QUASI-ONE-DIMENSIONAL ORGANIC CRYSTALS WITH IMPROVED THERMOELECTRIC PROPERTIES

A. Casian[1], I. Balmus[1], Z. Dashevsky[2], H. Scherrer[3], V. Dusciac[1], R. Dusciac[1]

[1]Department of Computers, Informatics and Microelectronics, Technical University of Moldova, MD-2004 Chisinau, Moldova

[2]Department of Materials Engineering, Ben-Gurion University of the Negev, P.O. Box 653, Beer-Sheva 84105, Israel

[3]Laboratoire de Physique des Materiaux, Ecole des Mines, Parc de Saurupt, 54042 Nancy, France

Abstract: Thermoelectric properties of quasi-one-dimensional (Q1D) organic crystals with the interference of two main electron-phonon interactions are considered. The electrical conductivity, thermopower, electronic thermal conductivity and thermoelectric figure of merit *ZT* are calculated for such crystals. Values of *ZT* much higher than unity are predicted.

Keywords: organic crystals, thermopower, thermoelectric figure of merit

The finding of materials with improved thermoelectric figure of merit *ZT* would widely increase the applications of thermoelectric devices. However, in spite of a large number of investigated materials, the maximum value of *ZT* ~1, achieved in bulk alloy Bi_2Te_3/Sb_2Te_3, could not be increased significantly. Recently, the search of materials with improved thermoelectric properties was enlarged by the emergence of different low–dimensional quantum–well (QW) structures. It has been demonstrated both theoretically and experimentally [1-2], that it is possible to improve significantly the thermoelectric properties of certain materials by preparing them in the form of quasi–two–dimensional or quasi–one-dimensional QW structures. The main improvement of thermoelectric properties in superlattices is due to the increase of the thermopower *S*, determined by the increasing density of states. A value of *ZT* ~ 2.4 at room temperature has been measured in *p*-type Bi_2Te_3/Sb_2Te_3 superlattice [3]. An increase of seven times of *ZT* relative to bulk Si has been observed in Si/Ge superlattice [4]. In PbTe/PbSeTe quantum dot superlattice structures *ZT* ~ 2 has been measured [5]. *ZT* ~ 2.2 at 800 K was found in some compounds of $AgPb_mSbTe_{2+m}$ type [6] with included microstructures. Our rigorous considerations of the thermoelectric properties of *n*- and *p*-type PbTe/PbEuTe QWs [7-9] have demonstrated that for several parameters of QWs and carrier concentrations a significant increase of the thermoelectric power factor *P* and figure of merit

ZT is possible. However, the technology for production of such structures is very complicated and expensive. On the other hand, the obtaining of materials with higher *ZT* would extend significantly the application of thermoelectric devices. Therefore, the search and investigation of novel materials with improved thermoelectric properties continues to remain an important and urgent problem from both scientific and practical points of view.

Presently, the Q1D organic compounds attract an especial attention. Such materials combine together the increase of the density of states, due to one dimensionality of the electronic spectra, and more complicated and diverse scattering mechanisms, determined by their molecular structure. In [10-12] we have already demonstrated that in Q1D organic crystals it is expected to obtain (under special conditions) extremely high mobilities and electrical conductivities. In the present paper we show that in such crystals it is possible to increase considerably also the thermopower and that such materials are very promising for thermoelectric applications.

Q1D organic compounds are composed of linear chains of molecules that are packed into a 3D crystalline structure. The overlapping of conduction electrons molecular orbitals along the chains is significant, whereas between the chains it is very small. As a result, the conduction mechanism along the chains is band-like and between the chains is hopping like. These particularities of electronic transport have determined a range of unusual properties of such crystals [13].

We will apply the physical model of a Q1D organic crystal described in [10]. It is important that the model takes into account simultaneously two main electron-phonon interaction mechanisms. The first one is determined by the variation of the transfer energy of an electron from one molecule to the nearest one along the chain, caused by the acoustic intermolecular vibrations of the crystalline lattice. This mechanism is similar to that of the deformation potential. The second interaction mechanism is determined by the variation of the polarization energy of molecules surrounding the conduction electron due to the same acoustic vibrations. It is similar to that of the polaron-phonon interaction. These interaction mechanisms have been considered in the literature, but we have applied them together for the first time to the Q1D organic crystals. It is very important because under special conditions the interference between above mentioned interactions can take place. Due to the interference, the electron-phonon interactions compensate each other for a narrow

strip of states in the conduction band. As a result, the relaxation time as a function of carrier energy takes the form of a Lorentzian. When the resonance energy E_0, which corresponds to the maximum of the Lorentzian, is placed into the conduction band, the carriers in the states near E_0 will have unusual long relaxation time, and, respectively, a very high mobility [10]. Due to the sharp dependence of the relaxation time on energy, these carriers will have simultaneously increased values of the thermopower. It is favorable to expect improved thermoelectric properties of such crystals.

The dependencies of electrical conductivity σ, thermopower S, electronic thermal conductivity κ^e and ZT are calculated after the formulae presented in [12] for a hypothetic crystal
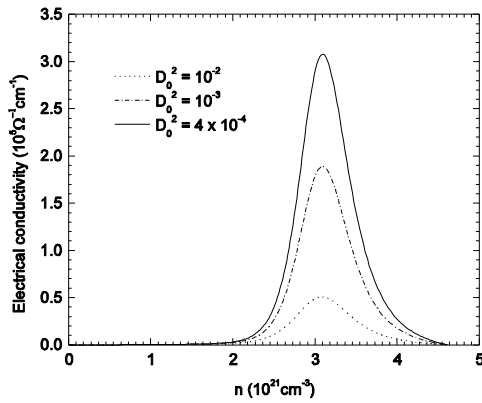

Fig. 1. The dependence of electrical conductivity σ on carrier concentration n.
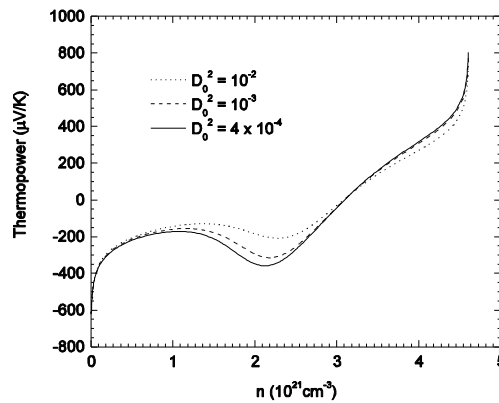

Fig. 2. The dependence of thermopower S on carrier concentration n.

with the parameters close to those of TCNQ chains in the TTF-TCNQ crystals. The parameter γ, which is the ratio of amplitudes of two mentioned electron-phonon interactions, is taken equal to 2, and the values of the parameter D_0, which describes the carriers scattering on impurities, are indicated in figures. From Fig. 1 it is seen that σ has a maximum and achieves high values due to the contribution of carriers with very long relaxation time. From Fig. 2 it is seen that S may also achieve high values, due to the increase of kinetic transport energy by carriers excited in the states near the resonance energy E_0. The dependence of S on parameter D_0 is less pronounced than for σ. Fig. 3 shows that κ^e also has a maximum as σ, but it is, relatively, not so big.

From Fig. 4 it is seen that ZT has a pronounced maximum of 10.5 at rather high carrier concentration $n=2.76\times10^{21}\text{cm}^{-3}$, when $\sigma = 2.13\times10^5\ \Omega^{-1}\text{cm}^{-1}$, $S = 120\mu\text{V/K}$ and $\kappa^e = 93$ mW/cmK. The main source of ZT enhancement is the growth of σ, due to both high carrier concentration and

increased mobility. κ^e is also high, but for the maximum value of *ZT* the Lorentz number is more that ten times less than it is expected according to the Wiedemann-Frantz law in the degenerate case. This is favorable for the increase of *ZT*. It is important that the crystals have pronounced Q1D
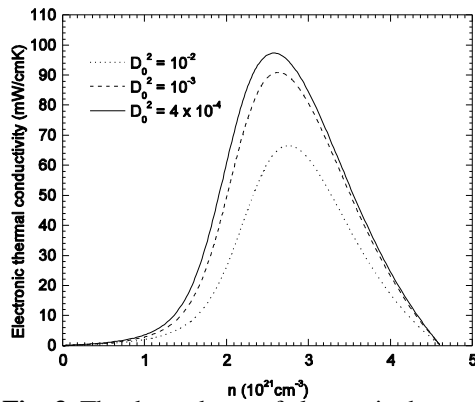

Fig. 3. The dependence of electronic thermal conductivity κ^e on carrier concentration *n*.
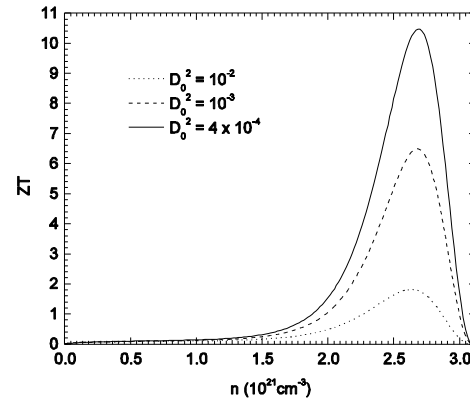

Fig. 4. The dependence of thermoelectric figure of merit *ZT* on carrier concentration *n*.

properties, high purity, and the carrier concentration be near to optimal one.

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