

# THERMOELECTRIC PROPERTIES OF A *p-n*-MODULE MADE OF ORGANIC MATERIALS

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**Abstract:** A thermoelectric module made from organic materials of *p*-type  $TTT_2I_3$  and *n*-type  $TTT(TCNQ)_2$  is proposed as an efficient device for direct waste heat-to-electricity conversion. Thermoelectric coefficients of the mentioned quasi-one dimensional organic crystals are modeled numerically as function of dimensionless Fermi energy on the base of more realistic three-dimensional physical model. More diverse and complicated internal interactions are considered. It is demonstrated that rather high values of thermoelectric figure-of-merit ( $ZT$ ) can be obtained by applying optimization procedures, such as the carrier's concentration tuning and the purification of the crystal. In this paper, the results are summarized and the average device  $ZT$  is calculated. The total efficiency of the *p-n* module is estimated for different values of the crystals parameters.

**Keywords:** Thermoelectric Module, Tetrathiotetracene-Iodide,  $TTT(TCNQ)_2$ , Organic Crystals, Quasi-one-dimensional crystal, Molecular Chain, Thermoelectric Figure-of-Merit, Efficiency.

## Introduction

Thermoelectric (TE) converters serve to convert the heat directly into electricity or the electricity into the cold. It is known that almost 90% of world annual energy consumption (which now is around 15 terawatt-years and is expected to achieve nearly 30 terawatt-years by 2050 [1]) is generated by heat engines that use fossil fuel combustion, oil, natural gas and coal as heat sources. These engines usually operate at 30–40 per cent efficiency. Thus, an enormous quantity of heat is lost to the environment. Automotive exhaust, industrial processes and home heating, all generate an enormous amount of unused waste heat. It is natural that there is a significant interest in finding cost-effective technologies for generating electricity from waste heat. It is expected that namely low cost and more efficient TE generators based on organic materials will serve for these goals.

Such devices have evident advantages compared with those that use traditional methods of electrical energy generation or refrigeration: no moving parts, long life, high reliability, no environment pollution, noiseless operation. In addition, they can be made very small and, relatively, no expensive. However, large application of thermoelectric converters is limited by their low efficiency that is determined by the low energy conversion efficiency of existing thermoelectric materials.

It is known that the main parameter that determines the possibility of a given material to be used in the TE converters of energy is the dimensionless thermoelectric figure of merit  $ZT$ , where  $T$  is the operating temperature. Now the largest commercially applied thermoelectric materials on the base of  $Bi_2Te_3$  have  $ZT \sim 1$  near room  $T$ . It is a rather low value. A value of  $ZT \geq 3$  would make the solid-state converters economically competitive with the ordinary used ones. Values of  $ZT$  even  $\sim 3.8$  have been reported in literature. However, such values have been obtained in very sophisticated, technologically complicated and very expensive structures. Nevertheless, it is demonstrated that such high values of  $ZT$  are possible.

In the last years, it is observed an increasing effort in the investigation of thermoelectric properties of organic materials [2-7] mainly in the scope to find low cost materials in order to convert even a part of low-grade waste heat to electricity. For example, in the highly conducting quasi-one-dimensional organic crystals values of  $ZT$  of the order of 10 were predicted [8]. These materials can be considered as bulk nanostructured, because they are formed of one-dimensional conducting chains of molecules displaced at approximately one nanometer one from other. They joint together the TE priorities of low-dimensional structures with increased density of states and of multi component systems with more diverse internal interactions. Moreover, it was shown that in these crystals, the Wiedemann-Franz law is violated and the Lorentz number can be diminished by several times in comparison with the standard values. It is favorable for TE applications. In poly(3,4-ethylenedioxythiophene) (PEDOT) doped by poly(styrenesulphonate) (PSS) thin films of *p*-type conductivity a value of the thermoelectric figure of merit  $ZT = 0.42$  at room temperature has been measured [4].

In present paper, the efficiency is estimated of a thermoelectric module constructed of an n-leg formed from an n-type TTT(TCNQ)2 and a p-leg from TTT2I3.

### Thermoelectric efficiency

The efficiency of a thermoelectric convertor for electricity generation is determined by the parameter  $\eta$ , defined as:

$$\eta = \frac{\text{energy provided to the load}}{\text{heat energy absorbed at hot junction}} \quad (1)$$

The possibility of a material to be used in a thermoelectric device is characterized by its dimensionless figure of merit  $ZT$ , given by

$$ZT = \frac{\sigma S^2 T}{\kappa}, \quad (2)$$

where  $\sigma$  is the electrical conductivity,  $S$  is the Seebeck coefficient and  $\kappa$  is the thermal conductivity of the considered material. Typical commercial thermoelectric devices are made out of  $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$  for room temperature applications and  $\text{PbTe}$  for high temperature applications and they have a  $ZT$  of around one. It is rather low value. Values of  $ZT$  as high as possible are needed. However, the requirements to increase in the same material simultaneously  $\sigma$  and  $S$  and to decrease  $\kappa$  are contradictory. For usual materials, the increase of  $\sigma$  leads to decrease of  $S$  and to increase of  $\kappa$ . New, more sophisticated materials are needed in order to overcome this problem.

The thermoelectric convertor is formed from a series of the thermocouples, each made up from two materials of n-and p-type. As an example, HZ-14 model developed by Hi-Z Company, has 6.27cm by 6.27cm ceramic area with 49 p-n pairs of bismuth telluride based semiconductors and a thickness of about 5mm [9]. The module provides 25W (5% efficiency) output for a temperature difference of 300°C.

The maximum efficiency  $\eta_{max}$  is given by

$$\eta_{max} = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + ZT_{av}} - 1}{\sqrt{1 + ZT_{av}} + \frac{T_c}{T_h}} \quad (3)$$

where  $T_h$  is the temperature at hot side,  $T_c$  is the temperature at the surface of cooled side and  $T_{av}$  is the average temperature  $T_{av} = (T_h + T_c)/2$ . The first factor in (3) is the efficiency of Carnot cycle.  $ZT_{av}$  is the dimensionless figure of merit of the device, which takes into consideration the thermoelectric figures of merit of both materials of n- and p-type. After geometrical optimization with respect to legs sections it is obtained

$$ZT_{av} = \frac{(S_p - S_n)^2 T_{av}}{[(\sigma_n^{-1} \kappa_n)^{1/2} + (\sigma_p^{-1} \kappa_p)^{1/2}]^2} \quad (4)$$

where  $\sigma_n$ ,  $\sigma_p$ ,  $S_n$ ,  $S_p$ ,  $\kappa_n$ , and  $\kappa_p$  are, respectively, the electrical conductivity, Seebeck coefficient and thermal conductivity of n- and p-type materials.

### Nanostructured material of p-type

It was demonstrated that the nanostructured crystals of  $\text{TTT}_2\text{I}_3$  are very promising thermoelectric materials of p-type [10-14]. The crystals have needle-like form of the length of 6-12 mm and thickness of 30-60  $\mu\text{m}$  and are made from segregate stacks or chains of TTT molecules and iodine [15]. However, only TTT chains are conductive. The crystal model is described in the tight binding and nearest neighbors' approximations as the most suitable for this class of materials. The carriers are holes. The matrix element of electron-phonon interactions takes into account two main interactions. The first interaction is similar to that of deformation potential. The second interaction is similar to that of polaron, but is determined by induced polarization of molecules surrounding the conduction hole. We for the first time have considered both these interactions together. This is very important because the interference between these interactions leads to compensation of both interactions for some states in the conduction band. As a result, the relaxation time and the carrier mobility for these states are increased considerably, especially in crystals with high degree of purity. This is very favorable for increase of the thermoelectric properties.

The crystal parameters are: the mass of TTT molecule  $M = 6.5 \times 10^5 m_e$  ( $m_e$  is the mass of the free electron); the lattice constants  $a = 18.35 \text{ \AA}$ ,  $b = 4.96 \text{ \AA}$ ,  $c = 18.46 \text{ \AA}$ ; the sound velocity along chains  $v_{s1} =$

$1.5 \times 10^3$  m/s. The transfer energies of a hole from the given molecule to the nearest one along lattice vectors  $\mathbf{b}$ ,  $\mathbf{a}$ ,  $\mathbf{c}$  are  $w_1$ ,  $w_2$ ,  $w_3$ ;  $w_1 = 0.16$  eV.  $w'_1$ ,  $w'_2$  and  $w'_3$  are the derivatives with respect to the intermolecular distance of transfer energies  $w_1$ ,  $w_2$  and  $w_3$ ;  $w'_1 = 0.26$  eV $\text{\AA}^{-1}$ .  $r = 4$  is the number of molecular chains through the transversal section of the elementary cell.  $\kappa_L = 0.6$  WK $^{-1}\text{m}^{-1}$  is the lattice thermal conductivity. The parameters  $d_1 = w_2/w_1 = w'_2/w'_1 = d_2 = w_3/w_1 = w'_3/w'_1 = 0.015$  were estimated by comparing the experimental and numerical results of transversal electrical conductivity. The parameters  $\gamma_1$ ,  $\gamma_2$  and  $\gamma_3$  have the means of the ratios of amplitudes of second interaction to the first one in the  $x$  direction of chains and in transversal directions  $y$ ,  $z$ , respectively.

The mean polarizability of TTT molecules was taken as  $\alpha_0 = 45$   $\text{\AA}^{-3}$  and this leads to  $\gamma_1 = 1.7$ . The parameters  $\gamma_2$  and  $\gamma_3$  have been calculated in [13, 14]. It was demonstrated [12] that the theory describes very well the temperature dependence of electrical conductivity  $\sigma_p$  along TTT chains in the interval from 180 K up to 300 K, the highest  $T$  for which measurements were made. For lower temperatures, probably the fluctuations of the dielectric phase appear which increase with decreasing  $T$  and lead to a lower increase of  $\sigma_p$  and finally to the metal-dielectric transition. The theory does not consider this low temperature phenomenon. The thermopower (Seebeck coefficient)  $S_p$  is less sensitive to the fluctuations of the dielectric phase and for  $S_p$  the theory agrees with the experimental data in a rather large temperature interval from 50 K up to 300 K. One may conclude that the elaborated physical model can be applied for the modeling and optimization of the thermoelectric properties of TTT $_2$ I $_3$  crystals near room  $T$ . The electrical conductivity  $\sigma_p$ , Seebeck coefficient  $S_p$  and electronic thermal conductivity  $\kappa_e$  have been calculated in a more complete 3D model in [14] as functions of the dimensionless Fermi energy  $\varepsilon_F$  in unities of  $2w_1$  for crystals with different degrees of perfection described by the parameter  $D_0$ . For  $D_0$  the following values were chosen: 0.1 which corresponds to crystals grown by gas phase method with stoichiometric electrical conductivity  $\sigma_{xx} \sim 10^6$   $\Omega^{-1}\text{m}^{-1}$ ; 0.02 which correspond to purer crystals grown also by gas phase method with somewhat higher  $\sigma_{xx} \sim 3 \times 10^6$   $\Omega^{-1}\text{m}^{-1}$ , and 0.005 which corresponds to even more perfect crystals with  $\sigma_{xx} \sim 6.6 \times 10^6$   $\Omega^{-1}\text{m}^{-1}$  not obtained yet. For these three sets of crystals, the impurity concentrations are expected to be  $5 \times 10^{18}$   $\text{cm}^{-3}$ ,  $10^{18}$   $\text{cm}^{-3}$  and  $2 \times 10^{17}$   $\text{cm}^{-3}$ , respectively, or crystal purity: 99.6%, 99.92% and 99.98%. These values of purity are achievable.

Some sets of values for  $\sigma_p$ ,  $S_p$  and  $\kappa_e$  are presented in the Table 1 below.

### Nanostructured material of $n$ -type

Organic crystals of  $n$ -type TTT(TCNQ) $_2$  have the aspect of dark-violet needles of length of 3 – 6 mm. The internal crystal structure consists of molecular chains of TTT and TCNQ arranged along one direction, further considered as  $x$  – axis. The lattice constants are  $c = 3.75$   $\text{\AA}$ ,  $b = 12.97$   $\text{\AA}$  and  $a = 19.15$   $\text{\AA}$ , taken as  $x$ ,  $y$  and  $z$  directions. The crystal model is also described in the tight binding and nearest neighbors' approximations, but the carriers are electrons. The overlap of molecular orbital of nearest molecules along the TCNQ chain generates a narrow conduction band of the width  $4w_1$  ( $\sim 19 k_0T_0$ ,  $T_0 = 300$  K), where  $w_1 = 0.125$  eV is the transfer energy of an electron from a given molecule to the nearest one in the  $x$  direction. In transversal to chains directions the transfer energies  $w_2 = d_1 \cdot w_1$  and  $w_3 = d_2 \cdot w_1$  are small and the transport mechanism is of hopping-type. The internal structure of TTT(TCNQ) $_2$  crystals is similar to that of TTT $_2$ I $_3$  and one can put  $d_1 = 0.015$  and  $d_2 = 0.01$  for  $y$  and  $z$  directions.

The numerical calculations of TE coefficients were performed for crystals with different degrees of purity and respectively  $D_0 = 0.1$ , 0.04, 0.02 at room temperature. The crystal parameters are:  $M = 3.72 \times 10^5 m_e$  ( $m_e$  is the mass of the free electron),  $v_{s1} = 2.8 \times 10^3$  m/s,  $w_1 = 0.125$  eV,  $w'_1 = 0.2$  eV $\text{\AA}^{-1}$ ,  $r = 2$ ,  $d_1 = 0.015$ ,  $d_2 = 0.01$ ,  $\kappa_L = 0.4$  WK $^{-1}\text{m}^{-1}$ . The parameters  $\gamma_2$  and  $\gamma_3$  were calculated in [15]. The electrical conductivity  $\sigma_n$ , Seebeck coefficient  $S_n$  and electronic thermal conductivity  $\kappa_n$  have been calculated in a more complete 3D model in [15] as functions of the dimensionless Fermi energy  $\varepsilon_F$  in unities of  $2w_1$  for crystals with different degrees of perfection described by the parameter  $D_0 = 0.1$ , 0.04, 0.02 at room temperature. Some sets of values for  $\sigma_p$ ,  $S_p$  and  $\kappa_e$  are presented in the Table 1 below.

### Conclusions

Let's consider a module constructed of an  $n$ -leg formed from a  $n$ -type TTT(TCNQ) $_2$  and a  $p$ -leg from TTT $_2$ I $_3$ .

In the Table 1 numerical data for  $\sigma_n$ ,  $\sigma_p$ ,  $S_n$ ,  $S_p$ ,  $\kappa_n$ , and  $\kappa_p$  are extracted from the Tables for the respective numerical calculations. The figure of merit  $ZT_{av}$  of the  $p$ - $n$ - module and maximum efficiency  $\eta_{max}$  are calculated after (4) and (3).

**Table 1.**

| $\sigma_n$ ,<br>$\Omega^{-1}\text{cm}^{-1}$ | $\varepsilon_F$<br>$n$ -leg | $S_n$<br>$\mu\text{VK}^{-1}$ | $\kappa_n = \kappa^e + \kappa^L$<br>$\text{Wm}^{-1}\text{K}^{-1}$ | $\sigma_p$<br>$\Omega^{-1}\text{cm}^{-1}$ | $\varepsilon_F$<br>$p$ -leg | $S_p$<br>$\mu\text{VK}^{-1}$ | $\kappa_p = \kappa^e + \kappa^L$<br>$\text{Wm}^{-1}\text{K}^{-1}$ | $ZT_{av}$ | $\eta_{max}$<br>% |
|---|-----------------------------|------------------------------|---|---|-----------------------------|------------------------------|---|-----------|-------------------|
| $7.2 \times 10^3$                           | 1.15                        | -92                          | 4.7   | $3.4 \times 10^3$                         | 0.15                        | 152                          | 2.0   | 0.94      | 7.3               |
| $6.3 \times 10^3$                           | 1.10                        | -97                          | 4.4   | $2.3 \times 10^3$                         | 0.10                        | 181                          | 1.0   | 1.3       | 9.1               |
| $9.2 \times 10^3$                           | 1.15                        | -124                         | 6.5   | $8.7 \times 10^3$                         | 0.15                        | 183                          | 3.5   | 1.3       | 9.1               |
| $7.1 \times 10^3$                           | 1.10                        | -128                         | 5.9   | $5.7 \times 10^3$                         | 0.10                        | 220                          | 2.7   | 1.8       | 11                |
| $8.2 \times 10^3$                           | 1.10                        | -152                         | 7.4   | $10 \times 10^3$                          | 0.10                        | 253                          | 3.7   | 2.7       | 13                |
| $11 \times 10^3$                            | 1.15                        | -148                         | 7.1   | $18 \times 10^3$                          | 0.15                        | 211                          | 3.9   | 3.1       | 14                |

The efficiency is not big, because we have chosen  $T_h = 480$  K, the highest  $T$  admitted by these organic materials.  $T_c = 300$  K and the temperature difference  $\Delta T = 180$  K. For such small  $\Delta T$ , the ideal Carnot efficiency is only 37.5%. Nevertheless, predicted generator efficiencies  $\sim 10$ -12 % for the conversion of low-grade waste heat are very good results. Moreover, these materials could be used in the low temperature cascade of TE generators working in larger  $\Delta T$  in order to improve the overall efficiency, because now does not exist thermoelectric materials which would have high efficiency in very large temperature intervals.

## References

1. A. Slaoui, R. T. Collins. MRS Bulletin, **32**, 211, 2007.
2. O. Bubnova, et al. *Optimization of the thermoelectric figure of merit in the conducting polymer poly(3,4-ethylenedioxythiophene)*, Nature Materials, **10**, 429, 2011.
3. P.J. Troni, I. Hoces, I. Singelin N. et al. *Thermoelectric Materials: A Brief Historical Survey from Metal Junctions and Inorganic Semiconductors to Organic Polymers*, Isr. J. Chem. 54, 534 – 552, 2014.
4. G-H. Kim, L. Shao, K. Zhang and K. P. Pipe. *Engineered doping of organic semiconductors for enhanced thermoelectric efficiency*. Nat. Mater. Vol. 12, 719, 2013.
5. J. Yang, Hin-Lap Yip and Alex K.-Y. Jen, *Rational Design of Advanced Thermoelectric Materials*, Advanced Energy Materials. 3, Issue 5, 549–565, 2013.
6. D. Wang et al., *Modeling thermoelectric transport in organic materials*, Phys. Chem. Chem. Phys., 2012,14, 16505-16520, DOI: 10.1039/C2CP42710A
7. W. Shi, J. Chen, J. Hi et al., *Search for Organic Thermoelectric Materials with High Mobility: The Case of 2,7-Dialkyl[1]benzothieno[3,2-b][1]benzothiophene Derivatives*, Chem. Mater. 26, 669–2677, 2014.
8. A. Casian in: Thermoelectric Handbook, Macro to Nano, Ed. by D. M. Rowe, CRC Press, 2006, Chap.36.
9. Hi-Z14 thermoelectric module. Available at <http://www.hi-z.com/hz-14.html>.
10. A. Casian, J. G. Stockholm, V. Duscic and V. Nicic, *Low-Dimensional Organic Crystal Tetrathiotetracene–Iodide as Thermoelectric Material: Reality and Prospects*, J. Nanoelectronics and Optoelectronics, **4**, 95, 2009.
11. A. I. Casian, I. I. Sanduleac, *Organic Thermoelectric Materials: new opportunities*, J. of Thermoelectricity, **3**, 2013.
12. A. Casian, I. Sanduleac. *Thermoelectric properties of tetrathiotetracene iodide crystals: modeling and experiment*, J. Electron. Mat., 43, 3740, 2014.
13. I. I. Sanduleac, A. I. Casian, J. Pflaum, *Thermoelectric Properties of Nanostructured Tetrathiotetracene Iodide Crystals in a Two-Dimensional Model*, J. of Nanoelectron. and Optoelectronics, **9**, 247-252, 2014.
14. A.I. Casian, J. Pflaum, I.I. Sanduleac. *Prospects of low dimensional organic materials for thermoelectric applications*, J. of Thermoelectricity, №1, 16-29, 2015.
15. A. Casian, I. Sanduleac, *Thermoelectric properties of nanostructured tetrathiotetracene iodide crystals: 3D modeling*, Mat. Today Proc., 2, 504, 2015.
- I. Sanduleac, A. Casian, *Modeling of thermoelectric properties of  $n$  – type organic crystals of  $\text{TTT}(\text{TCNQ})_2$ : 3D physical model*. J. Elec. Materials 2015, doi: 10.1007/s11664-015-4018-8.