Thermoelectric properties of oxysulfide $Bi_{1-x}Pb_xCuOS$ compounds

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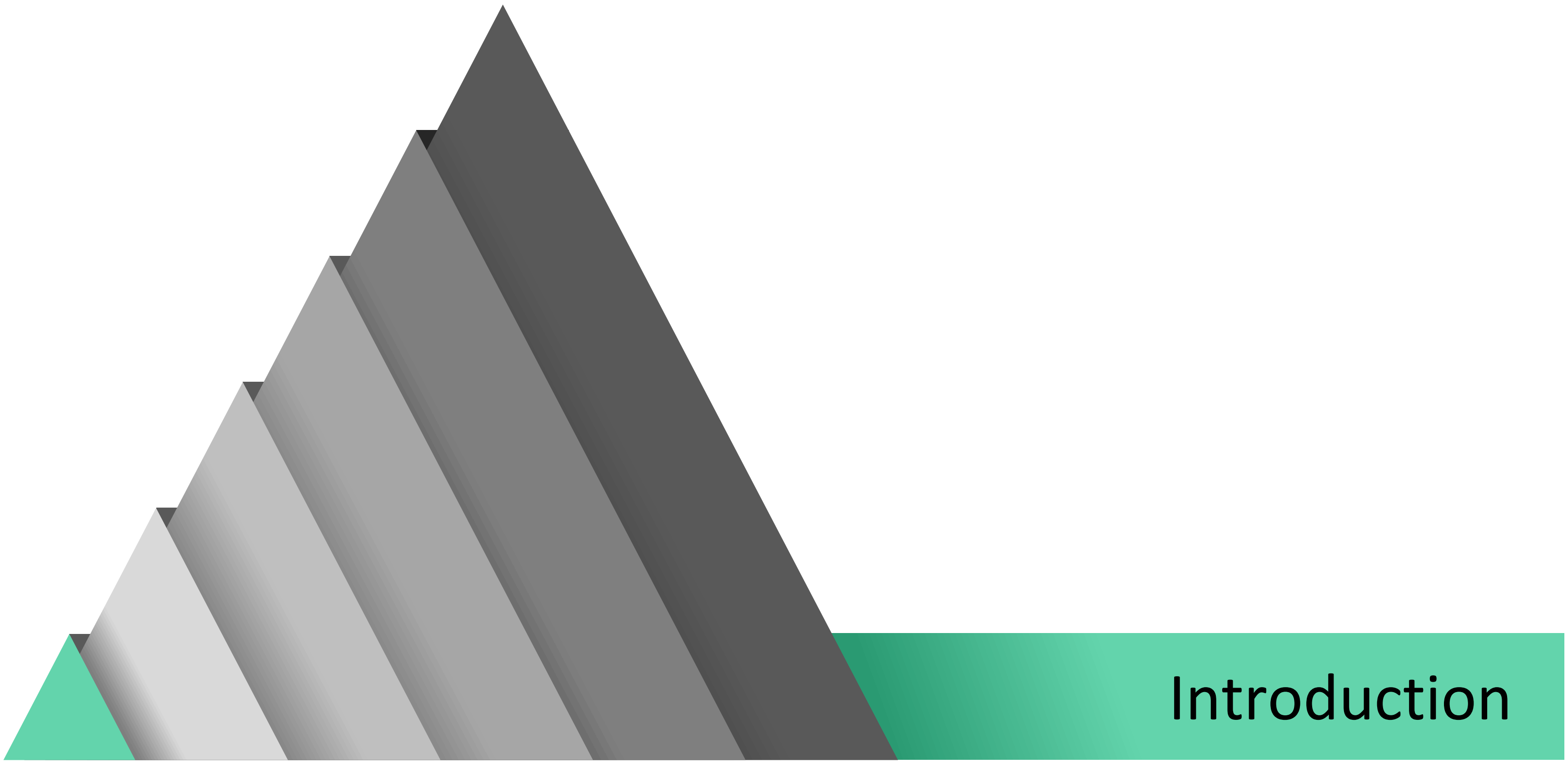
Plan



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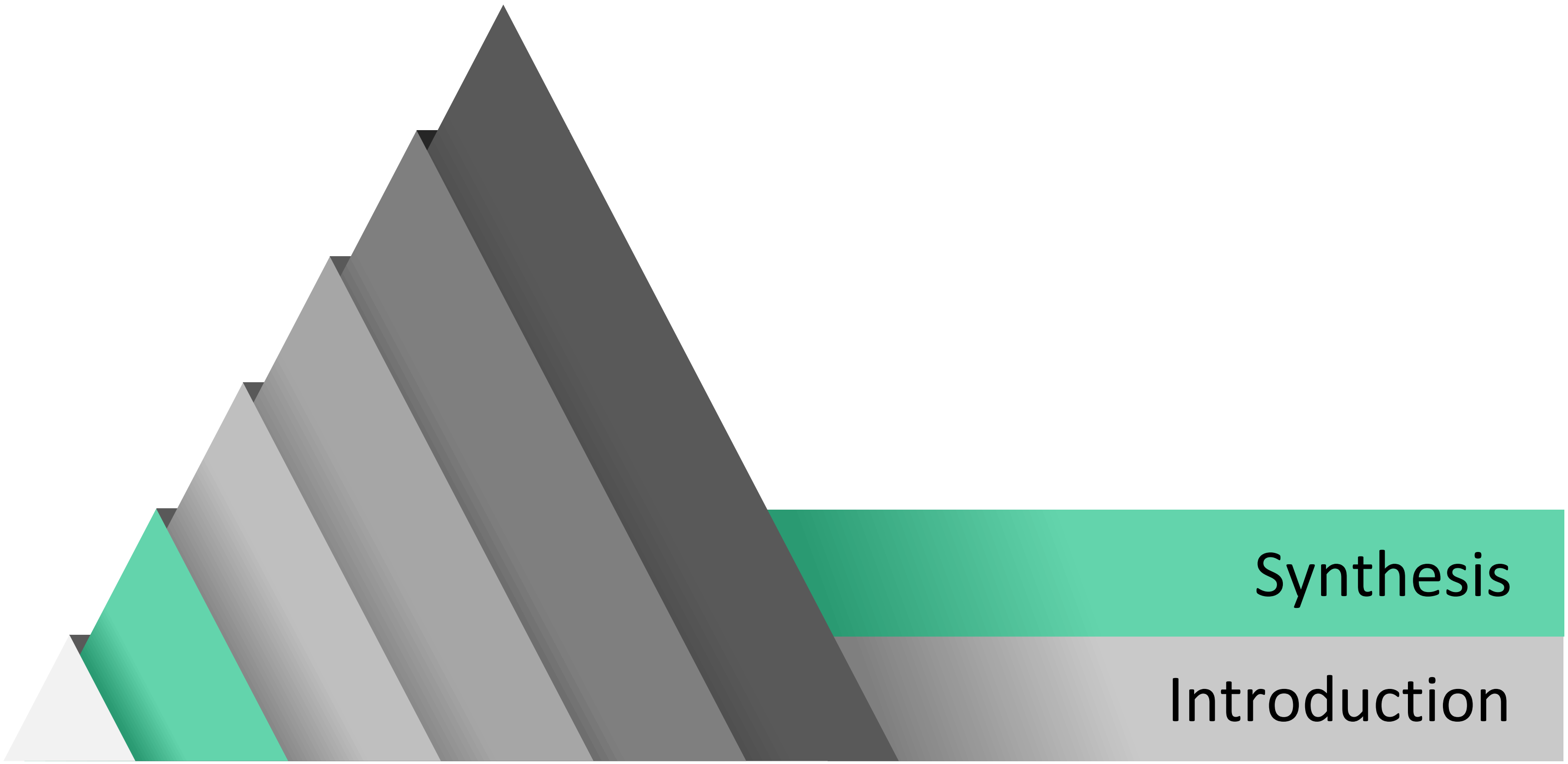

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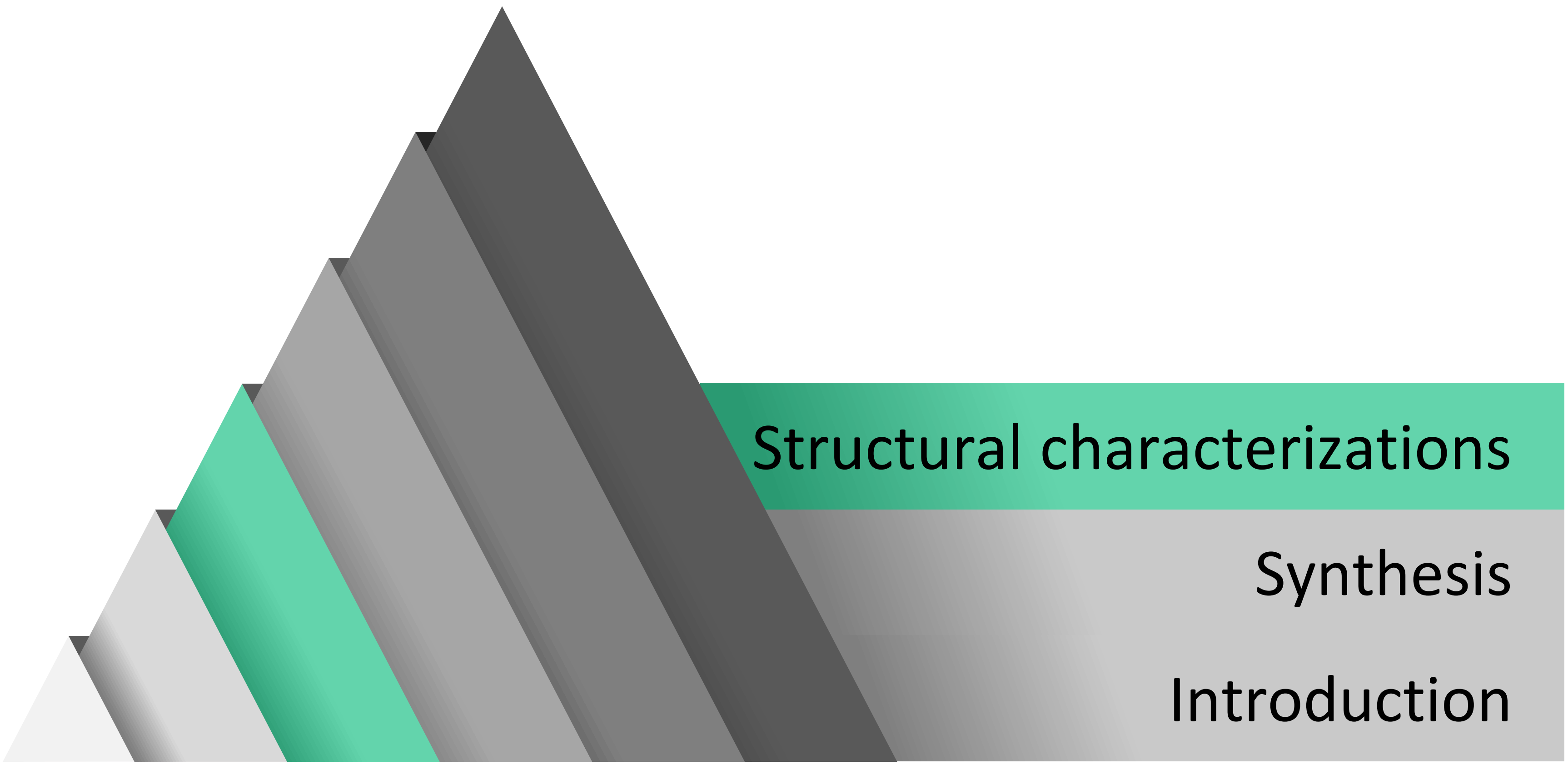

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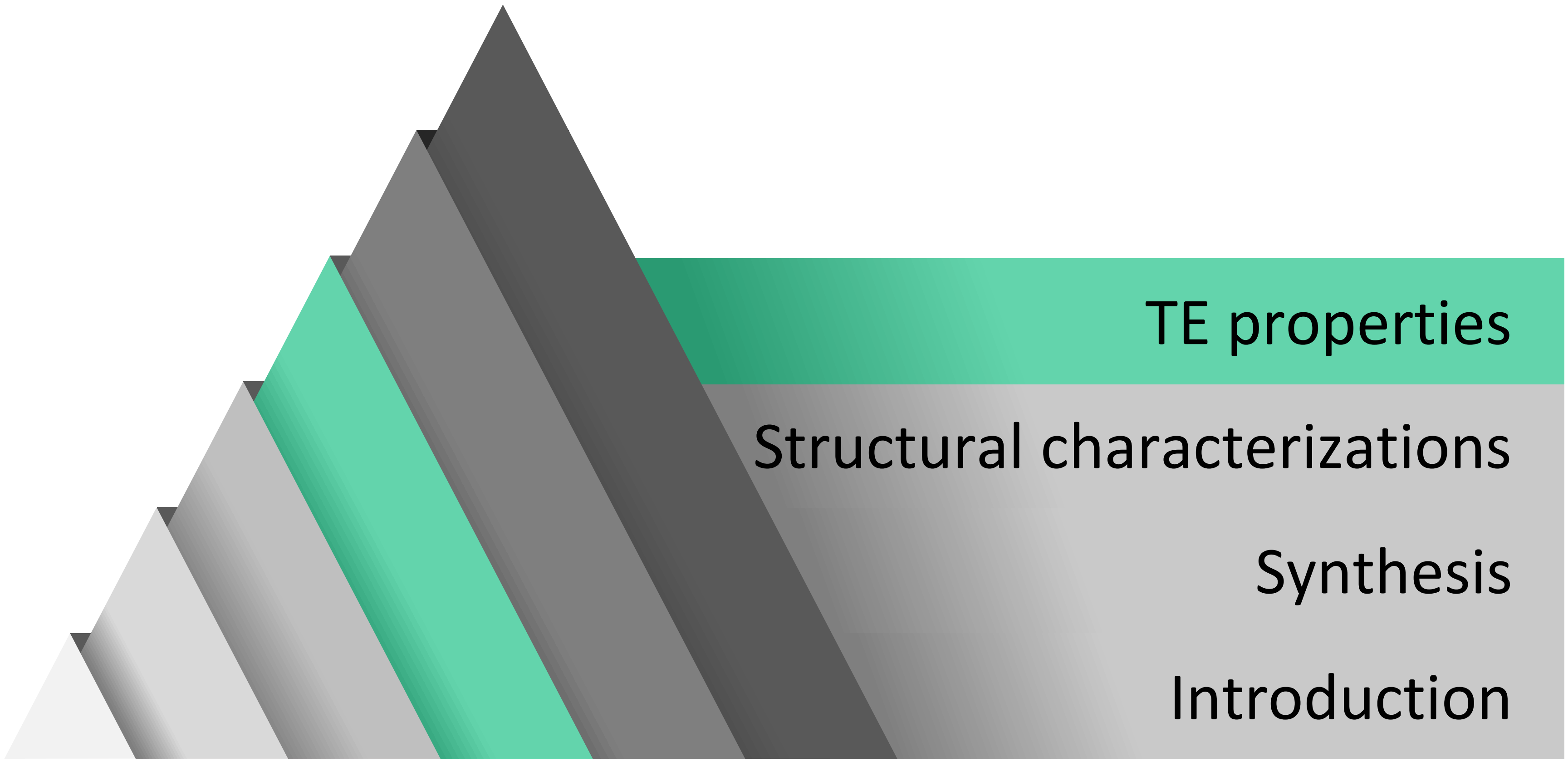
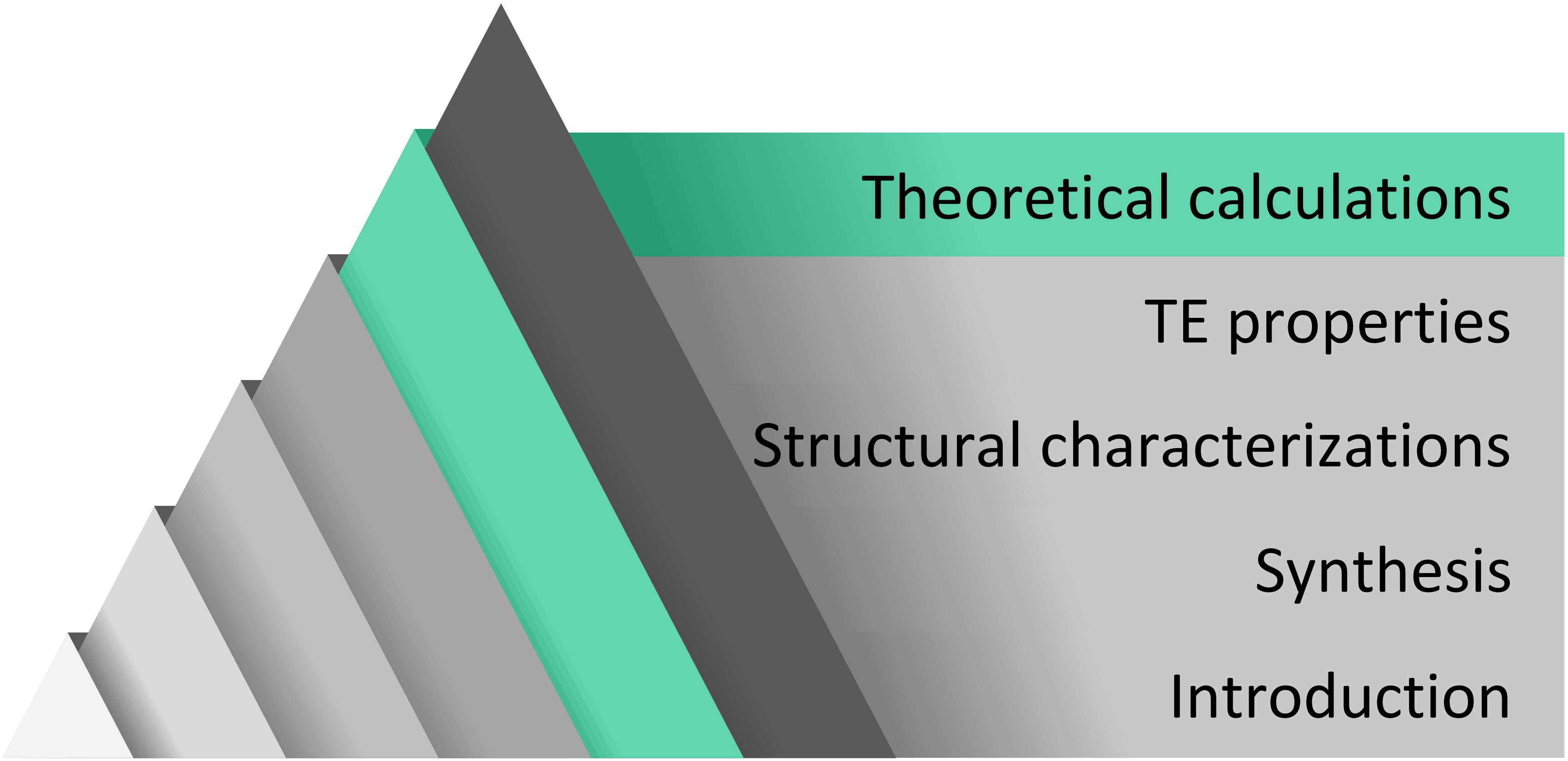

TE properties
Structural characterizations
Synthesis
Introduction

Plan


Theoretical calculations
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Conclusions

Theoretical calculations

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Introduction

1998	2010	2017
discovery of BiCuOCh (Ch = S, Se)[1]	1st TE study of BiCuOSe[2]	> 60 papers relative to BiCuOSe

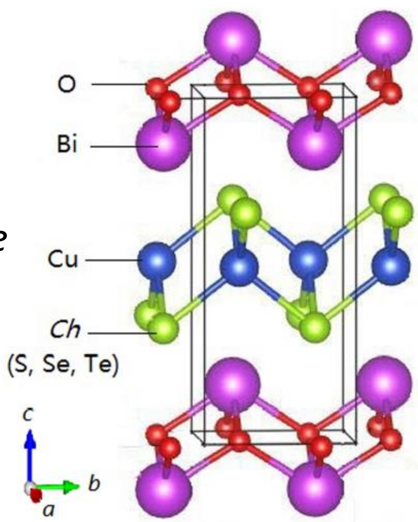
→ ZT_{max} = 1.4 @ 923 K

(3)

fluorite-like
$(Bi_2O_2)^{2+}$

anti-fluorite-like
$(Cu_2Ch_2)^{2-}$

fluorite-like
$(Bi_2O_2)^{2}$



Structure:

tetragonal, ZrSiCuAs type (*P4/nmm*)

- 2 layers alternately stacked along *c*
- covalent bonding inside the layers (4)
- ionic bonding between the blocks

→ anisotropy of electrical and thermal properties

→ low thermal conductivity

(1) Kusainova, A. M. *et al. J. Solid State Chem.* **1994**, *112*, 189–191.
(2) Zhao, L. D. *et al. Appl. Phys. Lett.* **2010**, *97*, 092118.
(3) Liu, G. *et al. J. Appl. Phys.* **2016**, *119*, 185109.
(4) Shein, I. R. *et al. Solid State Commun.* **2010**, *150* (13-14), 640–643.

Introduction

BiCuOCh (Ch = S, Se, Te) ➔ copper vacancies ➔ p-type [1]

[3,4]

	BiCuOSe	BiCuOS
gap (eV)	0.8	1.1
ρ_{RT} (mΩ cm)	~ 200	~ 8 x 10^5
κ_{RT} (W m^{-1} K^{-1})	1.05	1.1
ZT_{max} (673 K)	**0.31**	**0.07**

TE properties of BiCuOSe:

- stable in medium temperature range
- numerous successful substitutions : Ba^{2+}, Sr^{2+}, Mg^{2+}, Ca^{2+}, Pb^{2+}…
- when substituted and textured : ZT_{max} = 1.4 @ 923 K [2]

➔ Lack of studies on BiCuOS due to high resistivity

(1) Ueda, K. *et al. Thin Solid Films* **2002**, 411, 115–118.
(2) Sui, J. *et al. Energy Environ. Sci.* **2013**, 6, 2916–2920.
(3) Bérardan, D. *et al. Materials.* **2015**, 8, 1043–1058.
(4) Zhu, H. *et al. J. Eur. Ceram. Soc.* **2017**, 37, 1541–1546.

Synthesis

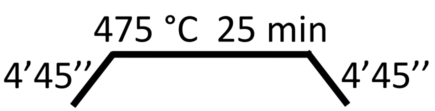
Bi_2O_3, Bi, Cu, S, (PbO)

Mechanosynthesis

- **synthesized in 3 h** vs sealed tubes (> 10 h) or hydrothermal synthesis (> 55 h) [1,2]
- scalable for mass production

Spark Plasma Sintering

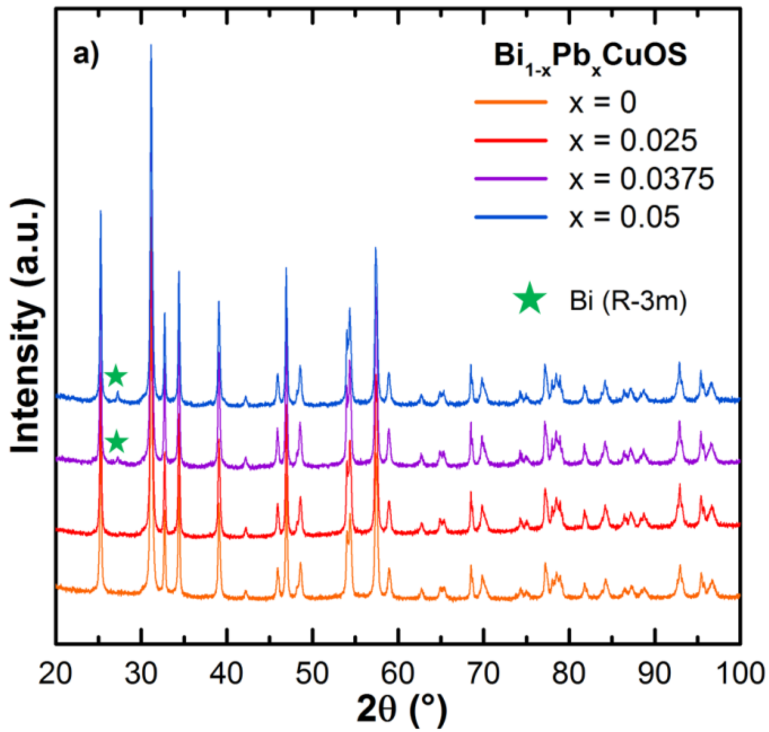
- short process duration, high density



pressure : 64 MPa

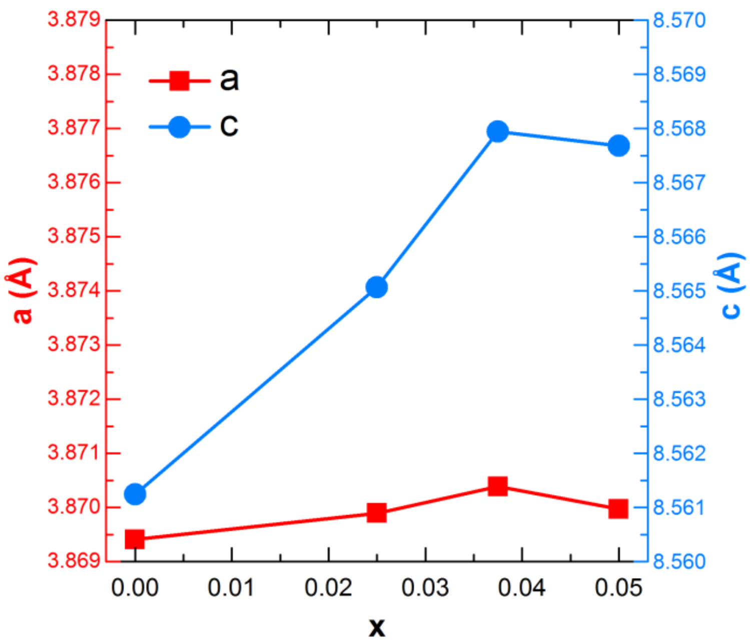
(1) Hiramatsu, H. *et al. Chem. Mater.* **2008**, 20, 326–334.
(2) Sheets, W. C. *et al. Inorg. Chem.* **2007**, *46* (25), 10741–10748.

Structural characterizations of $Bi_{1-x}Pb_xCuOS$ ($0 \leq x \leq 0.05$)



powder XRD after sintering :

- $x \leq 0.025$: single phase
- $x \geq 0.0375$: presence of ~ 1 % Bi metal



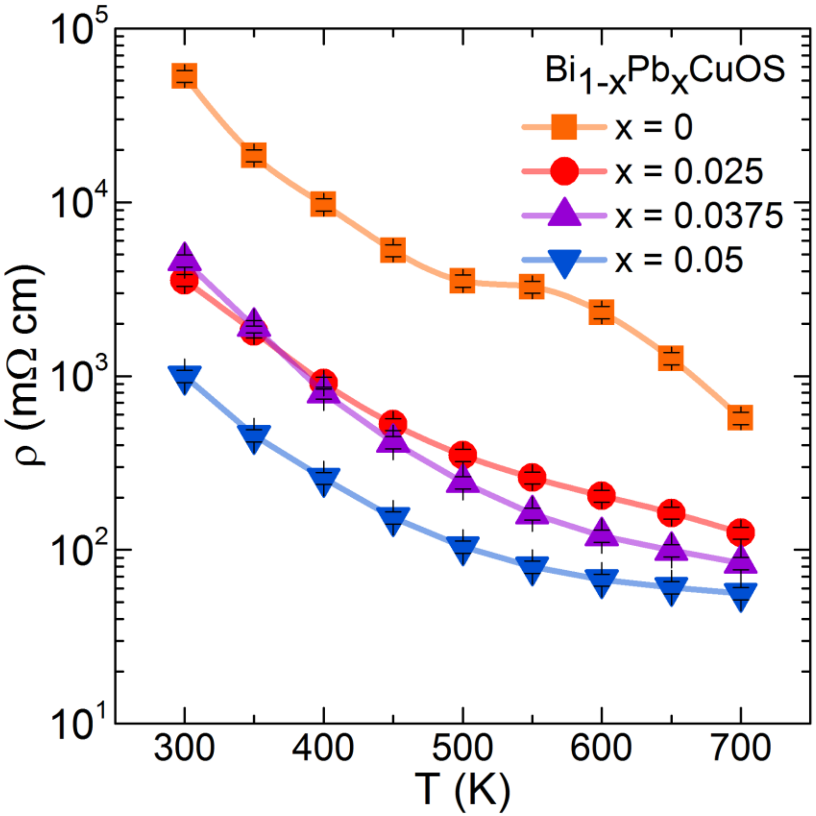
cell parameters (from Rietveld refinements) :

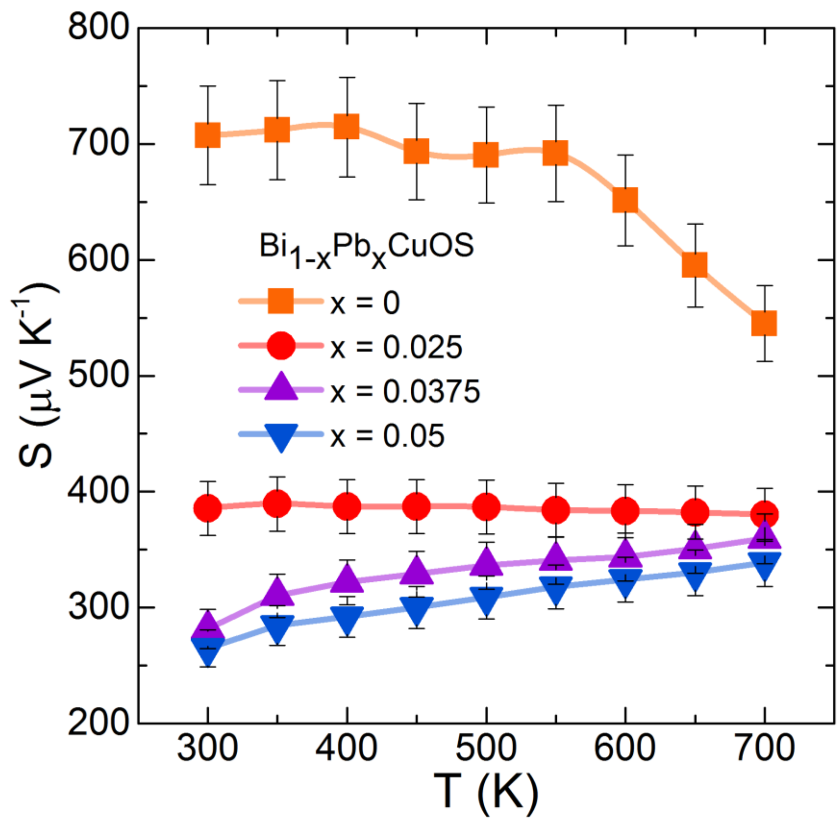
when x ↗:

- *a* and *c* ↗ ➔ substitution of Pb^{2+} (129 pm) on Bi^{3+} (117 pm) site
- *c* increases more than *a* ➔ weakening of Coulombic attraction between the layers $[(Bi_{1-x}Pb_x)_2O_2]^{(2-2x)+}$ and $[Cu_2S_2]^{(2-2x)-}$ (1)

(1) Barreteau, C. *et al.* Chem. Mater. 2012, 24, 3168–3178.

TE properties of $Bi_{1-x}Pb_xCuOS$ ($0 \le x \le 0.05$)



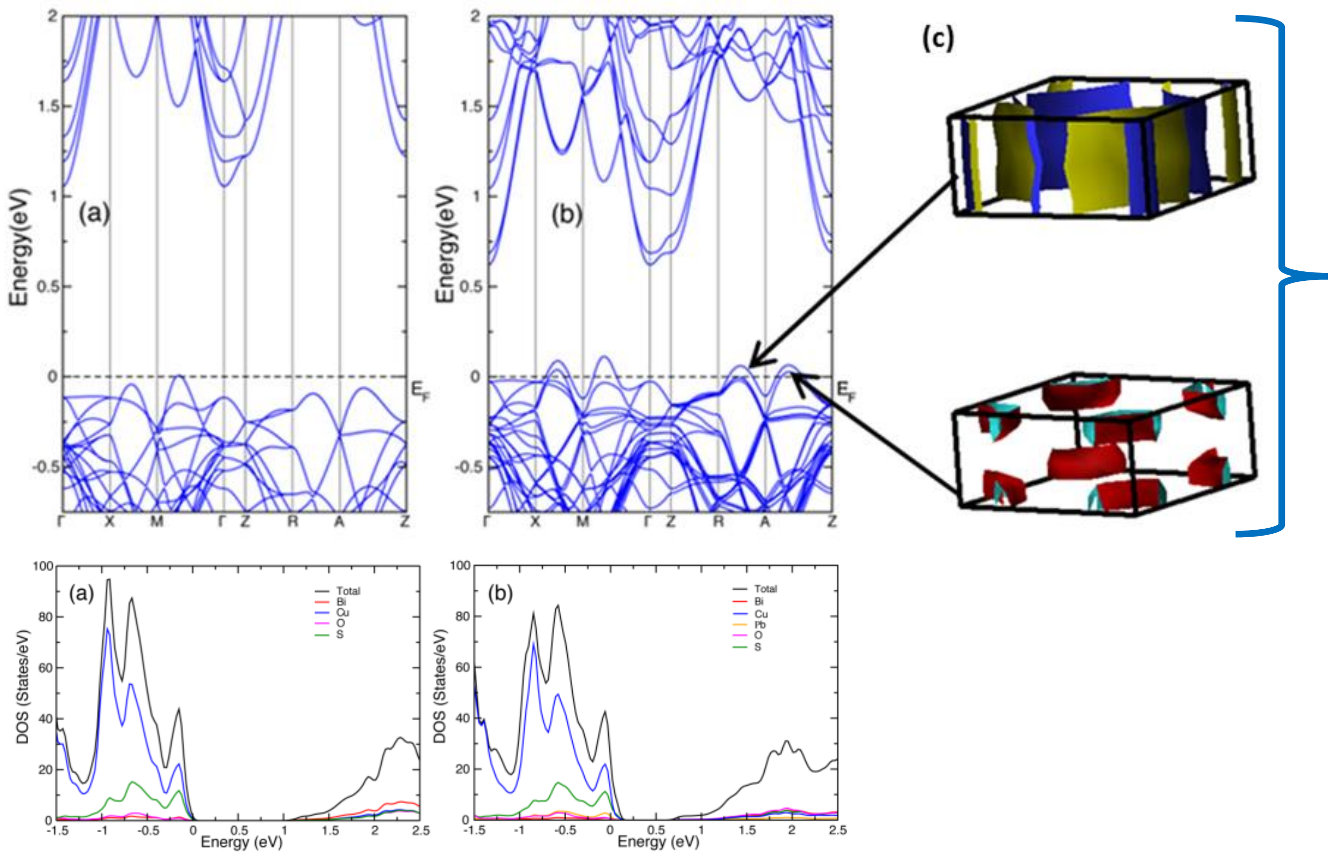


- when x ↗ : ρ ↘
- $\rho_{x=0.05}$ = 56 mΩ cm @ 700 K

- when x ↗: S ↘
- $S_{x=0.05}$ = 340 μV K^{-1} @ 700 K

DFT calculations

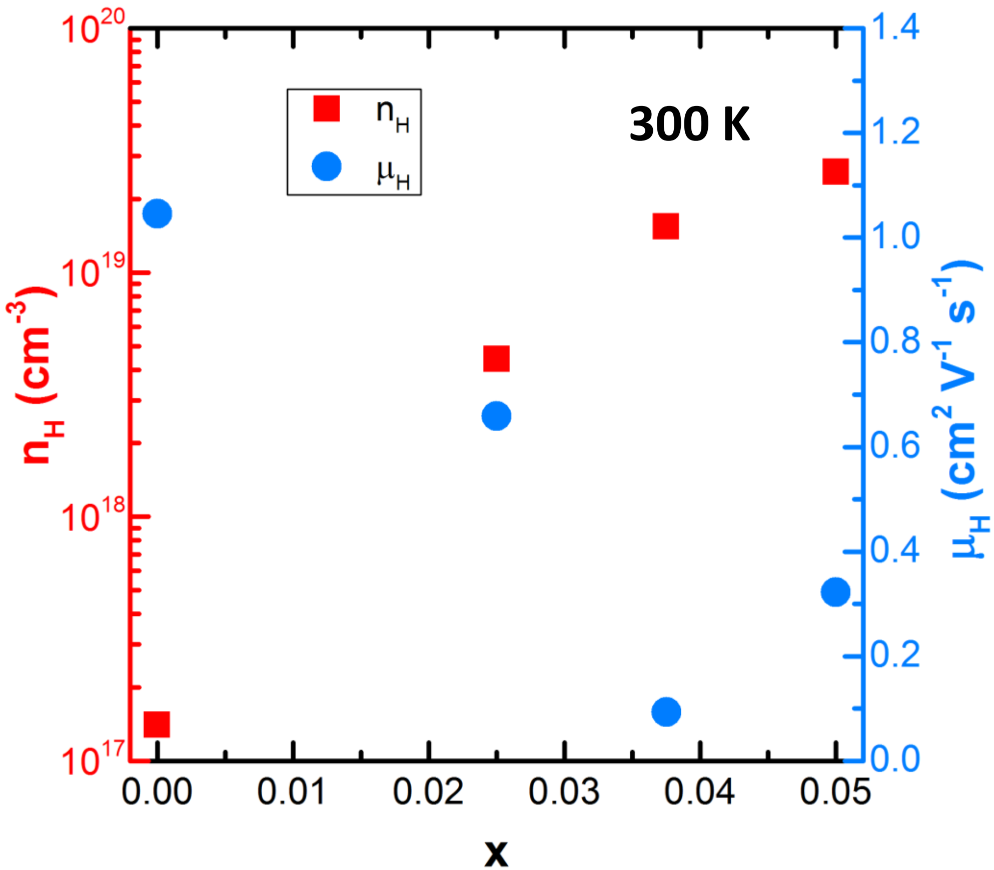
BiCuOS **$Bi_{93.7}Pb_{6.3}CuOS$**



Pb substitution increases the number of hole pockets

- band-gap decreases with Pb-doping
- top of VB : - hybridization between Cu *3d* and S *3p*
  - contribution of Pb *6s* in Pb-doped samples

TE properties of $Bi_{1-x}Pb_xCuOS$ ($0 \le x \le 0.05$)



when x ↗ :

- n ↗ ➔ confirms Pb^{2+} substitution
- n reaches 2.6×10^{19} cm^{-3} (x = 0.05)

↳ **too low to reach optimal PF**

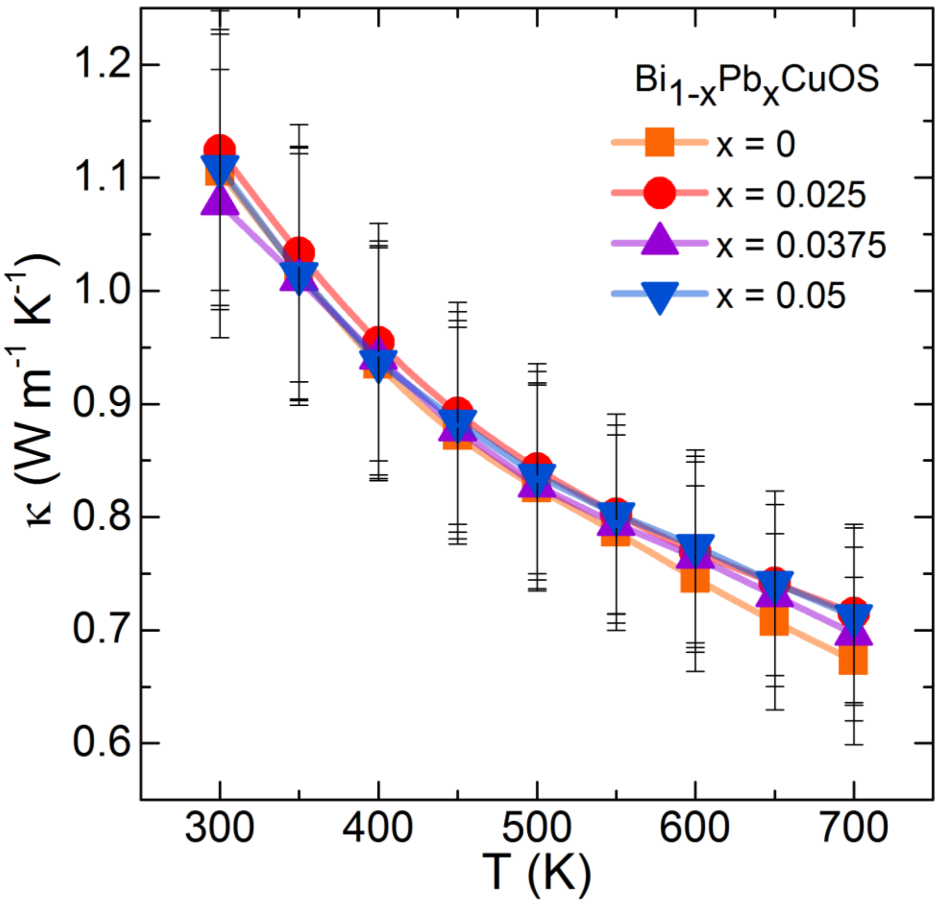
- μ ↘ until 0.3 $cm^2 V^{-1} s^{-1}$ (x = 0.05)

↳ **low mobility**

<u>hole effective mass estimated from Seebeck coefficient and the carrier concentration :</u>

x	0	0.025	0.0375	0.05
m*/me	1.71	1.81	1.85	2.2

TE properties of $Bi_{1-x}Pb_xCuOS$ ($0 \leq x \leq 0.05$)



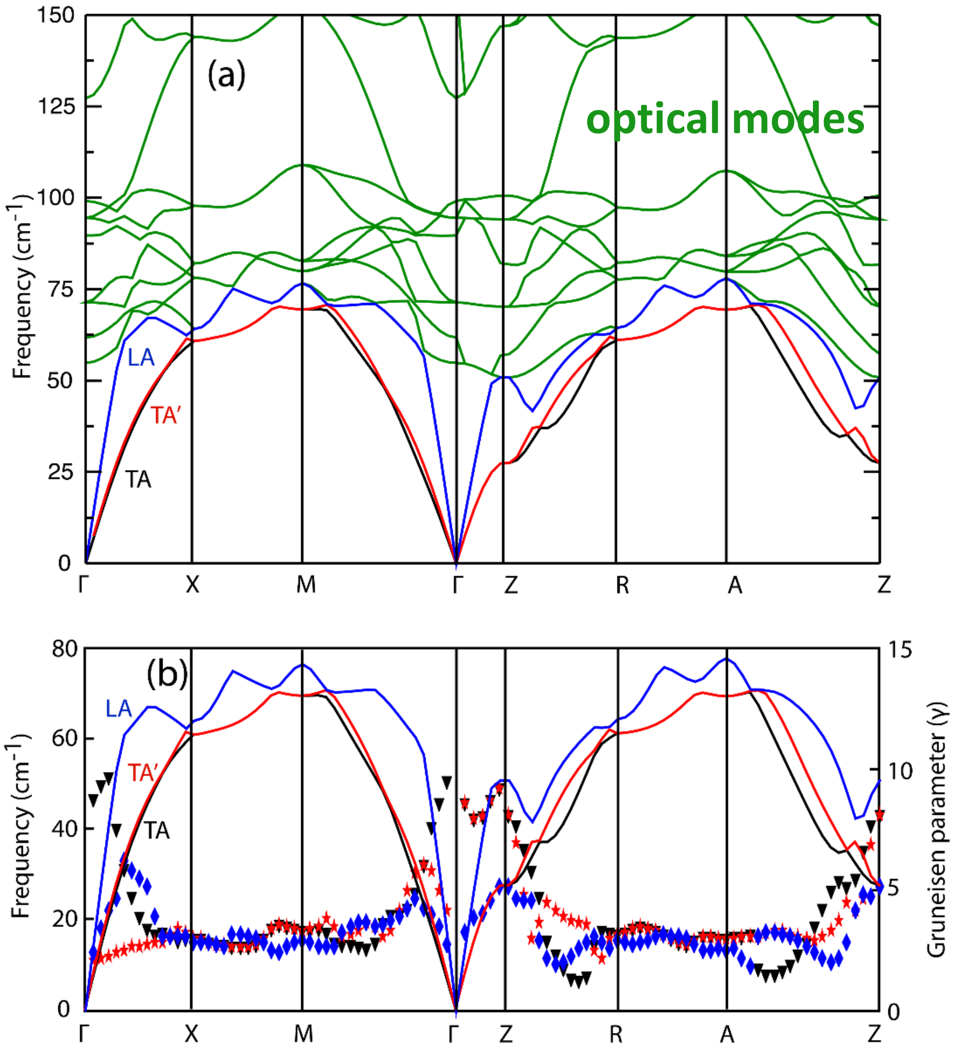
- when x ↗ : κ remains constant

Bi/Pb: - low mass fluctuation
- moderate size mismatch

- low κ ($\kappa_l >> \kappa_e$) ➔ layered structure, strong phonon scattering

$\kappa_{700\,K}$ ~ 0.70 W m^{-1} K^{-1}

Thermal conductivity of BiCuOS



phonon dispersion of BiCuOS:

- 3 acoustic modes with low boundary frequency

65 cm^{-1} along *Γ-X* and *Γ-M*

50 cm^{-1} along *Γ-Z* (001 direction)

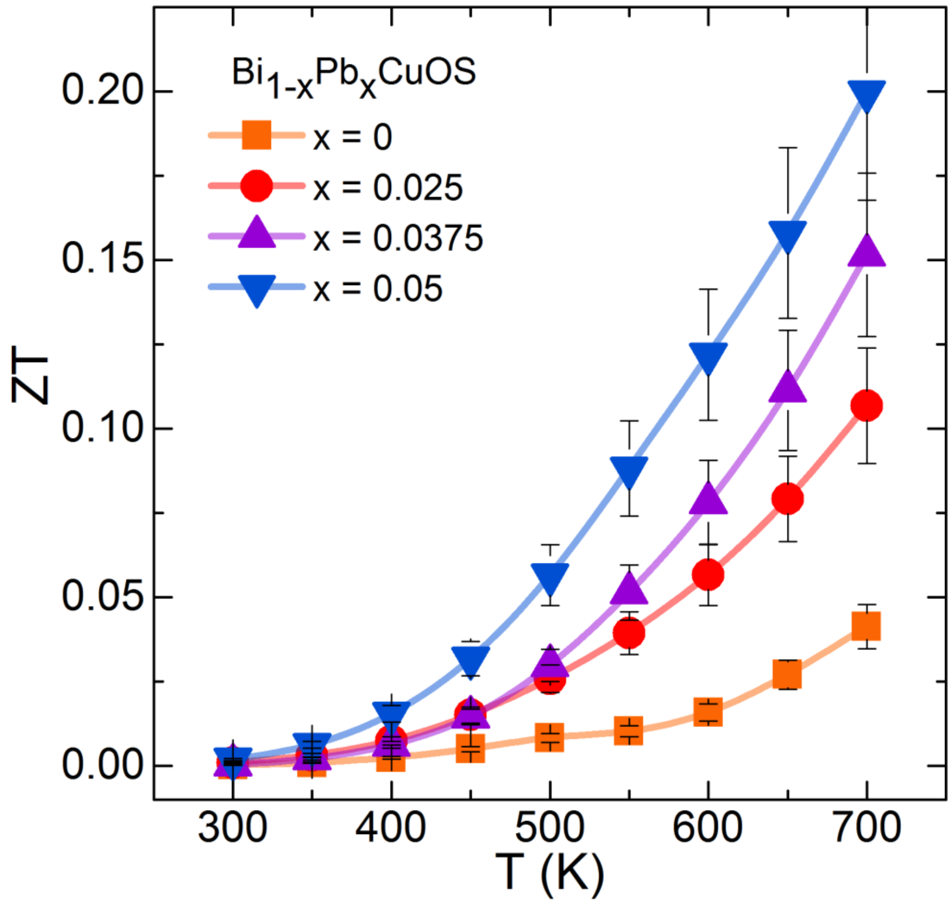
→ weak inter-layers bonding

Grüneisen parameters of BiCuOS :

- ~ 8 along *Γ-Z*

→ strong anharmonicity between the layers

TE properties of $Bi_{1-x}Pb_xCuOS$ ($0 \le x \le 0.05$)



- when x ↗ : n ↗ and ρ ↘ → ZT ↗
- ZT = **0.2** @ 700 K with **5 at%** Pb → **Best value among the oxysulfides**

Conclusions

XRD + charge carrier concentration ⇒ confirms Pb^{2+} substitution

⇓

~ 1 % Bi secondary phase when x ≥ 0.0375

when x = 0.05 : charge carrier concentration **x 185 at RT**

⇓

resistivity **divided by 53 at RT**

⇓

remains too high to reach optimal PF

+

low thermal conductivity

⇓

ZT = 0.2 @ 700 K with 5 at% Pb

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