TEMPERATURE DEPENDENCE OF THE THERMOELECTRIC POWER FACTOR OF TTT$_2$I$_3$ ORGANIC CRYSTALS

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Abstract. In this paper, the temperature dependence of the thermoelectric power factor of nanostructured organic crystals of tetrathiotetracene-iodide, TTT$_2$I$_3$ is presented. It has been demonstrated that such organic compounds are very good candidates for thermoelectric applications, and could be used for different purposes, such as direct conversion of thermal energy into electrical power, cooling systems or infrared sensors. The crystals admit non-stoichiometric compounds, and the thermoelectric properties are well tunable by manipulating the donor-acceptor ratio. In this paper, we have modeled the electrical conductivity, the thermopower and the power factor as a function of absolute temperature for different values of charge carrier concentration.

Key words. Nanostructured organic crystals, thermoelectric converters, electrical conductivity, thermopower, thermoelectric power factor.

1. Introduction

In the last time, the ecological problems facing humanity are becoming more and more serious and require an urgent solution. In the last decades, the scientific interest paid to the renewable energy sources has increased significantly. The possibility of direct conversion of host thermal energy into electrical power has been explored intensively, leading to the discovery of new materials and compounds with unusual and promising properties [1]. Important results have been reported recently in inorganic materials [2-4]. However, the expensive production technology and the small amount of raw inorganic materials are slowing the implementation of these materials. In this sense, organic compounds are more prospective, due to their cheap and eco-friendly production technology, lightweight and flexibility, well tunable

internal properties by simple chemical methods [5, 6]. The class of polymers with high electrical conductivity has been identified as very prospective thermoelectric materials. In this order, the highly conducting quasi-one-dimensional (Q1D) organic crystals of tetrat hiotetracene-iodide (TTT$_2$I$_3$) were intensively investigated for thermoelectric properties and large possibilities of enhancement [7].

The intensity of electrical power, generated by a thermoelectric element, is directly related to the power factor of the consisting materials. This parameter is directly proportional to the electrical conductivity and the square of thermopower (Seebeck coefficient):

$$P = \sigma S^2 \tag{1}$$

In ordinary materials, these two parameters are interconnected, meaning that while improving the electrical conductivity, the thermopower decreases. It has been demonstrated [8, 9] that in such organic compounds, both electrical conductivity and thermopower could be increased simultaneously, so as the carriers relaxation time as function of carrier energy achieves high maximum for a narrow strip of energetic states in the conduction band. This leads to a maximum of the power factor (1), limited by internal scattering processes.

The internal structure of TTT_2I_3 crystals consists of segregated molecular chains or stacks, resulting in an intra-chain spacing between two adjacent molecules, which is much smaller than the distance between neighboring chains. Along the chains, a narrow conduction band is generated by the overlap of electronic wave functions. The inter-chain overlap is very small and the preferential charge movement is along TTT molecular chains. The electrical conductivity of I iodine chains is negligible and crystals of TTT_2I_3 show a p – type behavior of electrical conductivity. Lattice constants are $a = 18.35$ Å, $b = 4.96$ Å, $c = 18.46$ Å, confirming Q1D structure with conducting direction along b. The two-dimensional (2D) physical model of the crystal is considering the main charge transport along TTT chains and the rarely electron jumps on neighbor chains in a direction.

The aim of this paper is to investigate the temperature dependences of the thermoelectric power factor in order to determine the optimal temperature interval and the prospective of using the TTT_2I_3 crystals as constructive part of thermo-electric converters.

2. The physical model of TTT_2I_3 crystals

In order to describe the charge transport in TTT_2I_3 crystals along TTT molecular chains, a temperature-dependent, two-dimensional (2D) physical model was elaborated. Along the main direction (b), a band-type transport mechanism is considered (with a bandwidth $4w_1 \sim 0.64$ eV, where w_1 is the transfer energy of an electron between the nearest TTT molecules along b direction). In transversal (a) direction, the overlap of electronic wave functions is significantly smaller, and we have considered a transfer energy $w_2 \sim 0.01 w_1$.

The Hamiltonian of the crystals has the form:

$$H = \sum_k E(\boldsymbol{k}) a_k^+ a_k + \sum_q \hbar \omega_q b_q^+ b_q + \sum_{k,q} A(\boldsymbol{k},\boldsymbol{q}) a_k^+ a_{k+q}(b_q + b_{-q}^+)$$

$$+ \left(I_i V_{0i} \sum_{l=1}^{N_i} e^{-iqr_l} + I_d V_{0d} e^{-E_0/k_0 T} \sum_{j=1}^{N_d} e^{-iqr_j} \right) V^{-1} \sum_{k,q} a_k^+ a_{k+q},$$

$$(2)$$

where

$$E(\mathbf{k}) = -2w_1[1 - \cos(k_x b)] - 2w_2[1 - \cos(k_y a)]$$

is the energy of carriers (holes), measured from the top of the conduction band, in the nearest-neighbor and tight-binding electrons approximations. The second term describes the acoustic phonons

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

where ω_1 and ω_2 are cut-off frequencies, and q_x, q_y are the projections of the quasi-wave vector $\boldsymbol{q}$.

Two main electron-phonon interaction mechanisms are considered in third term of (2). One interaction is similar to that of the deformation potential, and is determined by the variation of the transfer energies of an electron between the nearest TTT molecules due to acoustical phonons. The esond interaction is of polaron type, and is determined by the variation of polarization energy of molecules surrounding the carrier charge, due to the same acoustical phonons. The ratio of amplitudes of the second mechanism to the first one is described by dimensionless parameters γ_1 and γ_2 for b and a direction. Also, the scattering on

point-like impurities and thermally activated lattice dislocations is considered (see the last term of (2)). I_i and I_d are the energy of interaction of the electron with an impurity and with a defect within regions of volume V_{0i} and V_{0d}, respectively. E_a is the activation energy of a defect.

3. Electrical conductivity, Seebeck coefficient and the power factor

For a weak electric field and low temperature gradient, we have considered elastic scattering of charge carriers on acoustic phonons. The kinetic equation of the Boltzmann type was obtained by solving analytically the two-particle, temperature dependent, retarded Green functions. The obtained transport integrals have the form:

$$R_n = \int_0^2 d\varepsilon \int_0^\pi d\eta [\varepsilon + d(1-\cos\eta) - (1+d)\varepsilon_F]^n \varepsilon(2-\varepsilon) \times$$
$$\times n_{\varepsilon,\eta}(1-n_{\varepsilon,\eta})[s_0\sqrt{\varepsilon(2-\varepsilon)}cth(s_0T_0\sqrt{\varepsilon(2-\varepsilon)}/T) \times$$
$$\times \gamma_1^2(\varepsilon-\varepsilon_0)^2 + \frac{(w_2/w_1)^2}{8\varepsilon(2-\varepsilon)}(1+\gamma_2^2+2\sin^2\eta-2\gamma_2\cos\eta)$$
$$+ D_0 + D_1\exp(-E_a/k_0T)]^{-1}, \text{ where } s_0 = \hbar v_{s1}/(ak_0T_0).$$
(3)

where $\varepsilon = E(k_x)/2w_1$ and ε_F are the dimensionless kinetic energy of a hole along chains and Fermi energy in units of $2w_1$, respectively. $n_{\varepsilon,\eta}$ is the Fermi distribution function and $\eta = k_y a$ is the dimensionless quasi momentum. $\varepsilon_0 = (\gamma_1-1)/\gamma_1$ is the dimensionless resonance energy. The parameters D_0 and D_1 describe the scattering on point-like impurities and lattice dislocations, respectively. In our investigations we have considered $D_0 = 0.001$ and $D_1 = 0.8$. These values were estimated by comparison with experimentally reported data for electrical conductivity.

The transport integral from (3) can be ~~solved~~ calculated only numerically. The power factor of the crystal, along the TTT chains (x direction), has the form:

$$P_{xx} = \sigma_{xx}S_{xx}^2 \tag{4}$$

where σ_{xx} and S_{xx} are the electrical conductivity and the Seebeck coefficient, expressed as follows:

$$\sigma_{xx} = \sigma_0 R_0; S_{xx} = (k_0/e)(2w_1/k_0T)R_1/R_0;$$
$$\sigma_0 = 2e^2 Mv_{s1}^2 w_1^3 r / \pi^2 \hbar ab(k_0T)^2 w_1'^2 (T_0/T),$$
(5)

R_n are transport integrals (3), k_0 is the Boltzmann constant, e – elementary charge, M is the mass of TTT molecule, v_{s1} - the sound velocity along TTT chains, r is the number of molecular chains per elementary cell and w_1' is the derivative of transfer energy with respect to the intermolecular distance.

4. Numerical modeling of the results

For numerical calculations, we considered the following crystal parameters: $M = 6.5 \cdot 10^5 m_e$ (m_e is the mass of the free electron), $w_1 = 0.16$ eV, $w_1' = 0.26$ eVÅ^{-1}, $v_{s1} = 1.08 \cdot 10^3$ m/s, $\gamma_1 = 1.5$. In crystals with stoichiometric composition, the concentration of charge carriers is estimated to $n_h = 1.2 \cdot 10^{21}$ cm^{-3}. It was predicted theoretically [10], that the thermoelectric properties of TTT$_2$I$_3$ crystals can be significantly improved by diminishing the concentration of charge carriers.
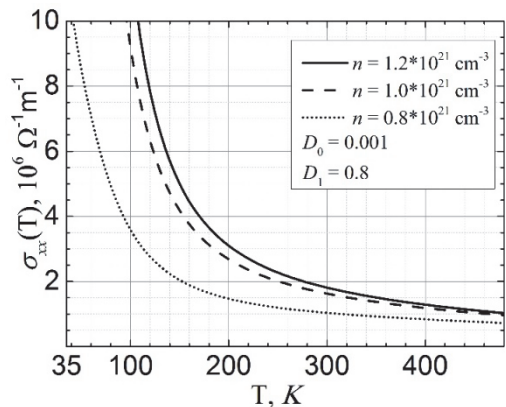

Fig.1. Longitudinal electrical conduc-tivity

as a function of temperature.

Experimentally, it was demonstrated the enhancement of thermoelectric properties of such structures by manipulating chemically the crystal composition [11, 12].

In this case, we have chosen three values of hole concentration: $n_h = 1.2, 1.0$ and $0.8 \cdot 10^{21}$ cm^{-3}, to which the dimensionless Fermi energies $\varepsilon_F = 0.32, 0.24$ and 0.17 correspond.

In Fig. 1, the electrical conductivity as a function of temperature is presented. For temperatures below ~ 100 K, a smooth metal-dielectric transition of Peierls type occurs. The phase transition in TTT$_2$I$_3$ crystals is described in [13]. This aspect is not considered in our physical model. For energy conversion applications, temperatures near room temperature or above should be considered. With the diminution of n_h, the electrical conductivity is diminished, for a wide range of temperatures.

For higher temperatures, the decrease of charge carrier mobility is caused by the increasing intensity of scattering processes on thermally activated lattice defects.

In Fig. 2, the Seebeck coefficient is presented as a function of absolute temperature T. In this case, the Seebeck coefficient increases significantly with the diminution of n_h. Experimentally values of $S_{xx} = 36$ μV/K were reported at room temperature for crystals with $\sigma_{xx} = 10^5$ Ω^{-1}m^{-1} [14]. Our numerical calculations predict values of $S_{xx} = 40, 60$ and 100 μV/K for : $n_h = 1.2, 1.0$ and $0.8 \cdot 10^{21}$ cm^{-3} at T = 300 K. In the last case, S_{xx} is more than 2,5 times higher than higher mentioned experimental value. It is observed that S_{xx} remains high for a large interval of temperatures around RT.

In Fig. 3, the thermoelectric power factor as a function of temperature is presented. For temperatures below ~ 100 K, due to the metal-dielectric phase transition, the physical model does not

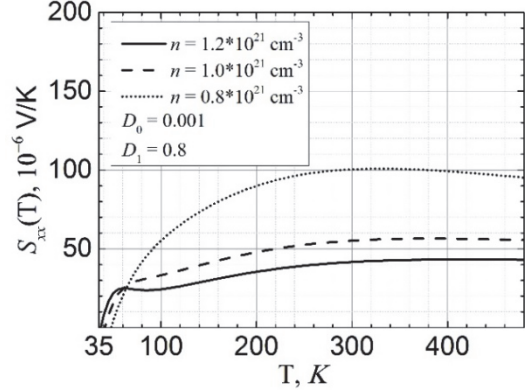describe appropriate the charge transport

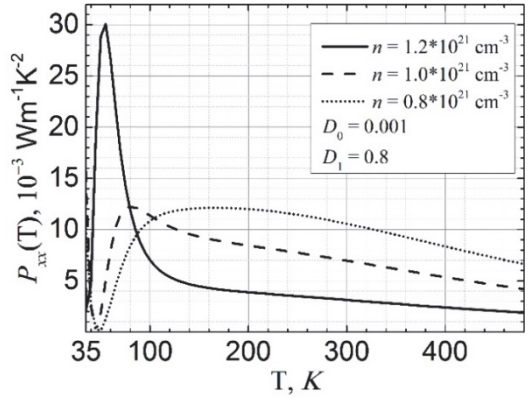Fig.2. Seebeck coefficient as a function of temperature

Fig.3. The power factor in longitudinal to TTT molecular chains direction.

For higher temperatures, it is observed that P_{xx} has a behavior with a maximum, displaced towards higher temperatures as the concentration of holes is diminished. This allowed us to predict that high values of power factor could be obtained at room temperature, by accurate tuning of carrier concentration.

For instance, at T = 300 K, values of $P_{xx} \sim 3; 7$ and $10 \cdot 10^{-3}$ Wm^{-1}K^{-2} are predicted for $n_h = 1.2, 1.0$ and $0.8 \cdot 10^{21}$ cm^{-3}. At T = 400 K $P_{xx} = 2.4 \cdot 10^{-3}$ Wm^{-1}K^{-2} in stoichiometric crystals and could be increased up to $8.3 \cdot 10^{-3}$ Wm^{-1}K^{-2}, if the concentration of carriers is diminished by 1.5 times. For comparison, in the most

widely used inorganic thermoelectric material, Bi_2Te_3, $P \sim 4 \cdot 10^{-3}$ $Wm^{-1}K^{-2}$ at T = 300 K [14].

5. Conclusions

The electrical conductivity, the Seebeck coefficient and the power factor of TTT_2I_3 crystals were calculated numerically for different parameters, as a function of temperature. It was found that the crystals could show very promising thermoelectric properties for a wide temperature range, from $\sim$ 200 K up to 450 K. For stoichiometric crystals at T = 300 K, a value of $P_{xx} \sim 3 \cdot 10^{-3}$ $Wm^{-1}K^{-2}$ can be obtained. By analyzing the results of numerical modeling, we predict that values up to $10 \cdot 10^{-3}$ $Wm^{-1}K^{-2}$ could be obtained at room temperature by diminishing the charge carrier concentration by 1. 5 times with respect to the stoichiometric one. It was demonstrated that optimized in such a way TTT_2I_3 crystals will still have an increased power factor for a temperature interval of 100 K below and above the room temperature.

Acknowledgments

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