QUASI-ONE-DIMENSIONAL TRANSPORT AND THERMOELECTRICITY: PEIERLS DISTORTION IN INDIUM SELENIDES

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Thermoelectric energy harvesting is a solid state technology to convert waste heat into electricity. Thermoelectric module has been used for limited purposes such as a deep space exploration and military uses. Even though it has long been studied intensively during a half century, the thermoelectric performance defined by the dimensionless thermoelectric figure-of-merit $ZT = S^2\sigma T/\kappa$, where S, σ, T, and κ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively, remains in a unity. It is widely known that the sharp density of states (DOS) near the Fermi level is a key element for a maximum thermoelectric figure-of-merit[1]. The resonant valence band control by an impurity doping is a method to control the DOS near the Fermi level. In the Tl-doped PbTe compound, the reported ZT was about 1.5 at 773 K[2]. Recently, a highly band degenerated materials of $PbTe_{1-x}Se_x$ was reported exhibiting an exceptionally high ZT of 1.8 at 850 K[3].

In order to lower the thermal conductivity κ with preserving the electrical conductivity σ, it was proposed that the phonons scatter and electrons can tunnel in a specific disordered solid which called the phonon glass and electron crystal (PGEC)[4]. The PGEC concept can be realized in rattling semiconductors and disordered nano composites[5–8]. Complex Zintl phase is an example of PGEC with low lattice thermal conductivity with high ZT of 1.4[9]. Up to now, the reported high ZT is mostly concentrated on the p-type materials while the research on the n-type materials is scarce. From the several years before, we studied the effect of Peierls distortion or charge density wave (CDW) on the thermoelectricity. Here we'll describe the fundamental concept of Peierls distortion and its applications on the thermoelectricity.

As we stated before, good thermoelectric materials have to meet the multiple requirements of high Seebeck coefficient, high electrical conductivity and low thermal conductivity, simultaneously. Because they are coupled each other, it is very difficult to control the parameters independently. The charge density wave has merits for controlling the thermoelectric parameters. Firstly, because the charge density wave is a low dimensional electronic transport property, it is anticipated the highly degenerated bands in a reduced dimensionality which may give rise to high Seebeck coefficient. Secondly, the charge density wave is a phenomenon from a strong electron-phonon coupling. The strong electron-phonon coupling induces phonon softening resulting in the decrease of phonon energy.

In terms of second order perturbation theory, the energy instability is revealed in a periodic lattices with strong electron-phonon coupling. The energy instability can be resolved by the lattice distortion which is called by the charge density wave (in a 2-D) and the Peierls (in a quasi 1-D electron system) lattice distortion[10]. The energy weakened phonon by phonon softening strongly scatters in a disordered lattice. Finally, the power factor can be maximized by controlling the energy gap driven by the Peierls or CDW lattice instability. Therefore, the high ZT can be possible in a Peierls distorted system due to high Seebeck coefficient, low thermal conductivity, and well controlled conductivity. One additional requirement for high ZT on CDW and Peierls system is the non-existence of electron-hole compensation which gives

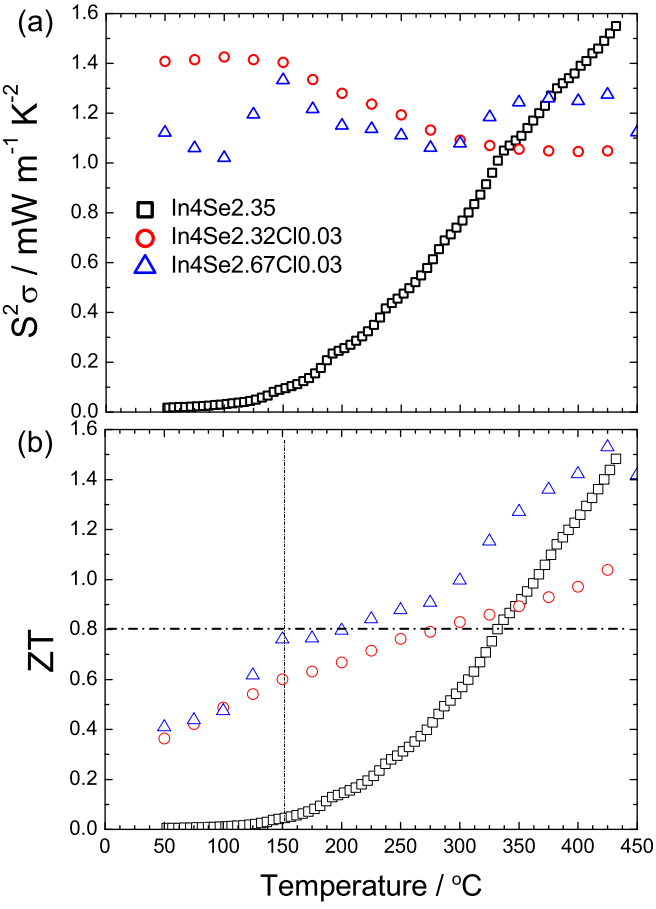

FIG. 1: (Color online) Temperature-dependent power factor $S^2\sigma$ (a) and dimensionless figure-of-merit ZT (b) of $In_4Se_{2.35}$ and $In_4Se_{3-\delta}Cl_{0.03}$ ($\delta = 0.33$ and 0.68)[17].

rise to low Seebeck coefficient[11].

The quasi-one-dimensional structure was revealed in the In_4Se_3 single crystal by the scanning tunnelling microscopy[12]. The quasi-one-dimensionality of In_4Se_3 is the intrinsic nature because it was characterized the nanowire-like clusters with 20 nm diameter along the chain direction[13]. The semiconducting band of about 1 eV was observed along the In chain direction on the compound. In order to tune the energy gap of the material, we employed selenium deficiency on the compound. The electronic band structure of In_4Se_{3-x} exhibited the strongly anisotropic property: the insulating energy gap along the *a*-axis, the hole localization along the *b*-axis, and the significant electronic band dispersion along the *c*-axis[14]. The quasi-one-dimensional structure and and hole localization with significant electronic transport are key ingredients for high *ZT*. The polycrystalline materials of In_4Se_{3-x} ($x = 0.05$) showed very high *ZT* of 0.63 as a *n*-type new materials. The nanostructural synthesis with mechanical ball milling and hot pressing on those compounds In_4Se_{3-x} ($x = 0.65$ and 0.8) increases *ZT* significantly up to a unity implying that the nanostructural process is promising in the compounds[15].

Because the basic concept of high *ZT* on those compounds is based upon the reduced dimensionality, the maximum thermoelectric performance is revealed along the chain direction. The anisotropic thermoelectric properties investigations on the bulk crystalline materials of $In_4Se_{3-\delta}$ showed exceptionally high *ZT* of 1.48 at 705 K for *n*-type materials[16]. The transmission electron microscopy confirmed the quasi-one-dimensional atomic chain along the *b*-direction. The Fermi surface calculation and electron diffraction showed the Fermi surface nesting and lattice dimerization along the *b*-direction. From the electronic susceptibility calculation, the Fermi surface nesting vector was calculated as the (0, 1/2, 1/16) indicating the lattice dimerization along the *b*-direction and long-range lattice modulation along the *c*-direction which is coincides with the electron diffraction result.

In spite of high *ZT*, the compounds are not optimized in terms of carrier density. The Boltzmann transport calculation has shown that the optimum chemical potential is of 0.8 eV while the chemical potential of $In_4Se_{2.35}$ is 0.22 eV. For the increase of chemical potential we performed chlorine doping because chlorine has one additional electron than selenium[17]. The results are shown in Fig. 1. Importantly, the power factors of chlorine doped samples are temperature insensitive and the *ZT* is increased further with maximum $ZT_{max} = 1.53$ at 425 °C which is the new record of high *ZT* in *n*-type materials. This is very important for practical applications because the operational temperature range is significantly improved from 150 °C to 450 °C by chlorine doping when we define the operational temperature as $ZT \geq 0.8$. By employing the selenium deficiency and chlorine doping concentration control, we anticipate that the *ZT* can be improved further.

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