

## Thermoelectric Properties of Tetrathiotetracene Iodide Crystals: Modeling and Experiment

Anatolie CASIAN and Ionel SANDULEAC

Department of Computers, Informatics and Microelectronics,  
Technical University of Moldova, Stefan cel Mare av. 168, Chisinau, Rep. of Moldova

A more complete physical model for nanostructured crystals of tetrathiotetracene-iodide that takes into account the interaction of carriers with the neighboring one-dimensional (1D) conductive chains and also the scattering on impurities and defects is presented. For simplicity the 2D approximation is applied. It is shown that this model describes very well the temperature dependencies of electrical conductivity in the temperature interval between 180 and 300 K and of Seebeck coefficient between 50 and 300 K, the highest temperature for which the measurements were reported. For lower temperatures it is needed to also consider the fluctuations of dielectric phase which appear before the metal-dielectric transition. It is found that the predictions made in 1D approximation are valid, if the crystal purity is not very high, the electrical conductivity is limited up to  $\sim 3.5 \times 10^6 \Omega^{-1} \text{m}^{-1}$  and the thermoelectric figure of merit up to  $ZT \sim 4$ .

**Key words:** Thermoelectric, organic crystal, tetrathiotetracene-iodide, Seebeck coefficient, thermal conductivity, thermoelectric figure of merit.

### INTRODUCTION

Organic materials attract more and more attention for thermoelectric applications as materials with much more diverse properties and less expensive in comparison with the known inorganic ones. Besides, organic materials usually have a very low thermal conductivity that is favorable for the improvement of thermoelectric efficiency. In poly(3,4-ethylenedioxy-thiophene) (PEDOT) a value of the thermoelectric figure of merit  $ZT = 0.25$  has been measured [1] and  $ZT \sim 1$  is predicted in this class of materials [2]. Reported in [1] data were analyzed in [3] and it was shown that the increase in the power factor in PEDOT is due mainly to the increase of ionized impurity scattering over the lattice scattering, leading to the increase of the thermopower. The peak power factor occurs for carrier density of  $\sim 1 \times 10^{26} \text{m}^{-3}$  higher than in inorganic thermoelectric materials and mobility of  $\sim 5 \times 10^{-4} \text{m}^2/\text{V s}$ .  $ZT$  was also enhanced due to low thermal conductivity of PEDOT  $\sim 0.37 \text{W/m K}$ . By minimizing the total dopant volume and increasing the ionization fraction,  $ZT = 0.42$  at room temperature was achieved [4] in PEDOT:PSS.

Both *n*-type and *p*-type organic thermoelectric materials with  $ZT$  values of 0.1 to 0.2 around 400 K were developed in [5]. A thermoelectric module containing 35 *n-p* single couples was fabricated which demonstrates an output power of 750  $\mu\text{W}$ , the highest for organic materials reported to this date. Prospects for polymer-based thermoelectric materials are discussed in [6].

The iodine-doped pentacene thin films can be potential candidates for good organic thermoelectric materials [7]. It is expected that the nanocomposite approach of organic and inorganic components could create new efficient thermoelectric materials [8-10]. And really, the highest value of  $ZT = 0.57$  at room temperature was measured in phenyl acetylene-capped silicon nano particles [11]. This result is obtained due to relatively high Seebeck coefficient  $S = 3.2 \times 10^3 \mu\text{V/K}$  and very low

thermal conductivity  $\kappa = 0.1 \text{Wm}^{-1}\text{K}^{-1}$ . For the description of thermoelectric transport in organic materials different theoretical models have been developed [12-15].

The quasi-one-dimensional (Q1D) organic crystals attract special attention. Such crystals join together the thermoelectric advantages of multi component systems with more diverse internal interactions and of low dimensional ones with increased electronic density of states. In molecular nanowires of conducting polymers values of  $ZT \sim 15$  and of thermoelectric power factor  $\sim 500 \mu\text{W/cm-K}$  at room temperature were predicted [16]. Such predictions are very important, because in this paper the charge and energy transport is described in the hopping model which is applicable in the case of polymers, but usually gives smaller mobility than the band model.

Still higher values of  $ZT$  were predicted by us in Q1D charge transfer organic crystals, if the crystal purity is sufficiently high [17]. However, the above predictions were made on the base of a simplified strictly one-dimensional crystal model. From experimental data it is known that in Q1D crystals the electrical conductivity  $\sigma$  along the molecular chains is almost by three orders of magnitude higher than in the direction transversal to chains. Although from this fact it follows that the interaction between the conductive molecular chains is weak, it is absolutely necessary to estimate the effect of interchain interaction and the restrictions on thermoelectric efficiency that this interaction involves.

The aim of the paper is to present a more complete physical model for highly conducting organic nanostructured crystals of tetrathiotetracene-iodide,  $\text{TTT}_2\text{I}_3$ , as thermoelectric material. The carrier interaction with the neighboring 1D conductive chains and also the scattering on neutral impurity and thermally activated structural defects are taken into account. The model becomes rather cumbersome, therefore for simplicity the 2D approximation is applied. It is shown that the