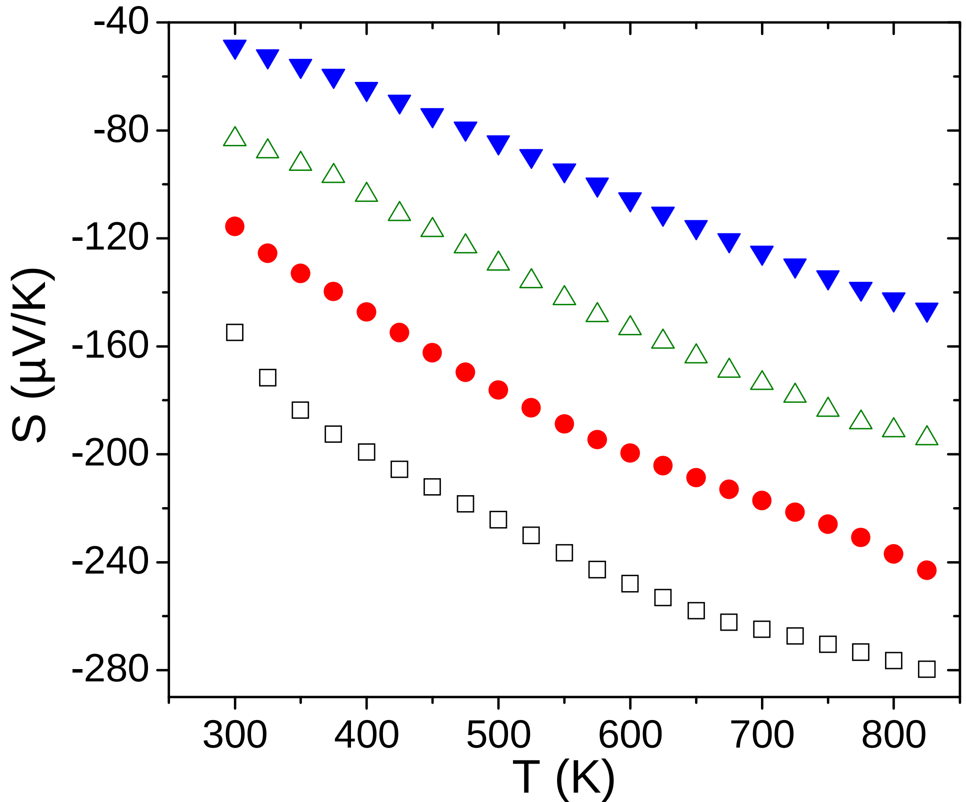
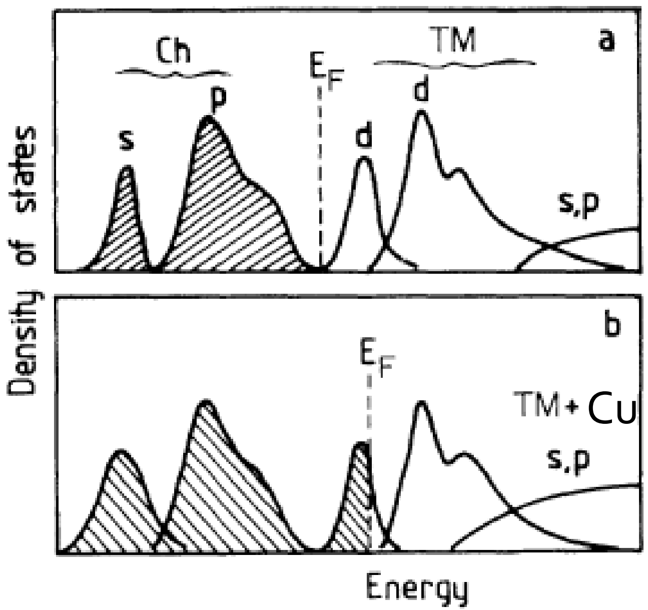


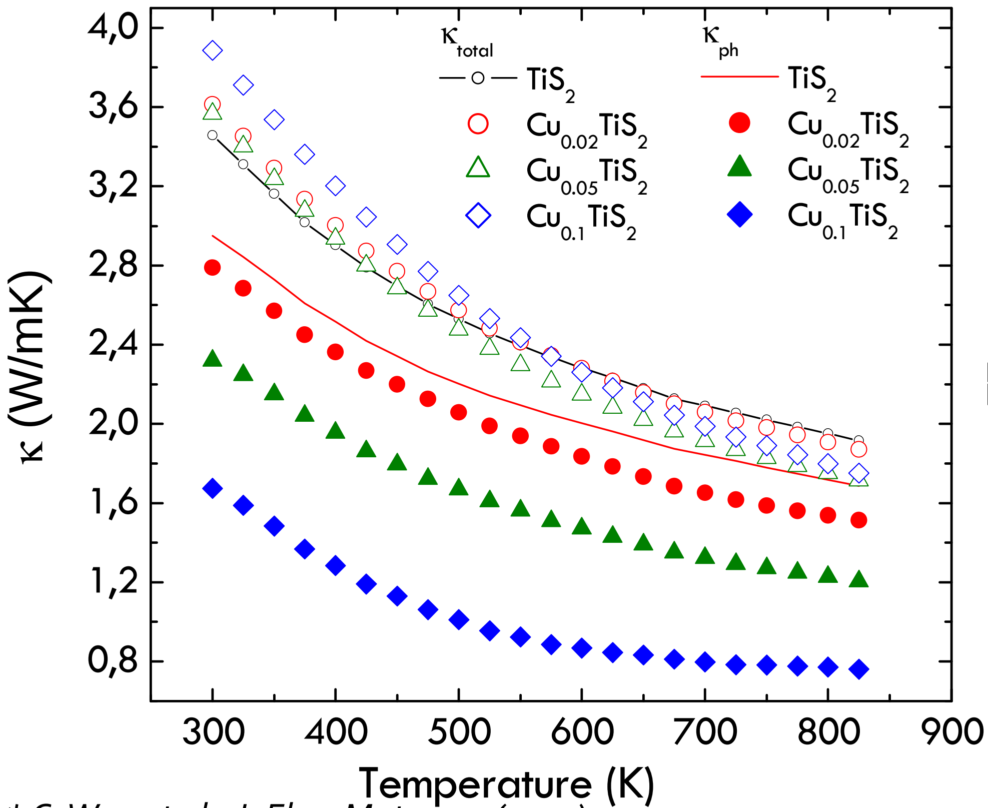


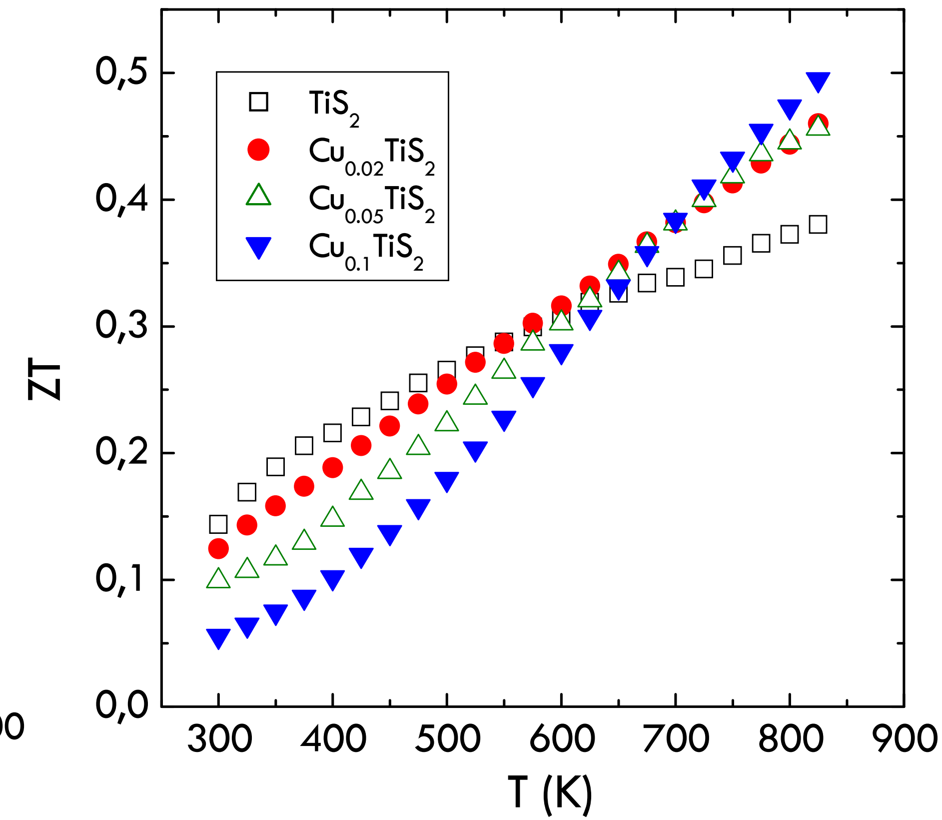
Intercalation in TiS_2

Thermal Properties

- Decrease in lattice Thermal cond.
- Phonon scaterring due to local Disorder
- Disruption of periodicity along the c axis*

- Moderate increase in ZT (0.35@ 700K)
- Rather high kappa values



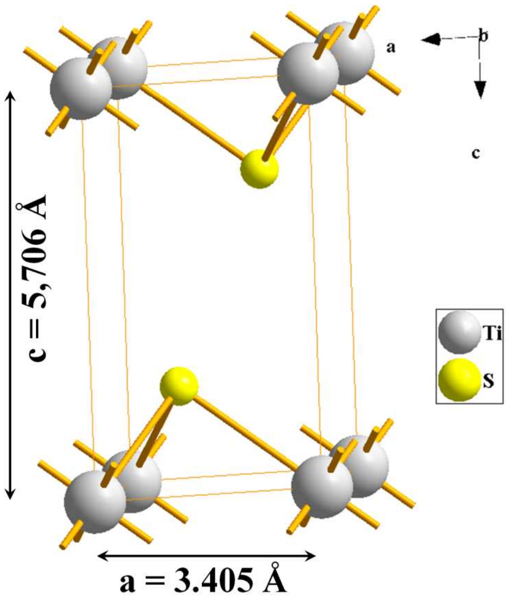


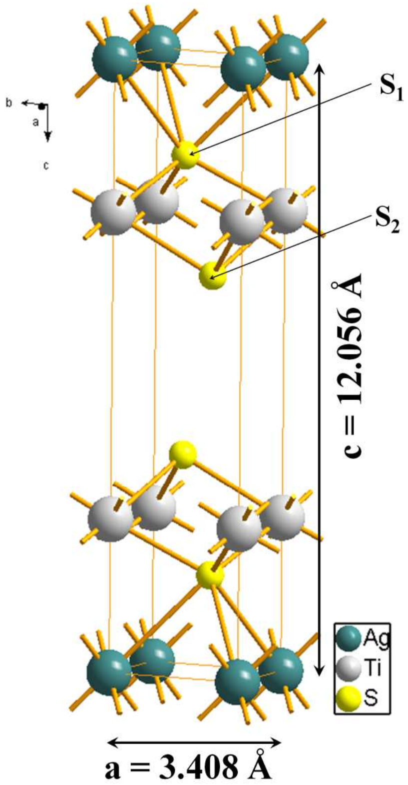
* *C. Wan et al., J. Elec. Mater. 40 (2011) 1271*

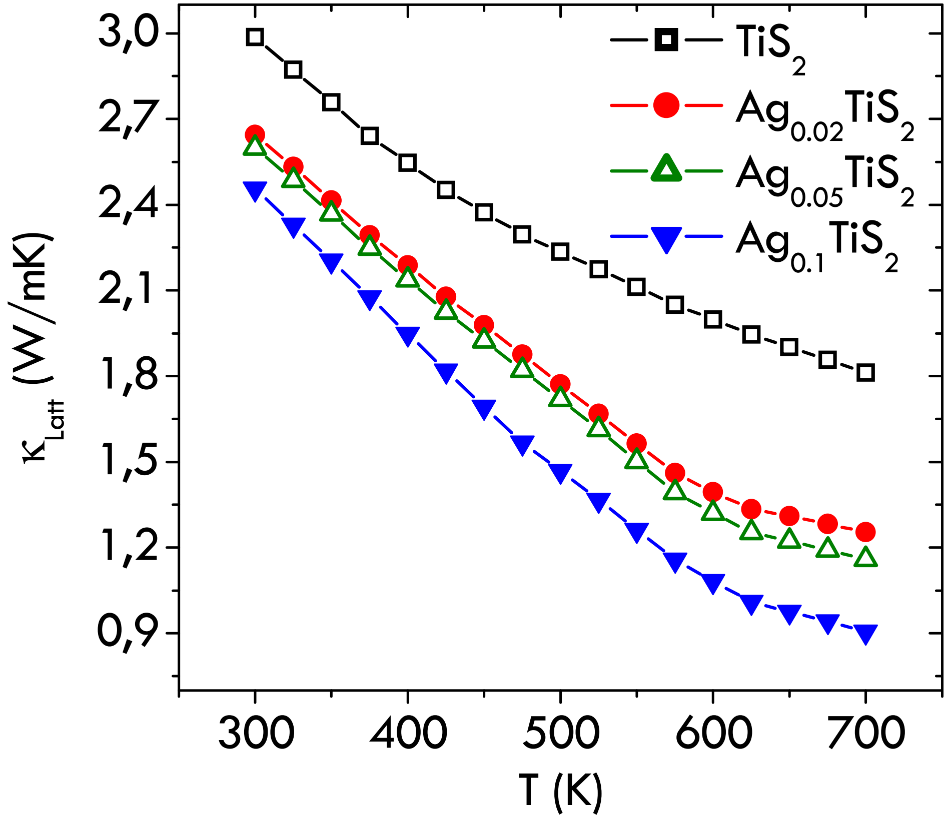
Intercalation in TiS_2

Ag_xTiS_2

- Different Intercalation mechanism
- Increase in ZT up to 0.46 @ 700K







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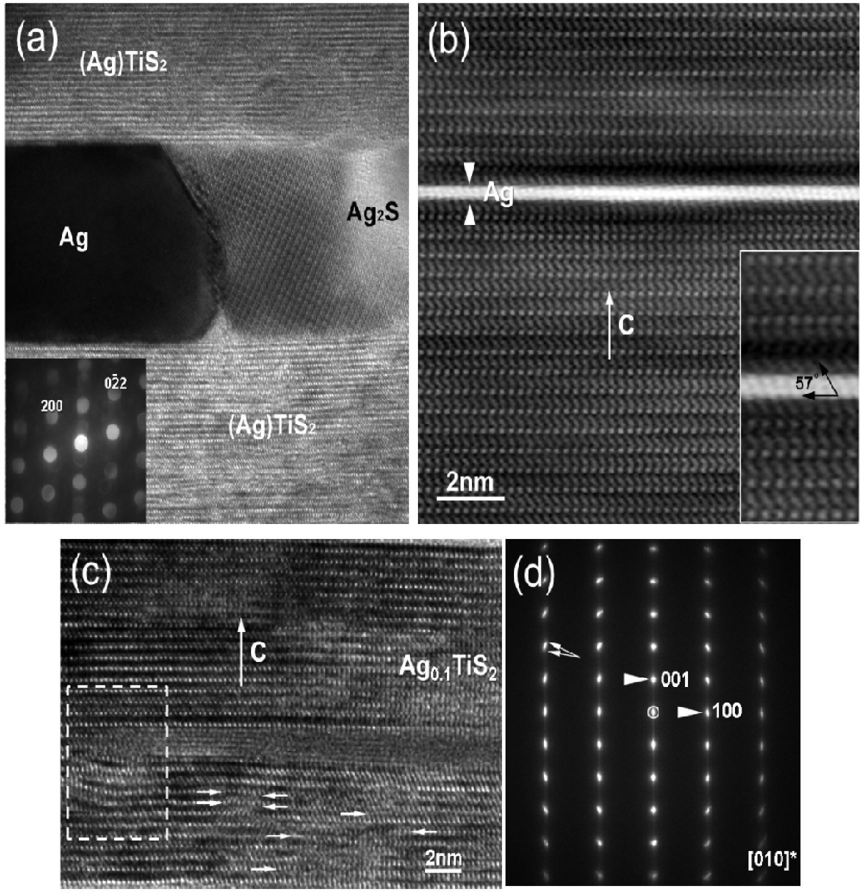

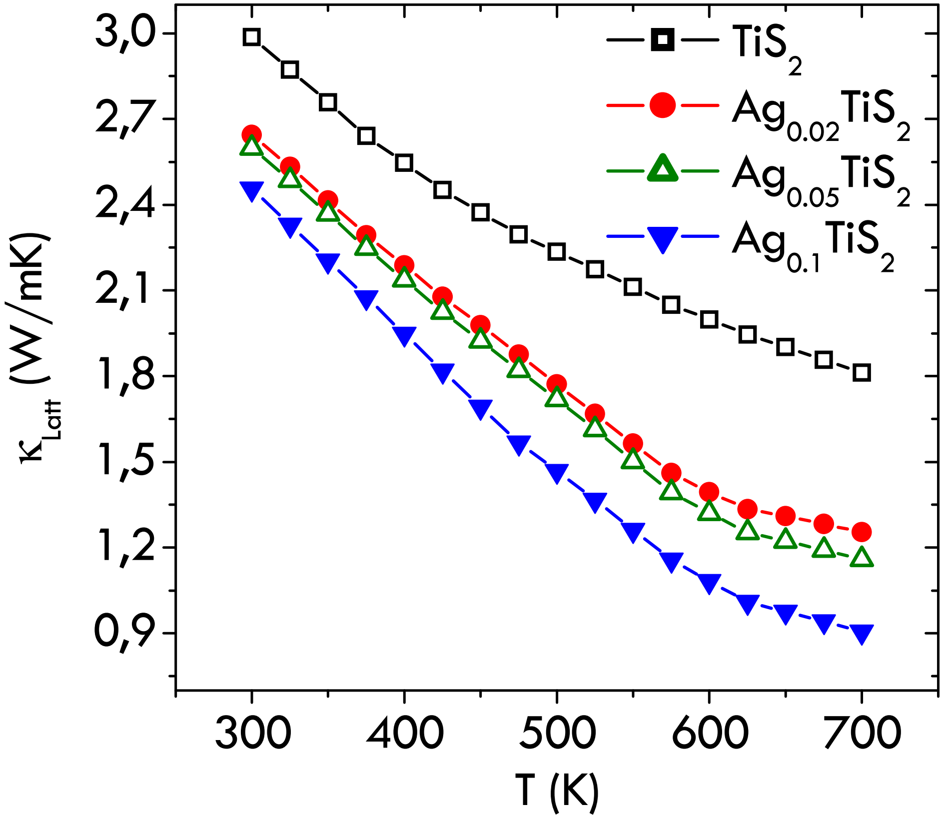

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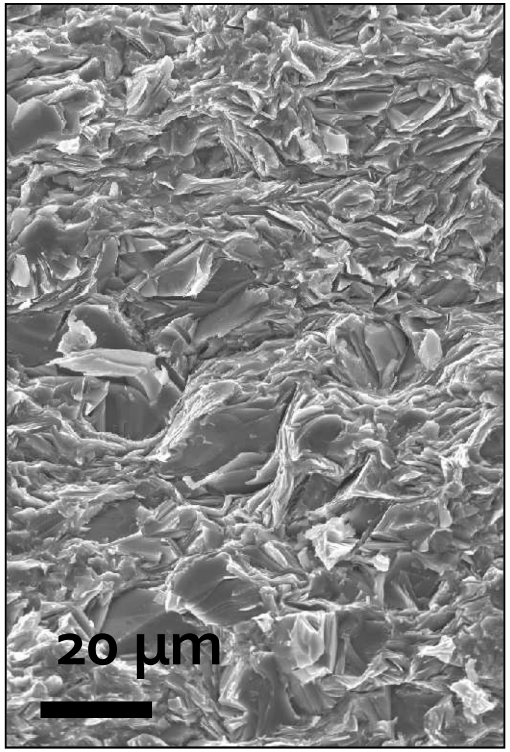

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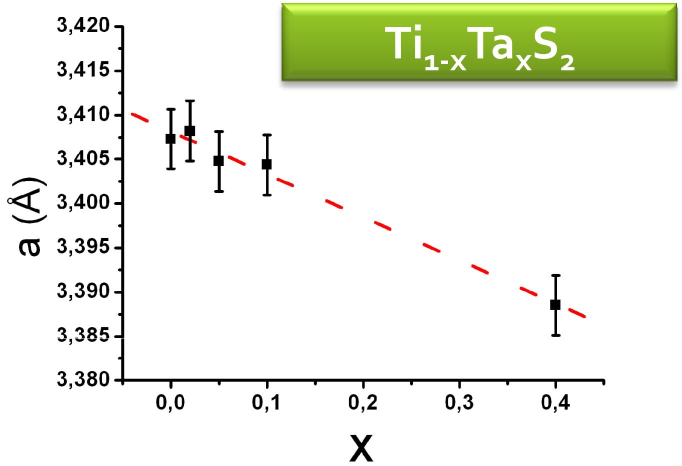
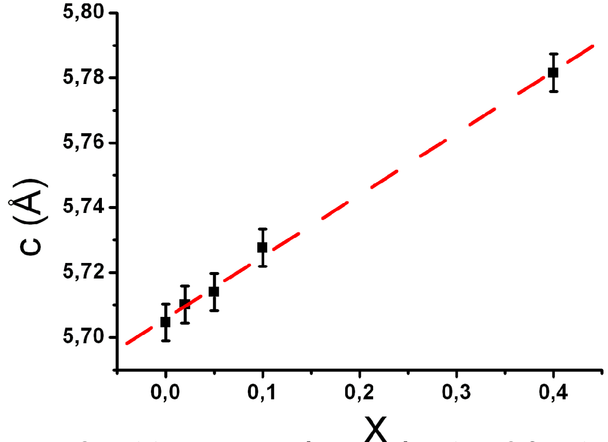
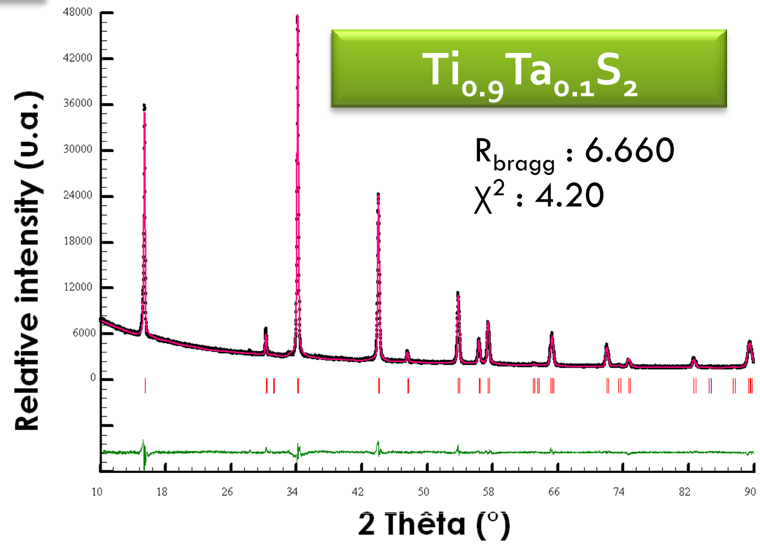
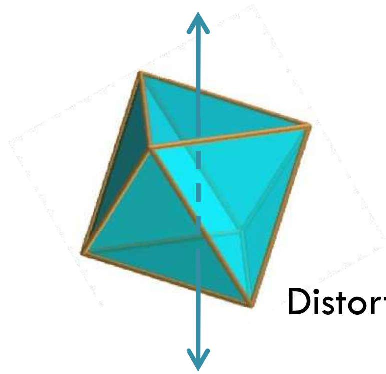
- Solid solution up to x=0.4







Trigonal distortion of octahedral coordination



Ta → r = 0.78Å
Ti → r = 0.745Å

Distortion along the 3-fold axis ***

*** *M. Shimakawa et al., MRB 32, 689 (1997)*

* *$Ti_{1-x}Ta_xS_2$, M. Beaumale et al. JAP, 2014.*

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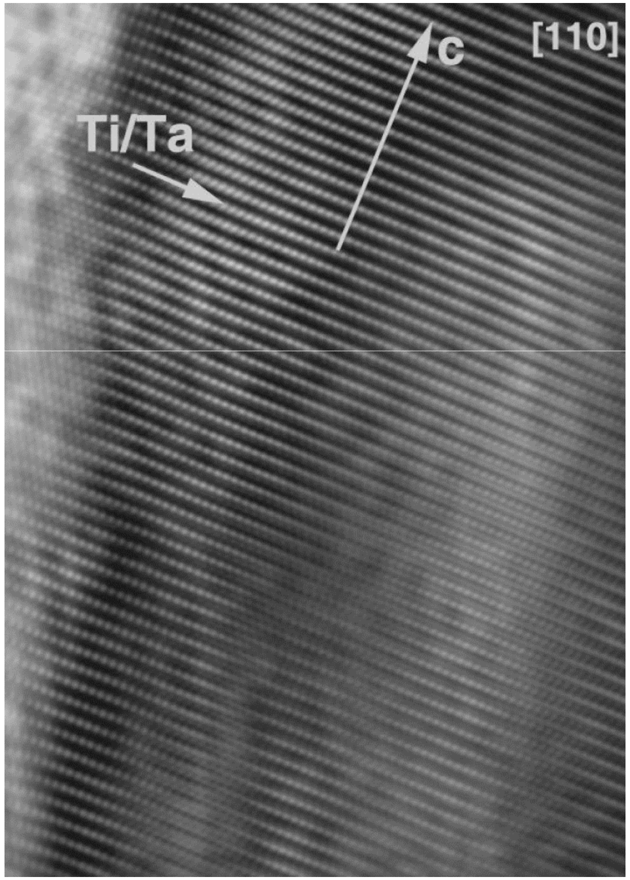

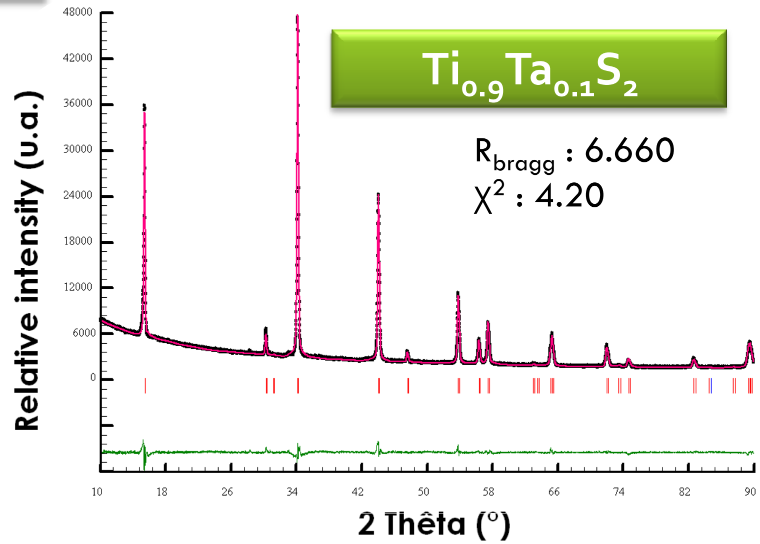

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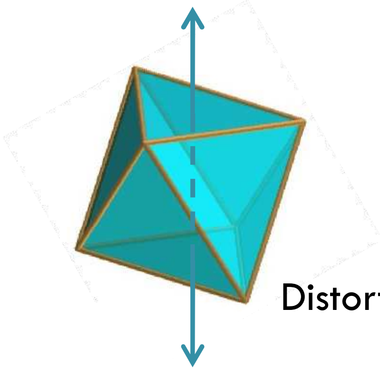

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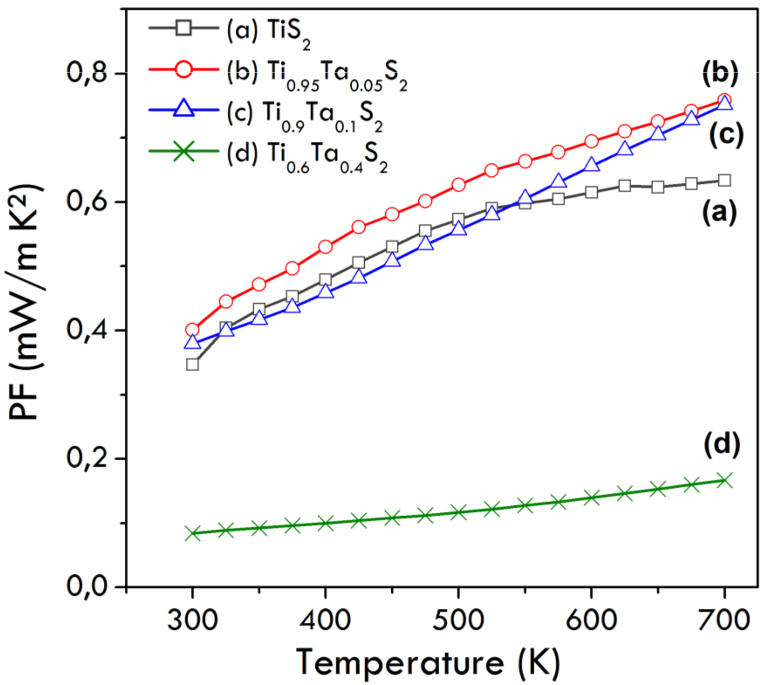
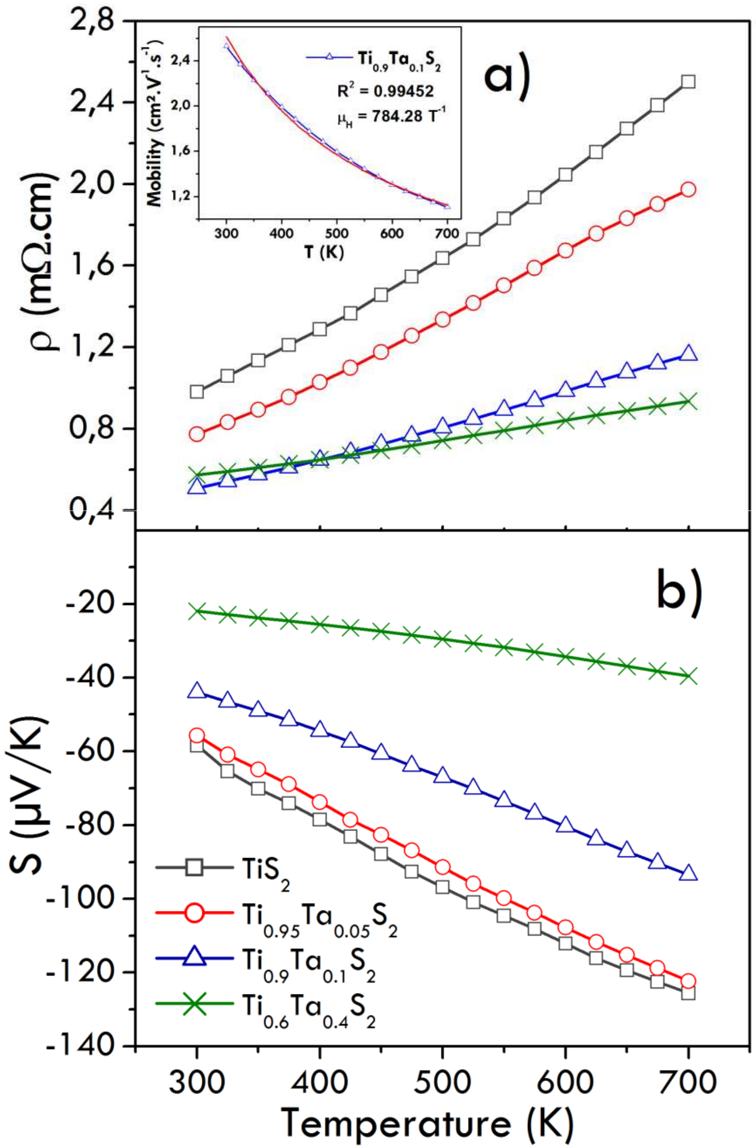
- Increase in carrier concentration
- Sulfur non stochiometry → low S





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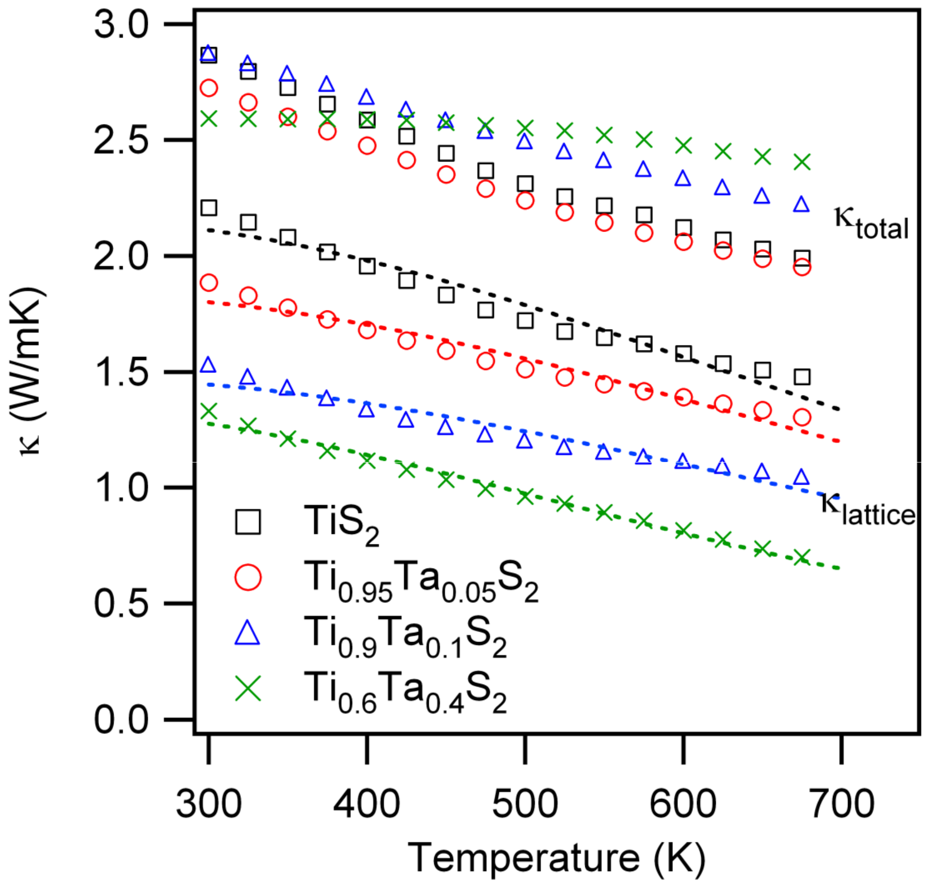
- ❑ Solid solution up to x=0.4
- ❑ Increase in carrier concentration
- ❑ Sulfur non stochiometry → low S
- ❑ Debye-Callaway → Mass fluctuation effect



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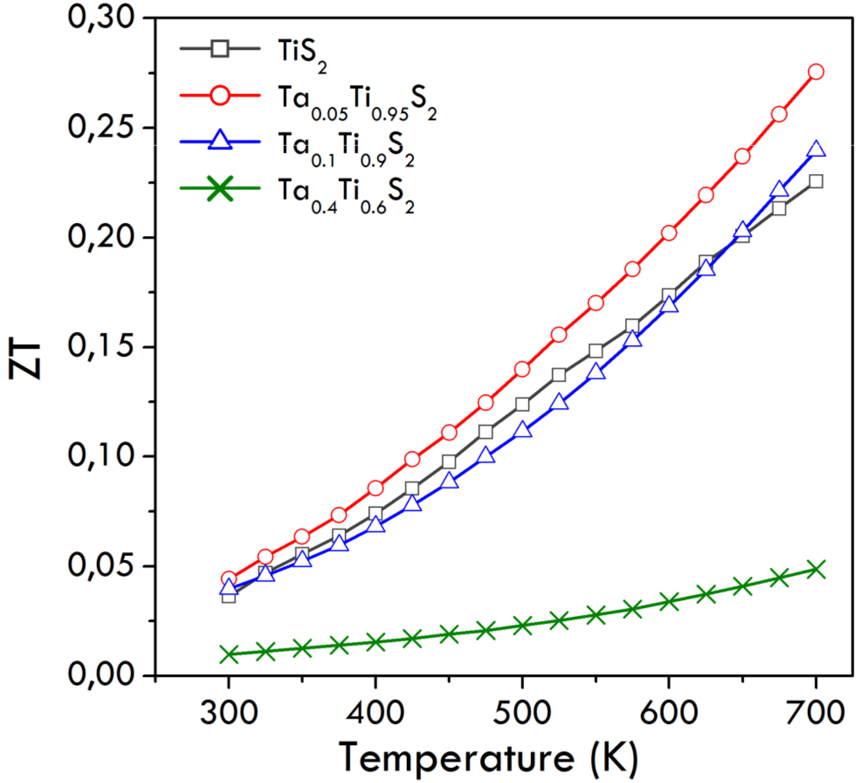
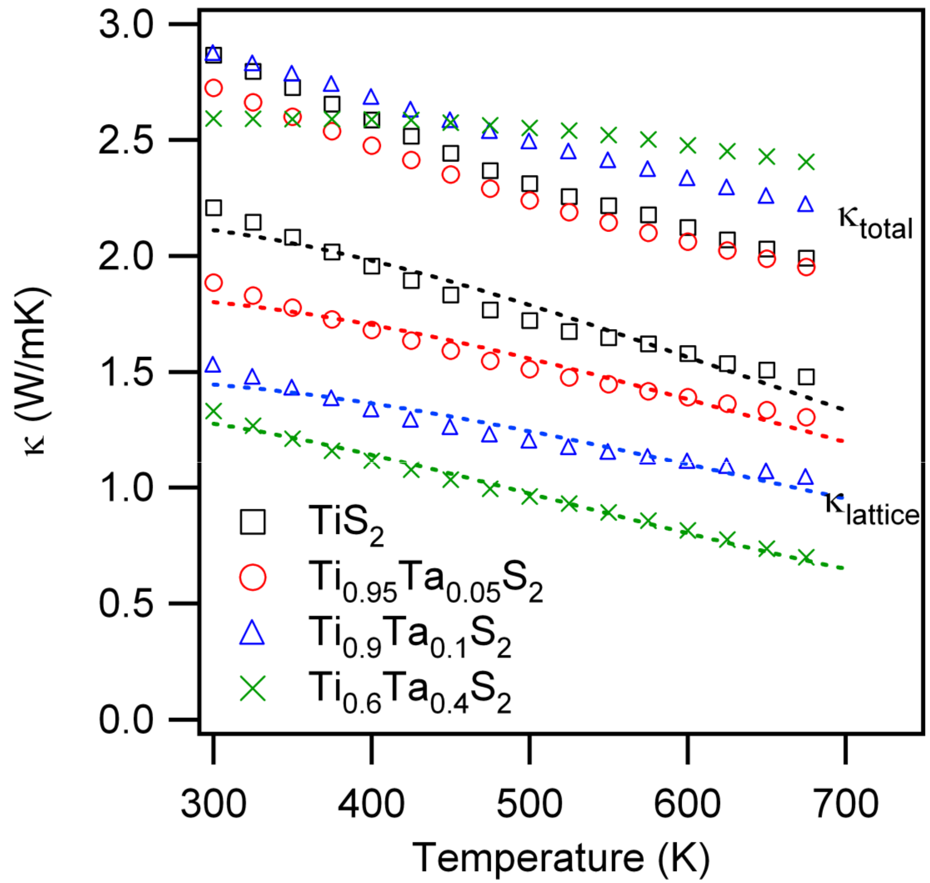
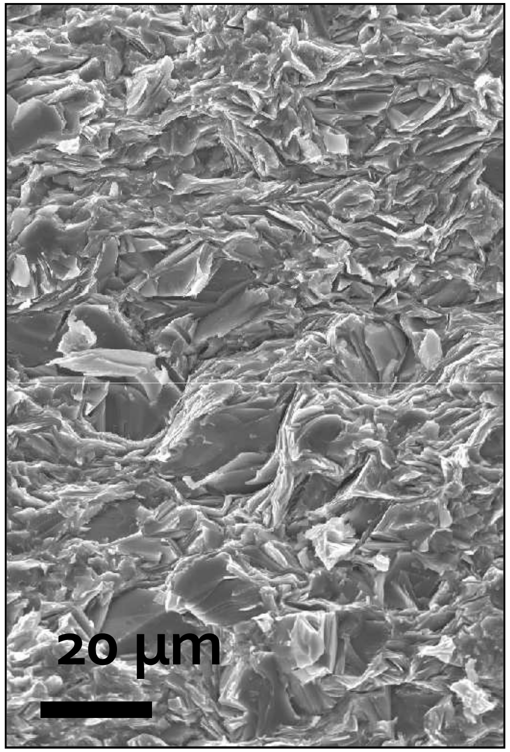




- Increase in ZT up to 0.27 @ 700K (x=0.05)
- Lower ZT due to sulfur loss (TiS_{2-x})

Summary



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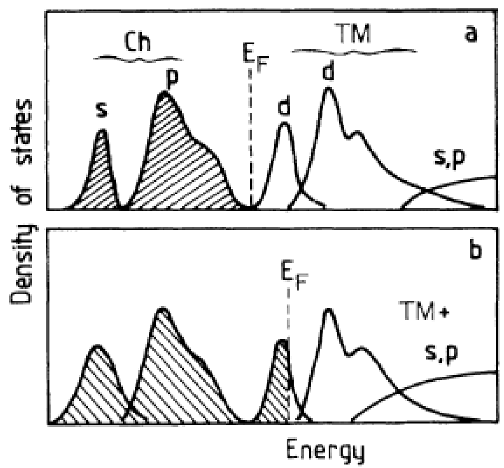
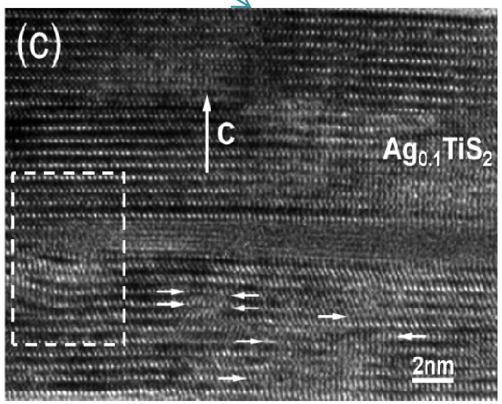
$Ti_{1+x}S_2$: Non stochiometry Approach

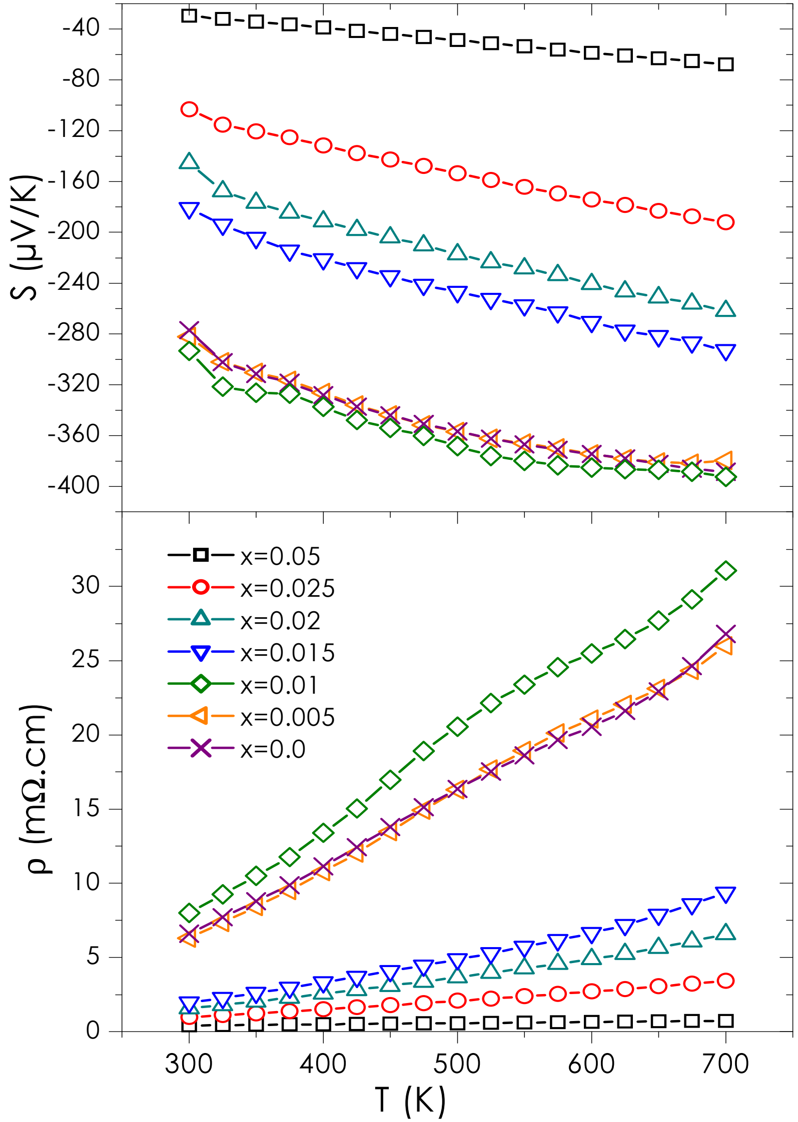
- S non Stoichio=Ti off-stoichiometry
  → intercalation

- Two effects within one chemical approach:

  - Optimization of PF (carrier conc.)
  - Structural disorder (intercalation)





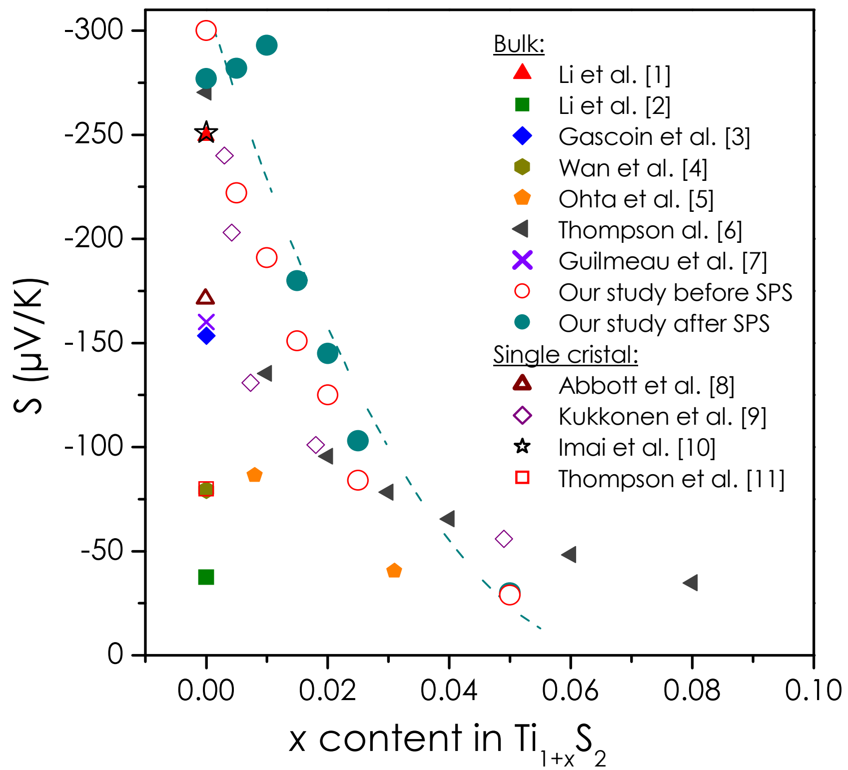


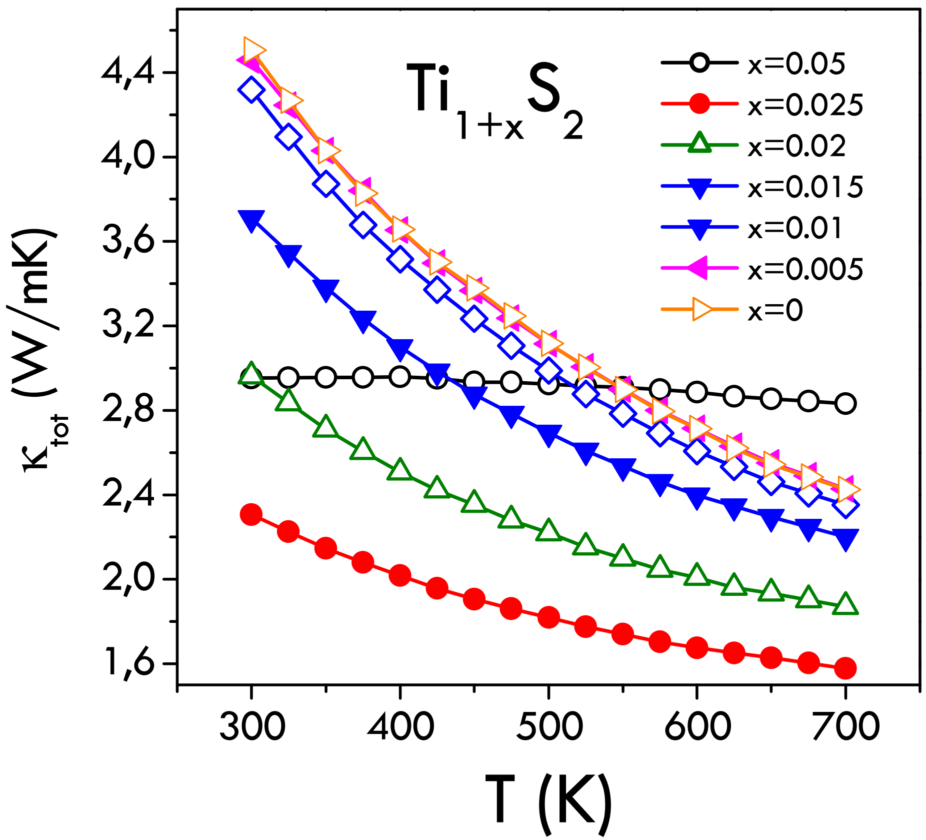
MS2 compounds | Intercalation | Substitution | **Non-stochiometry**

$Ti_{1+x}S_2$: Non stochiometry Approach

- ❑ Tuned carrier concentration
- ❑ Wide range of Seebeck coeff.

- ❑ Drastic decrease in κ_{tot}
- ❑ Ti intercalation → disorder
- ❑ ZT improved up to 0.45 @ 700K





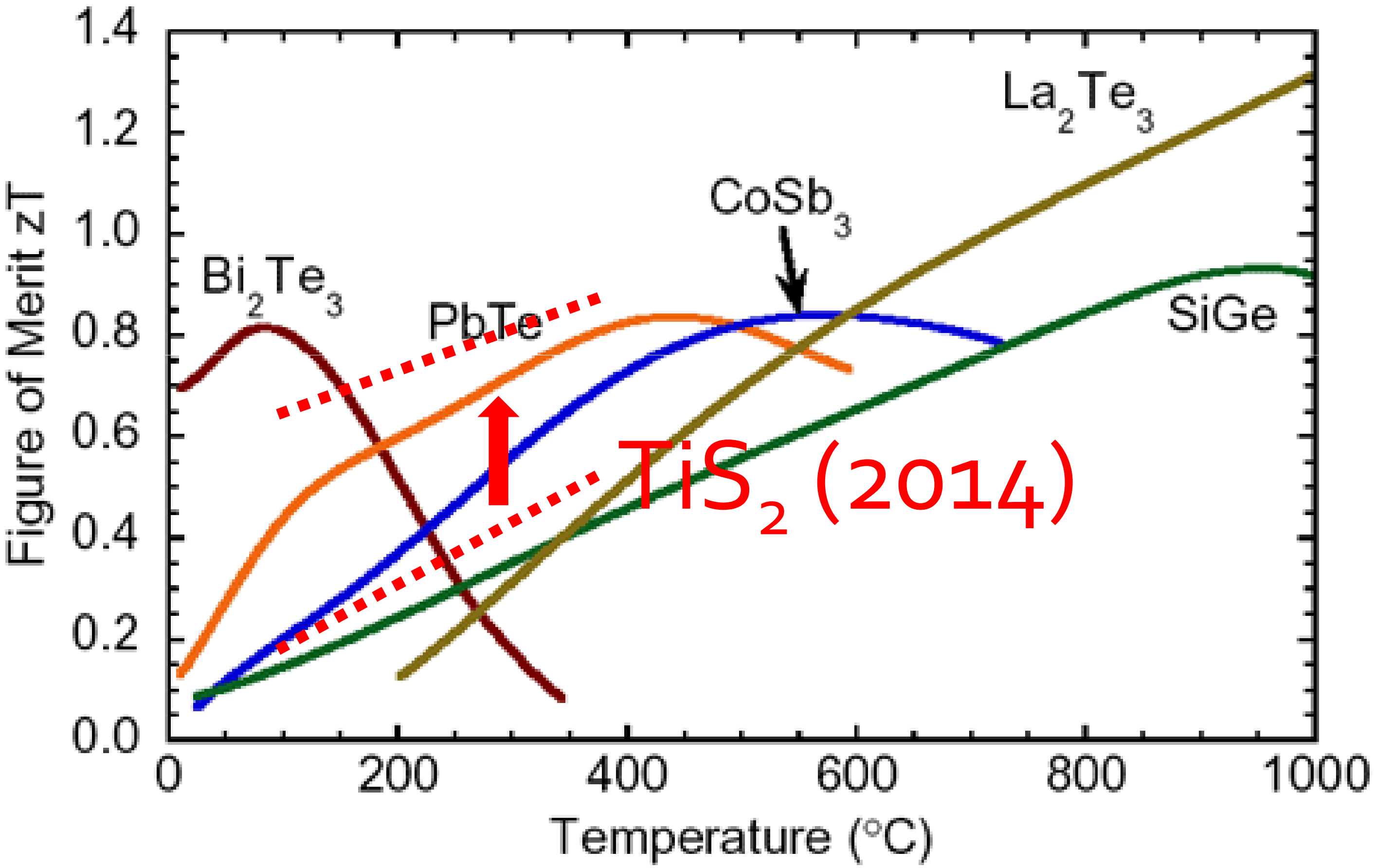
Conclusion

1. Intercalation, Substitution, Non Stochiometry
   Three potential approaches to decrease kappa.

2. Progress achieved with ZT>0.5 @ 700K

3. More efforts required to double ZT in the temperature range RT-700K

Conclusion



1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Figure of Merit zT
0
200
400
600
800
1000
Temperature (°C)
Bi2Te3
PbTe
CoSb3
La2Te3
SiGe
TiS2 (2014)

Acknowledgements

Marine Beaumale
Tristan Barbier
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Antoine Maignan

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Thank you
for your attention!!!!