Journal of ELECTRONIC MATERIALS, Vol. 42, No. 3, 2013
DOI: 10.1007/s11664-012-2374-1

Thermal Conductivity and *ZT* in Disordered Organic Thermoelectrics

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For decades, continuous attempts have been made to improve the figure of merit (*ZT*) of thermoelectrics. The theory behind the Seebeck effect itself is well researched, but the problem with *ZT* is related to materials properties that offset one another. This work analyzed the link between the site energy distributions and thermal conductivity of oxidized poly(3,4-ethylenedioxythiophene-tosylate) (PEDOT:Tos), which was reported to be a good organic thermoelectric. To understand how heat flow was affected by "disorder" in PEDOT:Tos and the associated electron–phonon interactions, we computed the values of the thermal conductivity κ and *ZT* using materials parameters extracted from the open literature. By varying the values of the parameters separately, we were able to identify their individual influence on κ and *ZT*. Our results suggest that *ZT* is most sensitive to changes in σ, the bandwidth of the density of states (DOS) of the transport sites, and less so to changes in n_{eff}, the effective carrier density. Our simulations also suggested that *ZT* could become exceptionally large (approaching a value of ~20) if σ were lowered to 1 meV to 2 meV. This would be a tremendous approach to increase *ZT* in oxidized PEDOT:Tos.

Key words: Disordered organic semiconductors, thermal conductivity, *ZT*, bandwidth of the DOS of the transport sites, electron–phonon interactions

INTRODUCTION

Recent studies have indicated that disordered thin films are capable of generating large values of *ZT* provided that the thermal conductivity κ is small.[1–3] The same should apply to organic thin-film thermoelectrics.[4,5] Quite obviously, we would ask the questions why and how disordered organic semiconductors can have small κ. To address this question, we examined the materials properties linked to κ and *ZT* in oxidized poly(3,4-ethylenedioxythiophene-tosylate) (PEDOT:Tos), which is known to have both large carrier density and low κ. Unlike inorganic semiconductors, organic semiconductors exhibit unique physical and transport properties including dispersive charge transport, field-dependent carrier mobility, and unconventional mobility–temperature characteristics.[6–8] A number of theories have been used to explain such observations, and most involved charge trapping. More specifically, carrier transport in disordered organic semiconductors is known to be dominated by hopping,[9] which involves a two-step process. Firstly, carriers have to escape from transport sites and migrate to new sites assisted by the local/external field. Such a charge transfer process may involve electron–phonon interactions via a polaron or a bipolaron (a polaron is composed of a charge and its accompanying polarization field, while a bipolaron is a bound pair of two polarons). As expected, the polaron and bipolaron mass will be large, and this reduces the carrier mobility. Hopping is also accompanied by energy transfer (and/or heat dissipation), which is affected by σ, the bandwidth of the density of states (DOS) of the transport sites. Nonlocal electron–phonon interactions have been shown to lower σ in small

(Received August 7, 2012; accepted November 27, 2012; published online December 20, 2012)