Extrinsic-to-intrinsic transition and sign changes of Seebeck coefficients for PbTe nanocrystals

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High efficiency thermoelectric (TE) materials have recently attracted much attention due to their applications in power generation from waste heat[1,2]It has been shown that *ZT* values of 1~2 can be achieved in several advanced TE materials, e.g. LAST[3], BiSbTe[4], doped PbTe[5], In_4Se_3[6] and Si nanowires[7,8]. Further improvements are still required to achieve an impact for commercial applications. The current strategy to further enhance the *ZT* values of TE semiconductors is focused on nanostructuring these TE materials[2] to increase the interface scattering of phonons resulting in reduced thermal conductivity[4,8] and incur the quantum size effect[9] leading to the enhancement of *S*.

Quantum confinement effect have been demonstrated in TE nanocrystals.[9] However, the quantum size effect on TE materials may also give rise to significantly varied charge carrier concentration, *n*,[10,11] mainly due to the increased band gap, which will affect many properties of TE semiconductors[12]. As direct tuning of *n* in nanocrystal system is not easy[11] due to self-purification process[13], the properties of TE nanocrystals can be much different from that of bulk counterparts. Herein, we report the observation of the extrinsic-to-intrinsic transition of PbTe nanocrystal in the temperature range of 575~650 K, upon which the sign of the Seebeck coefficients may change sign, e.g. from '+' to '-'. This phenomenon has not been systematically reported before for TE nanocrystals while it may affect the proper performance of TE modules in desired operation temperature range and should be considered during the design of the thermoelectric devices using semiconductor nanocrystals.

The PbTe nanowires and nanoparticles used for TE characterization were synthesized by solvothermal process[11,14]. The bulk ingots were prepared by solid state reaction of Pb and Te powder in a high temperature vacuum furnace (See figure 1).

The Seebeck coefficients characterized in the ULVAC ZEM-3 system indicate that all three types of samples are p-type with positive values of *S* (See figure 2). Increasing the measurement temperature, it clearly reveals sign changes of *S* from '+' to '-' for PbTe NPs (575 K) and NWs (~650 K), which can not be observed for the PbTe ingot within the measurement temperature range, e.g. 300~700 K. we concluded that the sign changes of Seebeck coefficients for PbTe nanocrystals are not close related to the change of the sample stoichiometry because such transition can be observed repeatedly for each sample during cycled measurements, e.g. each sample changed back to p- type with positive *S* when cooled down to room temperature and became n-type again at high temperature.

As the mobility play important roles to determine S in the intrinsic stage, field effect measurements are carried out on PbTe NW networks at the pre-selected temperature range of 300-675K to investigate μ_p and μ_e.

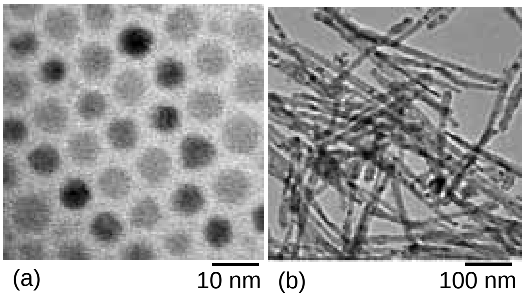

Figure 1 TEM images of as-prepared (a) PbTe NPs and (b) PbTe NWs.

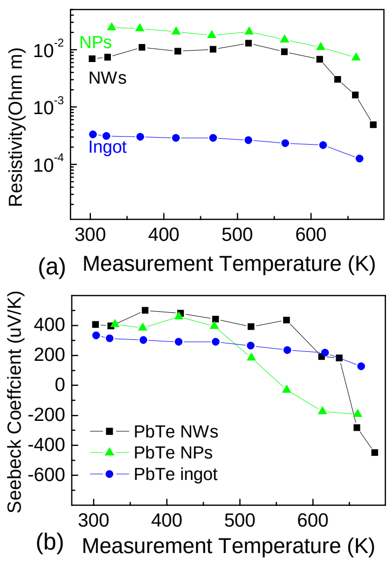

Figure 2 (a) Resistivity (b) Seebeck coefficients as a function of temperature for PbTe NWs, NPs and bulk ingots.

In summary, nanostructured PbTe, e.g. NWs and NPs, shows the extrinsic to intrinsic transition in the temperature range of 575-650 K, possibly due to their low extrinsic charge carrier concentration, while this phenomenon is not observed for bulk PbTe ingots up to 700 K. Such transition can lead to the sign change of Seebeck coefficient and may affect the proper performance of TE modules in their operation temperature range. As the adjustment of charge carrier concentration is not easy in nanocrystals due to self-purification process, such phenomenon should be considered carefully during the design of TE devices using nanostructured semiconductors.

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