ENHANCEMENT OF THERMOELECTRIC POWER FACTOR IN CRYSTALS OF TETRATHIOTETRACENE IODIDE

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Abstract: In this paper we analyze the usefulness of quasi-one-dimensional organic crystals of TTT_2I_3 as material for a thermoelectric generator or thermoelectric cooler. Therefore, the thermoelectric power factor is calculated in the frame of a more complete three-dimensional physical model, for different values of carrier concentration and purity level. It is demonstrated that the power factor of the crystal can be increased significantly, if some optimizing procedures are applied. These include the decrease of carrier concentration in comparison with the stoichiometric one and further purification.

Keywords: Thermoelectric Power Factor, Quasi-one-dimensional Organic Crystal, Numerical Modeling, Electrical Conductivity, Tetrathiotetracene-Iodide.

1. Introduction

In the context of rapid development of industrial sector, the demand for energy is rapidly growing. Consequently, the depletion of natural resources of coal, oil and gas represent a pressing issue and further development of the humanity directly depends on the intelligent solving of this problem. According to the newest global agreements [1], in order to avoid dangerous climate change by limiting global warming to well below 2°C, one expects to slow down the projected rise in energy-related carbon emissions. Major transformations in the global energy system are predicted over the next decades, with renewables and natural gas being the big winners in the race to meet energy demand growth until 2040.

The use of organic thermoelectric devices is a promising intelligent idea in this connection, with new environment-friendly technological solutions of energy conversion, the advantages of small size, high reliability, no pollutants and feasibility in a wide temperature range. The thermoelectric performance of a material is described by the dimensionless thermoelectric figure of merit ZT, where T is the operating temperature. $ZT = \sigma S^2 T / \kappa$, where σS^2 is the power factor and κ is the thermal conductivity of the material. In the last years, the wide commercialized thermoelectric devices are based on inorganic compound Bi_2Te_3 with $ZT \sim 1$ near room T. One estimates that in order to become economically competitive with the ordinary used convertors, the solid-state ones needs to achieve $ZT \geq 3$.

There are two main possibilities to increase ZT: the diminution of thermal conductivity and the enhancement of power factor. In conducting polymers and organic semiconductor the intrinsic thermal conductivity is relatively low, varying from 0.2 $Wm^{-1}K^{-1}$ for poly(3,4-ethylenedioxythiophene) complexes with (PEDOT:PSS) and 0.7 $Wm^{-1}K^{-1}$ for highly doped polyacetylene [2-4].

In TTT_2I_3 the contribution of the crystalline lattice is 0.6 $Wm^{-1}K^{-1}$. The thermal conductivity of conducting electrons is much significant, $3 - 5$ $Wm^{-1}K^{-1}$, depending on concentration. The enhancement of the power factor can be obtained by applying some doping procedures, which entails the increment of thermal conductivity of charge carriers. Thus, high ZT values are available for certain compromise values of the mentioned above quantities.

In this paper, the power factor of the TTT_2I_3 organic crystals is modeled numerically by using a more complete three-dimensional physical model.

2. The physical model of TTT₂I₃ crystals and the numerical results.

Tetrathiotetracene-iodide (TTT_2I_3) crystals are formed from segregate stacks or chains of TTT molecules and iodine. Two TTT molecules give one electron to iodine chain and a CT-complex (charge-transfer complex) is obtained. The charge transport is provided mainly by the holes, since the electrical conductivity of iodine chains is very low. A brief description of crystal structure is presented in [5, 6].

The Hamiltonian of the crystal is obtained in the frame of tight-binding electrons and nearest neighbour approximations:

$$H = \sum_k E(\boldsymbol{k})a_k^+a_k + \sum_q \hbar\omega_q b_q^+b_q + \sum_{k,q} A(\boldsymbol{k},\boldsymbol{q})(b_q + b_{-q}^+)a_k^+a_{k-q} + (I_iV_{0i}\sum_{l=1}^{N_i}e^{-i\boldsymbol{q}\boldsymbol{r}_l} + I_dV_{0d}e^{-E_0/k_0T}\sum_{m=1}^{N_d}e^{-i\boldsymbol{q}\boldsymbol{r}_m})V^{-1}\sum_{k,q}a_k^+a_{k-q} \quad (1)$$

The electron-phonon interaction consists of two main interaction mechanisms: of the deformation potential and of the polaron type. Both mechanisms are included in the matrix element of interaction $A(\boldsymbol{k}, \boldsymbol{q})$. $E(\boldsymbol{k})$ is the energy of electrons, ω_q is the frequency of longitudinal acoustic phonons and the last term describes the interactions with impurities.

The kinetic equation is deduced using the two-particle temperature dependent retarded Green function. numerical calculations of electrical conductivity σ_{xx}, thermopower S_{xx} and power factor P_{xx} along the molecular wires (*x* direction) are performed by considering the crystal parameters presented in [7].

In Fig.1. the electrical conductivity is presented as a function on dimensionless Fermi energy (ε_F) for three different values of the parameter describing impurity scattering (D_0). The crystals with $D_0 = 0.1$ are grown from gaseous phase with stoichiometric conductivity $10^6\ \Omega^{-1}m^{-1}$ [7]. In this case, the results of the one-dimensional (1D) physical model and those obtained in the frame of a more complete 3D model practically coincide. For stoichiometric crystals ($n = 1.2 \cdot 10^{21}$ cm^{-3}, or dimensionless Fermi energy $\varepsilon_F \sim 0.34$) we obtained $\sigma_{xx} \approx (8.5, 26, 60) \cdot 10^5\ \Omega^{-1}m^{-1}$ for $D_0 = 0.1, 0.02, 0.004$. It is observed that the electrical conductivity may be increased by optimizing the carrier concentration and further purification of crystals. The values $D_0 = 0.02$ and 0.004 are not obtained yet experimentally.

Fig.1. Electrical conductivity of TTT$_2$I$_3$ at RT for $D_0 = 0.1, 0.02, 0.004$

For stoichiometric TTT$_2$I$_3$ crystals, S_{xx} weakly depends on crystal perfection and is close to $S_{xx} \sim 35 - 40$ µV/K, reported experimentally [7]. If the concentration of charge carriers (holes) is diminished twice, from $n = 1.2 \cdot 10^{21}$ cm^{-3} down to $n = 0.6 \cdot 10^{21}$ cm^{-3} (with $\varepsilon_F \sim 0.12$), $S_{xx} \sim 260$ µV/K is expected for the purest crystals with $D_0 = 0.004$.
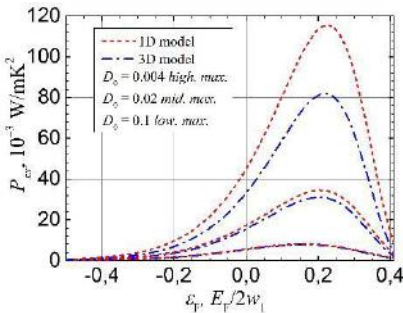
Fig.3. The Power Factor of TTT$_2$I$_3$ for $D_0 = 0.1, 0.02, 0.004$.
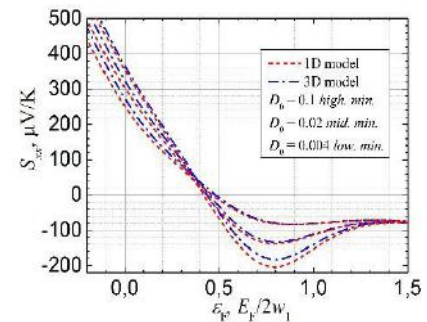
Fig.2. The Seebeck coefficient (S_{xx}) of TTT$_2$I$_3$ at RT for $D_0 = 0.1, 0.02, 0.004$.

In fig.3. the resulting power factor is presented. In stoichiometric crystals, because of low Seebeck coefficient, $P_{xx} \sim (4, 15, 40)$ mV/K, relatively low for thermoelectric applications. If the concentration of carrier is diminished down to $n = 0.8 \cdot 10^{21}$ cm^{-3} and the crystal is further purified, the power factor increases up to 80 mV/K or 2 times higher in comparison to Bi$_2$Te$_3$.
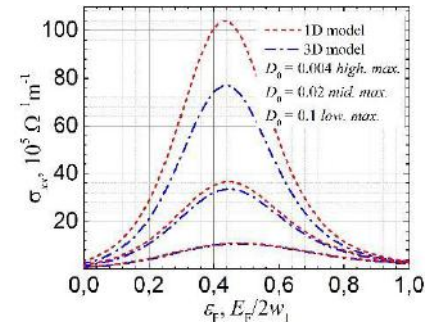
3. Conclusions:

The numerical modeling of the power factor and Seebeck coefficient demonstrates that quasi-one dimensional TTT$_2$I$_3$ organic crystals are prospective p – type materials for thermoelectric applications. It is expected that values of $P_{xx} \sim 80$ mV/K can be obtained for crystals with electrical conductivity $\sigma_{xx} \approx 60 \cdot 10^5\ \Omega^{-1}$ cm^{-1} and thermopower $S_{xx} \approx 260$ µV/K, after performing carrier concentration tuning and advanced purification.

4. References

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