

Thomson effect facilitates thermoelectric cooling

Journal:	<i>Materials Lab</i>
Manuscript ID	MATLAB-2024-0017
Manuscript Type:	Highlight
Date Submitted by the Author:	13-Dec-2024
Complete List of Authors:	Liu, Suyao; Beihang University, School of Materials Science and Engineering Qin, Bingchao; Beihang University, School of Materials Science and Engineering Zhao, Li-Dong; Beihang University, School of Materials Science and Engineering
Keywords:	Thomson effect, Entropy change, Thermoelectric cooling, Seebeck coefficient
Speciality:	Thermoelectrics, Energy Generation & Conversion

SCHOLARONE™
Manuscripts

Thomson effect facilitates thermoelectric cooling

Suyao Liu, Bingchao Qin*, Li-Dong Zhao*

School of Materials Science and Engineering, Beihang University, Beijing 102206, China

Corresponding author: qinbingchao@buaa.edu.cn; zhaolidong@buaa.edu.cn

Abstract

Thermoelectric technology is attracting increasing attention due to its application advantages in fields of waste heat recycling and solid-state cooling. Traditional thermoelectric cooling mainly depends on the Peltier effect, but its cooling capacity at cryogenic temperatures has been limited. Recent research conducted by Chen *et al.* has emphasized the potential of leveraging Thomson effect in thermoelectric cooling to attain substantial temperature drops. While conventional materials exhibit limited Thomson cooling due to insufficient change in carrier entropy, they found the electron phase transition in YbInCu_4 directly regulates the entropy of carriers, resulting in a significant enhancement of the temperature-normalized Thomson coefficient. This resulted in a stable temperature difference of over 5 K at about 38 K and a $\Delta T_{\text{max}}/T_{\text{hot}}$ value of about 15%, comparable to a conventional Peltier cooler at near-room temperatures. Here, we highlight that the approach goes beyond traditional focus solely on increasing ZT , and the results reveal the potential of solid-state thermoelectric cooling in cryogenic applications. Moreover, it opens up possibility of developing more efficient Thomson coolers by investigating other materials with strong electron interactions.

Keywords

Thomson effect, Entropy change, Thermoelectric cooling, Seebeck coefficient

Main text

Thermoelectrics is a specialized type of heat engine or pump that ingeniously employs charge carriers within materials as its working medium^[1]. By harnessing the entropy changes during its operational process, it achieves the mutual conversion between thermal and electrical energy, thereby creating a silent, vibration-free, and emission-less solid-state technology with widespread applications in fields such as power generation and electronic cooling^[2].

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record.

The Peltier Thomson effects constitute two fundamental theoretical bases of thermoelectric cooling, and the maximum cooling temperature difference ΔT_{\max} attainable through their synergistic action can be mathematically derived from a specific formula^{[3, 4][6, 7]}:

$$\Delta T_{\max} = \Delta T_{\max}^{\text{P}} + \Delta T_{\max}^{\text{T}} = \frac{1}{2} ZT_{\text{cold}}^2 + \frac{1}{4} ZT_{\text{hot}} T_{\text{cold}} \ln\left(\frac{S_{\text{hot}}}{S_{\text{cold}}}\right) \quad (1)$$

in which ZT and S represent the dimensionless figure of merit at cold (T_{cold}) or hot (T_{hot}) end temperatures and Seebeck coefficient. The Peltier effect demonstrates that the flow of charges induced by an electric current, resulting from a mismatch in chemical potentials, leads to an entropy variation at the interface between the thermoelectric material and electrode. This variation facilitates the extraction of heat at the cold junction.^[5, 8] Enhancing the dimensionless figure of merit ZT ($ZT = S^2\sigma T/(\kappa)$, in which σ and κ refer to the electrical conductivity and thermal conductivity) has become the ultimate goal in maximizing the temperature difference of Peltier coolers^[6]. However, for decades, no thermoelectric cooler has been able to achieve a cooling effect with a ΔT greater than 3 K at cryogenic temperatures of below 50 K.

Based on the Peltier effect and guided by thermodynamic principles, William Thomson predicted that the cooling effect extends not merely at the junctions but throughout the entire material^[7], as schematically shown in **Fig. 1a**. This overall effect, which entails entropy changes of charge carriers within thermoelectric materials, fundamentally amplifies cooling capabilities. Achieving substantial Thomson cooling capacity theoretically necessitates a material that exhibits a notable variation in the Seebeck coefficient, particularly between the designated hot (S_{hot}) and cold (S_{cold}) ends within the material.^[3] The significant difference observed indicates that the material has a substantial temperature-normalized Thomson coefficient (dS/dT) ^[6], which measures the degree of variation in the Seebeck coefficient along the temperature gradient from the hot to the cold end. Nevertheless, in standard thermoelectric materials, the changes in carrier entropy driven by temperature gradients are generally too small to generate a significant Thomson cooling effect, characterized by a dS/dT value less than $2\mu\text{V K}^{-2}$.^[8] Recently, Chen et al., in *Nature Materials*, have been inspired by conventional refrigeration systems that use working fluids experiencing phase transitions. They have exploited the phase changes of charge carriers (functioning as the operative medium) within materials to attain substantial entropy alterations.^[9] This approach significantly enhanced the

 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

contribution of Thomson effect to overall cooling, resulting in a considerable increase in the whole cooling temperature difference.

Current researches have been primarily focusing on enhancing Thomson effect by inducing rapid temperature-dependent variations in the Seebeck coefficient through lattice^[10] or magnetic phase transitions^[8, 11]. However, these types of phase transitions predominantly influence atomic configurational entropy or magnetic entropy changes, exerting limited influence on electronic entropy changes. Consequently, they are insufficient for achieving a significant temperature-normalized Thomson coefficient. To date, the sole measurements reported in literatures regarding Thomson coolers have demonstrated a $\Delta T_{\max}/T_{\text{hot}}$ value of merely 0.01%, which corresponds to a $\Delta T_{\max} = 30$ mK at $T_{\text{hot}} = 300$ K^[8]. Additionally, these phase transitions often pose additional challenges in terms of performance stability and mechanical integrity, making them unreliable for potential applications.

Chen *et al.* have discovered a unique electronic phase transition in YbInCu₄ that directly influenced the entropic state of charge carriers. Consequently, the temperature-normalized Thomson coefficient ($\tau/T = dS/dT$) underwent a substantial increase, reaching a peak magnitude of ~ 10 $\mu\text{V K}^{-2}$. Further investigation unveiled that this electronic phase transition was precipitated by a sudden shift in the hybridization dynamics between the itinerant and localized $4f$ electrons of the Yb element. Resultantly, the stable cooling temperature difference in devices was realized, starting from approximately 38 K and extending over a range of more than 5 K, which corresponded to a $\Delta T_{\max}/T_{\text{hot}}$ value of approximately 15%. This cooling performance was comparable to that of traditional Peltier coolers, which can attain a $\Delta T_{\max}/T_{\text{hot}}$ ratio of around 20% (ΔT_{\max} of ~ 60 K at T_{hot} of 300 K)^[6]. Moreover, at cryogenic temperatures, this novel thermoelectric cooler exhibits a substantially superior performance compared to the current state-of-the-art Peltier cooler based on Bi_{1-x}Sb_x alloys^[6], as shown in **Fig. 1b**, demonstrating important application prospects in electronic cooling by utilizing Thomson effect.

While numerous investigations on thermoelectrics have been mainly focusing on merely increasing the ZT value to enhance the device efficiency, the study by Chen *et al.*, leveraging unique electronic phase transitions and Thomson effect, introduced a novel strategy to enhance the performance of thermoelectric coolers. Furthermore, it revealed the significant potential of solid-state thermoelectric cooling in cryogenic applications. Besides YbInCu₄, there could be other materials featuring robust electronic interactions that exhibit electronic phase transitions at or significantly

below room temperature. These materials hold promise for enabling the advancement of more efficient Thomson cooling technologies, thereby catering to practical applications across a diverse temperature range. This research not only validates an innovative approach within the thermoelectric cooling domain, but also provides comprehensive insights into the immense and untapped potential of this methodology for future applications, thereby paving the way for novel advancements and innovations in the field of solid-state cooling.

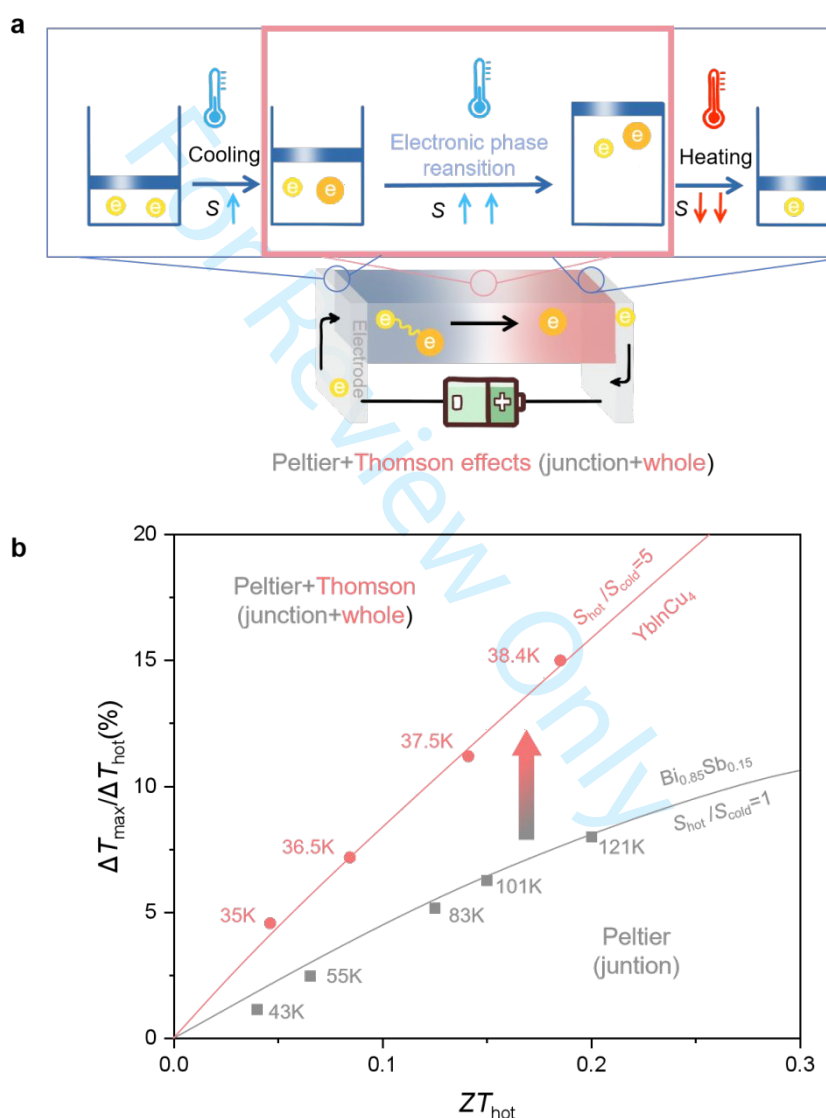


Figure 1. Thomson effect facilitates thermoelectric cooling. **a**, Schematic of enhanced thermoelectric cooling by combining the Peltier and Thomson effects. **b**, Large improvement in the relative cooling temperature difference ($\Delta T_{max}/T_{hot}$) compared with that of state-of-the-art $Bi_{1-x}Sb_x$ -based Peltier coolers^[6]. Figures were redrawn from reference^[9].

Acknowledgments

This work was supported by the National Science Fund for Distinguished Young Scholars (51925101) and Tencent Xplorer Prize, the National Natural Science Foundation of China (52450001 and 22409014), the China National Postdoctoral Program for Innovative Talents (BX20230456), and China Postdoctoral Science Foundation (2024M754057).

Conflict of interest

The authors declare no conflict of interest.

Author contributions

This highlight was drafted by Suyao Liu and revised by Dr. Bingchao Qin and Prof. Li-Dong Zhao. All authors have approved the final version of the manuscript.

References

- [1] Qin, B.; Kanatzidis, M. G.; Zhao, L.-D. *Science*, 2024, 386, 6719.
- [2] Zhang, Q.; Deng, K.; Wilkens, L.; Reith, H.; Nielsch, K. *Nat. Electron.*, 2022, 5, 6.
- [3] Snyder, G. J.; Toberer, E. S.; Khanna, R.; Seifert, W. *Phys. Rev. B*, 2012, 86, 4.
- [4] Goldsmid, H. J. *<Introduction to Thermoelectricity>*. 2009, 121.
- [5] Qin, Y.; Qin, B.; Wang, D.; Chang, C.; Zhao, L.-D. *Energy Environ. Sci.*, 2022, 15, 11.
- [6] Mao, J.; Chen, G.; Ren, Z. *Nat. Mater.*, 2021, 20, 4.
- [7] Thomson, W. *P Roy Soc Edinb*, 1857, 3, 4.
- [8] Modak, R.; Murata, M.; Hou, D.; Miura, A.; Iguchi, R.; Xu, B.; Guo, R.; Shiomi, J.; Sakuraba, Y.; Uchida, K.-i. *Appl. Phys. Rev.*, 2022, 9, 1.
- [9] Chen, Z.; Zhang, X.; Zhang, S.; Luo, J.; Pei, Y. *Nat. Mater.*, 2024, <https://doi.org/10.1038/s41563-024-02039-z>.
- [10] Byeon, D.; Sobota, R.; Delime-Codrin, K.; Choi, S.; Hirata, K.; Adachi, M.; Kiyama, M.; Matsuura, T.; Yamamoto, Y.; Matsunami, M. *Nat. Commun.*, 2019, 10, 1.
- [11] Nakagawa, K.; Yokouchi, T.; Shiomi, Y. *Sci. Rep.*, 2021, 11, 1.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

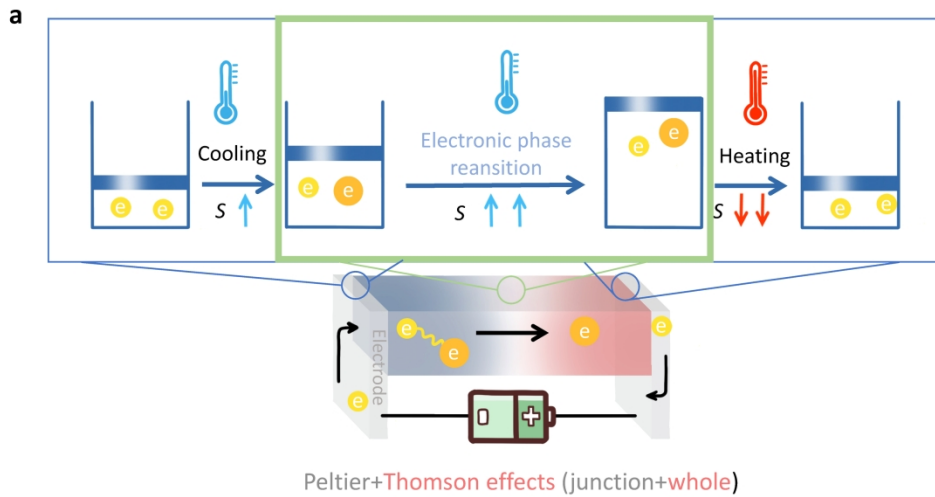
This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record.

Accepted Article

For Review Only

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record.



Peltier+Thomson effects (junction+whole)

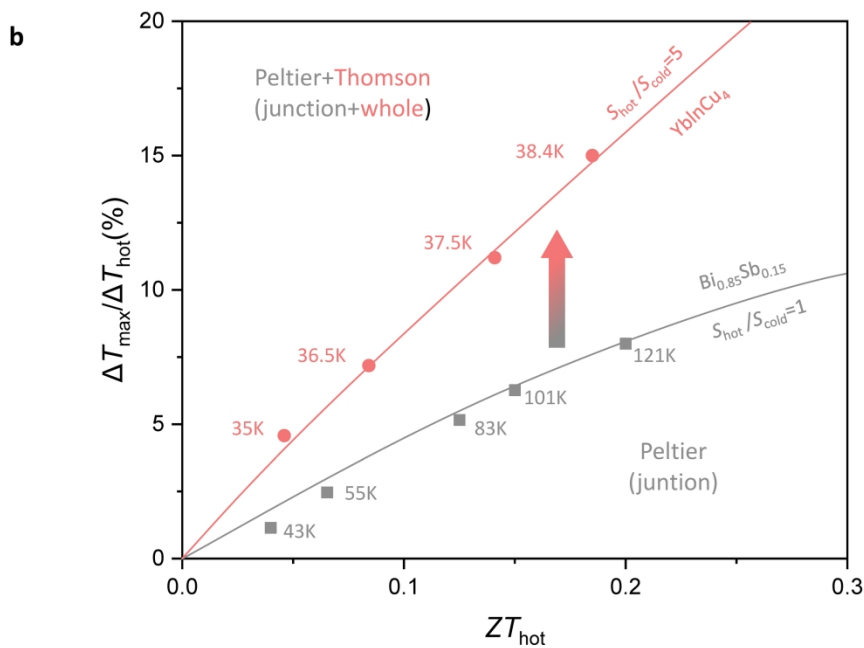


Figure 1

242x297mm (300 x 300 DPI)