ISE 2021
July 22

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Energy and Materials LAB
University of Trento

DIPARTIMENTO DI

INGEGNERIA CIVILE, AMBIENTALE E MECCANICA

Effect of structural disorder on the thermoelectric behavior of Cu_2SnS_3 (CTS)

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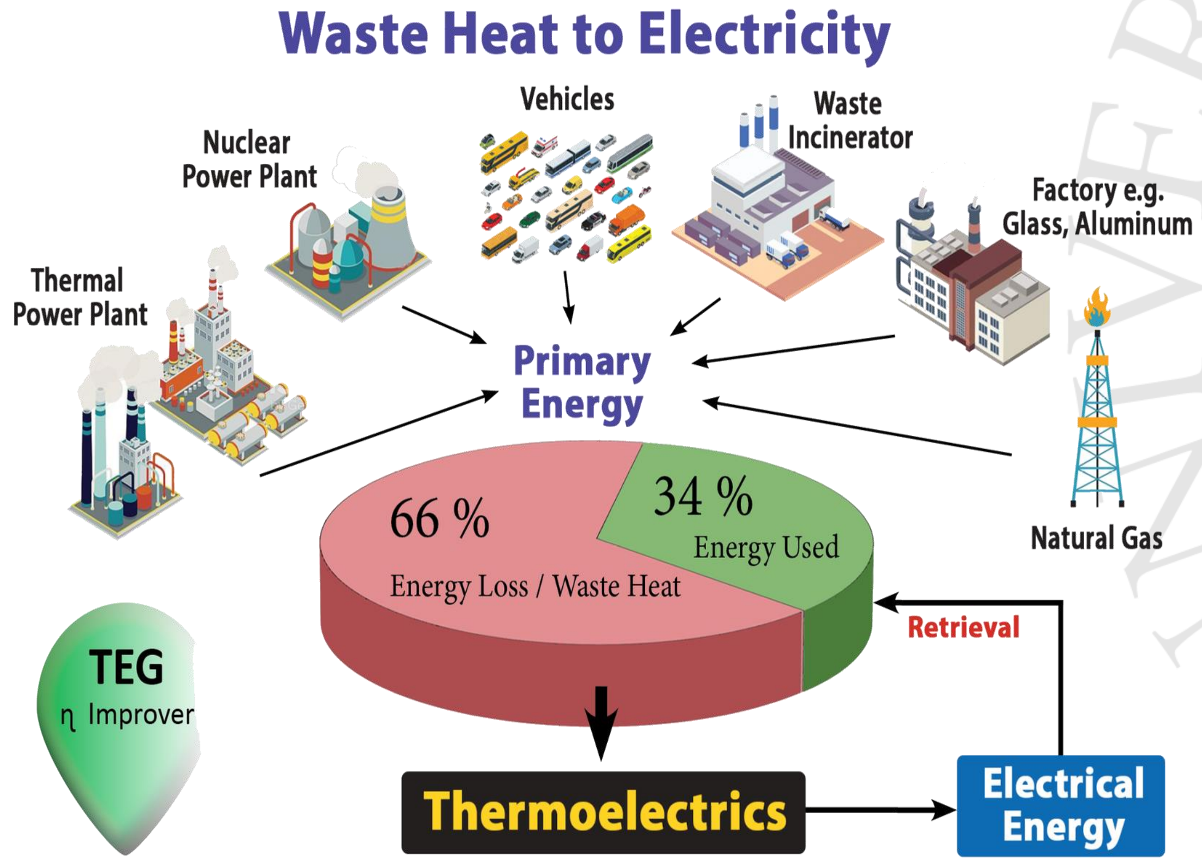
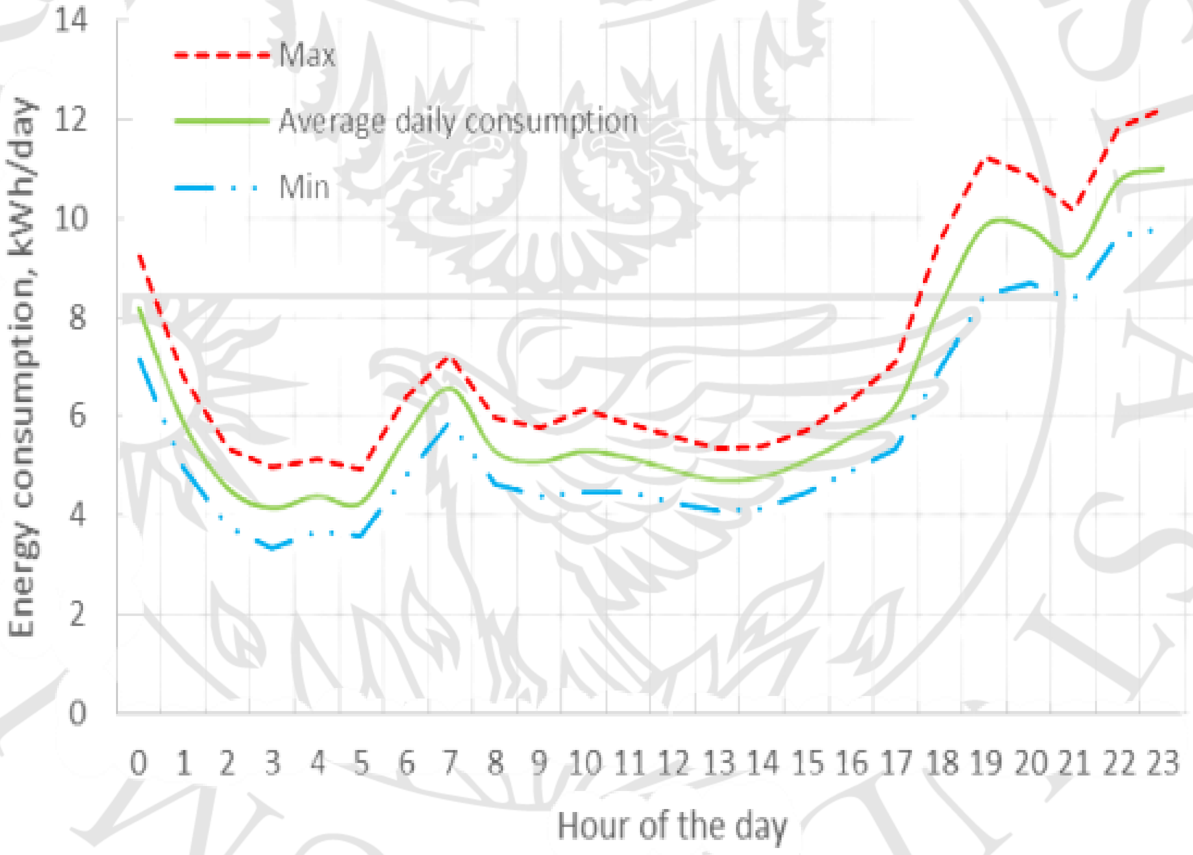
Thermoelectricity: Direct conversion of temperature gradient into voltage and vice versa.



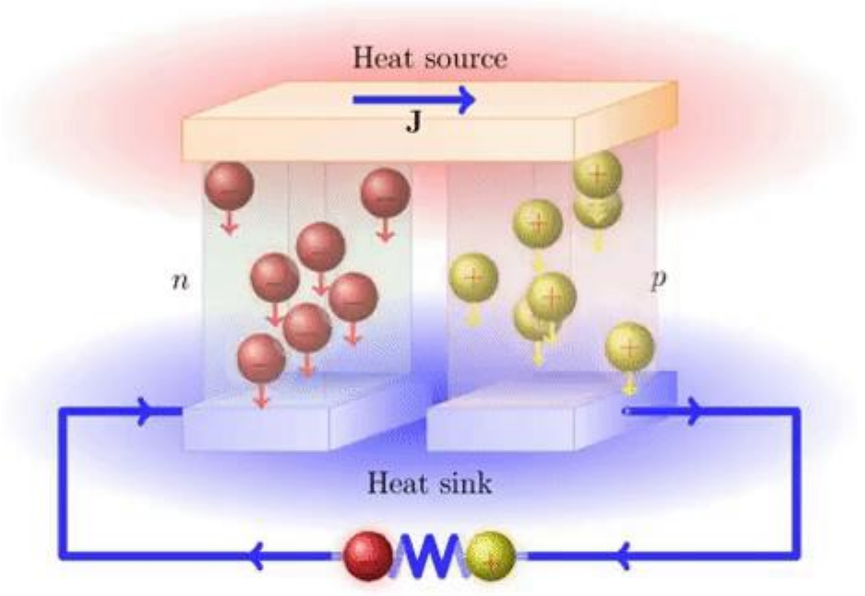


Power Consumption during a typical day

Nicola et al., IOP Conf. Series: Earth and Environmental Science 172 (2018) 012035

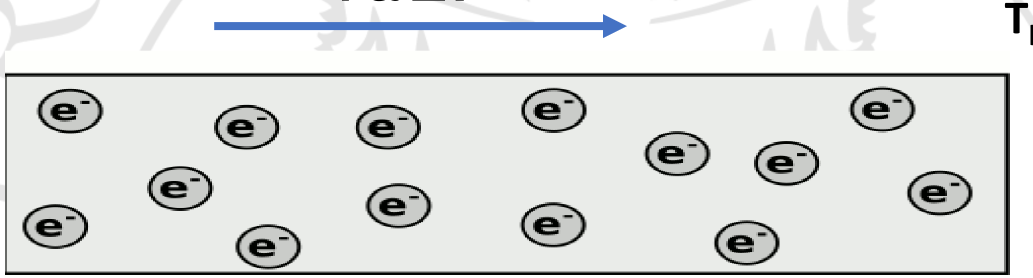
TEG & A simple case:

Thermoelectric Generator
[Seebeck effect]



I & ΔV

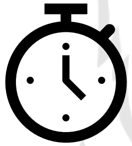
T_L T_H



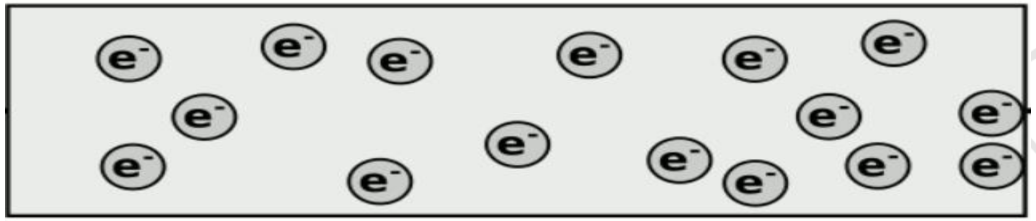
Seebeck Coefficient

$S = \frac{\Delta V}{\Delta T}$

Charge Carriers & Heat



$T_H = T_L$



ΔV→0, I→0, & S→0

Optimal thermoelectric materials: High figure of Merit (zT)

$$S = AT\left(\frac{m^*}{n^{3/2}}\right)$$

High

$$P.F. = S^2\sigma$$

$$\sigma = \frac{1}{\rho} = ne\mu$$

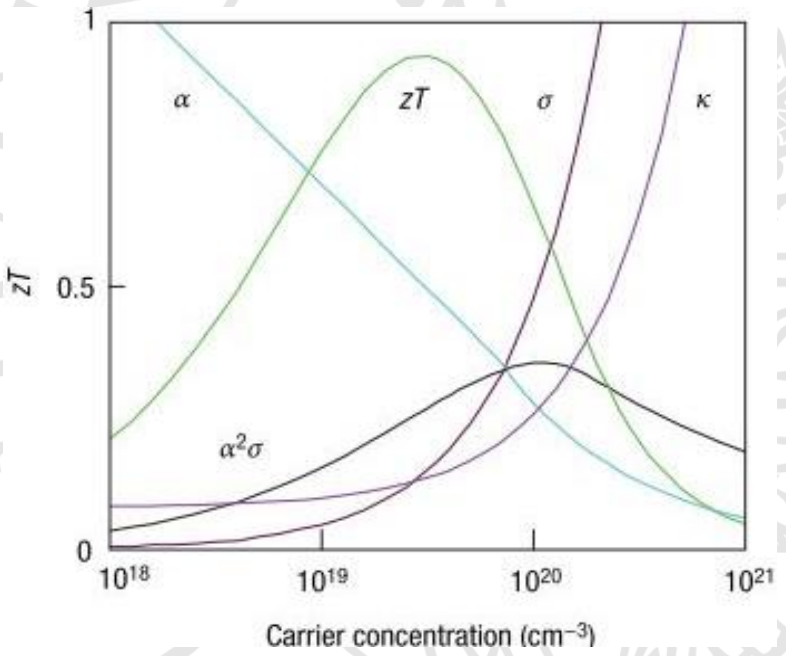
$$zT = \frac{S^2\sigma}{\kappa}T$$

Low

$$\kappa_e = L\sigma T = Lne\mu T$$

$$\kappa = \kappa_e + \kappa_l$$

$$\kappa_l = {}^1/_3\, cvl$$



T=Temperature

P.F.= Power factor
κ = Thermal conductivity

S = Seebeck coefficient
σ = Electric conductivity

κ_l= Lettice thermal conductivity
κ_e= Electronic thermal conductivity

n= Carrier concentration
µ= Mobility

A= Constant
m*= Effective mass of charge carriers
e= Charge of electron
L= Lorentz number

c = Specific heat per unit volume
v = Average phonon velocity
l= Average mean free path

Heavily doped Semiconductors or **Semimetals**

Phonon-Glass Electron-Crystal or **Phonon-Liquid Electron-Crystal**

Snyder et al., Nature Materials, Volume7 pages105–114 (2008)

State of art and applications:

Solid Sate generators ,long-lasting, noise free, flexible.

Several potential application

Low efficiency, η ≤10%

Voyager 1,
Voyager 2,
Galileo,
Ulysses,
Cassini,
&
New Horizons
spacecraft.

Room temperature: Bi_2Te_3 T: 300K-600K

Medium temperature: SnSe, PbTe   T : 600K-900K

High temperature: SiGe , T > 1000K

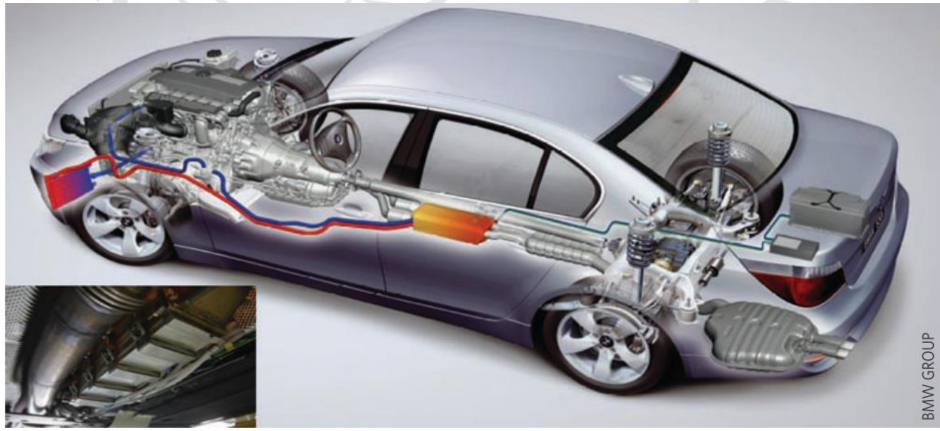


Figure 1 | Integrating thermoelectrics into vehicles for improved fuel efficiency. Shown is a BMW 530i concept car with a thermoelectric generator (yellow; and inset) and radiator (red/blue).

Cronin B. Vining, Nature Materials, Volume 8, pages83–85 (2009)

Cu_2SnS_3: Copper-Tin Sulfide (Eco-friendly, Earth-abundant, Cost-effective)

V. A. Kovalenkar in 1983. (A new sulfide of Cu and Sn)

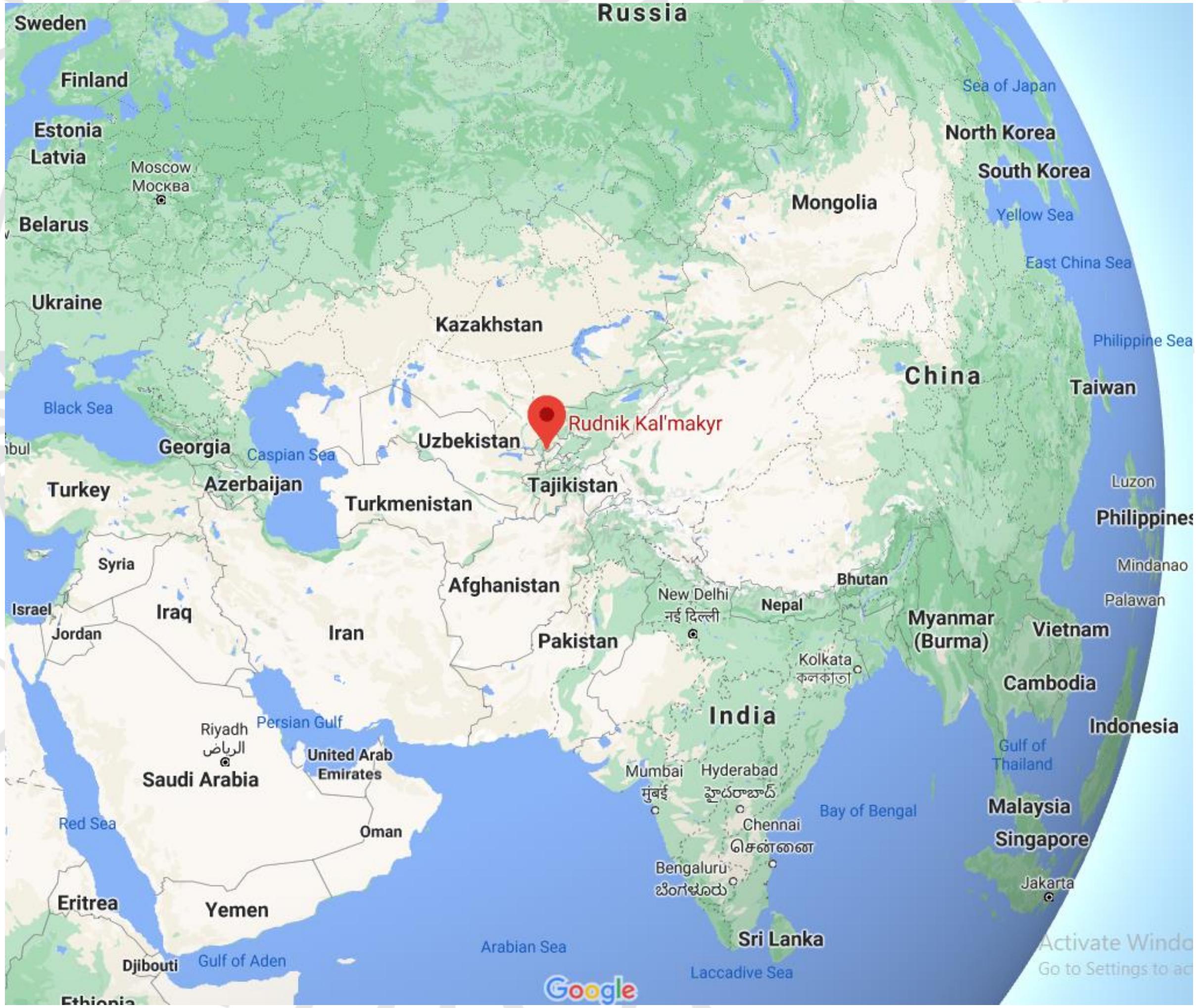
Goldfieldite-Famatinite-Tetrahedrite ores

Kochbulak deposits (Uzbekistan)

XRD study: Triclinic (SG:*P1*)

Closely related to Kuramite (Cu_3SnS_4)

Mohit (Cu_2SnS_3) CTS



Kovalenker, V. A. Cu_2SnS_3, A New Sulfide of Tin and Copper. Int. Geol. Rev. 1983, 25, 117–120

Applications: Photovoltaic devices, Drug delivery, Transistor , Thermoelectric etc.

PV Application: Tunable bandgap(0.6-1.7 eV) and High optical absorption coefficient (~10cm^{-1})

Thermoelectric Applications: p-type, medium temperature (~450K-750K) in 2016

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journal homepage: http://www.elsevier.com/locate/jalcom

Enhanced thermoelectric properties of earth-abundant Cu_2SnS_3 via In doping effect

CrossMark

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State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing, 100084, PR China

SCIENTIFIC REPORTS

OPEN

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Eco-friendly *p*-type Cu_2SnS_3 thermoelectric material: crystal structure and transport properties

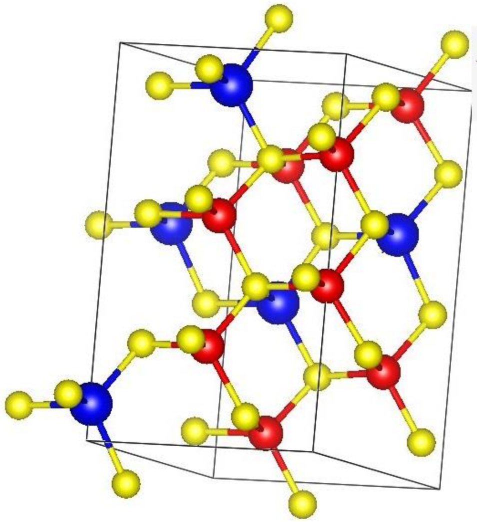
Yawei Shen[1], Chao Li[2], Rong Huang[2], Ruoming Tian[3], Yang Ye[1], Lin Pan[1,4], Kunihito Koumoto[3], Ruizhi Zhang[5], Chunlei Wan[6] & Yifeng Wang[1,4]

Tan et al. J. Alloys Compd. 2016, 672, 558−563. ; Shen et al. Sci. Rep. 2016, 6, 32501

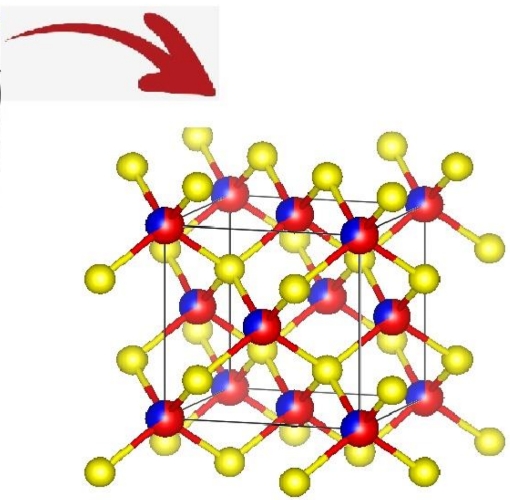
Thermoelectric exploration:

Production method in the Literature: Solid-State Reaction using elemental powders.

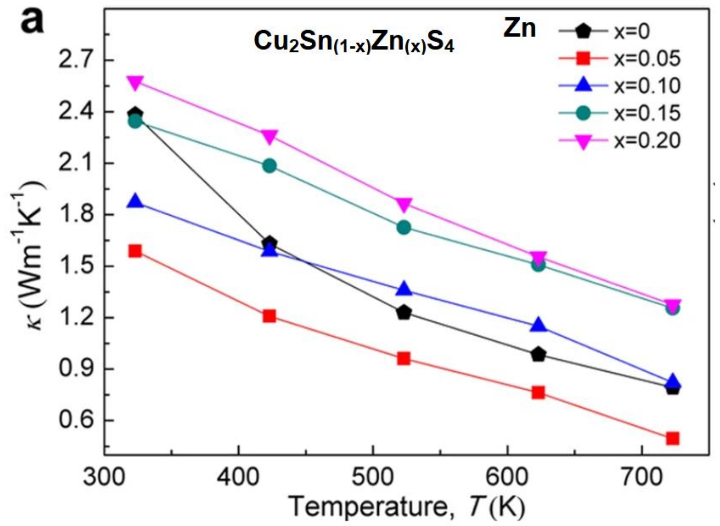
Disordered polymorph via acceptor doping: In, Zn,Mn, Ni, Fe, and Co.



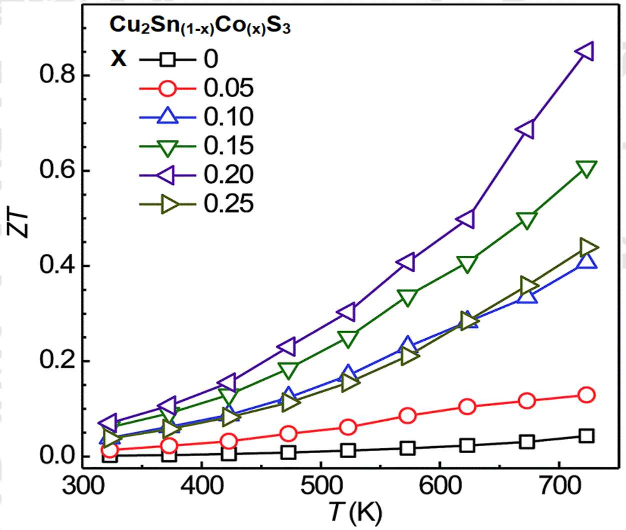
Monoclinic (Ordered)



Cubic (Disordered)



Ultra-low Thermal Conductivity

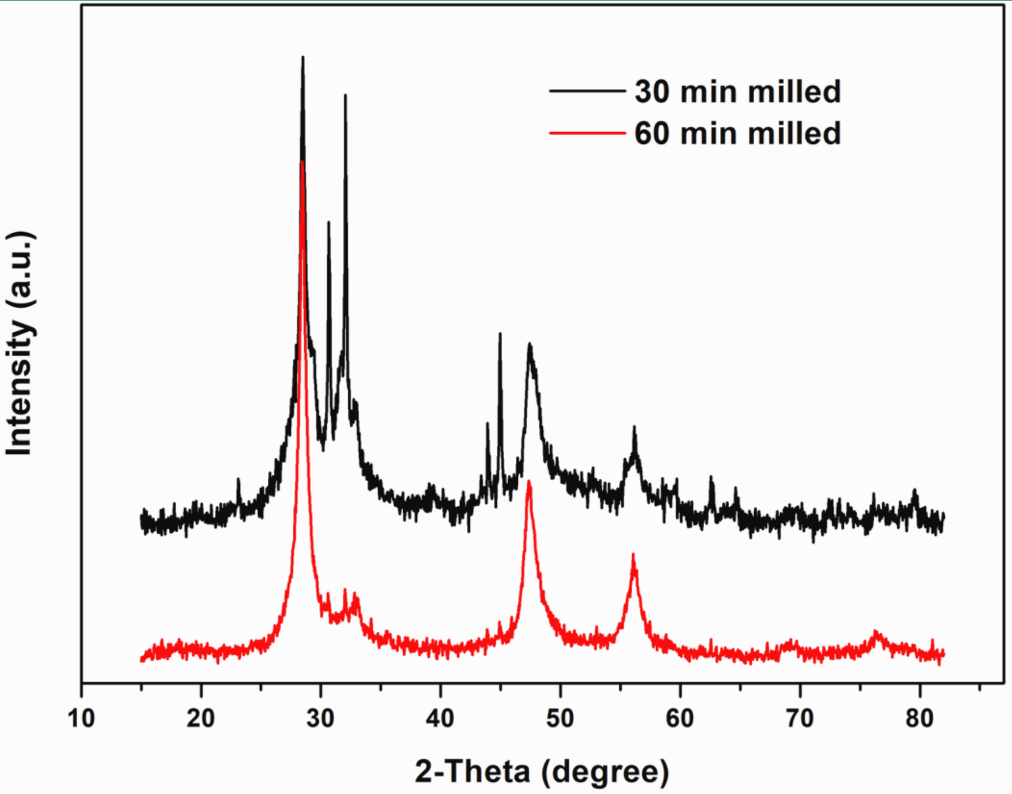


High zT

Zhang et al. J. Alloys Compd. 2019, 780, 618–625.; Xu et al. J. Alloys Compd. 2017, 728, 701–708.; Zhao et al. J. Appl. Phys. 2019, 125, 095107.; Zhao et al. J. Mater. Chem. A 2017, 5, 23267–23275.

Production:

High energy reactive ball milling. (Simple, fast, Scalable)



Elemental powder (1h) or Binary sulfieds (30min).
Powder/Ball = 1/100.

Ω=-540 rpm & r=300 rpm

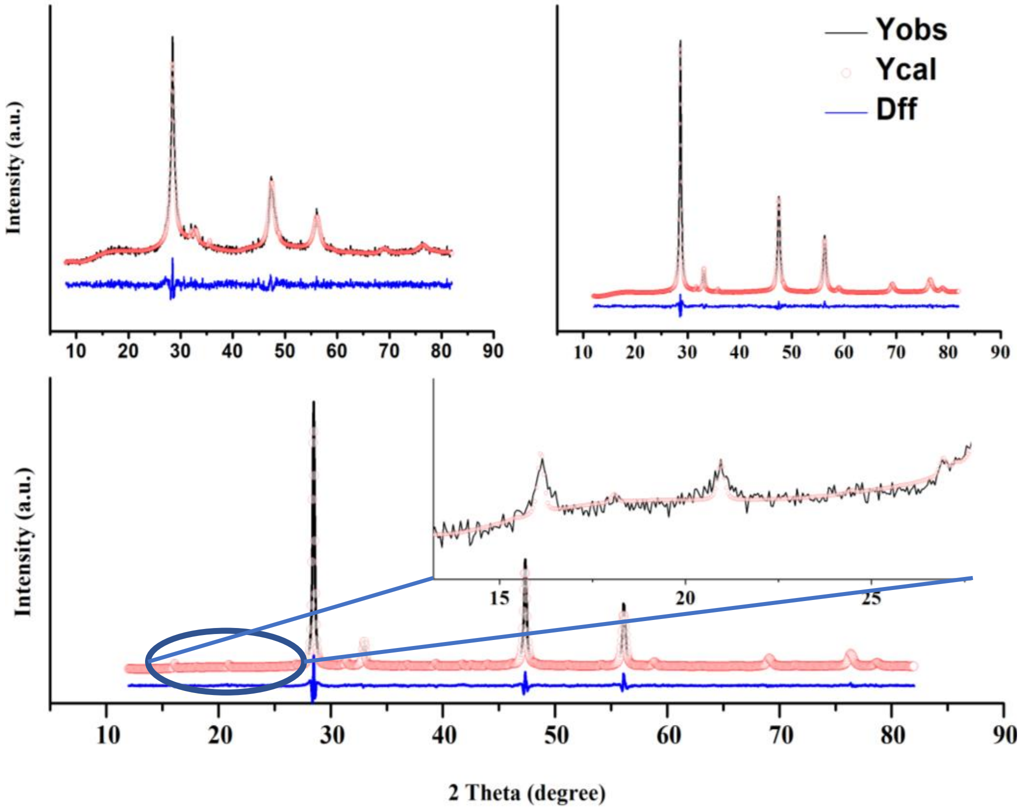
O_2 & H_2O < 10 PPM

Elemental powder
30 min milled: Cu, Sn, CuS, SnS, & CTS
60 min milled: CTS with amorphous fraction

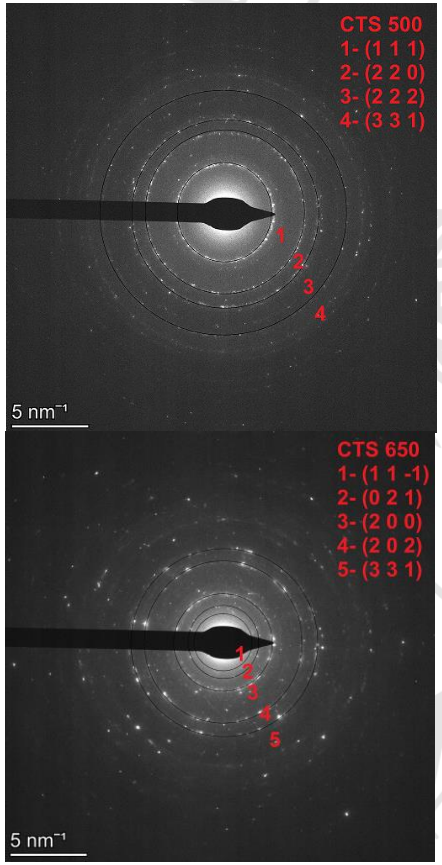
Lohani et al. J. Alloys Compd. 2020, 830, 154604.

Structural and chemical analysis:

XRD : Rietveld Refinement

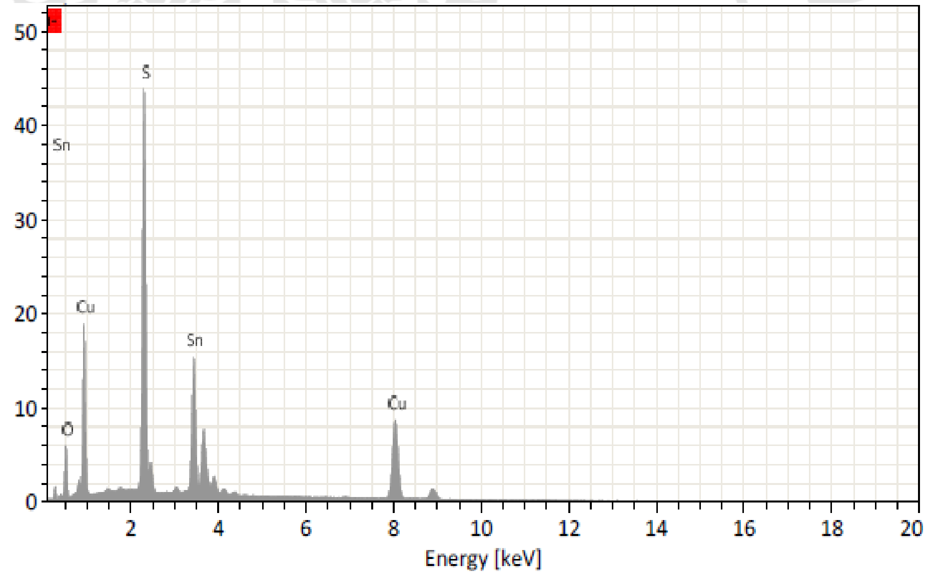


SAED



EDXS

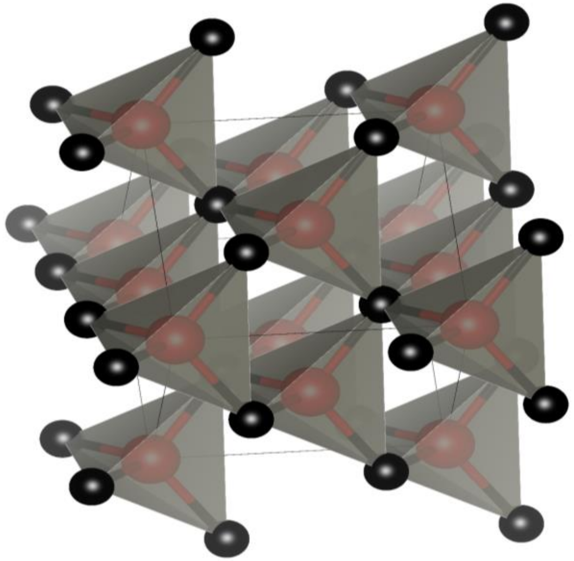
Atom[%] ~ Sn : Cu : S = 1 : 2 : 3



Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Oxygen	8	14852	10.36	10.98	30.61	1.40	13.52
Sulfur	16	205201	23.40	24.79	34.48	0.86	3.69
Copper	29	73369	31.18	33.04	23.19	0.87	2.78
Tin	50	138729	29.44	31.19	11.72	0.89	3.04
		Sum	94.39	100.00	100.00		

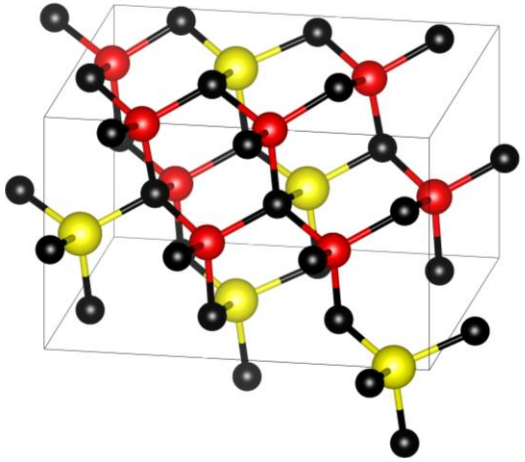
Computational methods: Chalcogenide

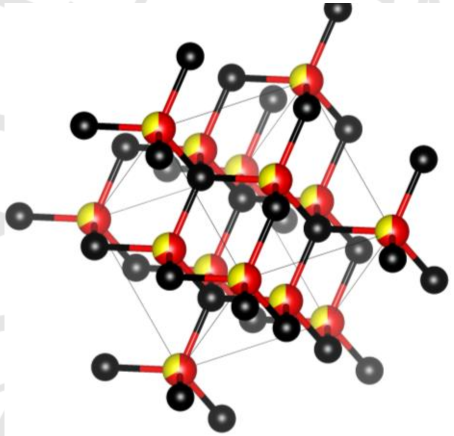
ZnS **Zn** **S**



Wycoff positions: Zn- 4a & S- 4C

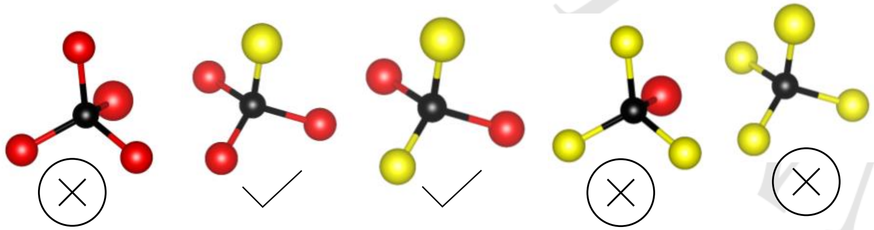
Cu **Sn** **S**





Partial occupancy
2/3 Cu & 1/3 Sn

$S{-}Cu_iSn_{(4-i)}$; $i \in \{0, \ldots, 4\}$,



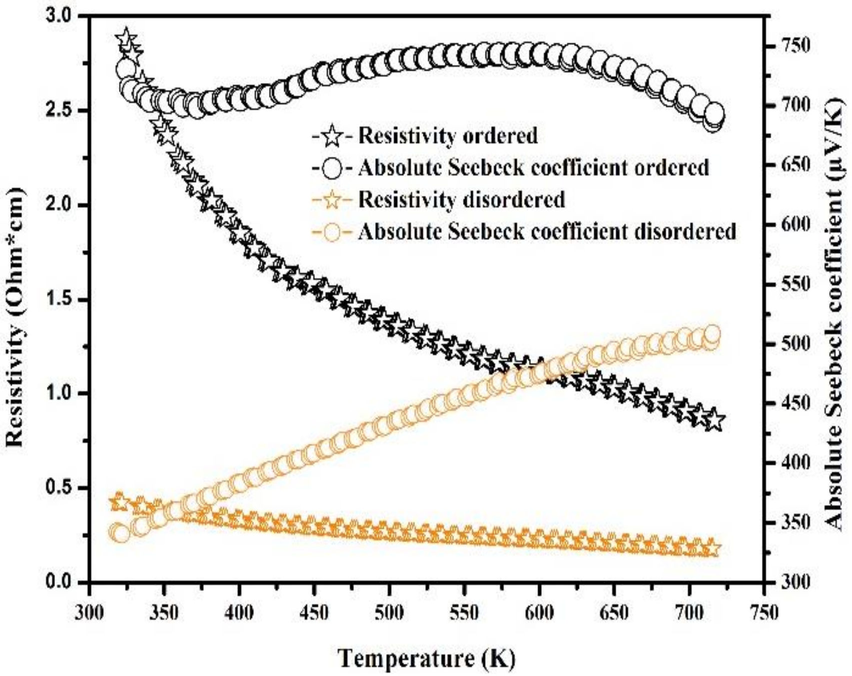
Ordered:

24-atoms (8-Cu, 4-Sn, and 12-S)

Disordered:

Sn-rich (21-Cu, 11-Sn, and 32-S)
Sn-poor (22- Cu, 10-Sn, and 32-S)

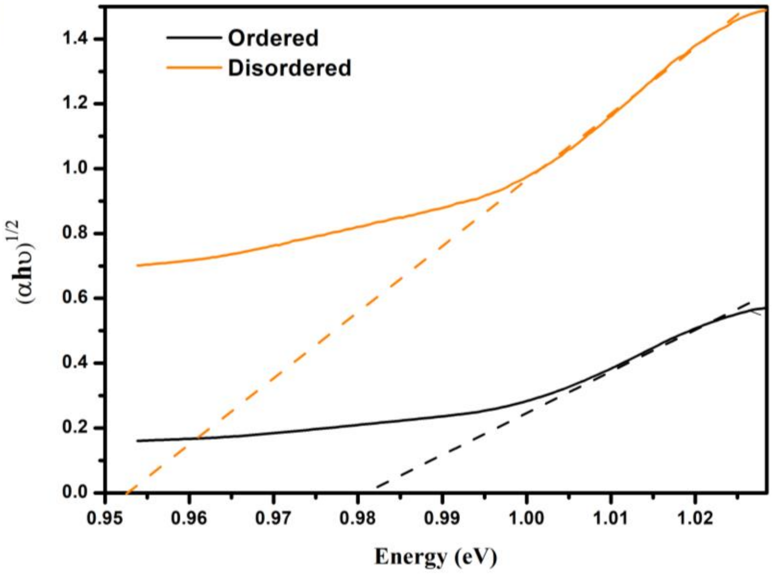
Thermopower and Resistivity:

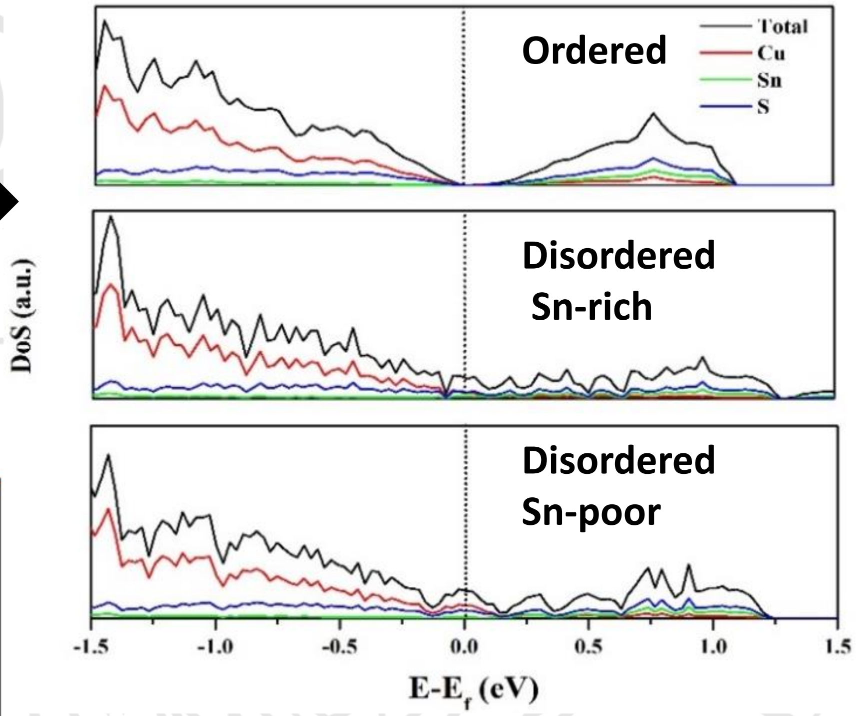


p-type
Non-degenerate SC

DFT-VASP

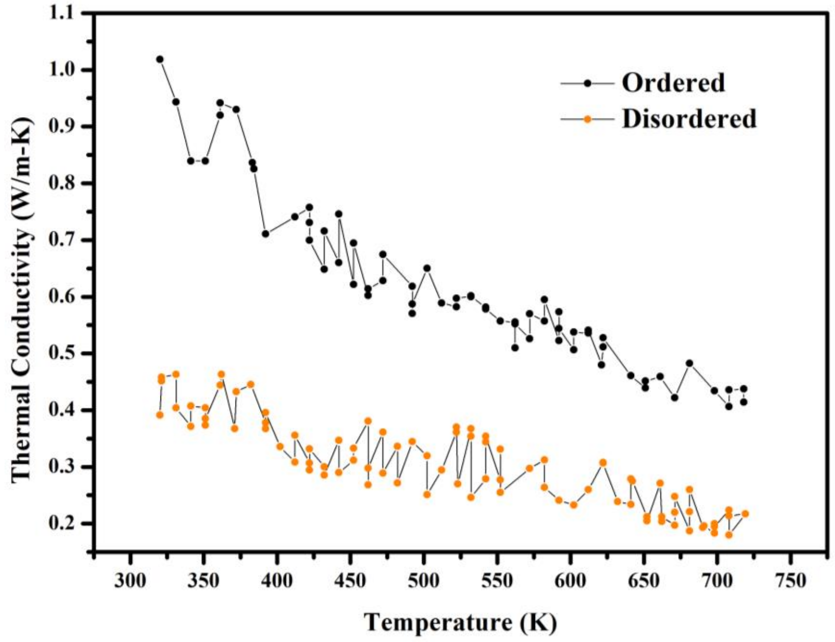
Generalized Gradient Approximation (GGA)





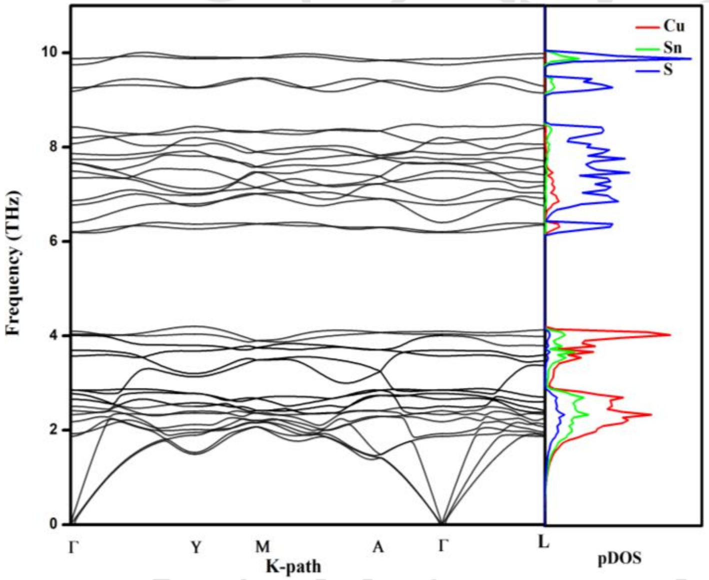
p-type nature
Valence band: : Cu-3d S-3p
Conduction band: Sn-5S S-3p

Thermal conductivity:

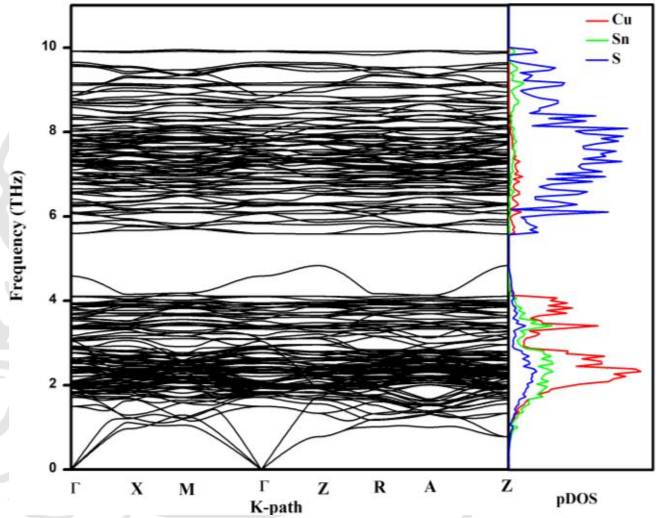


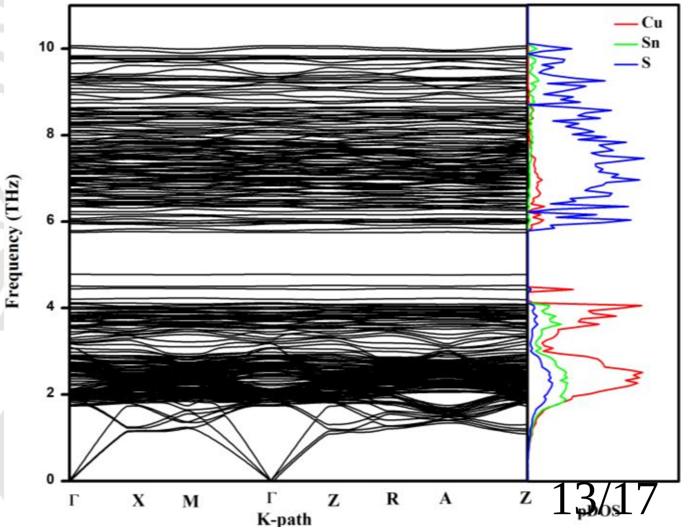
As most of high resistivity SC,
Main contribution of k is due to k_l.

Ordered



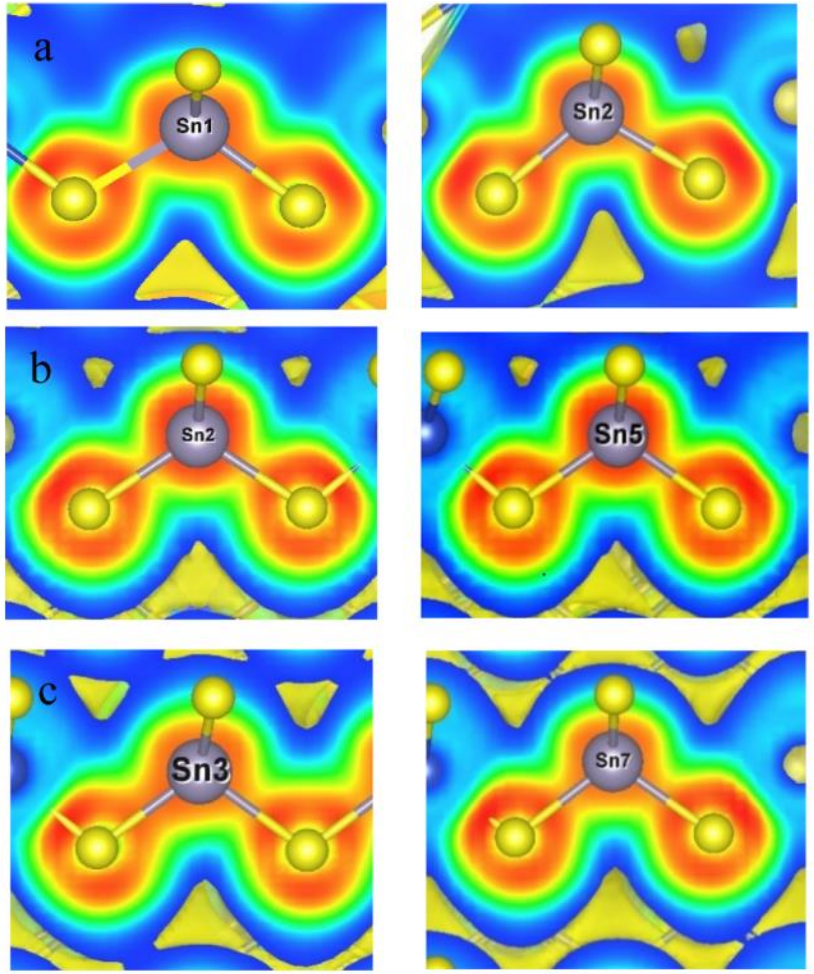
Disordered





Using Phonopy :
Low freq. modes: heavy atoms (Cu/Sn)
Low freq. modes : Ordered Cu domination & disordered Sn domination.
Similar V_g for acoustical but flat optical.
Low lying optical modes. (heat traps)

ELF and Grüneisen Parameter

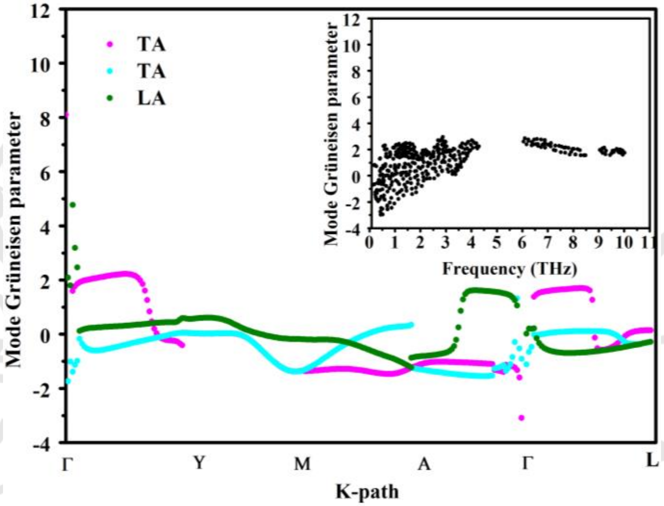


**Ordered-
Similar
Electron
Localization**

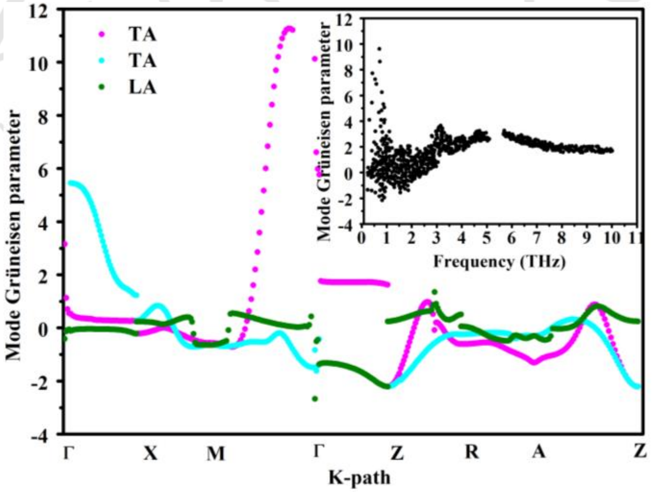
**Disordered-
Inhomogeneous
Electron
Localization**

**Grüneisen Parameter:
Quasi-harmonic
approximation,
Volume change by ±1%.**

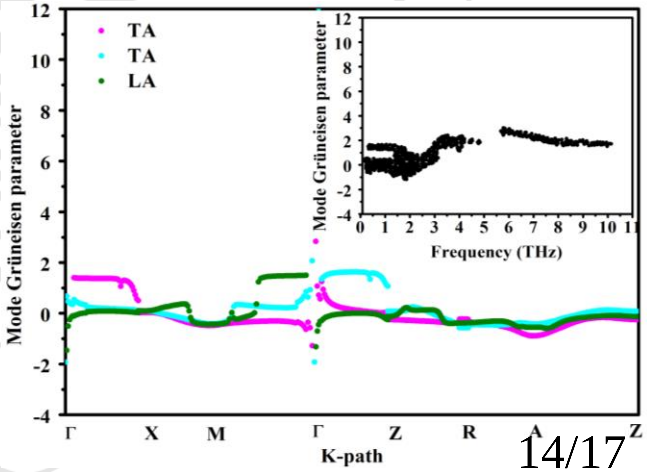
Ordered



Disordered Sn-rich

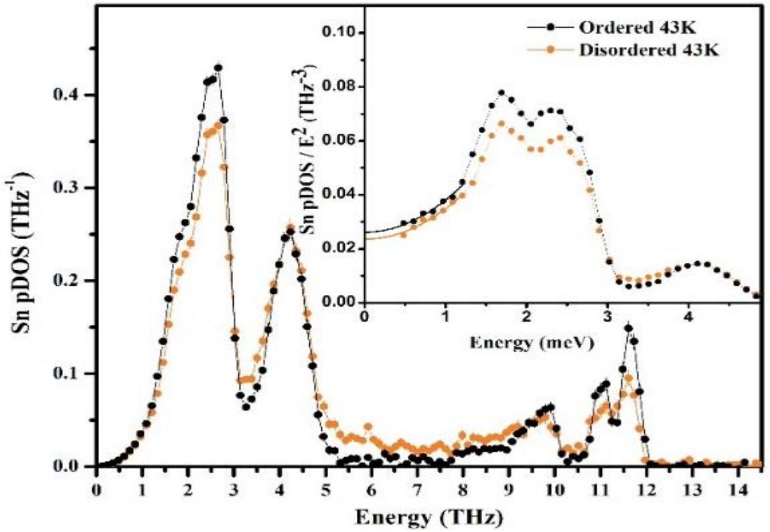


Sn-poor



Nuclear Inelastic scattering (NIS): *PETRA III (DESY, Hamburg)*

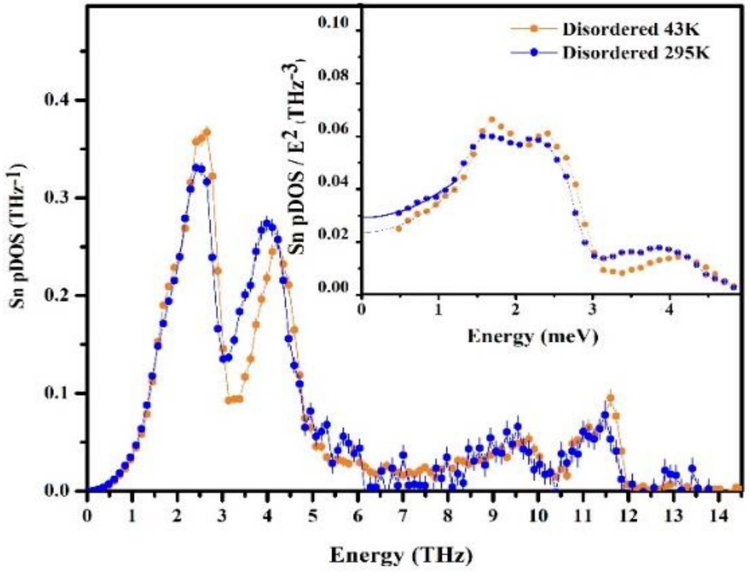
Ordered and Disordered @ 43K



Broad Phonon-band (5-9 THz).

Similar Debye energy and V_g.

Disordered @ 43K and 295K



Significant mode softening for acoustical part.

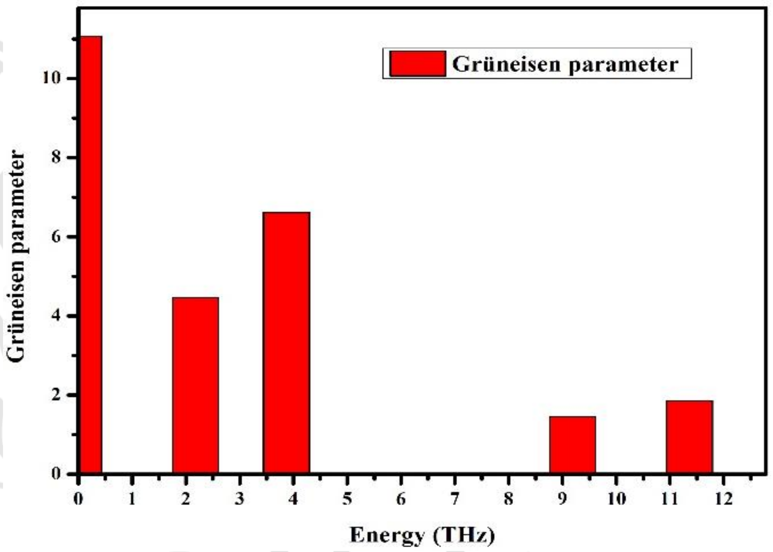
High Debye level.

Relative energy shifts ΔE/E.

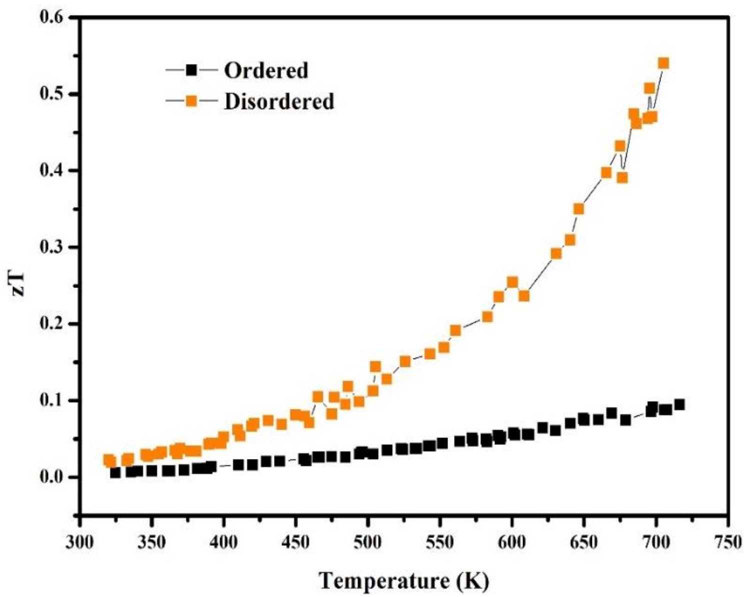
S-XRD in temp: relative volume change ΔV/V.

Grüneisen parameter (γ_i)= (ΔE/E)/(ΔV/V).

High γ_i for 0 and 4THz Energy peak.



Conclusions:



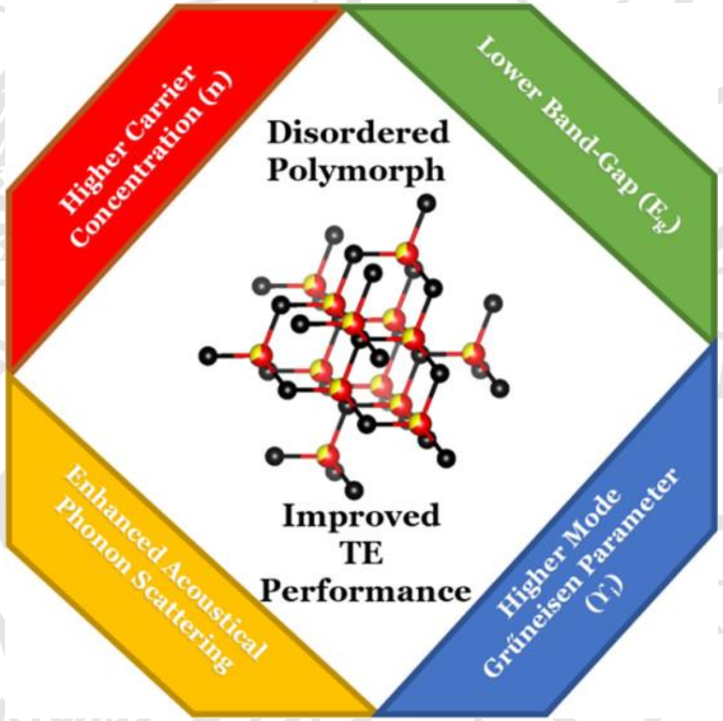
Higher zT → lower band gap and low thermal conductivity.

Low k → Low lying Optical modes & Significant variation of Sn bonding leads to strong anharmonicity.

In general,

Structural disorder enhances TE performance.

Stabilized new crystallographic phases especially disordered (e.g., CZTS, Colusites) using high energy reactive ball-milling.



Future scope: Stabilize new disordered structures and exploration of disordered structures with doping.

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Article

Experimental and *Ab Initio* Study of Cu_2SnS_3 (CTS) Polymorphs for Thermoelectric Applications

Ketan Lohani, Himanshu Nautiyal, Narges Ataollahi, Carlo Fanciulli, Ilya Sergueev, Martin Etter, and Paolo Scardi*

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Ultra-low thermal conductivity and improved thermoelectric performance in disordered nanostructured copper tin sulphide (Cu_2SnS_3, CTS)

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[b] National Research Council of Italy-Institute of Condensed Matter Chemistry and Technologies for Energy (CNR-ICMATE), Lecco Unit, Via Previati 1/E, 23900, Lecco, Italy
[c] Institute of Photonics and Nanotechnologies IFN, National Research Council CNR CSMFO Lab. & Fondazione Bruno Kessler FBK, Centro Materiali e Microsistemi CMM, Via alla Cascata 56/C, 38123, Trento, Italy

Acknowledgement:

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Dr. Narges Ataollahi
Dr. Carlo Fanciulli
Dr. Ilya Sergueev
Dr. Martin Etter
Prof. Paolo Scardi & Whole Family of Energy Materials Lab, UniTrento

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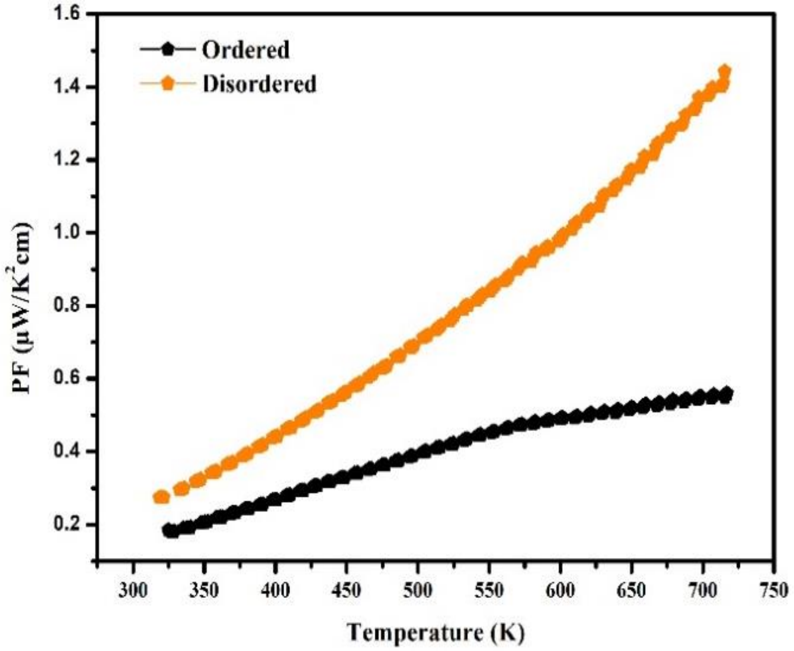
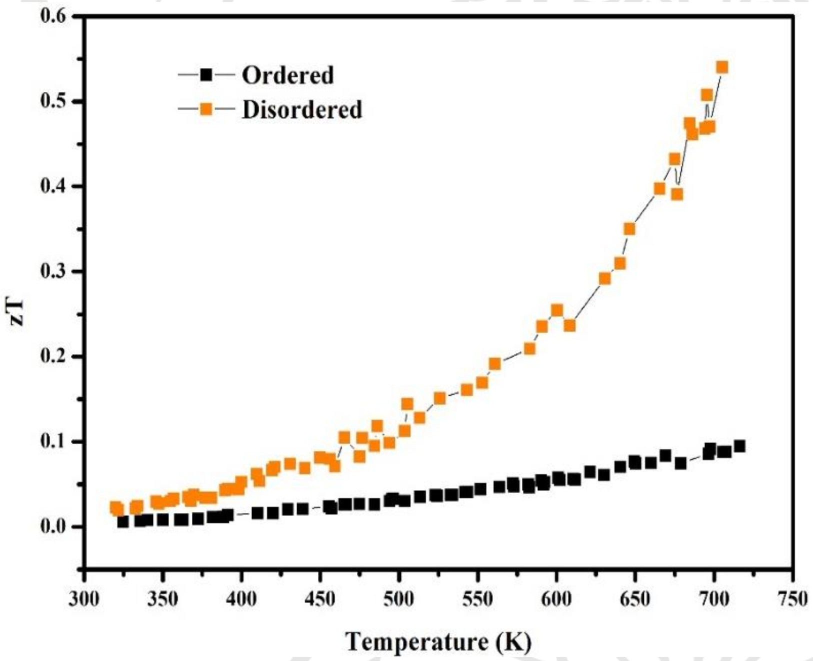
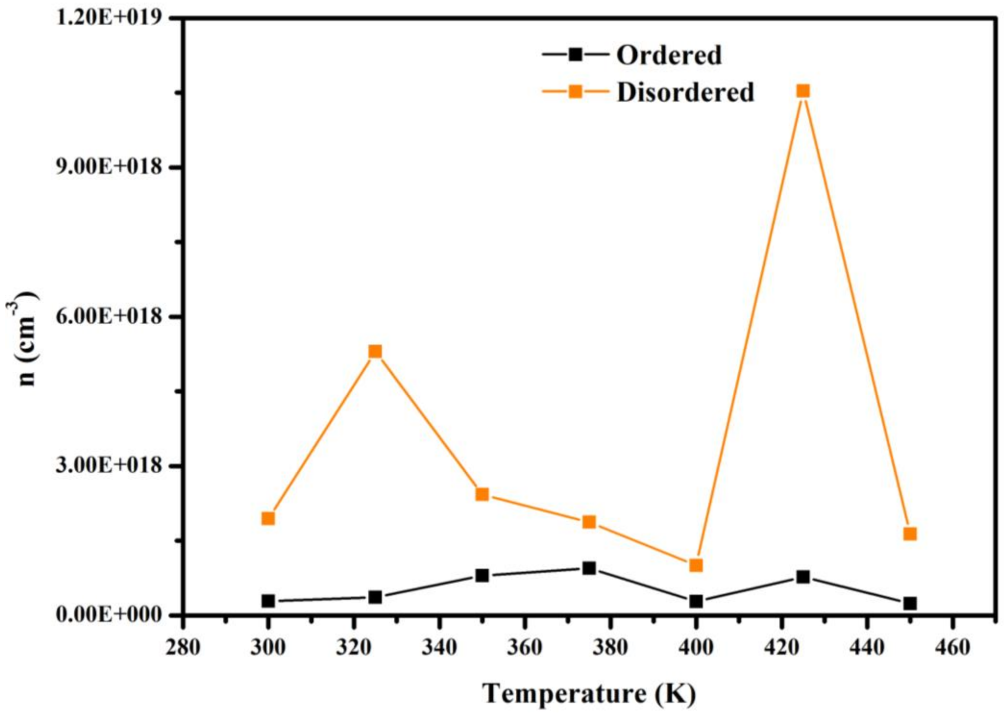
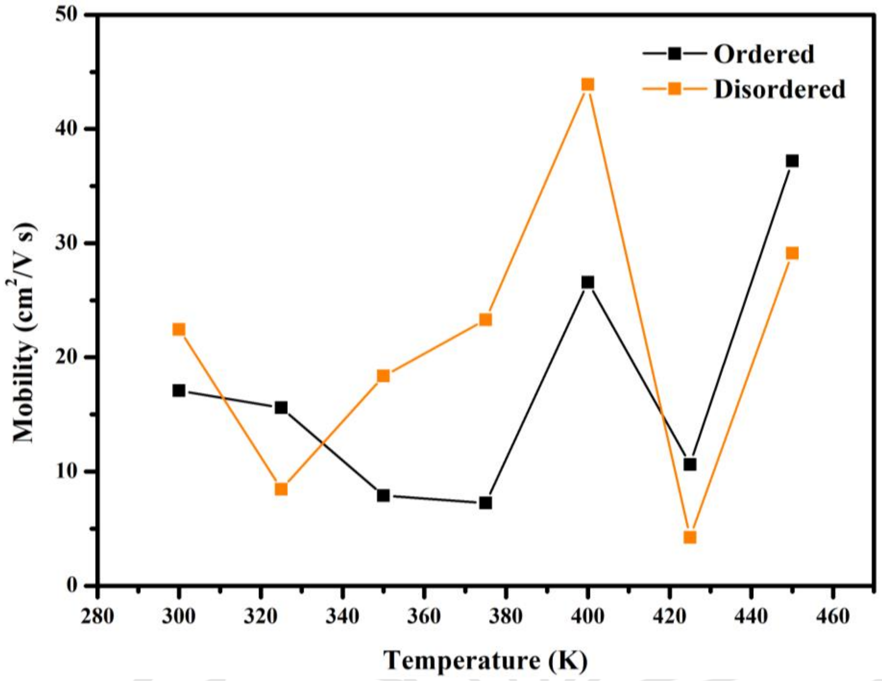
Supporting Information:


Ordered
Disordered
PF (μW/K²cm)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
300
350
400
450
500
550
600
650
700
750
Temperature (K)


Ordered
Disordered
zT
0.6
0.5
0.4
0.3
0.2
0.1
0.0
300
350
400
450
500
550
600
650
700
750
Temperature (K)

Carrier concentration (n) and mobility (μ):





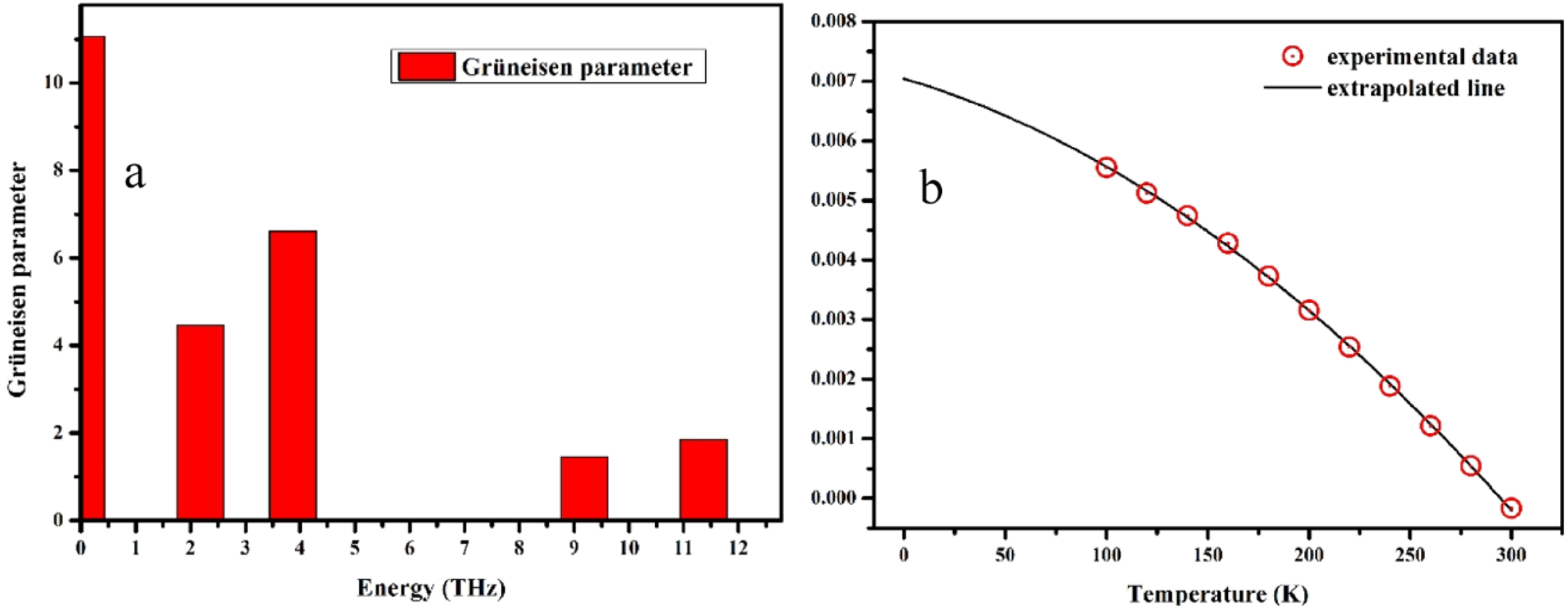


Figure 12. Grüneisen parameters of the specific phonon peaks of the disordered compound obtained from the NIS measurements at 43 and 295 K (a) and relative volume change $\Delta V/V_{295K}$ from the XRD data collected in temperature range 300−100 K (b).

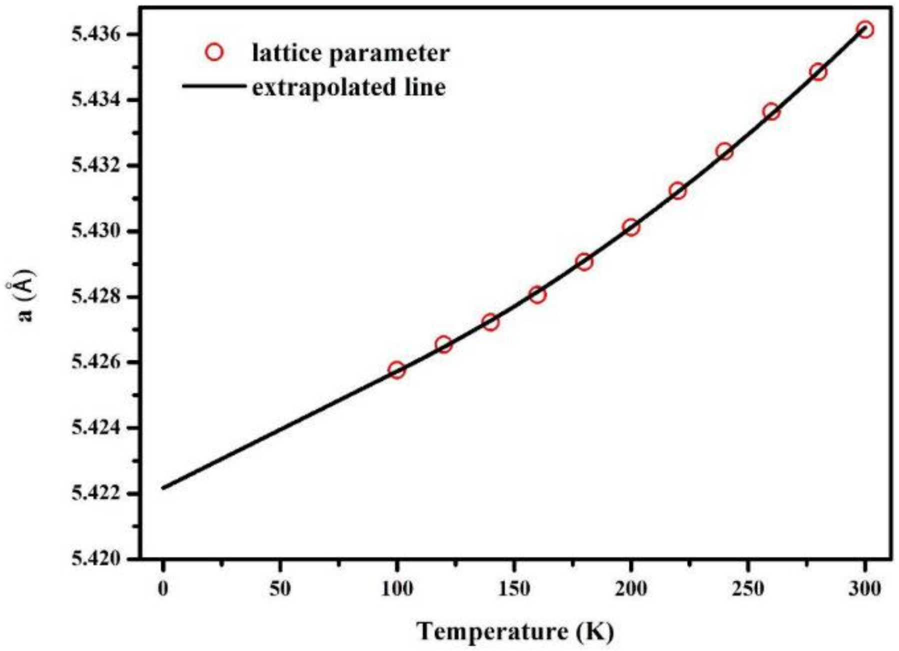


Figure S6. The lattice parameter of disordered (cubic) CTS in temperature range 300K to 100 K shown in table S1 with a parabolic fit.

Temperature	Lattice Parameter		Cell Volume	
K	a (Å)	e.s.d.	V (Å³)	e.s.d.
300	5.43614	2.80E-04	160.64699	0.02444
280	5.43485	2.70E-04	160.53262	0.02408
260	5.43364	2.70E-04	160.42521	0.02374
240	5.43243	2.60E-04	160.31784	0.02332
220	5.43123	2.60E-04	160.212	0.02292
200	5.43012	2.60E-04	160.11347	0.02256
180	5.42907	2.50E-04	160.02093	0.02225
160	5.42806	2.50E-04	159.93181	0.02196
140	5.42722	2.40E-04	159.85763	0.02156
120	5.42654	2.40E-04	159.79713	0.02133
100	5.42576	2.40E-04	159.72824	0.02095

Table S1. Lattice parameter (a) and cell volume (V) for the disordered (cubic) CTS in temperature range 300 K to 100 K.

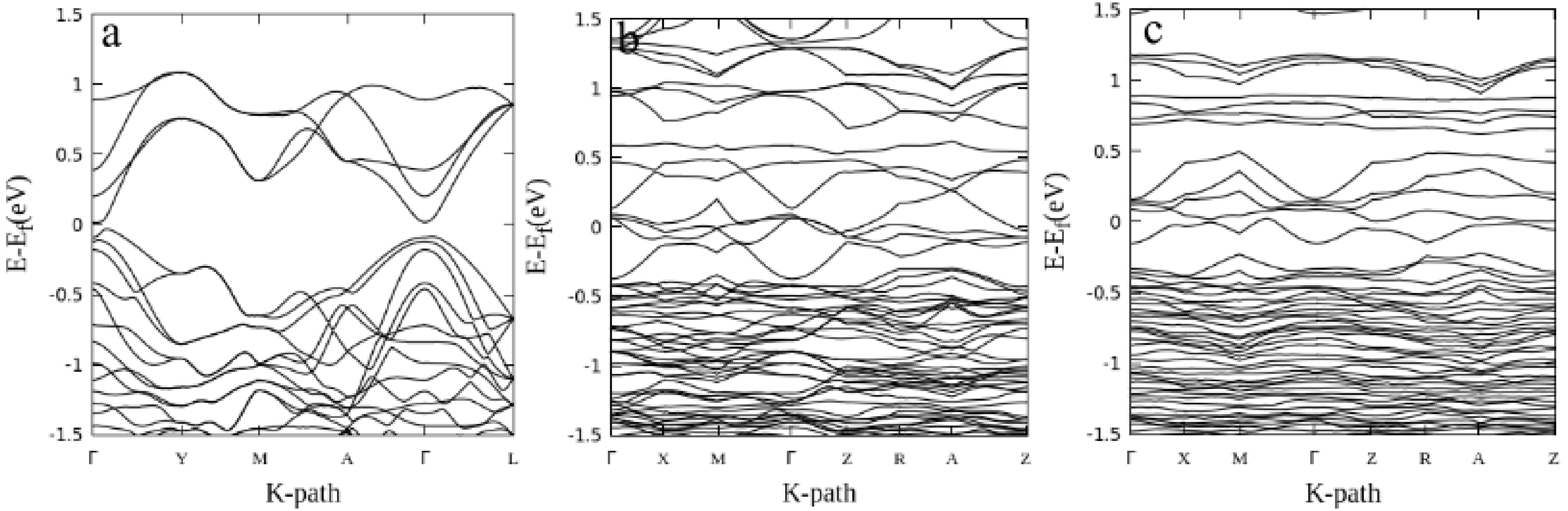


Figure S3. Band structures for ordered (a), Sn-rich disordered (b), and Sn-poor disordered (c) cells.