



Thermoelectric Properties of a p-n Module Based on TTT_2I_3 and $\text{TTT}(\text{TCNQ})_2$ Organic Crystals

Sanduleac Ionel

Technical University of Moldova, Faculty of Electronics and Telecommunications,
Av. Stefan cel Mare 168, MD-2004, Chisinau, Republic of Moldova,
e-mail: ionel.sanduleac@mt.utm.md, Web: fizica.utm.md

Abstract—In this paper the thermoelectric properties of $p - n$ thermoelectric module of organic nanostructured crystals is investigated. A thermoelectric module (TM) is a device designed for direct conversion of heat to electricity or for cooling effect by applying a small electrical current at the pairs legs. TMs are embedded in a various of devices: thermal generators for energy harvesting at industrial scale, personalized mini devices for power generation or local cooling effect for integrated circuits. In modern medical devices, TMs are used for accurate temperature control in PCR (polymerase chain reaction), biological samples and vaccines transportation, continuous temperature monitoring and others. However, most commercialized TMs nowadays are made of inorganic compounds with a low rate of energy conversion. By the other side, organic materials are more reliable, flexible with a higher efficiency at low temperature gradients. Earlier, it was established theoretically that organic crystals of TTT_2I_3 of p - type and $\text{TTT}(\text{TCNQ})_2$ of n - type are very prospective materials for thermoelectric applications at near-to-room temperature. For temperatures not exceeding ~ 400 K, it is expected that crystals properties will not change significantly. The charge transport and thermoelectric properties are predicted to significantly enhance by some manipulations with carrier and impurity concentrations. In the following, the electrical conductivity, the output voltage, and the maximum power factor of a p - n module made of these crystals is calculated numerically for different combinations of crystals parameters and temperature gradients.

Keywords—thermoelectricity; organic crystals; TTT_2I_3 ; $\text{TTT}(\text{TCNQ})_2$; thermoelectric module; Seebeck coefficient; thermoelectric efficiency

I. INTRODUCTION

Thermoelectric (TE) phenomena are related with the electrochemical and thermal properties of a physical system (metal or semiconductor) leading to electrical current generation when a temperature gradient is applied or to local cooling effect when a difference of electrical potential is applied to the material [1]. The maximum

efficiency of the energy conversion process of a material at a given temperature is determined by the thermoelectric figure of merit ZT [2]:

$$ZT = \sigma S^2 T / \kappa \quad (1)$$

where σ is the electrical conductivity, S - thermopower (Seebeck coefficient), T - absolute temperature and κ - the total (electronic and phononic) thermal conductivity. For TMs used as temperature sensor, another quantity is very important, namely the power factor, describing the current power delivered by device for given temperature:

$$P = \sigma S^2 \quad (2)$$

Since the mid of 20th century, the main focus was on the TE properties of classic inorganic materials, such as Bi_2Te_3 , PbTe , and SiGe alloys. A threshold of ZT around 1 was achieved [3]. Over the last decades, the interest in this field has expanded rapidly, due to the novel techniques, such as low-dimensional structures, nanocomposites, band engineering and carrier filtering.

For instance, in $\text{Pb}_{0.91}\text{Cr}_{0.09}\text{Te}$ codoped with Iodine, fabricated by melt growth process, values of $\sigma = 625 \Omega^{-1}\text{cm}^{-1}$, $S = 275 \mu\text{VK}^{-1}$, $P = 47.3 \mu\text{Wcm}^{-1}\text{K}^{-2}$ and $ZT \sim 2.2$ were reported at $T = 550\text{K}$ [4]. In high-conductive $\text{PbTeCd}_{0.02}$, $\sigma = 2000 \Omega^{-1}\text{cm}^{-1}$, $S = -143 \mu\text{VK}^{-1}$, $P = 47.3 \mu\text{Wcm}^{-1}\text{K}^{-2}$ and $ZT \sim 1.5$ was obtained by melt spinning and rapid induction hot pressing at $T = 773\text{K}$ [5]. In skutterudites $\text{Ba}_{0.09}\text{La}_{0.04}\text{Yb}_{0.14}\text{Co}_4\text{Sb}_{12}$ the effect of dopants, nanocomposites, and filler atoms has led to $\sigma = 2220 \Omega^{-1}\text{cm}^{-1}$, $S = -161 \mu\text{VK}^{-1}$, $P = 57.5 \mu\text{Wcm}^{-1}\text{K}^{-2}$ and $ZT \sim 1.4$ at $T = 850\text{K}$ [6]. However, all the inorganic TE compounds reported in the last two decades are efficient at high temperatures, while for low, near-to room temperatures, their TE efficiency is very low.

Organic compounds, by the other side, offer the possibility to operate at low temperature, with high TE performance. The main advantage of organic TE materials is low thermal conductivity, leading to significant enhancement of ZT (see formula 1). In this sense,

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materials with high electrical conductivity are desired. This can be obtained by using high-conducting organic crystals or by including carbon materials, particularly carbon nanotubes (CNT), in the structure of the polymer. From the recent advances, one can highlight the following: $\sigma = 77000 \Omega^{-1}\text{cm}^{-1}$, $S = 65 \mu\text{VK}^{-1}$, $P = 176 \mu\text{Wcm}^{-1}\text{K}^{-2}$ and $ZT \sim 0.12$ in PANI/SWCNT at $T = 298\text{K}$ [7]. Simultaneous enhancement of electrical conductivity and Seebeck coefficient was obtained in organic thermoelectric SWNT/PEDOT:PSS nanocomposites ($\sigma = 1700 \Omega^{-1}\text{cm}^{-1}$, $S = 55.6 \mu\text{VK}^{-1}$, resulting in a high power factor $P = 526 \mu\text{Wcm}^{-1}\text{K}^{-2}$ [8].

The most successful p-type material developed to date is undoubtedly, poly(3,4-ethylenedioxy thiophene) polystyrene sulfonate (PEDOT:PSS) [9].

Thermoelectric devices, based on organic materials have been reported by many authors. For instance, an organic power generator consisting of 55 legs in a vertical architecture exhibits a maximum power output of 0.128 μW at temperature difference of 10K [10]. By using metal-organic conducting polymers as the n-type and p-type materials Zhu's group reported a maximum power of 750 μW and an output voltage of 0.26 V from a TM consisting of 35 legs under a temperature difference of 82K[11].

In this paper, we present the results of numerical modelling a p-n device made of highly conductive nanostructured organic crystals of TTT_2I_3 and $\text{TTT}(\text{TCNQ})_2$ under different temperature gradients. Earlier, theoretical investigations have revealed very promising TE properties of these crystals if carrier concentration is accurately tuned and the purification process is performed [12].

II. THERMOELECTRIC COEFFICIENTS

Crystals of TTT_2I_3 and $\text{TTT}(\text{TCNQ})_2$ consist of stack-like packages of molecules, arranged in linear chains in perpendicular-to stack direction. This direction is considered below as x - direction of a cartesian coordinate system. The stack y and z axes are defining the stack plane. In x direction, the significant overlap of HOMO (higher occupied molecular orbitals) of neighboring molecules ensures high longitudinal electrical conductivity for both crystals, according to experimentally reported data [13, 14]. In y and z directions, the distance between neighbor molecules is of three or four times larger, the HOMO overlap is small and the transversal electrical conductivity is of three orders of magnitude lower than the longitudinal one. In crystals of TTT_2I_3 the main charge carriers are holes, travelling along TTT chains. In crystals of $\text{TTT}(\text{TCNQ})_2$ the carriers are electrons on TCNQ chains. Considering a small electric field and low temperature gradient, the transport processes can be derived by using the method of retarded, two-particle Green functions [12]. Thermoelectric coefficients can be calculated numerically as:

$$\sigma_{xx} = \sigma_0 R_0, S_{xx} = \pm 2 |w_1| / eT \cdot R_1 / R_0 \quad (3)$$

where

$$\sigma_0 = 2e^2 M v_{s1}^2 |w_1|^3 z / [\pi^3 \hbar abc (k_0 T)^2 w_1'^2] \cdot (T_0 / T)^2 \quad (4)$$

here k_0 is the Boltzmann constant, e – elementary charge, z is the number of molecular chains per elementary cell. a, b, c are lattice constants, w_1 is the transfer energy of a charge carrier from the given molecule to the neighbor, and w_1' is the derivative with respect to the intermolecular distance. The upper sign in S_{xx} is for p – type crystals and the lower - for n – type. R_n are the transport integrals:

$$R_n = \iiint_{[-\pi, \pi]} dx dy dz |\sin x|^3 [1 - \cos x + d_1(1 - \cos y) + d_2(1 - \cos z) - (1 + d_1 + d_2)\varepsilon_F]^n n_k(1 - n_k) / \{ (1 \mp |\gamma_1| [1 + \beta_{xx}(T - T_0)]^5 \cos x)^2 + D_0 + D_1 e^{(-E_0/k_0 T)} + d_1^2(1 + 2 \sin^2 y \mp 2 |\gamma_2| \cos y + |\gamma_2|^2) / 8 \sin^2 x + d_2^2(1 + 2 \sin^2 z \mp 2 |\gamma_3| \cos z + |\gamma_3|^2) / 8 \sin^2 x \} \quad (5)$$

here the upper sign in “ \mp ” is for p – type crystals and the lower for n – type. n_k is the Fermi distribution function in terms of dimensionless quasi-momentum $\mathbf{k} = (k_x b, k_y a, k_z c)$ and $\varepsilon_F = E_F / 2w_1$ is the dimensionless Fermi energy. The parameters $d_1 = w_2 / w_1$ and $d_2 = w_3 / w_1$ describe the ratio of transfer energies. D_0 describes the scattering on point-like impurities and D_1 – the scattering on thermally activated lattice dislocations. The thermal expansion of the lattice is considered in the coefficient β_{xx} only for the direction of molecular chains.

The expressions for output voltage and the maximum power of a p - n module can be figured out as [15]:

$$U_0 = m(S_p - S_n)\Delta T, P_{\max} = U_0^2 / 4R_g \quad (6)$$

where m is the number of thermocouples in the module, S_p and S_n are the Seebeck coefficients of p, respectively, n legs and ΔT is the temperature difference between hot and cold side. The expression for P_{\max} is obtained for the optimized case, when the internal electrical resistance of TM R_g and the load electrical resistance are equal. The internal electrical resistance can be calculated as:

$$R_g \cdot l = 1 / \sigma_p + 1 / \sigma_n \quad (7)$$

here σ_p and σ_n are longitudinal electrical conductivities and l is the length of legs.

III. NUMERICAL RESULTS

The electrical conductivity and the Seebeck coefficient (3) were calculated by solving numerically the integrals (5) for the following crystals parameters: TTT_2I_3 : $M = 6.5 \cdot 10^5 m_e$ (m_e is the mass of the free electron), $w_1 = 0.16 \text{ eV}$, $w_1' = 0.26 \text{ eV}\text{\AA}^{-1}$, $v_{s1} = 1.5 \cdot 10^3 \text{ m/s}$, $z = 4$, $d_1 = d_2 = 0.015$, $D_0 = 0.001$, $D_1 = 0.3$, $E_0 = 0.024 \text{ eV}$. $\text{TTT}(\text{TCNQ})_2$: $M = 3.72 \cdot 10^5 m_e$, $w_1 = 0.125 \text{ eV}$, $w_1' = 0.22 \text{ eV}\text{\AA}^{-1}$, $v_{s1} = 2.8 \cdot 10^3 \text{ m/s}$, $z = 2$, $d_1 = 0.01$, $d_2 = 0.015$, $D_0 = 0.001$, $D_1 = 0.3$, $E_0 = 0.024 \text{ eV}$. The crystals parameters

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were estimated by fitting the numerical results of electrical conductivity and Seebeck coefficient with experimentally reported ones [13, 14].

In Fig.1., the electrical conductivity and thermopower of TTT₂I₃ crystals as a function of dimensionless Fermi energy are presented. It is observed that in case of stoichiometric concentration of conducting holes $n_h = 1.25 \cdot 10^{21} \text{ cm}^{-3}$ (to which corresponds a dimensionless Fermi energy $\varepsilon_F = 0.35$), $\sigma_{xx} = 9 \cdot 10^3 \Omega^{-1} \text{ cm}^{-1}$ and $S_{xx} = 60 \mu\text{V/K}$, which is very close to the experimentally reported values in [13]. Bud, as it is observable from Fig.1., If ε_F is diminished down to 0.18 (which corresponds to the diminution of holes concentration by two times), the electrical conductivity decreases $\sigma_{xx} = 3.6 \cdot 10^3 \Omega^{-1} \text{ cm}^{-1}$ and the Seebeck coefficient increases up to $S_{xx} = 150 \mu\text{V/K}$. This indicates on the enhancement of thermoelectric properties.

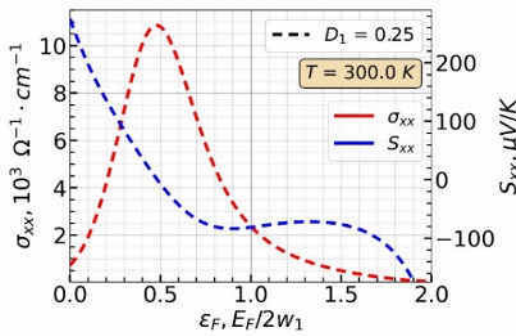


Figure 1. Electrical conductivity and Seebeck coefficient of TTT₂I₃ crystals as function of dimensionless Fermi energy

In Fig.2., the electrical conductivity and Seebeck coefficient of TTT(TCNQ)₂ crystals are presented.

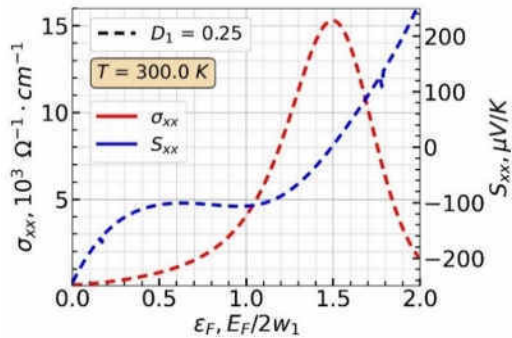


Figure 2. Electrical conductivity and Seebeck coefficient of TTT(TCNQ)₂ crystals as function of dimensionless Fermi energy.

In case of *n*-type crystals, the concentration of charge carriers has to be increased in order to achieve high thermoelectric voltage. For stoichiometric concentration of conducting electrons $n_e = 1.22 \cdot 10^{21} \text{ cm}^{-3}$ (to which corresponds a dimensionless Fermi energy $\varepsilon_F = 0.35$), $\sigma_{xx} = 0.46 \cdot 10^3 \Omega^{-1} \text{ cm}^{-1}$ and $S_{xx} = -120 \mu\text{V/K}$. If additional doping with donors is performed, increasing the concentration n_e by 2 times with respect to the stoichiometric one (i.e., $\varepsilon_F = 1.05$), the Seebeck coefficient does not change significantly, $S_{xx} = -110 \mu\text{V/K}$, but electrical conductivity will increase with an order of

magnitude $\sigma_{xx} = 4.6 \cdot 10^3 \Omega^{-1} \text{ cm}^{-1}$. This is very promising, since according to (2), the delivered power factor will increase also. In the following, it is interesting to modelate a *p*-*n* pair (or a set of pairs) of these crystals in power generation regime.

In Fig.3. the output voltage and the maximum power output of a *p*-*n* module made of 10 pairs of legs under a temperature gradient $\Delta T = 20\text{K}$ is presented. The length of a single leg was considered $l = 0.05 \text{ m}$. The modeling was performed as a function of the dimensionless Fermi energy of *n*-type TTT(TCNQ) crystals, considering stoichiometric TTT₂I₃ crystals. The dimensionless parameter D_1 was estimated by comparison with experimental data reported in [13], which correspond to crystals grown from gaseous phase. In the following, we have considered the same D_1 value for TTT(TCNQ)₂.

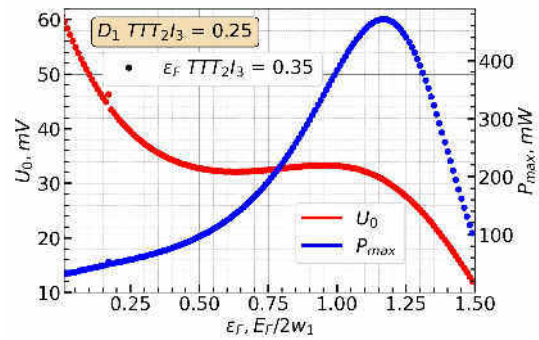


Figure 3. Output voltage and maximum power output generated by 10 *p*(TTT₂I₃) – *n*(TTT(TCNQ)₂) pairs at temperature difference of 20K, as function of dimensionless Fermi energy of *n* leg. *p* leg - undoped.

It is observed that for stoichiometric concentration of conducting electrons in TTT(TCNQ)₂ (i.e., $\varepsilon_F = 0.35$) the TM can deliver an output voltage $U_0 = 35 \text{ mV}$ with a maximum power $P_{\max} = 70 \text{ mW}$. If n_e is increased by two times (i.e., $\varepsilon_F = 1.05$), the output voltage practically does not change $U_0 = 33 \text{ mV}$ but the maximum power increase by six times $P_{\max} = 420 \text{ mW}$. If the optimization procedure is applied to TTT₂I₃ crystal (i.e., $\varepsilon_F = 0.18$), significant achievements can be obtained (see Fig.4).

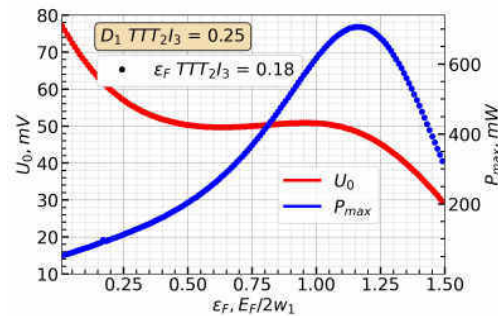


Figure 4. Output voltage and maximum power output generated by 10 *p*(TTT₂I₃) – *n*(TTT(TCNQ)₂) pairs at temperature difference of 20K, as function of dimensionless Fermi energy of *n* leg. *p* leg - optimized.

In Fig.4. the same TM is modeled as a function of dimensionless Fermi energy of *n*-type TTT(TCNQ) crystals, considering optimized TTT₂I₃ crystals. It is observed that in this case, high values of output voltage

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and maximum power can be obtained: $U_0 = 50$ mV and $P_{\max} = 660$ mW.

Thus, the strategy for improving thermoelectric properties of a TM made of TTT_2I_3 and $\text{TTT}(\text{TCNQ})_2$ crystals consists of accurate tuning of charge carrier concentration. The purification process is very important, since the diminution of D_1 leads to even more high values of U_0 and P_{\max} . The temperature dependence of σ_{xx} and S_{xx} is very important, since when applying a temperature difference to the ends of p and n legs, the working temperature is distributed along the leg.

In Fig.5., the temperature dependence of electrical conductivity and Seebeck coefficient of $\text{TTT}(\text{TCNQ})_2$ optimized crystals is presented.

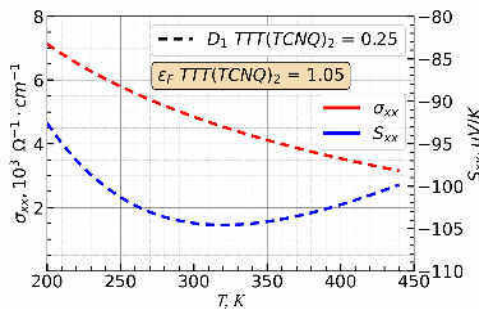


Figure 5. Electrical conductivity and Seebeck coefficient of TTT_2I_3 crystals as function of dimensionless Fermi energy

As one can observe, the electrical conductivity decreases with the increase of temperature. This effect is linked to the intensification of electron-phonon scattering. The Seebeck coefficient is less sensible to the temperature variations and practically remains constant for a large range of temperatures. The domain below 200K was not considered, since for lower temperatures, a more detailed physical model has to be developed. For TTT_2I_3 the temperature dependence was calculated in [16]. It was also revealed that for a temperature range from $\sim 300\text{K}$ to 400K the electrical conductivity and the Seebeck coefficient does not change significantly. From these reports results that at near-to room temperatures, the thermoelectric properties of the crystals practically remain unchanged.

IV. CONCLUSIONS

The electrical conductivity σ_{xx} , the Seebeck coefficient S_{xx} of p -type TTT_2I_3 and n -type $\text{TTT}(\text{TCNQ})_2$ crystals were calculated numerically and modeled as a function of dimensionless Fermi energy of charge carriers. It was obtained that the tuning of this parameter can lead to significant improvement in thermoelectric properties of the crystal. Also, a thermoelectric module made of 10 p - n thermocouples of these organic crystals was modeled for different values of internal parameters of the crystals. A temperature difference of 10 K was assumed and the length of legs was considered as 0.05m. The output

voltage U_0 and the maximum power delivered P_{\max} were calculated. It is predicted that one can achieve values of $\sigma_{xx} = 3.6 \cdot 10^3 \Omega^{-1}\text{cm}^{-1}$ and $S_{xx} = 150 \mu\text{V/K}$ for p -type and of $\sigma_{xx} = 46 \cdot 10^3 \Omega^{-1}\text{cm}^{-1}$ and $S_{xx} = -110 \mu\text{V/K}$ for n -type if the charge carrier concentration is tuned. In this case, the thermoelectric module should deliver $U_0 = 50$ mV of voltage and $P_{\max} = 660$ mW of maximum power. These results are very promising for high-efficient thermoelectric converters.

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