

Possibilities to Improve the Thermoelectric Properties of *n*-type Organic Crystals

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Abstract — In the last years, organic materials attract more and more attention for thermoelectric applications as materials with more diverse properties, accessible raw components and obtained by cost-effective environmentally friendly production technology. For thermoelectric converters materials of both *p*- and *n*-type are necessary. Usually, the materials of *n*-type have lower values of the thermoelectric figure of merit ZT , then those of *p*-type. Therefore, it is important to search materials of *n*-type with improved thermoelectric performance. In this paper, the thermoelectric properties of *n*-type organic crystals of tetrathiotetracene–tetracyanoquinodimethane, TTT(TCNQ)₂, are modeled and optimal parameters in order to increase ZT are determined. It is obtained that, if the carrier concentration is increased by 2.3 times with respect to stoichiometric one and the crystals are further purified, values of $ZT \sim 1.2$ are expected, higher than reported until now in organic crystals of *n*-type.

Index Terms — organic crystals, electrical conductivity, Seebeck coefficient, thermal conductivity, thermoelectric figure of merit.

I. INTRODUCTION

Thermoelectric materials are used in thermoelectric converters that serve to transform directly a temperature difference into electricity without a rotating generator, or electricity into cooling without a compressor. It is known that the possibility of a given material to be applied in a thermoelectric devices is determined by the dimensionless thermoelectric figure of merit $ZT = \sigma S^2 T / \kappa$, where σ is the electrical conductivity, S is the Seebeck coefficient, κ is the thermal conductivity of the given material, and T is the temperature. Values of ZT as high possible are needed.

The most widely applied commercial materials on the base of Bi₂Te₃ have $ZT \sim 1$. This is rather low value. In order that the thermoelectric generators or refrigerators be economically competitive with the ordinary ones, device materials must have $ZT > 3$.

In ordinary materials, such high values of ZT could not be realized because usually the increase of electrical conductivity σ leads to decrease of the Seebeck coefficient S and to increase of thermal conductivity κ and vice versa. Therefore, the search of more sophisticated materials and structures, in order to overcome this interdependence of σ , S and κ , is an important and urgent problem of material science.

In the last decades, the quasi-two-dimensional, Q2D quantum structures, Q1D quantum wires and Q0D quantum dot structures have been intensively developed [1]. In such structures the quantization of electronic spectrum leads to increase of electronic density of states and to increase of the

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Seebeck coefficient and power factor $P = \sigma S^2$. In addition, the phonon scattering at the interfaces or the reengineering of phonon spectrum leads to decrease of thermal conductivity. In Bi₂Te₃-Sb₂Te₃ 2D superlattices $ZT = 2.4$ has been reported [2]. Harman has reported higher value of $ZT \sim 3$ in PbTeSe quantum dot superlattices [3]. $ZT \sim 3.5$ and even ~ 3.8 have been reported too [4, 5]. However, these values

of ZT have been obtained in very sophisticated and very expensive nanostructures. The main source of ZT increase in such structures comes from the decrease of thermal conductivity, although the increase of the power factor has been also observed. However, the possibility to obtain values of $ZT > 3$ has been demonstrated.

In the last years, the organic materials attract more and more attention of investigators and engineers. Usually, such materials have more diverse and often unusual properties in comparison with the inorganic materials. In addition, they are less expensive, do not pollute atmosphere and admit cost effective production technologies.

Thus, $ZT \sim 0.42$ at $T = 300$ K [6] has been reported in PEDOT: PSS thin films, and $ZT \sim 0.44$ in PEDOT nanowire/PEDOT hybrid composites [7]. First-principles calculations have shown [8] that the polypyrrole (PPy), has promising thermoelectric properties.

It has predicted that the quasi-one-dimensional (Q1D) organic crystals can have prospect thermoelectric properties [9]. From the structural point of view, such crystals are formed from linear chains or stacks of molecule. The overlapping of electronic wave functions along the chains is significant, whereas between the stacks it is by two or three order of magnitude smaller. Many organic crystals have Q1D structure, for example, the ion-radical salts of the tetrathiofulvalene-

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tetracyanoquinodimethane (TTF-TCNQ) type, a set of compounds with charge transfer.

For the production of thermoelectric converters, it is necessary to have materials of both *p*- and *n*-type. We have predicted [10, 12] in *p*-type crystals of tetrathiotetracene-iodide, TTT₂I₃, values of $ZT \sim 3 - 4$ after optimization of physical parameters. In *n*-type crystals of tetrathiotetracene-tetracyanoquinodimethan, TTT(TCNQ)₂ values of $ZT \sim 0,8 - 1,0$ were calculated [13, 14]. It is observed experimentally that the organic materials of *n*-type usually have lower values of thermoelectric figure of merit ZT , than the materials of *p*-type. Previous results also confirm this conclusion.

The aim of this paper is to demonstrate that in *n*-type crystals of TTT(TCNQ)₂ is still possible to improve the thermoelectric properties by additional crystal purification and optimization of carrier concentration.

II. CRYSTAL PHYSICAL MODEL

Crystals of TTT(TCNQ)₂ consist of segregate stacks of planar molecules of TTT and TCNQ. The lattice constants are $c = 3.75 \text{ \AA}$, $b = 12.97 \text{ \AA}$ and $a = 19.15 \text{ \AA}$ [15], showing a pronounced Q1D structure with conductive TCNQ chains along *c* direction. The TTT molecules are donors and those of TCNQ are acceptors. The crystal electronic structure is complicated, but in the case of relatively weak electrical fields and weak temperature gradients, we can consider only the lowest molecular orbitals. The overlap of TCNQ orbitals determines the transfer energies w_1 along stacks and w_2, w_3 in transversal directions. Due to crystal quasi-one-dimensionality, $w_1 \gg w_2, w_3$. For TCNQ stacks $w_1 = 0.125 \text{ eV}$ that determines a conduction band along TCNQ stacks of the width $\Delta = 4w_1 = 0.5 \text{ eV}$ [16]. Thus, along TCNQ stacks the conduction mechanism is of band type, and in transversal directions is of hoping type. For TTT stacks, the transfer energies are much smaller and the charge transport along these stacks can be neglected. Thus, the charge carriers are electrons.

The crystal model is described in the tight binding and nearest neighbors approximations. The energy of an electron, measured from the bottom of conduction band is

$$E(\mathbf{k}) = 2w_1(1 - \cos k_x c) + 2w_2(1 - \cos k_y b) + 2w_3(1 - \cos k_z a), \quad (1)$$

where k_x, k_y and k_z are the projections of the carrier wave vector \mathbf{k} on *x* along TCNQ stacks and on *y* and *z* in transversal directions. The frequency of longitudinal acoustic phonons is:

$$\omega_q^2 = \omega_1^2 \sin^2(q_x c / 2) + \omega_2^2 \sin^2(q_y b / 2) + \omega_3^2 \sin^2(q_z a / 2), \quad (2)$$

where ω_1, ω_2 and ω_3 are limit frequencies and q_x, q_y, q_z are the projections of the quasi-wave vector \mathbf{q} , $\omega_1 \gg \omega_2, \omega_3$.

The crystal model takes into account two main electron-phonon interactions. One interaction is of deformation potential type. The coupling constants are proportional to

the derivatives of transfer energies with respect to the intermolecular distances, w_1', w_2', w_3' . The second mechanism is similar to that of polaron with the coupling constant proportional to the mean polarizability of TCNQ molecules, α_0 . The ratios of the amplitudes of second interaction mechanism to those of first one along TCNQ chains and in the transversal directions are described by the parameters

$$\gamma_1 = 2\alpha_0 e^2 / (w_1' c^5), \gamma_2 = 2\alpha_0 e^2 / (w_2' b^5), \quad (3)$$

$$\gamma_3 = 2\alpha_0 e^2 / (w_3' a^5).$$

It is important that between above-mentioned two electron-phonon interactions a compensation can take place for some strip of states in the conduction band. As a result, the relaxation time as function of carrier energy obtains a pronounced maximum for mentioned states. The carriers from these states will have increased mobility. It is favorable for the improvement of thermoelectric properties. The height of the relaxation time maximum is determined by the strength of interchain interaction and by the electron scattering on impurities and defects. At room temperatures, the latest scattering is described by a single dimensionless parameter D_0 . The latter is proportional to the impurity and defect concentration and may be made very small in pure and perfect crystals. Unlike the *p*-type crystals, in the *n*-type ones the maximum of relaxation time corresponds to states from the second half of the conduction band. This means that in order to draw the Fermi level nearer to the maximum of the relaxation time it is necessary to increase the carrier concentration.

Further we will consider that a weak electrical field and a weak temperature gradient are applied along the direction *x* of conductive TCNQ stacks, and the transport takes place in the same *x* direction too. The kinetic equation is deduced applying the method of two-particle temperature dependent retarded Green functions. Near room temperature the scattering of electrons on acoustic phonons can be considered as elastic and the kinetic equation takes the form of Boltzmann one. As result, the electrical conductivity σ_{xx} , thermopower S_{xx} , power factor P_{xx} , electronic thermal conductivity κ_{xx}^e and the thermoelectric figure of merit $(ZT)_{xx}$ can be expressed through the transport integrals [14]. However, the transport integrals can be calculated only numerically.

III. RESULTS AND DISCUSSIONS

The crystal parameters are: $M = 3.72 \cdot 10^5 m_e$ (m_e is the mass of free electron), the sound velocity along the TCNQ stacks $v_{s1} = 2.8 \cdot 10^3 \text{ m/s}$, $w_1 = 0.125 \text{ eV}$, and $w_2 = d_1 w_1, w_3 = d_2 w_1, d_1 = 0.015, d_2 = 0.01, w_1' = 0.22 \text{ eV \AA}^{-1}$, the number of TCNQ molecules in the unit cell $r = 2, w_2' = d_1 w_1', w_3' = d_2 w_1'$, the lattice thermal conductivity $k_{xx}^L = 0.4 \text{ WK}^{-1} \text{ m}^{-1}$. The mean polarizability of TCNQ molecules is taken from DFT calculations [17] and equals $\alpha_0 = 10 \text{ \AA}^{-3}$. For stoichiometric crystals the carriers concentration is $n = 1.1 \cdot 10^{21} \text{ cm}^{-3}$, to which it corresponds the dimensionless Fermi energy $\varepsilon_F = E_F / 2w_1 = 0.35$, where E_F is the Fermi energy. The crystals are not very perfect, therefore the

measured electrical conductivity [15] varies in the interval between 20 and 160 $\Omega^{-1}\text{cm}^{-1}$. The Seebeck coefficient is $\sim 60 - 65 \mu\text{VK}^{-1}$. The calculations of thermoelectric

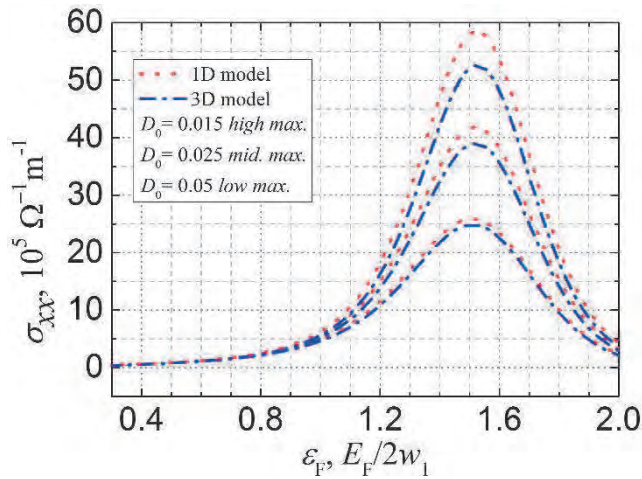


Fig.1. Electrical conductivity σ_{xx} along chains as a function of Fermi energy ϵ_F for $\gamma_1 = 1.8$.

coefficients were performed at room temperature for more perfect crystals, to which the values $D_0 = 0.05, 0.025$ and 0.015 correspond. In stoichiometric crystals, the electrical conductivity σ_{xx} feebly depends on degree of crystal perfection and for given interval of D_0 is $\sim 450 \Omega^{-1}\text{cm}^{-1}$, as it is seen from Fig.1. However, with the increase of carrier concentration n or ϵ_F , σ_{xx} grows rapidly. If n increases two times (up to $n = 2.2 \cdot 10^{21} \text{cm}^{-3}$ or $\epsilon_F = 1.04$), σ_{xx} achieves values $4.8 \cdot 10^3 \Omega^{-1}\text{cm}^{-1}$, $5.1 \cdot 10^3 \Omega^{-1}\text{cm}^{-1}$ and $5.8 \cdot 10^3 \Omega^{-1}\text{cm}^{-1}$ for $D_0 = 0.05, 0.025$ and 0.015 , respectively. The deviation of 3D model from that of 1D is observed only for the most perfect crystals with $D_0 = 0.025$ and 0.015 . For $\epsilon_F > 1.5$, σ_{xx} begins to decrease, because the carriers become holes and their concentration decreases.

In Fig. 2 the dependences of the Seebeck coefficient S_{xx} along chains on Fermi energy ϵ_F are presented. S_{xx} is negative because the carriers in this interval of concentration are electrons. It is seen that the Seebeck coefficient feebly depends on parameter D_0 .

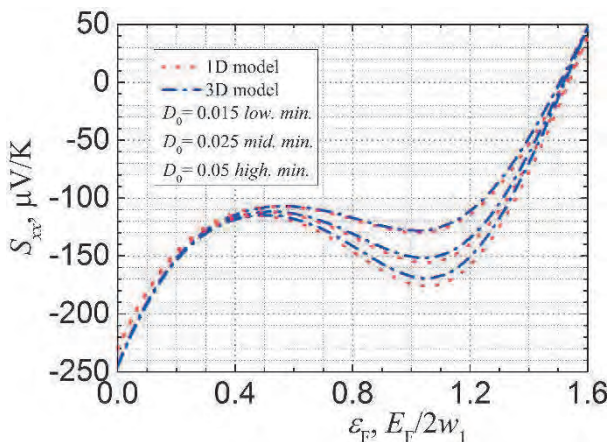


Fig.2. Seebeck coefficient S_{xx} along chains as a function of Fermi energy ϵ_F for $\gamma_1 = 1.8$.

For stoichiometric crystals $S_{xx} \approx -120 \mu\text{V/K}$. However, if n increases two times, up to $\epsilon_F = 1.04$, S_{xx} achieves rather

high values of $-130 \mu\text{V/K}$, $-150 \mu\text{V/K}$ and $-170 \mu\text{V/K}$. It is also seen that for crystals of given perfection, the results of 3D and 1D approximations are practically the same in the whole interval of ϵ_F . For $\epsilon_F > 1.5$, the carriers become holes and S_{xx} is positive.

In Fig.3 the dependences of the power factor P_{xx} along chains on Fermi energy ϵ_F are presented. The power factor

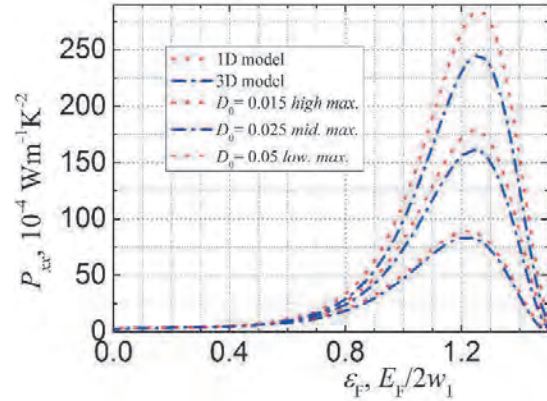


Fig.3. Electronic thermal conductivity κ_{xx}^e along chains as a function of ϵ_F for $\gamma_1 = 1.8$.

is the parameter that determines the possibility of given material to be applied in nonselective detectors of infrared irradiation. It is seen that in stoichiometric crystals the power factor is very small. However, if ϵ_F increases, P_{xx} grows quickly achieving rather high values. When $\epsilon_F = 1.04$, P_{xx} obtains values of $80 \cdot 10^{-4}$, $160 \cdot 10^{-4}$ and $235 \cdot 10^{-4} \text{W/m} \cdot \text{K}^2$, as compared with $40 \cdot 10^{-4} \text{W/m} \cdot \text{K}^2$ in Bi_2Te_3 .

The dependences of the electronic thermal conductivity κ_{xx}^e along the chains on Fermi energy ϵ_F are presented in Fig.4. It is seen that for stoichiometric crystals κ_{xx}^e is small, but grows rapidly with the increase of ϵ_F , achieving at $\epsilon_F = 1.04$ (or $n = 2.2 \cdot 10^{21} \text{cm}^{-3}$) values 4.2, 5.5 and 6.0 $\text{W/m} \cdot \text{K}$ for $D_0 = 0.05, 0.025$ and 0.015 , respectively. These values are much bigger than the lattice thermal conductivity k_{xx}^L .

Thus, at this n almost complete thermal conductivity is maintained by electrons. Form the comparison of Fig.1 and Fig.4 one can observe that the maximums of κ_{xx}^e are displaced to lower values of ϵ_F or n with respect to σ_{xx} . This leads to increase of the Lorenz number. Unfortunately, this

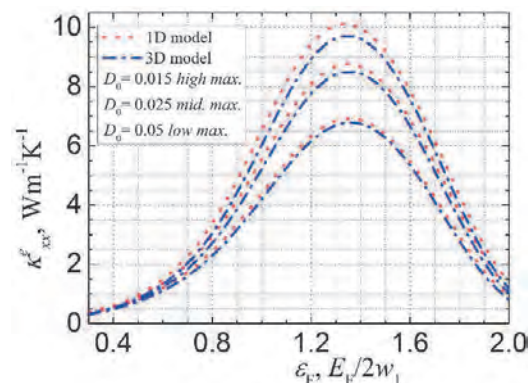


Fig.4. Electronic thermal conductivity κ_{xx}^e along chains as a function of ϵ_F for $\gamma_1 = 1.8$.

fact is not favorable for the increase of the thermoelectric figure of merit of n -type materials and can determine their poorer thermoelectric properties with respect to those of p -type materials.

The dependences of thermoelectric figure of merit $(ZT)_{xx}$ on Fermi energy ε_F are presented in Fig. 5. It is seen that in not very perfect crystals with $D_0 = 0.05$ the values of $(ZT)_{xx}$

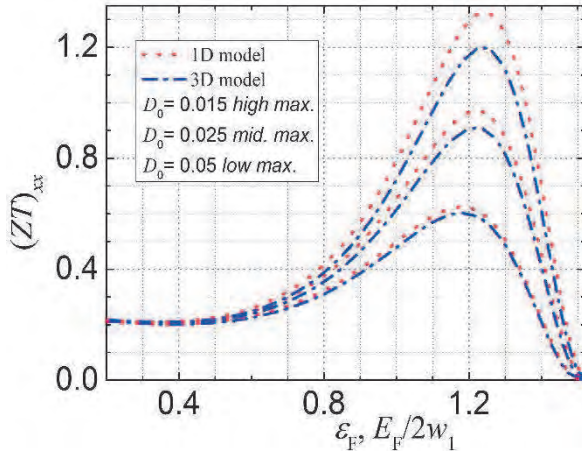


Fig.5. ZT along chains as a function of Fermi energy ε_F for $\gamma_1 = 1.8$.

for the 3D model practically coincide with those for 1D model. For stoichiometric crystals $(ZT)_{xx}$ takes very small values. However, when ε_F increases, $(ZT)_{xx}$ grows rapidly. Thus, if ε_F grows up to 1.04 ($n = 2.2 \cdot 10^{21} \text{ cm}^{-3}$, two times higher than the stoichiometric concentration), values of $(ZT)_{xx} = 0.48, 0.62$ and 0.75 are expected for $D_0 = 0.05, 0.025$ and 0.015 , respectively. Even $(ZT)_{xx} = 1.2$ is predicted in the most perfect crystals at $\varepsilon_F = 1.24$ ($n = 2.5 \cdot 10^{21} \text{ cm}^{-3}$), the highest calculated until now value in TTT(TCNQ)₂ crystals. The thermoelectric parameters of such crystals are $\sigma_{xx} \approx 15 \cdot 10^5 \text{ } \Omega^{-1} \text{ m}^{-1}$, $P_{xx} = 235 \cdot 10^{-4} \text{ W/m} \cdot \text{K}^2$, $\kappa_{xx} \approx 9 \text{ W/m} \cdot \text{K}$ and $S_{xx} \approx -150 \text{ } \mu\text{V/K}$. In spite of high values of the electrical conductivity, of Seebeck coefficient and of the power factor, the thermoelectric figure of merit is not sufficiently high, because the electronic part of the thermal conductivity is very high, 4.5 higher than in Bi₂Te₃.

IV. CONCLUSIONS

Organic materials of n -type usually have lower values of thermoelectric figure of merit ZT , than the materials of p -type. Therefore, the search of possibilities to increase ZT of n -type organic materials is an important and urgent problem of materials science. The modeling of thermoelectric properties have showed that in crystals of TTT(TCNQ)₂ it is possible to increase ZT up to 1.2, if the carrier concentration is increased by 2.3 times, up to $n = 2.5 \cdot 10^{21} \text{ cm}^{-3}$, and additional purification is performed.

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