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STATE OF THE ART AND NEW POSSIBILITIES TO INCREASE THETHERMOELECTRIC FIGURE OF MERIT OF ORGANIC MATERIALS

In this paper, a short review of promising thermoelectric organic materials is provided. It is shown that organic compounds, under appropriate synthesis and after accurate tuning of electronic properties by manipulating the internal molecular structure, may become serious substitutes of classical inorganic thermoelectric materials. A big step forward constitutes the implementation of new trends of nanotechnology in designing the thermoelectric structures. In this order, we provide the most important results, achieved in several low-dimensional thermoelectric structures, such as quantum-dot superlattices or molecular nanowires of conducting polymers. More specifically, the latter structures may become very promising thermoelectric materials, if we refer to the predicted values of ZT ~ 15. Whereas these predictions were made in the frame of simple one-dimensional physical model, in a more realistic physical model the values of ZT ~ 1.1 for an n- type and ZT ~ 4 for a p-type compound are predicted.

Key words: Thermoelectricity, organic compound, thermoelectric figure-of-merit, thermoelectric efficiency, the coefficient of performance.

Introduction

According to IEA (International Energy Agency) World Energy Outlook 2016, in 2040 the energy sector will look in the following way. It is expected a 30 % increase in energy demand, mostly from developing countries, 37 % of power generation will be from renewables, compared to 23 % in 2016, 150 million vehicles compared to 1.3 m, 50 % growth in demand for natural gas, overtaking the coal in the global energy mix. The level of oil consumption will constitute 103 million barrels per day, compared to 92.5 mb/d in 2015. The average annual growth of carbon emissions in energy sector will constitute 0.5 %, compared to 2.4 % per year since 2000 [1].

This situation will take place in 2040, if the nations will abide the pledges made as part of Paris Agreement, which entered into force on 4 November 2016. This is a major step forward in the fight against global warming. The agreement sets out a global action plan to put the world on track to avoid dangerous climate change by limiting global warming to well below 2 °C. One of the major Governments agreements is to undertake rapid actions thereafter in accordance with the best available science. In this order, one expects to slow down the projected rise in energy-related carbon emissions, from an average of 650 million tons per year since 2000, to around 150 million tons per year in 2040.

The era of fossil fuels appears far from over and underscores the challenge of reaching more ambitious climate goals. As a result of major transformations in the global energy system that will take place over the next decades, renewables and natural gas are the big winners in the race to meet energy demand growth until 2040. Therefore, to achieve the 2 °C target, the energy sector must be carbon-neutral by 2100. It is expected a growth of renewables from ~ $4.7 \cdot 10^{12}$ kWh in 2012 to ~ $10.6 \cdot 10^{12}$ kWh in 2040.

The use of thermoelectric efficient devices may constitute a cornerstone in this huge process of building a new technological future. Thermoelectricity offers new environment-friendly technological solutions of energy conversion, with the advantages of small size, high reliability, no pollutants and feasibility in a wide temperature range.

In the period of 60's – 70's, all attempts to improve thermoelectric figure-of-merit *ZT* led to the establishment of a threshold value of *ZT* ~ 1 in classical semiconductors [2]. Later, it turned out that *ZT* cannot be increased too much mainly because of the interconnectivity of the electrical conductivity and thermal conductivity of a material. Consequently, it concluded that researches that are more thorough are needed in the field of thermoelectric properties of materials. As a result, in 1970 the International Thermoelectric Society (ITS) is founded. In the period between 60's and 90's, no significant progress is achieved, the best thermoelectric materials being *Bi2Te*3 and its alloys with *ZT* ~ 1 for near room temperatures [3], and *PbTe* for higher temperature range. There were no efficient thermoelectric materials for the temperature range 600 – 700 K [4]. Only at the beginning of the 90's the scientific community is attracting new attention to thermoelectric materials, mainly driven by the energy crisis and the problem of environmental conservation. As a result, many new discoveries are made, including the possibility to improve the thermoelectric properties by manipulating the crystal structure or composition of the material. Two main investigation areas are delimited: bulk thermoelectric materials and low dimensional systems [5]. During the mid of the 20'th century until now, many big ideas have served as guiding principles in focusing research and advancing knowledge. These include the use of heavy atom masses and complex unit cells, alloy scattering of phonons, bulk nanostructuring, phonon glass/electron crystal, quantum confinement of electrons, hierarchical nanostructuring, anharmonicity, and band engineering [6]. Recently, a large number of research demonstrated that organic materials, bulk or nanostructured, may become very promising thermoelectric materials [7].

In terms of internal structural arrangement, thermoelectric materials can be classified in two broad categories: bulk TE materials and nanostructured TE materials. In recent years, an increasingly strong interlacing of these categories is noticed. Bulk material approach is related to the structures with many atoms in the basic region of the crystal. In this case, the physical properties are more or less isotropic and do not change when the extraction or addition of any number of atoms is performed. In a low-dimensional system, the movement of electrons, phonons or photons is described by the wave vectors, which are defined in two dimensions (2D), or one dimension (1D). When the dimensionality is reduced, the quantum and surface effects are more pronounced, which leads to new physical properties, different from the bulk ones. In terms of the number of dimensions, different low dimensional systems can be distinguished, such as 2D quantum structures, quantum wires (1D) and quantum dots structures (0D). The density of energetic states dramatically changes, when the dimensionality is reduced. This phenomenon leads to significant changes in electronic and thermal transport properties [8, 10]. Note that recently [11] it has been shown that the thermal conductivity of indium tin oxide films with nanogranular structure may be strongly suppressed due to the enhancement of phonon scattering on grain boundaries and reaches ultra-low values ~ 0.84 ± 0.12 Wm^{-1}K^{-1} at room temperature. Taking into account high values of the thermoelectric power factor [12], such films demonstrate promising thermoelectric properties.

Recently, the scientific community has focused more and more on the research of organic thermoelectric materials, particularly conjugated polymers. Among the most important benefits of these materials are: abundant raw materials, cheap and environmentally friendly production technology, flexibility and extensive possibilities to manipulate the molecular structure. Because of the instability of organic materials at high temperatures, the application of these materials as thermoelectric convertors is limited to low or moderate temperatures [13]. One of the big advantages

of organic compounds is their low thermal conductivity, compared to the majority of inorganic materials. This property is very important for a thermoelectric material, since the reduction of parasitic heat loss allows high ZT values. However, the electrical conductivity of most organic compounds is relatively low. At the same time, physical properties can be optimized effectively using chemical methods and molecular doping procedures. In recent years, a rapid development of the electronics on organic basis is noticed. This has led to the synthesis of hundreds of organic semiconductor compounds with high charge carrier mobility, similar to that of polycrystalline silicon [14].

Usually, the conjugated polymers manifest high doping reversibility, mechanical flexibility and satisfactory electric conductivity along the backbone. However, polymeric materials are often heterogeneous, because of the coexistence of crystalline and non-crystalline regions; the layering of the stack is difficult to control and the mass distribution of molecules is large. The overcome of these obstacles can be achieved by applying various synthesis schemes. The electrical conductivity, as well as the Seebeck coefficient, depends on the concentration of charge carriers, the chemical structure of monomers, as well as the spatial arrangement of the molecules. In the organic materials, like in the inorganic ones, the thermal transport consists of the contribution of the lattice and of the charge carriers. However, the Wiedemann-Franz law is often violated due to the strong coupling between electric charges and the lattice vibrations. As a result, the contribution of charge carriers to thermal conductivity is low. As an example, one reports that if the electrical conductivity of PA (polyacetylene), PANI (polyaniline) and PPY (polypyrrole) samples is increased by three orders of magnitude, the total thermal conductivity increases only from 0.1 $W·m^{-1}K^{-1}$ to 1 $W·m^{-1}K^{-1}$ [15].

Significant improvement of thermoelectric properties is reported for PEDOT: PSS thin films with high electrical conductivity, treated with hydrophilic solvents (ethylene glycol or DMSO): $ZT \sim 0.42$ at $T = 300$ K [16]. The value of power factor $P = 1.27$ $\mu Wm^{-1}K^{-2}$ was reported in PP-PEDOT thin films [7]. It is estimated that the thermoelectric figure-of-merit $ZT \sim 1.02$, but this result should be verified experimentally, by accurately measuring the thermal conductivity. The PEDOT nanowire/PEDOT hybrid composites have demonstrated a power factor P as high as 446.6 $\mu W·m^{-1}$ K^{-2} and $ZT \sim 0.44$ at room temperature [17].

Recently, it has been demonstrated [18] that in freestanding PEDOT films both electrical conductivity and Seebeck coefficient were increased simultaneously by controlling the synthesis conditions, achieving a power factor ~ 7.9 $\mu W·m^{-1}K^{-2}$. It is a very important result. First-principles calculations [19] based on density-functional theory (DFT) and the Boltzmann transport equation have shown that the polypyrrole (PPy), which is one of the conducting polymers, has promising thermoelectric properties.

Development of a thermoelectric generator from *p*-type optimized PEDOT: TOS and *n*-type non-optimized *TTF – TCNQ/PVC* was reported. This device can generate a power of $P \sim 0.128$ μW at $T = 10$ K and 0.27 μW at $T = 30$ K, a very important result for medical use [16]. At the same time, another promising research direction is the use of mixed organic-inorganic compounds [20]. As an example, in phenyl acetylene doped with silicon nanoparticles, $ZT = 0.57$ at $T = 300$ K was reported [21]. Research progress has been obtained in the study of thermoelectric property of Poly (M-ett) (M = metal, ett = ethylenetetrathiolate), which provides the best performance of *n*-type organicthermoelectric materials [22].

Highly conducting *Q1D* organic crystals

The small-molecule based organic compounds are another class of promising thermoelectric organic materials. This class of materials includes charge-transfer complex compounds and molecular

semiconductors. Particularly, our research is focused on the investigations of thermoelectric properties of charge-transfer quasi-one-dimensional organic compounds such as tetrathiafulvalene-tetracyanoquinodimethane (*TTF – TCNQ*), tetrathiotetracene-tetracyanoquinodimethan (*TTT(TCNQ)₂*) and tetrathiotetracene-iodide (*TTT₂I₃*) [23, 24, 25]. The abovementioned crystals belong to the class of quasi-one-dimensional (*Q1D*) organic crystals. The main characteristic of these compounds is the presence of a predominant direction in the internal structure. The molecules arrange in longitudinal chains, generating parallel segregated stacks. The distance between neighboring chains is much larger than the distance between two adjacent molecules along the chain. Due to this structural peculiarity, the physical properties of the crystal, such as electrical and thermal conductivity, are strongly anisotropic. In such a compound, the molecules from one chain play the role of acceptors and from another chain – of donors. As example, in *n*-type *TTF – TCNQ* and *TTT(TCNQ)₂*, *TTF* and *TTT* molecules are strong donors and *TCNQ* molecules – acceptors. In *p*-type *TTT₂I₃*, the electric charge is transferred from *TTT* molecular chains to iodine chains and the carriers are holes. The pronounced quasi-one dimensionality of internal structure imposes some peculiarities in the movement of charge carriers. Along the longitudinal direction, the overlap of π-electron wave functions generates a narrow conduction band, providing a metallic-type electrical conductivity. In transversal to the chain direction, due to the significant interchain distance, the overlap of electron wavefunctions is insignificant and the charge transport is of hopping type. However, because the interchain interactions are very small, we will describe the transport in longitudinal direction in the first approximation in a 3D band model.

The cornerstone idea of this physical crystal model is that two main electron-phonon interactions may compensate each other under some special conditions. As a result, for a narrow region of energetic states in the conduction band, the relaxation time of charge carriers increases significantly, being limited by scattering on impurity. However, in real-existing crystals the interchain interaction is present with more or less influence. Consequently, the relaxation time is limited not only by the impurity scattering, as one assumed in the 1D model, but also by the scattering on the neighboring molecular chains. Due to this, the simpler 1D physical model was improved by taking into consideration the interaction of the nearest chains in one plane (2D model) [26 – 28]. These works allowed us to conclude that for crystals with low purity level, the interchain interaction is insignificant. Contrarywise, for high-purity crystals, the abovementioned interchain interaction becomes important, diminishing significantly the relaxation time of the carriers. As a result, *ZT* is reduced considerably. In order to describe more accurately the thermoelectric properties of quasi-one dimensional organic crystals of *TTT(TCNQ)₂* and *TTT₂I₃*, a more complete physical model was elaborated, taking into account the interaction of carriers with the neighboring molecular chains (3D model) [29 – 31] and with impurities.

The Hamiltonian of the crystals has the form:

$$H = \sum_{k} E(\boldsymbol{k}) a_k^+ a_k + \sum_{q} \hbar\omega_q b_q^+ b_q + \sum_{k,q} A(\boldsymbol{k},\boldsymbol{q})\left(b_q + b_{-q}^+\right) a_k^+ a_{k-q}$$
$$+ \left(I_i V_{0i} \sum_{l=1}^{N_i} e^{-iqr_l} + I_d V_{0d} e^{-E_0/k_0 T} \sum_{m=1}^{N_d} e^{-iqr_m} \right) V^{-1} \sum_{k,q} a_k^+ a_{k-q}$$

(1)

The first term describes the energy of charge carriers in the tight binding and nearest neighbor approximations. For electrons, the energy *E*(*k*) is measured from the bottom of the conduction band. For holes – from the top of the valence band. a_k^+, a_k are the creation and annihilation operators for a charge carrier with the wave vector *k*. The second term describes the energy of acoustic longitudinal phonons, considered in the harmonic and tight-binding approximations. For not very high temperatures and weak electric fields, the optical phonons can be neglected. b_q^+, b_q are the creation and

annihilation operators for a phonon with the wave vector $\boldsymbol{q}$ and frequency $\omega(\boldsymbol{q})$. In these crystals, due to high molecule polarizability, two main interaction mechanisms of charge carriers with phonons take place. The first mechanism is of the deformation potential type, determined by the variation of transfer energies with respect to the intermolecular distances. The second interaction mechanism is similar to that of a polaron. In this case, the interaction is caused by the variation of induced polarization energy of molecules surrounding the charge carrier. Both abovementioned interactions are included in the matrix element $A(\boldsymbol{k}, \boldsymbol{q})$:

$$\left| A(\boldsymbol{k},\boldsymbol{q}) \right|^2 = 2\hbar / \left(NM\omega_q \right) \Big\{ w_1'^2 \left[\sin(k_x b) - \sin((k_x - q_x)b) \mp \gamma_1 \sin(q_x b) \right]^2 +$$
$$+ w_2'^2 \left[\sin(k_y a) - \sin((k_y - q_y)a) \mp \gamma_2 \sin(q_y a) \right]^2 + w_3'^2 \left[\sin(k_y c) - \sin((k_y - q_y)c) \mp \gamma_3 \sin(q_y c) \right]^2 \Big\} \tag{2}$$

where M is the mass of TTT or $TCNQ$ molecule, N is the number of molecules in the basic region of the crystal. w_1', w_2' and w_3' are the derivatives with respect to the intermolecurar distances of transfer energies w_1, w_2, w_3 of a carrier from a given molecule to the nearest ones along lattice vectors a, b, c. The parameters γ_1, γ_2 and γ_3 have the means of the ratios of amplitudes of second interaction to the first one in the direction of chains and in transversal directions. In (2) the upper sign corresponds to p-type TTT_2I_3 with the conducting x direction along $\boldsymbol{b}$. The lower sign corresponds to n-type $TTT(TCNQ)_2$ with the conducting x direction along $\boldsymbol{c}$.

Even the purest crystals contain a certain amount of impurities. In this physical model for the crystal, two most important types of impurities are considered (the last two terms in (1)): point-like neutral impurity centers and temperature-activated defects. The latter are related to different coefficients of thermal expansion for the chains of different composition. In (1) r_l, r_m are the radius vectors of impurities and defects; I_i, V_{0i}, N_i are, respectively, the energy of carrier interaction with an impurity, the volume of impurity action and the number of impurities; I_d, V_{0d}, N_d are the same for defects. E_0 is the activation energy of a such defect, V is the volume of the basic region of the crystal. At room temperature, the scattering of charge carriers on both types of impurity centers is described by the dimensionless parameter D_0, which is proportional to the impurity and defect concentration and may be very small in pure and perfect crystals.

The thermoelectric properties are investigated by considering a weak electrical field and a weak temperature gradient applied along the conductive chains. At room temperature, the kinetic energy of the charge carriers along the transversal directions is much smaller than the kinetic energy in the longitudinal direction. Due to this, it is possible to neglect the transversal kinetic energy of carriers in the scattering processes. So as the crystal model contains many interactions, in the linear approximation with respect to applied field the general expression for electrical conductivity tensor is deduced applying the method of two-particle retarded Green functions depending on temperature. The equation for the two-particle Green function contains the three-particle Green functions, for which new equations are written. In the latter the higher order Green functions are expressed through the two-particle ones and in such a way the chain of equations for the two-particle Green function is closed. After some transformations, the equation for Green function takes the form of a generalized Boltzmann kinetic equation. Considering carrier scattering on acoustic phonons at room temperature as elastic, the relaxation time of charge carriers is expressed through the probability of the scattering process. As a result, the linearized kinetic equation is solved analytically. Let us consider that the electrical field and the temperature gradient are applied in x direction and the transport is directed in the same x direction. Then the electrical conductivity σ_{xx}, Seebeck coefficient S_{xx}, electronic thermal

conductivity and the thermoelectric figure-of-merit $(ZT)_{xx}$ can be expressed analytically through the mass operator of the Green function. The latter is an analog of the inverse relaxation time of carriers.

Crystals of *p*-type *TTT₂I₃*

Modeling of the thermoelectric properties can be realized only numerically. In Fig. 1 (*a* and *b*) the longitudinal electrical conductivity and thermal conductivity of TTT_2I_3 crystals with different degree of purity as function of dimensionless Fermi energy $\varepsilon_F = E_F/2w_1$ are presented, where E_F is the Fermi energy.
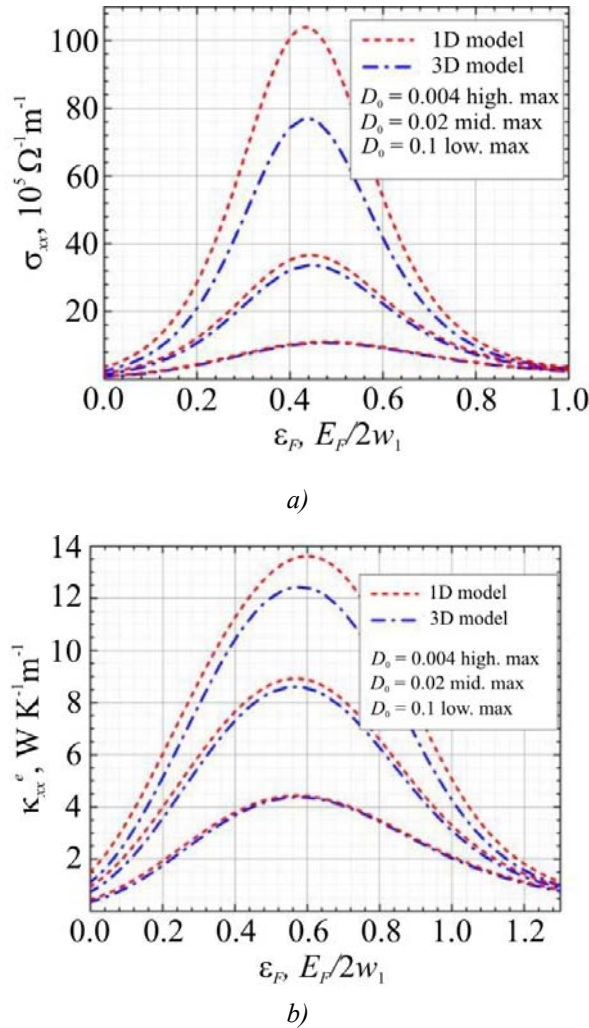

a)

b)

Fig. 1. a) Electrical conductivity σ_{xx} and b) electronic thermal conductivity
along the direction of molecular chains as a function of dimensionless
Fermi energy for quasi-one-dimensional organic crystal of TTT_2I_3.

The crystal parameters are the same as in [30], only more perfect crystals are considered. The value $D_0 = 0.1$ corresponds to not very pure TTT_2I_3 crystals, grown from gaseous phase with stoichiometric conductivity 10^6 $\Omega^{-1}m^{-1}$ [25]. In this case, the 1D and 3D models practically coincide in the entire region of ε_F variation. The value $D_0 = 0.02$ corresponds to purer crystals with stoichiometric conductivity $\sigma_{xx} \sim 3 \cdot 10^6$ $^{-1}m^{-1}$ not synthesized yet. It is seen that the deviation between the 1D and 3D models remains small. In this case, the scattering probability of carriers on neighbouring chains is much smaller than the scattering on impurities and the simpler 1D model is yet applicable. Only for ultra-pure hypothetic crystals, with $D_0 = 0.004$ and stoichiometric conductivity $\sigma_{xx} \sim 6.2 \cdot 10^6 m^{-1}$, the impurity scattering processes are smaller and the mentioned interchain interaction becomes important.

In this case, the more complete 3D physical model should be applied. In TTT_2I_3 crystals the stoichiometric concentration of charge carriers is $n = 1.2 \cdot 10^{21}$ cm^{-3}, to which corresponds $\varepsilon_F \sim 0.37$. It is seen that with the increase of carrier concentration, σ_{xx} grows rapidly.

From Fig. 1b it is observed that the electronic thermal conductivity is less sensitive to interchain interaction. Usually, the lattice thermal conductivity of organic crystals is low (for TTT_2I_3 $\kappa_{xx}^{L} \sim 0.6$ WK^{-1}m^{-1}). In the purest stoichiometric crystals $\kappa_{xx}^{e} \sim 9$ WK^{-1}m^{-1}, much higher than κ_{xx}^{L}. If the carrier concentration grows, κ_{xx}^{e} increases considerably. Also, by comparing Fig. 1a and b, one can observe that the maxima of σ_{xx} are slightly displaced toward lower values of ε_F for TTT_2I_3 with respect to the maxima of κ_{xx}^{e}. This is related to the phenomenon of violation of the Wiedemann-Franz law in these crystals [32] and is favourable for the improvement of thermoelectric properties.

In Fig. 2a and b, the Seebeck coefficient S_{xx} and thermoelectric figure-of-merit $(ZT)_{xx}$ along the molecular chains as a function of dimensionless Fermi energy are presented.

For stoichiometric TTT_2I_3 crystals, S_{xx} weakly depends on crystal perfection and is close to $S_{xx} \sim 35 - 40$ µV/K, reported experimentally. It is observed (Fig. 2a) that S_{xx} is less sensitive to the interchain interactions and it increases considerably with the decrease of ε_F. If the hole concentration is diminished twice, from $n_h = 1.2 \cdot 10^{21}$ cm^{-3} (with $\varepsilon_F \sim 0.37$) down to $n_h = 0.6 \cdot 10^{21}$ cm^{-3} (with $\varepsilon_F \sim 0.12$), $S_{xx} \sim 260$ µV/K is expected for the purest crystals with $D_0 = 0.004$.

In stoichiometric case the figure-of-merit $(ZT)_{xx}$ is quite low (Fig. 2b, $(ZT)_{xx} \sim 0.1$ for $\varepsilon_F \sim 0.37$).
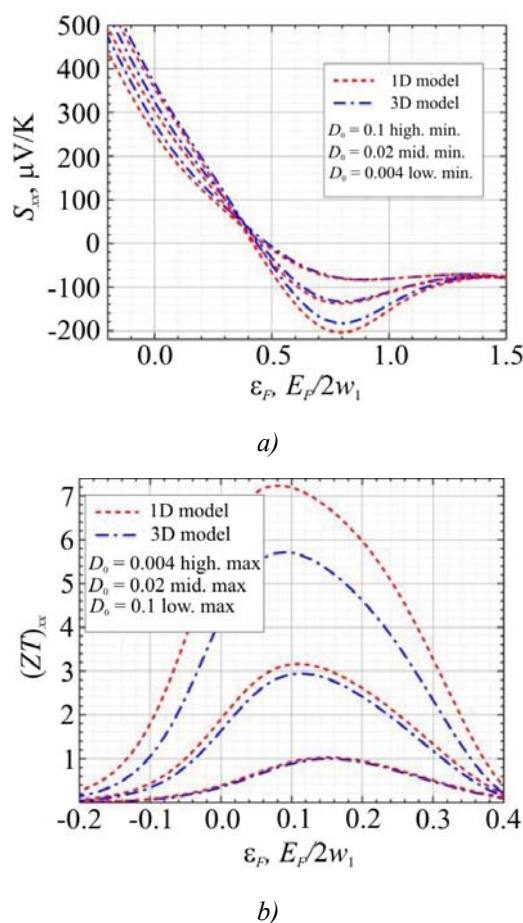

a)

b)

Fig. 2. a) The Seebeck coefficient S_{xx} and b) thermoelectric figure-of-merit $(ZT)_{xx}$
along the direction of molecular chains as a function of dimensionless
Fermi energy for quasi-one-dimensional organic crystals of p – type TTT_2I_3.

If the concentration of conducting holes is diminished twice, the Seebeck coefficient increases significantly and, even if the electrical conductivity decreases, this leads to a significant increase of $(ZT)_{xx}$ up to ~ 2.9 for crystals with $D_0 = 0.02$ and up to ~ 5 for those with $D_0 = 0.004$, very promising results. Thus, in order to increase $(ZT)_{xx}$ in TTT_2I_3 crystals, it is necessary to diminish the hole concentration and increase the crystal purity.

Crystals of *n*-type *TTT*(*TCNQ*)$_2$

The crystals of *n*-type $TTT(TCNQ)_2$ are less studied. Thus, the purity of reported crystals should not be very high. Due to this, somewhat higher values for D_0 were considered, meaning a more large concentration of impurities and defects than in TTT_2I_3 crystals. Other parameters are from [31].
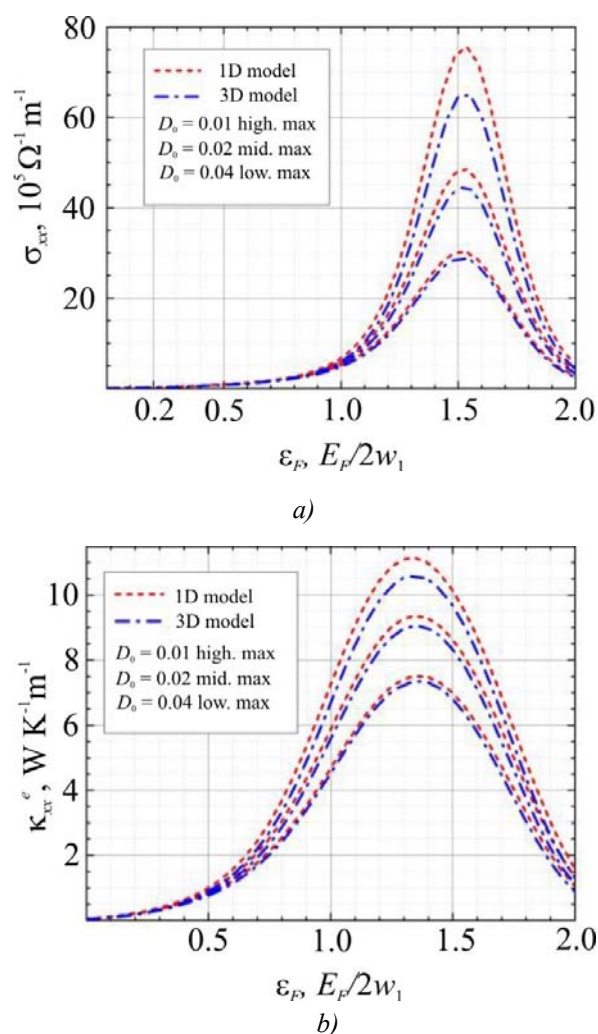

Fig. 3 a) Electrical conductivity σ_{xx} and b) electronic thermal conductivity along the direction of molecular chains as a function of dimensionless Fermi energy for quasi-one-dimensional organic crystal of n- type TTT(TCNQ)$_2$.

In the case of $TTT(TCNQ)_2$ the Seebeck coefficient is negative, because the charge carriers are electrons (Fig. 4*a*)

In stoichiometric crystals, $n_e = 1.1 \cdot 10^{21}$ cm^{-3} (or $\varepsilon_F \sim 0.35$), $S_{xx} \sim 120$ μV/K is expected. If the concentration of electrons is increased twofold ($\varepsilon_F \sim 1.05$) with respect to the stoichiometric value, $S_{xx} = -136$ μV/K, -160 μV/K and -180 μV/K is expected for the crystals with $D_0 = 0.04$, 0.02 and 0.01.
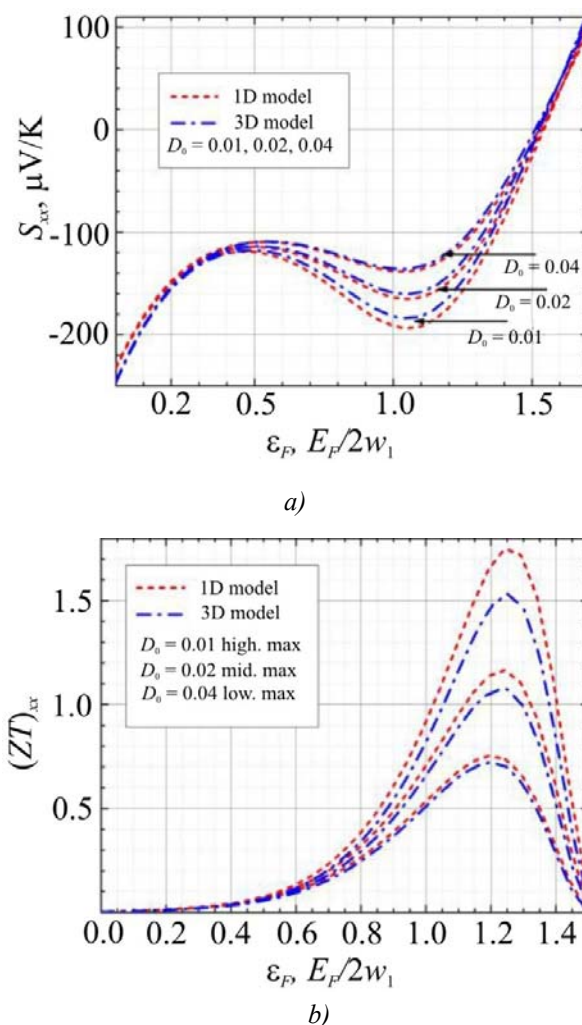
a)

b)

Fig.4. a) The Seebeck coefficient S_{xx} and b) thermoelectric figure-of-merit $(ZT)_{xx}$
along the direction of molecular chains as a function of dimensionless
Fermi energy for quasi-one-dimensional organic crystals of n – type TTT(TCNQ)$_2$.

It is observed (Fig. 4b) that in the case of stoichiometric crystals, the thermoelectric figure-of-merit *ZT* is quite low, even for crystals with high level of purity. This is explained by the simultaneous increase of electrical and thermal conductivity with increasing the purity of the crystal. However, if carrier concentration is properly tuned, the crystal enters the region of strong compensation of the abovementioned electron-phonon interactions. After that, if doped crystals are further purified, the electrical conductivity increases, but the thermal conductivity has a slower increasing rate. As a result, for *n*-type $TTT(TCNQ)_2$ and $D_0 = 0.01$ the following values are predicted: $ZT \sim 0.9$ for $\varepsilon_F = 1.05$ and $ZT \sim 1.1$ for $\varepsilon_F = 1.07$. In order to increase $(ZT)_{xx}$ in $TTT(TCNQ)_2$ crystals it is necessary to increase the electron concentration and increase the crystal purity.

Conclusions

Recent advances in the field of organic thermoelectric materials are reported. A more detailed evaluation of thermoelectric properties of quasi-one-dimensional organic crystals *p*-type TTT_2I_3 and *n*-type $TTT(TCNQ)_2$ is performed. It is expected that crystals of this type are very promising for thermoelectric applications, if the thermoelectric properties are optimized by accurate tuning of carrier

concentration and further purification of the crystal. Thus, the values of thermoelectric figure-of-merit $ZT \sim 5$ can be obtained in relatively pure TTT_2I_3 crystals, if the concentration of conducting holes is diminished twice with respect to the stoichiometric one. As it is well known, the thermoelectric properties of *n*-type materials are usually lower that in the case of *p*-type. However, the values of $ZT \sim 1$ are predicted for ultra-purified $TTT(TCNQ)_2$ crystals, if the concentration of conducting electrons is increased twice with respect to the stoichiometric one. The obtained results open up new possibilities for the implementation of organic compounds in new competitive thermoelectric devices. Partially the results have been implemented in the frame of the H2ESOT project [33], supported by FP7 program of EU Commission. For further improvement, a more detailed physical model should be elaborated.

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