Paper ID: MS-231

Unusually High Thermoelectric Figure of Merit in Monocrystalline Metallic Vanadium Dioxide Nanobeams and Its Potential as a Thermoelectric Material

MD. Samirul Islam[1], Md. Mujahid Ul Islam[1], Md. Firojjaman[1], Tauhidur Rahman[1], Sadat Rafi[2]

[1]Department of Mechanical Engineering, Rajshahi University of Engineering and Technology, Rajshahi-6204, Bangladesh
[2]Department of Electrical and Electronic Engineering, Rajshahi University of Engineering and Technology, Rajshahi-6204, Bangladesh
E-mail: samirulislamratul@gmail.com

Abstract

The thermoelectric figure of merit (ZT) is a dimensionless term which indicates the ability of a material to efficiently produce thermoelectric power and it depends on the material's Seebeck coefficient, electrical conductivity, thermal conductivity and temperature. For a higher efficiency, a high thermoelectric figure of merit is desired and for that Seebeck coefficient, electrical conductivity and temperature need to be high and thermal conductivity needs to be low. Due to the violation of Wiedemann-Franz law, in the absence of quasi-particles, monocrystalline metallic Vanadium Dioxide (VO_2) follows the above illustration which gives it an unusually high value of ZT. This makes VO_2 an efficient thermoelectric material. This paper thoroughly discusses the reasons behind this anomalously high value of ZT and explores the prospects of VO_2 as an efficient thermoelectric material for thermocouples and thermoelectric coolers.

Keywords: Vanadium Dioxide, Wiedemann-Franz law, thermoelectric figure of merit, Ansys.

1. Introduction

Thermoelectric phenomena arise out of the intercoupled electrical and thermal currents in a material. The thermoelectric effect is the direct conversion of temperature differences to electric voltage and vice versa. A thermoelectric device creates voltage when there is a different temperature on each side. Conversely, when a voltage is applied to it, it creates a temperature difference. At the atomic scale, an applied temperature gradient causes charge carriers in the material to diffuse from the hot side to the cold side [1]. This effect can be used to generate electricity, measure temperature or change the temperature of objects. Because the direction of heating and cooling is determined by the polarity of the applied voltage, thermoelectric devices can be used as temperature controllers.

The term "thermoelectric effect" encompasses three separately identified effects: the Seebeck effect, Peltier effect, and Thomson effect. Seebeck effect is the production of an electromotive force and consequently an electric current in a loop of material consisting of at least two dissimilar conductors when two junctions are maintained at different temperatures. Peltier effect is the cooling of one junction and the heating of the other when electric current is maintained in a circuit of material consisting of two dissimilar conductors. Thomson effect is the evolution or absorption of heat when electric current passes through a circuit composed of a single material that has a temperature difference along its length. This transfer of heat is superimposed on the common production of heat associated with the electrical resistance to currents in conductors.

Thermoelectric effects are correlated to thermoelectric figure of merit. The ability of a given material to efficiently produce thermoelectric power is related to its dimensionless figure of merit (ZT) [1] expressed as,

$$ZT = \sigma S^2 T / k \tag{1}$$

which depends on the Seebeck coefficient *S*, thermal conductivity *k*, electrical conductivity σ, and temperature T. The Seebeck coefficient of a material is a measure of the magnitude of an induced thermoelectric voltage in response to a temperature difference across that material, as induced by the Seebeck effect. The SI unit of the Seebeck coefficient is volts per kelvin (V/K), although it is more often given in microvolts per kelvin (μV/K) [2].

Thermoelectric effects are utilized in various thermoelectric devices like thermocouples, thermoelectric generators (TEG), thermoelectric coolers or peltier coolers (TEC) etc. Materials with a high figure of merit is desired in these devices as thermoelectric efficiency depends on the figure of merit, ZT [3]. An unusually high thermoelectric figure of merit can be observed in monocrystalline metallic Vanadium Dioxide (VO_2) compared to other common metals and alloys [6] which opens the door to the possibility of designing better thermoelectric devices.

2. Figure of merit of VO_2 and violation of Wiedemann-Franz law

There is no theoretical upper limit to ZT, and as ZT approaches infinity, the thermoelectric efficiency approaches the Carnot limit. However, no known thermoelectric material has a ZT > 3 [3]. In metals, thermal conductivity approximately tracks electrical conductivity according to the Wiedemann–Franz law, as freely moving valence electrons transfer not only electric current but also heat energy. However, the general correlation between electrical and thermal conductance does not hold for other materials, due to the increased importance of phonon carriers for heat conduction in non-metals. The Wiedemann–Franz law states that the ratio of the electronic contribution of the thermal conductivity (κ) to the electrical conductivity (s) of a metal is proportional to the temperature (T) [4].

$$\frac{k}{\sigma} = LT \tag{2}$$

Theoretically, the proportionality constant L, known as the Lorenz number, is equal to

$$L = \frac{k}{\sigma T} = 2.44 \text{ x } 10^{-8} \text{ W}\Omega\text{K-2} \tag{3}$$

Experiments have shown that the value of L, while roughly constant, is not exactly the same for all materials. Kittel gives some values of L ranging from $L = 2.23 \times 10^{-8}$ $W\Omega K^{-2}$ for copper at 0 °C to $L = 3.2\times10^{-8}$ $W\Omega K^{-2}$ for tungsten at 100 °C [5]. For a metal to have a high thermoelectric figure of merit, it is required to have high electrical conductivity and low thermal conductivity. But in electrically conductive solids, the Wiedemann-Franz law requires the electronic contribution to thermal conductivity to be proportional to electrical conductivity which limits the figure of merit. A large violation of the Wiedemann–Franz law near the metal-insulator transition (MIT) phase at the temperature range of 240K to 340K in Mono crystalline Metallic Vanadium Dioxide Nanobeams was reported. Anomalously low electronic thermal conductivity was observed in correspondence with the electrical conductivity. The unusually low electronic thermal conductivity is a signature of the absence of quasi particles in a strongly correlated electron fluid where heat and charge diffuse independently [6]. In a Fermi liquid, the same quasi particles that transport charge also carry heat. Therefore, in most normal metals the charge and heat conductivities are related via the Wiedemann-Franz law. But in the case of VO_2, The violation of the Wiedemann–Franz law is attributed to the formation of a strongly correlated, incoherent non-Fermi liquid, in which charge and heat are independently transported [6]. VO_2 undergoes the metal-insulator transition at 340 K, accompanied by a first-order structural phase transition from the monoclinic insulating (I) phase to the tetragonal metallic (M) phase on heating [8]. Moreover using single-crystal VO_2 nanobeams with effective beam size of 432nm, where the single crystallinity and freestanding configuration eliminate extrinsic domain and strain effects. This sample geometry ensures that both heat and charge flow in the same path along the nanobeams length direction [6].
Also in solids, conduction is mediated by the combination of vibrations and collisions of molecules, of propagation and collisions of phonons, and of diffusion and collisions of free electrons. Thus the thermal conductivity in solids are written as,

$$k_{tot} = k_e + k_{ph} \tag{4}$$

Where k_{tot} is the total thermal conductivity, k_e is the electronic contribution to thermal conductivity and k_{ph} is the thermal conductivity due to phonon conductance. Phonon is a collective excitation in a periodic, elastic arrangement of atoms or molecules in condensed matter, like solids and some liquids, often designated a quasiparticle which represents an excited state in the quantum mechanical quantization of the modes of vibrations of elastic structures of interacting particles [6].

Table 1. Data of VO_2 at 340K temperature

K^M_e $(Wm^{-1}K^{-1})$	σ (S/m)	S (V/K)	ZT_e	Ref.
0.72	8×10^5	-18×10^{-6}	1.224×10^{-1}	6

In insulators, due to the scarcity of free electrons, k_e can be considered zero. So in case of the insulator phase (I) of VO_2, k^I_{tot} is equal to k^I_{ph} which in this case is 5.80 W/ (m. K). In regular metals, both k_e and k_{ph} need to be accounted for to determine k_{tot}. The values of k^M_e and k^M_{ph} for the metallic phase (M) are 0.72 W/ (m. K) and 5.15 W/(m.K). But in absence of quasi particles, the effective value of k^M_{tot} becomes equal to k^M_e. So from (1), effective figure of merit or electronic figure of merit ZT_e becomes 0.1224 [6].

3. VO_2 in contrast with commonly used metals and thermocouple materials

The thermoelectric properties of a material such as thermal conductivity, electrical conductivity, Seebeck coefficient are temperature sensitive. An example is given in Fig. 1. , from which it is apparent that the highest Seebeck coefficient for VO_2 is at the vicinity of its metal-insulator transition phase that is around 340K temperature. It is also evident that the metals in which quasi-particles are present, such as copper, silver and gold has somewhat similar values of Seebeck coefficient over the range of temperatures. Whereas VO_2, in absence of quasi-particles, has a much higher value of Seebeck coefficient which increases far more greatly with the increase of temperature as it is transitioning from insulator to metal phase.

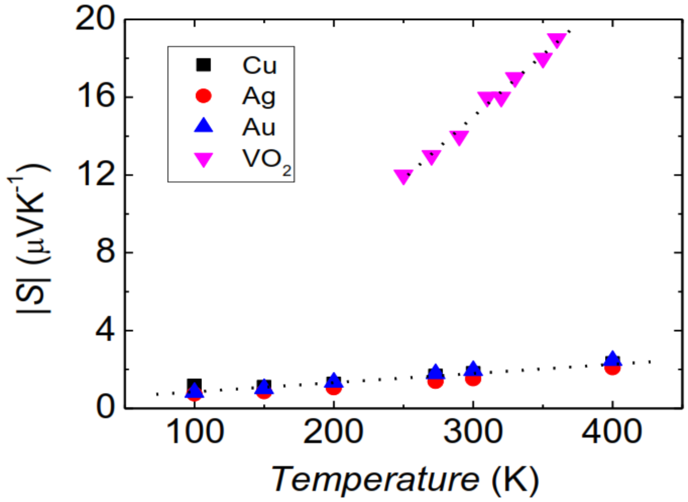

Fig. 1. Comparison of the temperature dependent Seebeck coefficient of VO2 (absent of quasi-particles) with normal, good metals (present of quasi-particles), such as Cu, Ag, and Au [6].

The Table 2. shows the thermal conductivity, electric conductivity, Seebeck coefficient and figure of merit of some of the most commercially used thermocouple materials and other common metals along with VO_2.

Table 2. Thermoelectric properties of various metals and alloys at 340K

Metal name	Thermal conductivity *($Wm^{-1}K^{-1}$)*	Electric conductivity *(S\m)*	Seebeck Coefficient *(V\K)*	Figure of merit	Ref
VO_2	0.72	8×10^5	-18×10^{-6}	1.2×10^{-1}	6
Copper	394	5.96×10^7	6.5×10^{-6}	2.18×10^{-3}	10
Gold	293	4.10×10^7	6.5×10^{-6}	2.02×10^{-3}	11, 12
Silver	419	6.301×0^7	6.5×10^{-6}	2.17×10^{-3}	11, 12
Platinum	72	9.43×10^6	1×10^{-6}	2×10^{-3}	15
Chromel	19	1.42×10^6	2.51×10^{-6}	1.6×10^{-2}	16
Alumel	29.7	3.40×10^6	2.53×10^{-6}	1.6×10^{-3}	13
Iron	68.965	1×10^7	45×10^{-6}	9.5×10^{-2}	11
Constantan	19.5	2×10^6	-35×10^{-6}	4×10^{-2}	10

The Fig. 2. demonstrates the variation of thermoelectric figure of merit with respect to thermal conductivity of various metals and alloys. It is clear that vanadium dioxide's thermal conductivity is lowest and the Seebeck coefficient and the figure of merit is the highest in comparison with other common materials like copper, silver, gold etc. For its high value of Seebeck coefficient and high value of ZT, it has the potential to be a good thermocouple material.

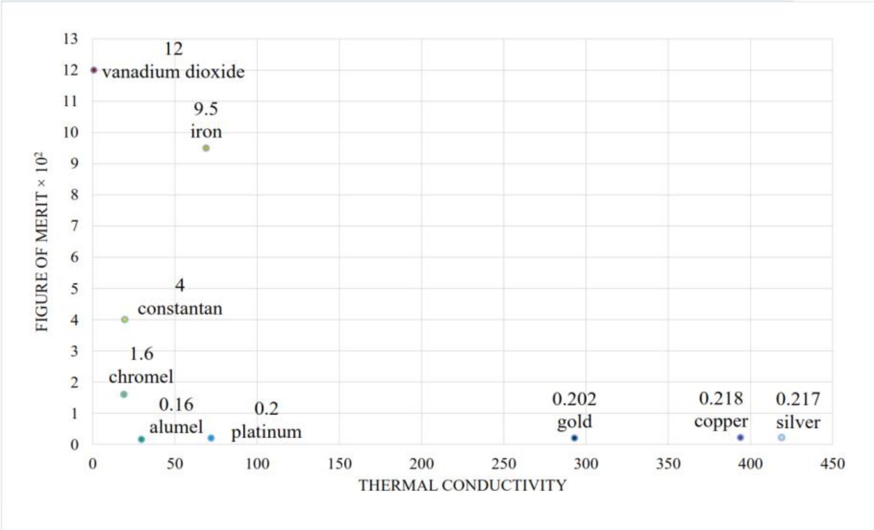

Fig. 2. Thermal conductivity vs figure of merit of various materials from Table. 2.

4. Prospects of VO_2 as a thermoelectric material in TEG/TEC

Thermoelectric generator (TEG) and thermoelectric cooler (TEC) are thermoelectric devices which depend on the principle of thermoelectric effect. TEG is a device which can produce electrical energy by converting temperature differences. Whereas in case of TEC, when voltage is applied in one direction, one side of the device creates heat while the other side absorbs heat, becoming cold. The efficient performance of TEG and TEC depend on the thermoelectric property of material used in respective devices which can be measured by the thermoelectric figure of merit ZT [17]. Bismuth Telluride (Bi_2Te_3) is the most commonly used material in TEG/TEC for higher efficiency due to its ZT value of 0.8 [18].

4.1. Compatibility factor

The materials used in TEG/TEC are guided by the compatibility factor. A material's compatibility factor s is defined as,

$$s = \frac{\sqrt{1-\mathrm{ZT}}-1}{ST} \tag{5}$$

When the compatibility factor from one segment to the next differs by more than a factor of about two, the device will not operate efficiently [19]. In the case of using P type Bi_2Te_3 along with VO_2, the compatibility factor stays within the acceptable range which is an indication of a potential practical use of the TEG/TEC utilizing Bi_2Te_3 along with VO_2.

4.2. Simulation of TEG/TEC

Two simulations were designed in Ansys Workbench to demonstrate the viability of this TEG/TEC. A basic geometry identifying a single cell was drawn on Solidworks. This basic geometry was created in accordance with widely popular model of TEC of Bismuth Telluride (Bi2Te3) but in an enlarged scale of a single cell. The geometry and all the Ansys parameters were kept the same in both simulations to get a clear comparison.

For the first simulation using P type and N type Bi_2Te_3, the parameters are given in table 3. And For the second simulation using P type graphene and N type Bi_2Te_3, the parameters are given in table 4. The Results are given in Table 5.

Table 3. Thermoelectric properties of Bi_2Te_3

Name of the component	*S* *(μv/k)*	*ρ* *(Ωm)*	*k* *($Wm^{-1}K^{-1}$)*	*ZT*	Ref.
P type Bi_2Te_3	140	0.6× 10-5	1.3	0.8	20
N type Bi_2Te_3	-150	4× 10-5	0.21	0.8	21

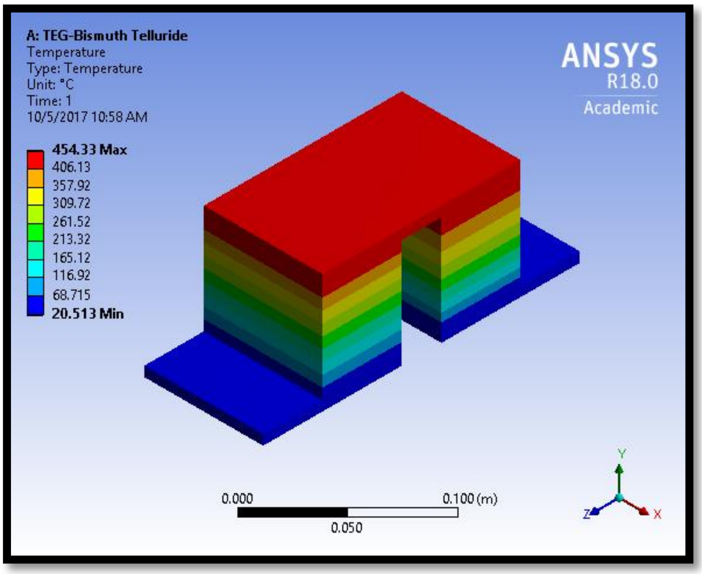

Fig 3. Simulation of TEG/TEC using P type and N type Bi_2Te_3 (Heat Distribution)

Table 4. Thermoelectric properties of P type Bi_2Te_3 and VO_2

Name of the component	*S* (*μv/k*)	*ρ* (*Ωm*)	*k* ($Wm^{-1}K^{-1}$)	*ZT*	Ref.
P type graphene	140	0.6× 10-5	1.3	0.8	20
VO_2 (as N type material)	-18	1.25× 10-6	0.72	0..12	6

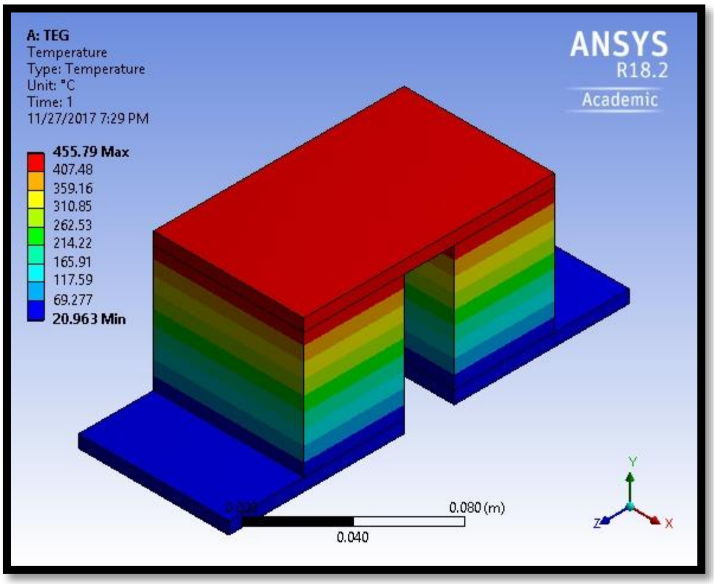

Fig 4. Simulation of TEG/TEC using P type Bi_2Te_3 and VO_2 (Heat Distribution)

Table 5. Results

Name of the simulation	Generated current (*A*)	Heat absorbed (*W*)
P type and N type Bi_2Te_3	84.452	54.579
P type Bi_2Te_3 and VO_2	61.198	59.668

Although the generated current for VO_2 is less than that of the Bi_2Te_3, the absorbed heat is higher. The results of the simulation confirms that VO_2 has the potential of becoming an effective TEC material.

5. Conclusion

The violation of the Wiedemann-Franz law allows metallic Vanadium Dioxide to have a unique set of thermoelectric properties. The combinations of higher electrical conductivity in correspondence with lower thermal conductivity and a relatively high Seebeck coefficient makes VO_2 an ideal candidate for various thermoelectric applications where metals or alloys are widely used, such as in thermocouples. VO_2 seems to show all the necessary properties required to be a good thermocouple material. The compatibility factor and the subsequent simulations also show that VO_2 has a lot of potential as an N type material for thermoelectric coolers. Further research is needed to reduce the production cost of nanostructured VO_2 so that it can be used in various thermoelectric devices in a cost effective way. This material's unique properties are sure to open some new doors in scientific researches and in various engineering applications.

6. References

[1] Howard E., and Theodore O. Poehler, eds. *Innovative thermoelectric materials: polymer, nanostructure and composite thermoelectrics*. World Scientific, 2016.

[2] Blundell, Stephen J., and Katherine M. Blundell. *Concepts in thermal physics*. OUP Oxford, 2009.

[3] Tritt, Terry M., and M. A. Subramanian. "Thermoelectric materials, phenomena, and applications: a bird's eye view." MRS bulletin 31, no. 3 (2006): 188-198.

[4] Jones, William, and Norman Henry March. *Theoretical solid state physics: Perfect lattices in equilibrium*. Vol. 1. Courier Corporation, 1973.

[5] Kittel, Charles. *Introduction to solid state physics*. Wiley, 2005.

[6] Lee, Sangwook, Kedar Hippalgaonkar, Fan Yang, Jiawang Hong, Changhyun Ko, Joonki Suh, Kai Liu et al. "Anomalously low electronic thermal conductivity in metallic vanadium dioxide." *Science* 355, no. 6323 (2017): 371-374.

[7] Schwabl, Franz, *Advanced Quantum Mechanics,* Springer, 4th edition, pp. 253, 2008.

[8] Eyert, Volker. "The metal-insulator transitions of VO2: A band theoretical approach." *arXiv preprint cond-mat/0210558* (2002).

[9] Jones, Alison, and Brenda Sufrin. EU competition law: text, cases, and materials. Oxford University Press, 2016.

[10] Davis, Joseph R., ed. *Copper and copper alloys*. ASM international, 2001.

[11] Brandes, E. A., G. B. Brook, and P. Paufler. "*Smithells Metals Reference Book*", Butterworth- Heinemann Ltd., Oxford, 1976.

[12] Matula, Richard Allen. "Electrical resistivity of copper, gold, palladium, and silver." Journal of Physical and Chemical Reference Data 8, no. 4 (1979): 1147-1298.

[13] Horton, J. L., T. G. Kollie, and L. G. Rubin. "Measurement of B versus H of alumel from 25 to 180° C." Journal of Applied Physics 48, no. 11 (1977): 4666-4671.

[14] Pila, Justine, and Paul Torremans. European Intellectual Property Law. Oxford University Press, 2016.

[15] Moore, J. P., and R. S. Graves. "Absolute Seebeck coefficient of platinum from 80 to 340 K and the thermal and electrical conductivities of lead from 80 to 400 K." Journal of Applied Physics 44, no. 3 (1973): 1174-1178.

[16] Getting, I. C., and G. C. Kennedy. "Effect of Pressure on the emf of Chromel- Alumel and Platinum- Platinum 10% Rhodium Thermocouples." Journal of Applied Physics 41, no. 11 (1970): 4552-4562.

[17] Wood, C. "Materials for thermoelectric energy conversion." Reports on progress in physics 51, no. 4 (1988).

[18] Kim, K. T., Kim, K. J., & Ha, G. H. (2010). Thermoelectric Properties of P-Type Bismuth Telluride Powders Synthesized by a Mechano-Chemical Process. Electronic Materials Letters, 6(4), 177–180.

[19] Snyder, G. Jeffrey, and Tristan S. Ursell. "Thermoelectric efficiency and compatibility." Physical review letters 91, no. 14 (2003).

[20] [7] Kim, K. T., Kim, K. J., & Ha, G. H. (2010). Thermoelectric Properties of P-Type Bismuth Telluride Powders Synthesized by a Mechano-Chemical Process. Electronic Materials Letters, 6(4), 177–180

[21] Le, Phuoc Huu, Chien-Neng Liao, Chih Wei Luo, and Jihperng Leu. "Thermoelectric properties of nanostructured bismuth–telluride thin films grown using pulsed laser deposition." Journal of Alloys and Compounds 615 (2014): 546-552.