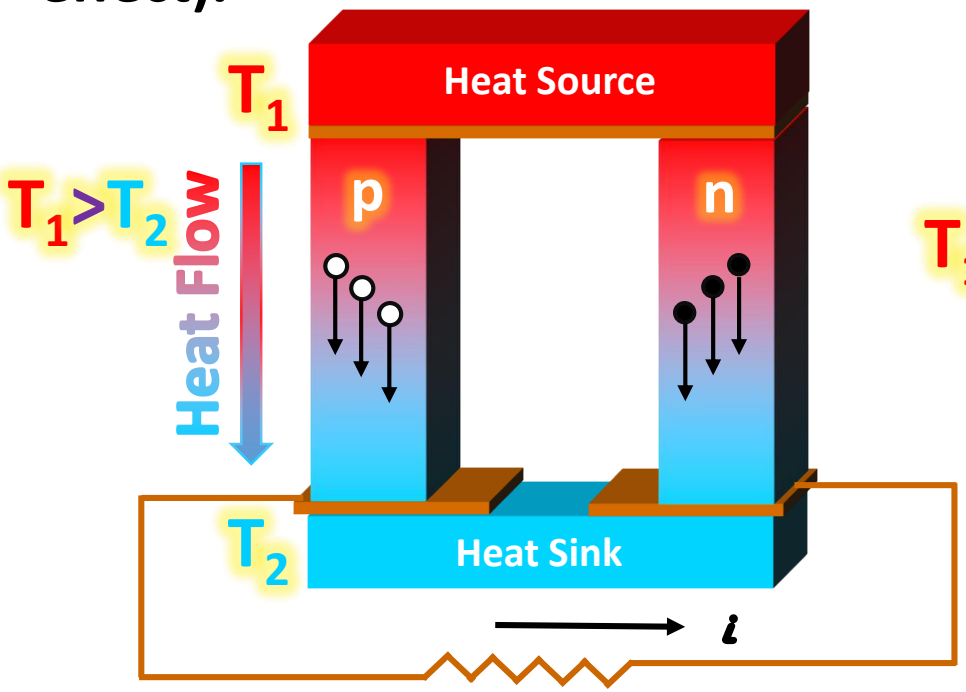
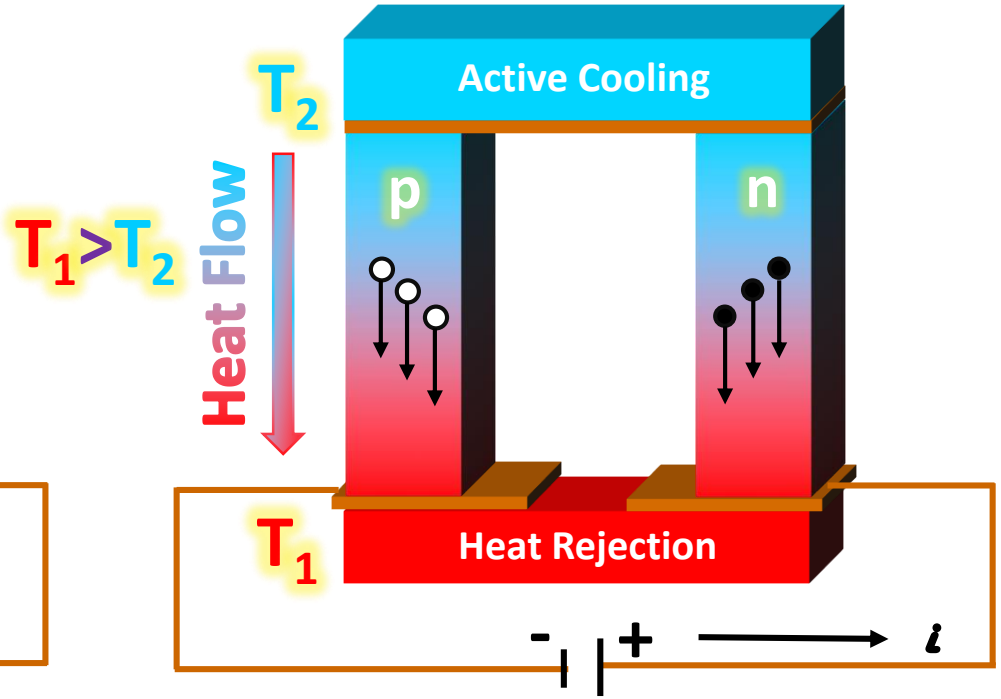
Computational Exploration of Ultralow Lattice Thermal Conductivity and High Figure of Merit in p-type Bulk RbX_2Sb (X=K, Na)

What are thermoelectric materials?

- Materials that generate electricity due to temperature difference(Seebeck effect) or flow of electricity through which result temperature difference(Peltier effect).



Seebeck Effect
"Electricity from waste-heat"



Peltier Effect
"Refrigeration without any moving part"

What are thermoelectric materials? (contd.)

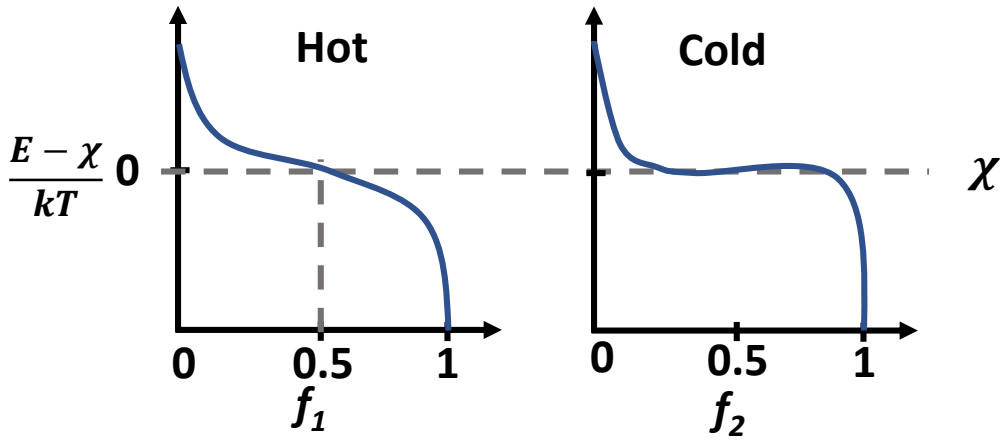
- Electricity flows due to voltage difference and voltage difference comes from the difference in electrochemical potential.
- In thermoelectric materials the voltage difference comes from the temperature difference (for Seebeck effect).

$$I = \frac{1}{q}\int_{-\infty}^{+\infty} dE\, G(E)(f_1 - f_2)$$

Current flow — Conductance

$$f_i = \frac{1}{1 + e^{(E-\chi_i)/kT_i}}$$

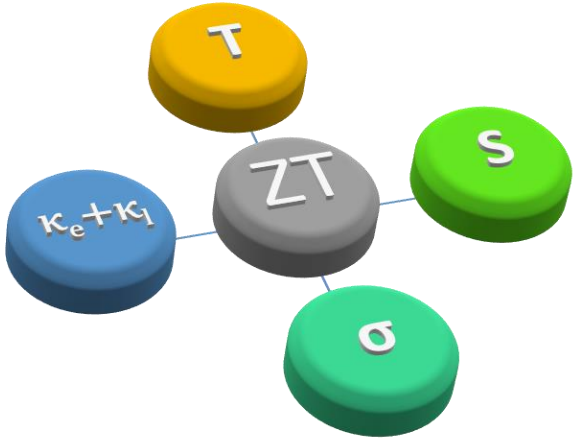
Fermi function — Electrochemical potential



Why we are interested in thermoelectric materials?

- **Major cause of global warming is the waste heat.**
- **Almost 75% of the energy produced by the mankind are squandered as waste heat.**
- **The waste heat can be used as the renewable energy source for the generation of electricity by the aid of the Seebeck effect of thermoelectric materials.**

Figure of merits



Seebeck Coefficient Electrical conductivity

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_l}$$

$S^2\sigma T$ ← Absolute Temperature

$\kappa_e + \kappa_l$ ← Lattice Thermal Conductivity

κ_e ← Electrical Thermal Conductivity

ZT ← Figure of merit

$$S = \frac{\Delta V}{\Delta T}$$ ← ability to generate voltage difference due to unit temperature difference

Interdependencies of the parameters

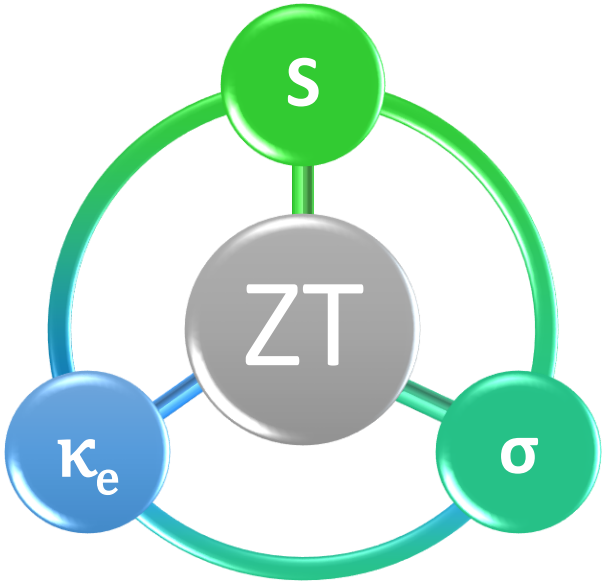
Energy Electrochemical potential

$$S(T,\chi) = \frac{\int_{-\infty}^{\infty} dE \left(-\frac{\partial f(E,T,\chi)}{\partial E}\right)\sigma(E)(E-\chi)}{qT\int_{-\infty}^{\infty} dE \left(-\frac{\partial f(E,T,\chi)}{\partial E}\right)\sigma(E)} \quad \text{...(1)}$$

$$\sigma(T,\chi) = \int_{-\infty}^{\infty} dE \left(-\frac{\partial f(E,T,\chi)}{\partial E}\right)\sigma(E) \quad \text{...(2)}$$

$$\kappa_e = \kappa_0 - T\sigma S^2 = L\sigma T \quad \text{...(3)}$$

Lorenz Constant



f(E, T, χ) ← Fermi function.

κ_0 ← Electrical thermal conductivity under closed circuit condition.

Contradictory relations between the parameters

$$S = \frac{2k_B^2 T}{3e\hbar^2}\left(\frac{\pi}{3n}\right)^{2/3} m_d^*, \quad \text{where } m_d^* \propto m_b^* = \frac{\hbar^2}{\frac{d^2 E_{edge}}{dk^2}}$$

Charge carrier concentration

DOS effective mass

band effective mass

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_l}$$

$$\sigma = \frac{ne^2\tau}{m_b^*} = ne\mu, \text{ where } \tau = \frac{m_b^* \mu}{e}$$

← Charge carrier mobility

Charge carrier relaxation time

$$\kappa_e = \kappa_0 - T\sigma S^2 = L\sigma T$$

Metal

High electrical conductivity

+

Semiconductor

High Seebeck coefficient

+

Glass

Low thermal conductivity

=> Good thermoelectric material

Our present work with bi-alkali antimonides

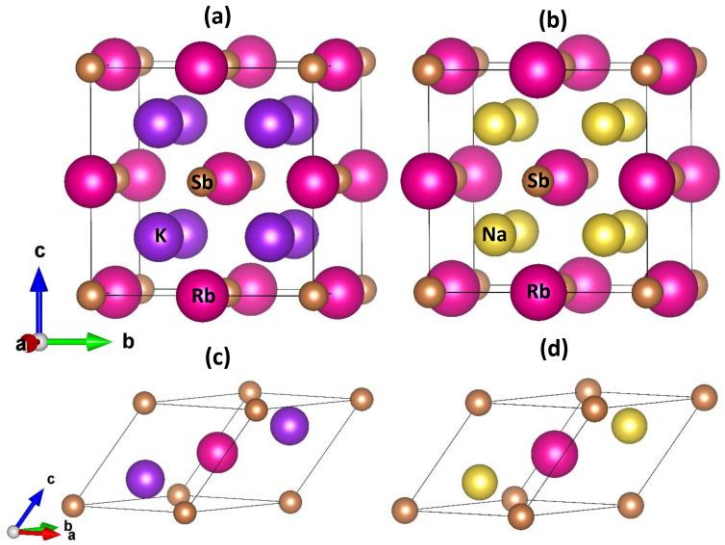


Figure 1: Conventional unit cells (a), (b) and primitive unit cells (c), (d) of RbK_2Sb and $RbNa_2Sb$, respectively

- Cubic crystal structure with space group Fm-3m (No. 225)
- 16 atoms per conventional unit cell
- 4 atoms per primitive unit cell

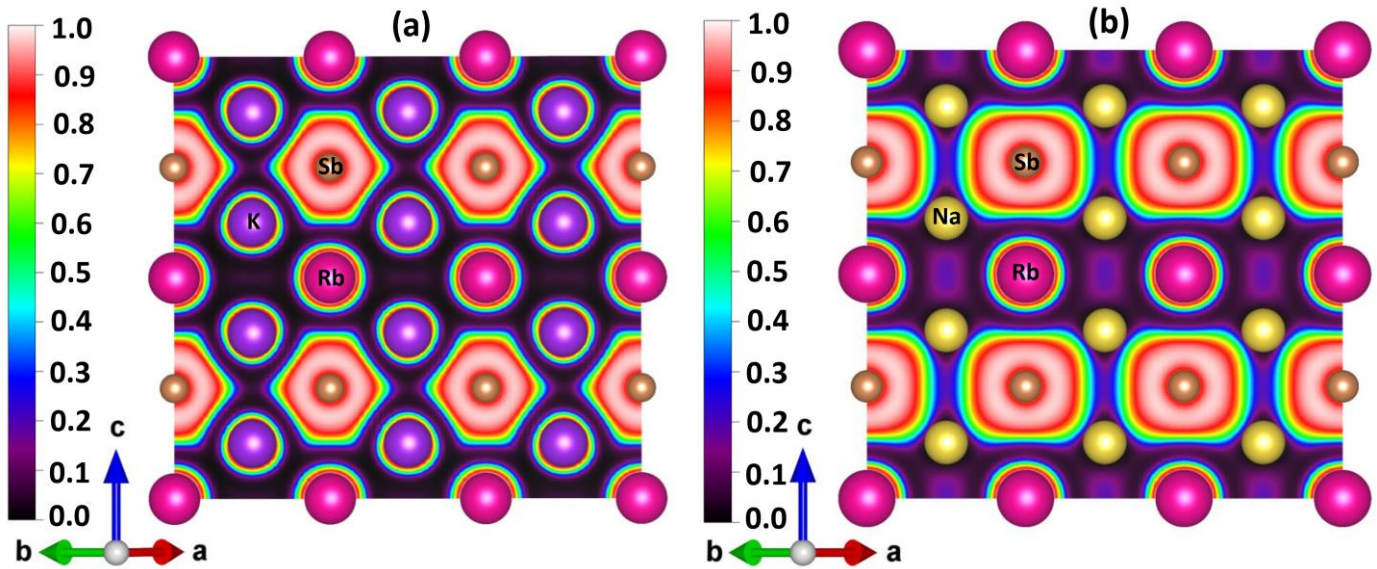


Figure 2: Electron localization function plot along the (110) plane of (a) RbK_2Sb and (b) $RbNa_2Sb$.

From Figure 2:

- Negligible ELF values between the atom pairs for both systems
- Electrons are tightly bound to the atoms resulting in very poor overlaps between the atom pairs
- Represent ionic characteristic of the bonds in both the systems

Stability of the systems

- ❖Negative formation energy (-0.41 and -0.44 eV/atom for RbK2Sb and RbNa2Sb, respectively): **Thermodynamically stable**
- ❖Thermally stable from ab Initio molecular dynamics simulation at 700 K

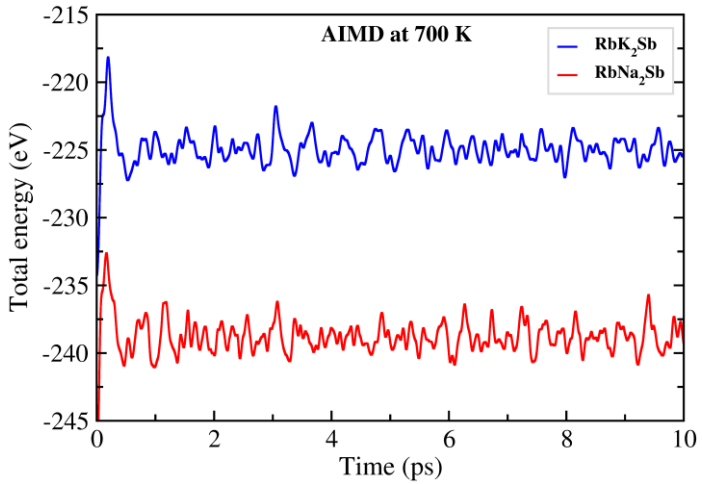


Figure 3: AIMD plot at 700 K up to 10 ps

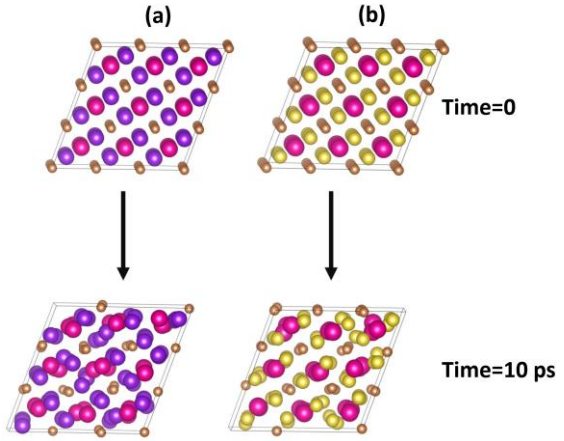


Figure 4: Structures of (a) RbK_2Sb and (b) $RbNa_2Sb$ after 10 ps of AIMD simulation.

- ❖Satisfies the Born stability criteria in terms of elastic stiffness constants: **Mechanically stable**
- ❑Born criteria for cubic systems: $C_{11}-C_{12}>0$, $C_{11}+2C_{12}>0$ and $C_{44}>0$

Stability of the systems (contd.)

❖Non-negative phonon frequencies: Dynamically stable

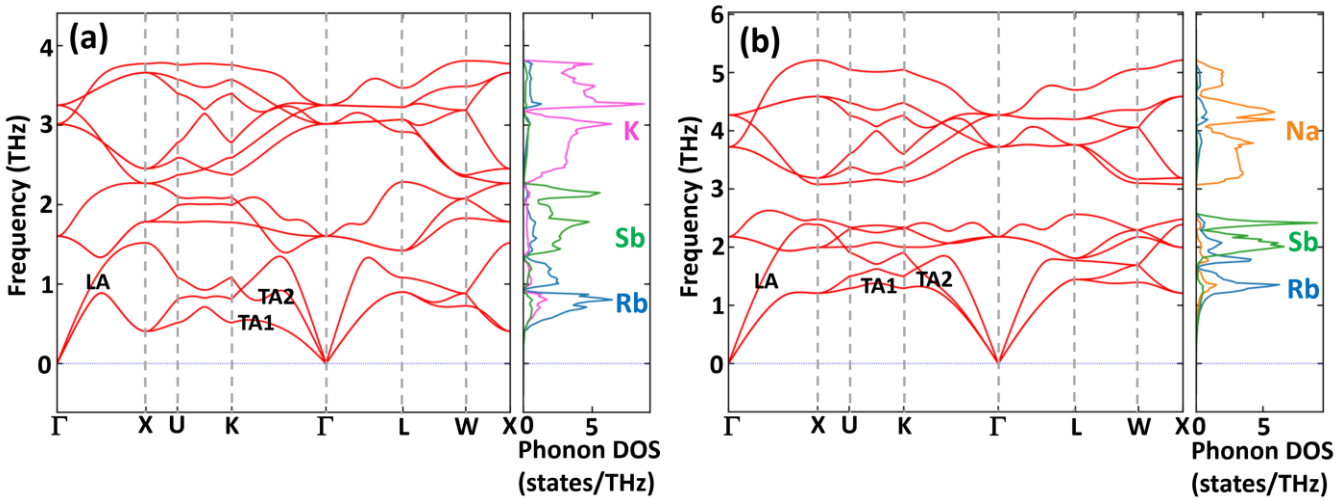


Figure 5: Phonon dispersion and phonon density of state of (a) RbK_2Sb, (b) $RbNa_2Sb$

- 4 atoms per primitive unit cell
- 3x4=12 degrees of freedom: 12 phonon modes =3 acoustic (2TA+1LA)+9 optical (3 low frequency + 6 high frequency)
- $M_K > M_{Na}$: $\omega(RbK_2Sb) < \omega(RbNa_2Sb)$
- Avoided crossing in RbK_2Sb phonon dispersion.
- Flattening of the acoustic bands of the RbK_2Sb
- In RbNa2Sb: low frequency optical and acoustic bands overlap

Electronic structure

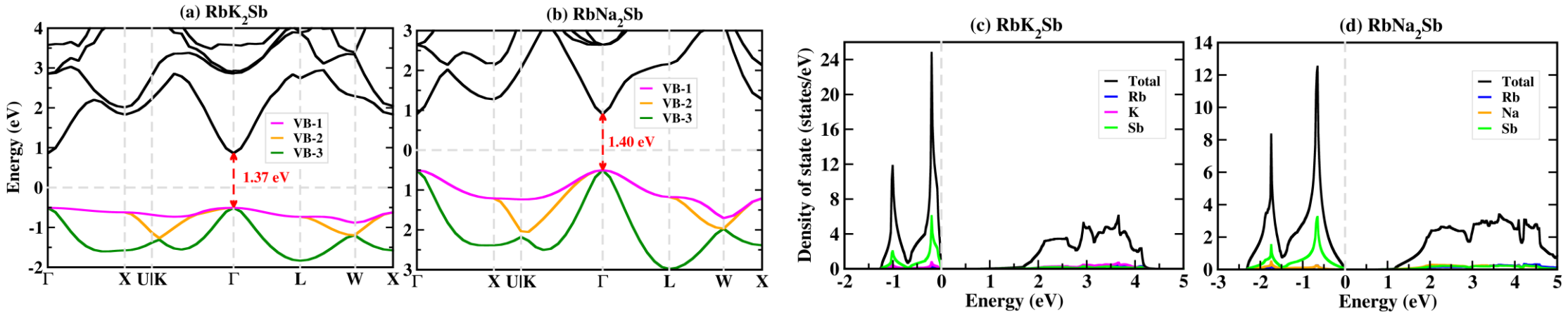


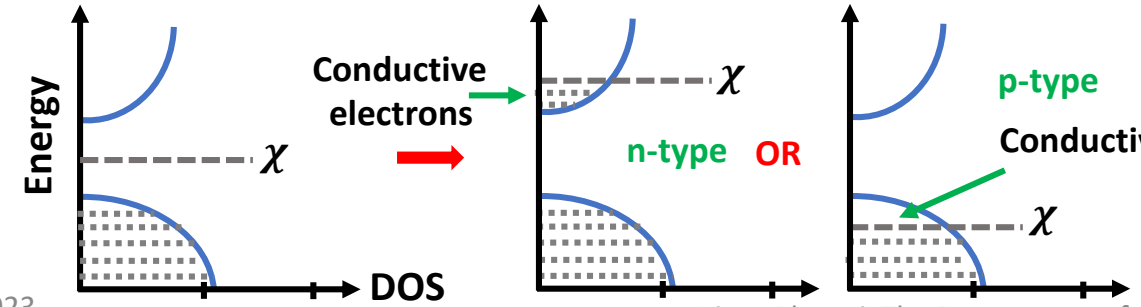
Figure 6: Electronic band structure using HSE06 functional: (a) RbK_2Sb, (b) $RbNa_2Sb$ and electronic DOS: (c) RbK_2Sb, (d) $RbNa_2Sb$

	VB-1			VB-2			VB-3		
Systems	$\Gamma \to X$	$\Gamma \to K$	$\Gamma \to L$	$\Gamma \to X$	$\Gamma \to K$	$\Gamma \to L$	$\Gamma \to X$	$\Gamma \to K$	$\Gamma \to L$
RbK_2Sb	-9.830	-8.780	-2.442	-9.830	-1.826	-2.442	-0.156	-0.169	-0.161
$RbNa_2Sb$	-0.856	-0.907	-0.877	-0.856	-0.830	-0.877	-0.112	-0.114	-0.104

Table 1: Hole effective masses (m_h^*/m_e)

	CB		
Systems	$\Gamma \to X$	$\Gamma \to K$	$\Gamma \to L$
RbK_2Sb	0.136	0.136	0.128
$RbNa_2Sb$	0.113	0.117	0.107

Table 2: Electron effective masses (m_e^*/m_e)



$$S = \frac{2k_B^2 T}{3e\hbar^2}\left(\frac{\pi}{3n}\right)^{2/3} m_d^*, \quad \text{where } m_d^* \propto m_b^* = \frac{\hbar^2}{\frac{d^2 E_{edge}}{dk^2}}$$

Thermoelectric properties

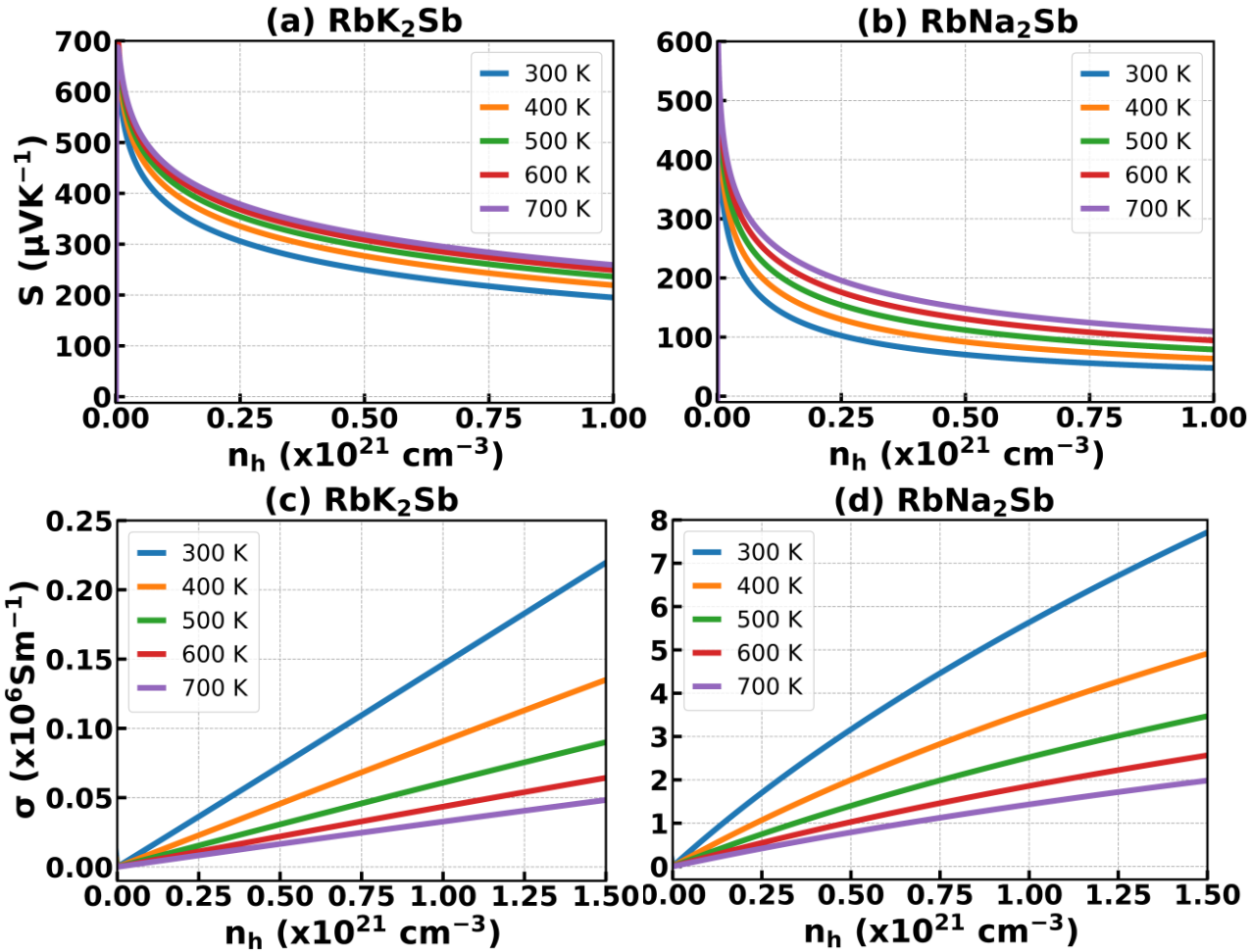


Figure 7: Seebeck coefficient of p-type (a) RbK_2Sb, (b) $RbNa_2Sb$ and electrical conductivity of p-type (c) RbK_2Sb, (d) $RbNa_2Sb$ as a function of hole concentration

	RbK_2Sb		$RbNa_2Sb$	
Temperature (K)	$\mu\ (cm^2V^{-1}S^{-1})$	$\tau\ (fs)$	$\mu\ (cm^2V^{-1}S^{-1})$	$\tau\ (fs)$
300	2.28	12.8	451.38	220
400	1.48	8.3	291.35	142
500	1.05	5.9	209.28	102
600	0.80	4.5	157.98	77
700	0.64	3.6	125.15	61

Table 3: Hole mobilities and relaxation times

$$S = \frac{2k_B^2T}{3e\hbar^2}\left(\frac{\pi}{3n}\right)^{2/3}m_d^*, \quad \text{where } m_d^* \propto m_b^*$$

$$\sigma = \frac{ne^2\tau}{m_b^*} = \frac{ne^2\mu}{e}, \text{ where } \tau = \frac{m_b^*\mu}{e}$$

$$\kappa_e \propto \sigma$$

Thermoelectric properties (contd.)

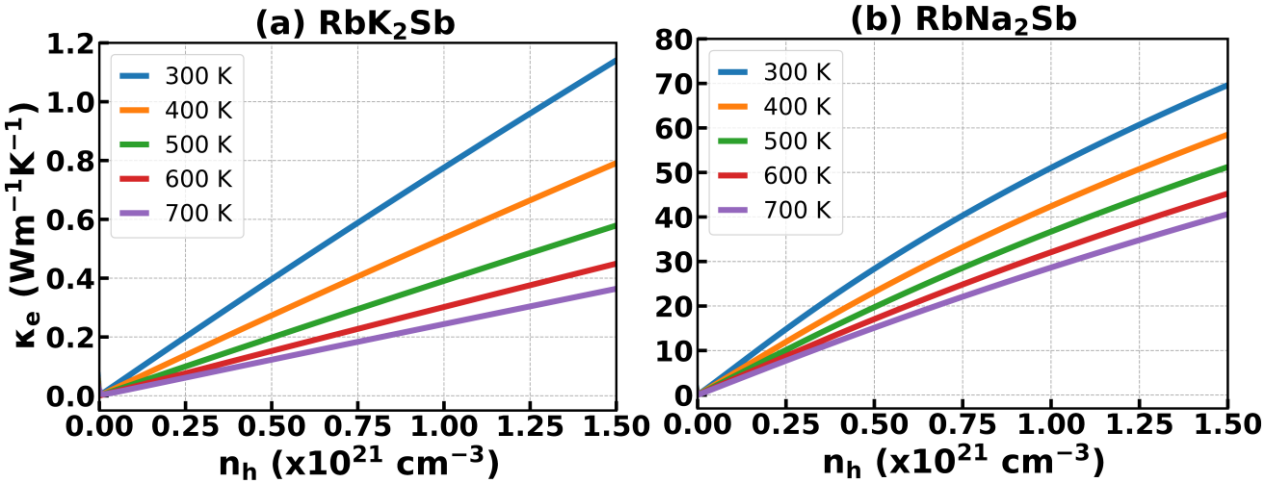


Figure 8: Electronic thermal conductivity of p-type (a) RbK_2Sb, (b) $RbNa_2Sb$ as function of hole concentration

$$\kappa_e \propto \sigma \qquad ZT=\frac{S^2\sigma T}{\kappa_e+\kappa_l}$$

Lattice thermal conductivity

Specific heat at constant volume

$$\kappa_l(T) = \frac{1}{3} < \tau >< v_g^2 > C_v(T)$$

Average relaxation time

Mean square group velocity

Systems	300 K	400 K	500 K	600 K	700 K
RbK_2Sb	0.35087	0.26307	0.21044	0.17536	0.15031
$RbNa_2Sb$	0.53243	0.39974	0.31997	0.26673	0.22868

Table 5: Lattice thermal conductivities at different temperatures

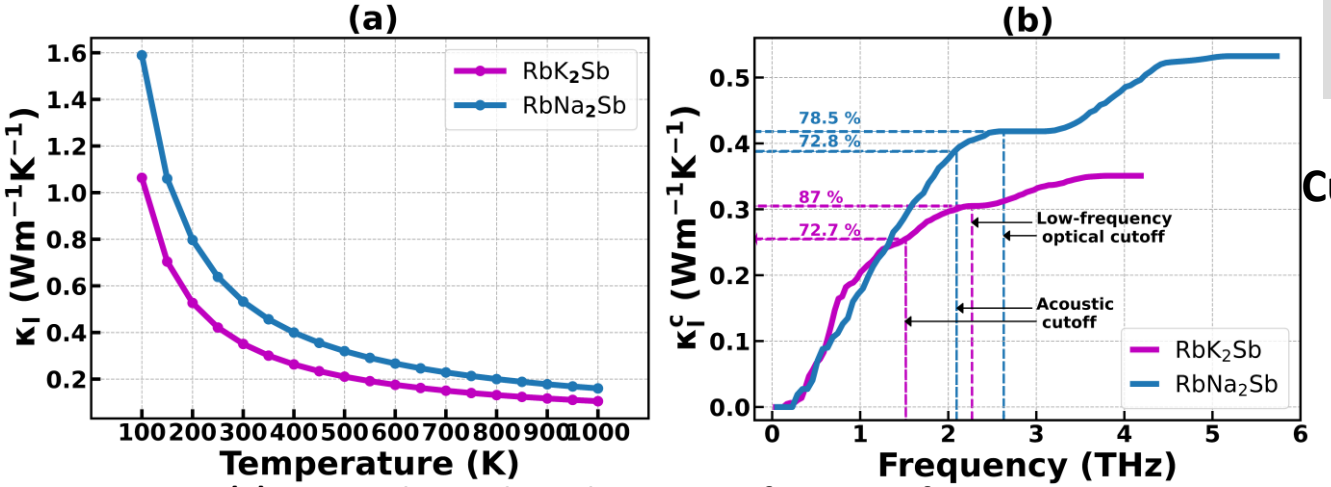


Figure 9: (a) Lattice thermal conductivity as function of temperature (b) Cumulative lattice thermal conductivity as function of frequency

Cumulative lattice thermal conductivity

Mode specific phonon frequency

$$\kappa_l^c(\omega) = \int_0^{\omega} \frac{1}{N}\sum_s \kappa_{l,s}\delta(\omega_s - \omega')d\omega'$$

Contribution to lattice thermal conductivity from phonon mode *s*

Thermoelectric properties (contd.)

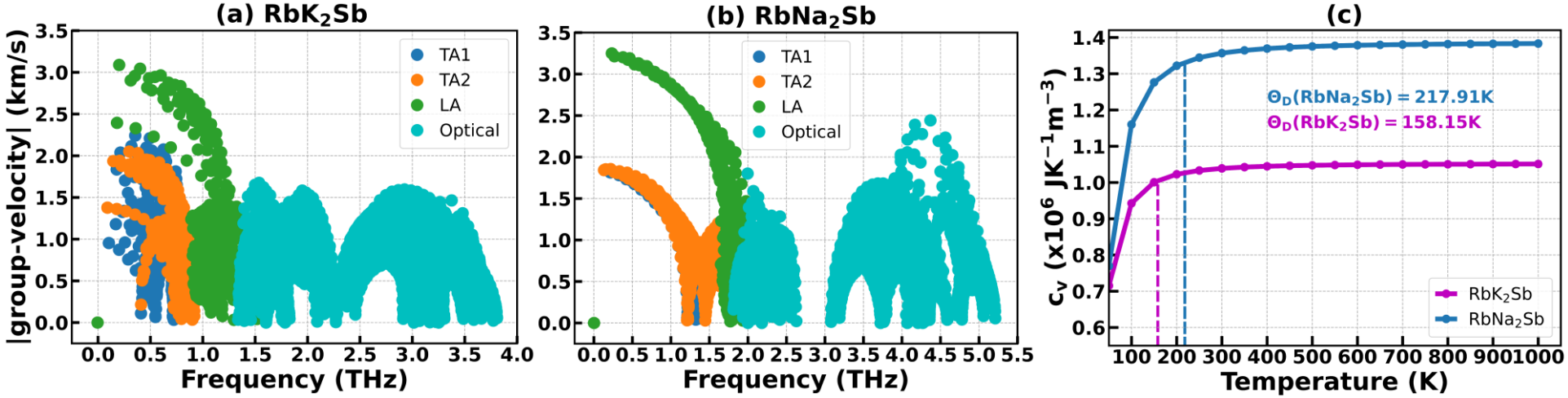


Figure 10: Mode specific group velocity as a function of phonon frequency for (a) RbK2Sb, (b) RbNa2Sb. (c) Specific heat at constant volume as a function of temperature

Debye temperature is the Temperature of the crystal's Highest normal vibrational mode, i.e., above θ_D all the phonons get excited.

Systems	$v_{g,LA}$(km/s)	$v_{g.TA1}$(km/s)	$v_{g,TA2}$(km/s)
RbK_2Sb	3.08	2.24	2.05
$RbNa_2Sb$	3.25	1.85	1.86

Table 6: Maximum mode specific group velocities at the vicinity of the Γ-point

Comparable and even lower than many TE materials reported earlier like 2D α-Te (>4 km/s), $Ti_{3-x}Mo_xC_2T_2$(x=0.5,1,1.5,2.5,2.5, T=-OH/-O/-F)(>6 km/s), 2D BP/MoS2 vdW hetero-bilayer(>12 km/s) etc.

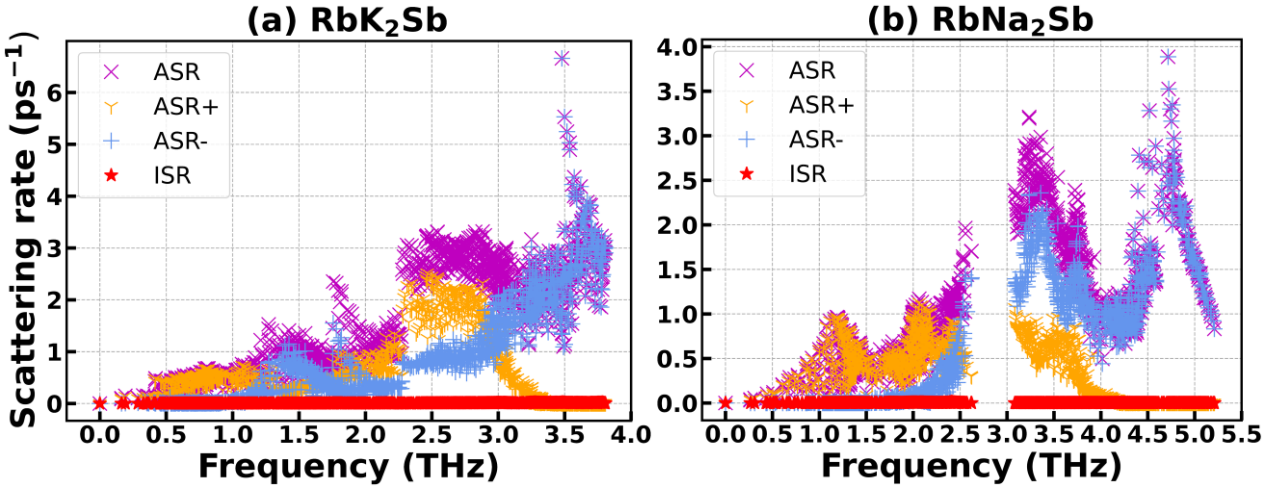


Figure 11: Scattering rates as functions of phonon frequency for (a) RbK_2Sb, (b) $RbNa_2Sb$

Thermoelectric properties (contd.)

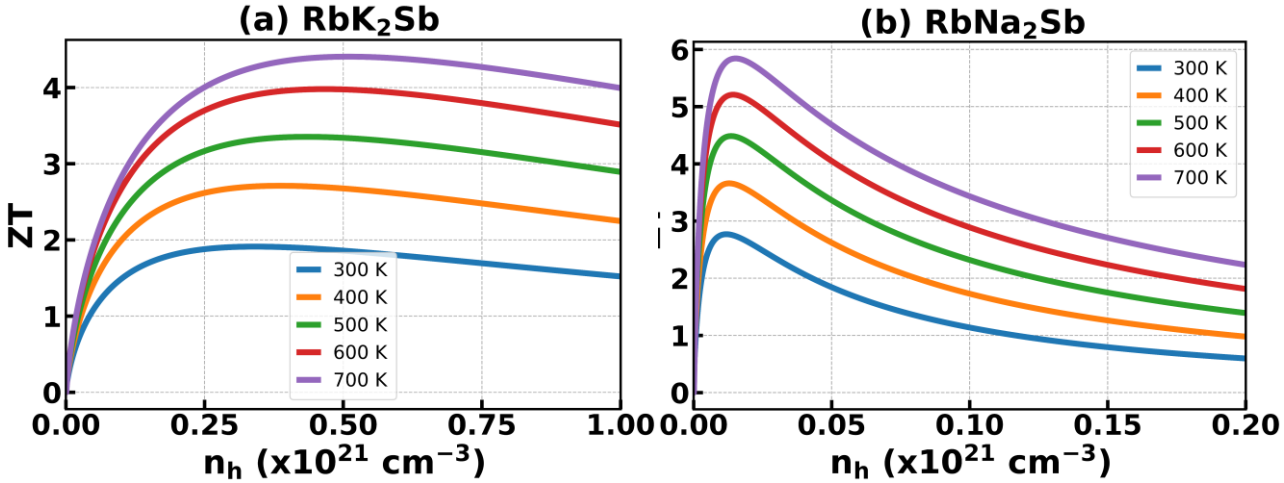


Figure 12: ZT as function of hole concentration at the temperature range 300-700 K for (a) RbK_2Sb, (b) $RbNa_2Sb$

Systems	300 K	400 K	500 K	600 K	700 K
RbK_2Sb	1.91	2.71	3.35	3.97	4.40
$RbNa_2Sb$	2.76	3.65	4.48	5.20	5.84

Table 7: $(ZT)_{max}$ for p-type RbK2Sb and RbNa2Sb at the temperature range 300-700 K

(ZT)max for other full-Heusler compounds reported earlier:

- **n- and p-type Ba_2AuBi shows ZT as high as 5 and 2 at 800 K** [1]
- **Predicted ZT for n-type Sr_2BiAu is 4.9 at 700 K** [2]
- **Predicted ZT for n-type Sr_2SbAu is 3.4 at 750 K** [2]
- **ZT for n-type Sr_2AsAu is 3.3 at 700 K** [3]

Conclusion:

The bi-alkali antimonides, we have studied can be considered as better thermoelectric materials as compared to the other full-Heusler compounds

References and acknowledgments

References:

[1] Park, J.; Xia, Y.; Ozoli¸nˇs, V. High Thermoelectric Power Factor and Efficiency from a Highly Dispersive Band in Ba2BiAu. *Phys. Rev. Appl.* **2019**, *11*, 014058.

[2] Park, J.; Xia, Y.; Ganose, A. M.; Jain, A.; Ozoli¸nˇs, V. High Thermoelectric Performance and Defect Energetics of Multipocketed Full-Heusler Compounds. *Phys. Rev. Appl.* **2020**, *14*, 024064.

[3] Wang, W.; Dai, Z.; Wang, X.; Zhong, Q.; Zhao, Y.; Meng, S. Low Lattice Thermal Conductivity and High Figure of Merit in n-type Doped Full-Heusler Compounds X2YAu (X= Sr, Ba; Y= As, Sb). *Int. J. Energy Res.* **2021**, *45*, 20949-20958.

Acknowledgements: We sincerely acknowledge the financial supports from CSIR (HRDG), Government of India [sanction no.01(3086)/21/EMR-II]. We also sincerely acknowledge the financial supports from UGC-BSR Mid-Career, Government of India [sanction no. F.19-257/2021(BSR)]. Myself sincerely acknowledge CSIR (HRDG), Government of India for providing me the JRF NET fellowship [sanction no. 09/202(0114)/2020-EMR-I].

THANK YOU