Spark Plasma Sintering Nanostructured Thermoelectrics

Qinghui Jiang and Mike Reece
School of Engineering and Materials Science, Queen Mary University of London, Mile end road, London, E1 4NS, UK

There is an increasing demand for alternative energy technologies to reduce our reliance on fossil fuels. One approach is to use thermoelectric (TE) materials to scavage waste heat energy and to convert it into useful electrical energy. Thermoelectric materials have the additional potential advantages that they can be: small, inexpensive, lightweight, quiet and pollution-free(Fig.1). In this project, two strategies were used to reduce lattice thermal conductivity and then improve the zT: one is phonon-glass substitution within the unit cell by creating point defects such as interstitials and vacancies; another is the introduction of more interfaces on the nanometre scale. Using these approaches, we identified promising optimised compositions, controlled the grain morphology and size, and sintered powders by Spark Plasma Sintering (SPS), to produce doped Bi_2Te_3 and $CoSb_3$-based bulk layer-textured nanomaterials with significantly enhanced zT. Meanwhile, we also pursued sulphide system because of their low cost and no-toxicity.

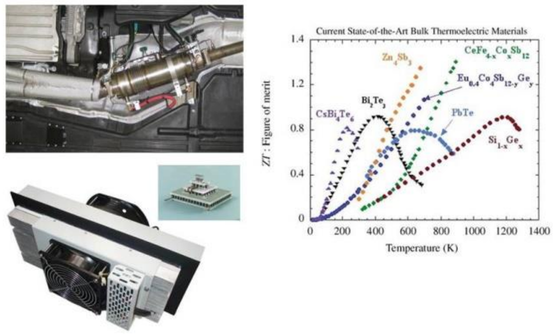

Fig. 1 current state-of-the-art-bulk thermoelectric materials

Compared with melting process in a furnace, ball milling method is a safe, low cost and easy controlled. We prepared Bi_2Te_3/$CoSb_3$ powders with the Sb, Se, Yb and Te doping by ball milling various metal powders. The powders were sinteredinto bulk samples.The optimum processing conditions and composition with best TE properties were determined. The materials were characterized from room temperature to high temperature (200 ^oC for Bi_2Te_3 and 700 ^oC for $CoSb_3$);Seebeck coefficient, electric conductivity, thermal conductivity and zT. We investigated the effect of the doping on the TE properties. For Bi2Te3, Sb doped is p- typewith a zT value about 1~1.1, which is similar with that of the commercial ingot.

Yb-stuffed and Te-substituted $CoSb_3$ has a *zT* value of ~0.7 at 600 K due to its very low lattice thermal conductivity (1.17 W m^{-1} K^{-1} at ~550 K). Yb rattles inside the cage-like structure of $CoSb_3$ which effectively reduces the phonon mean free path and results in a lattice thermal conductivity comparable to those of costly nanostructured $CoSb_3$ materials.

By combining the densification of nanostructured powders and a two-step hot forging process, hierarchical nanostructured p-type $Bi_{0.5}Sb_{1.5}Te_3$ alloys with good preferred orientation was successfully fabricated. The Seebeck coefficient in the direction perpendicular to the pressing force, which is highly anisotropic, is much greater than that of the material sintered via one-step sintering. The second step of spark-plasma-sintering hot forging induced interface modifications and crystal defects which produced both higher Seebeck value, and lower thermal conductivity due to more effective and preferential scattering of phonons than electrons. As a result, a 50%

enhancement of ZT value (from 1 to above 1.5) in the well-orientated nanostructured alloys was obtained(as shown in Fig. 2).

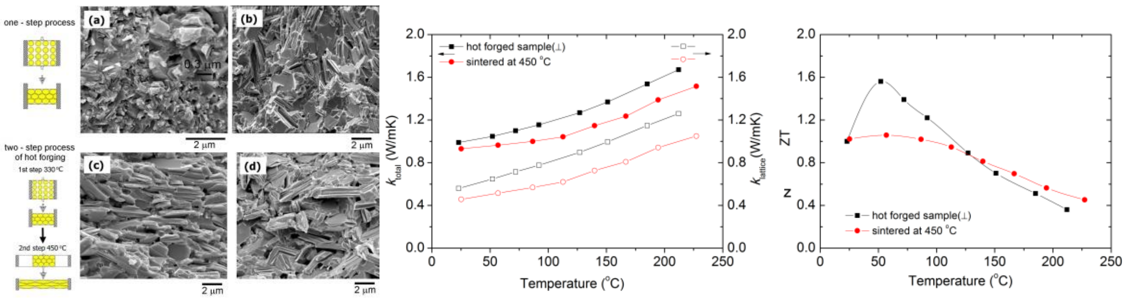

Fig. 2 SEM pictures and thermoelectric properties of BiSbTe

We introduced nano twin grain boundaries into the materials via dynamic plastic deformation and densified the powders under high pressure at room temperature or sinter the powders via spark plasma sintering. The samples have ultra-low thermal conductivity (0.3~0.5 W/m K). After the optimization of SPS sintering condition, the maximum zT value (about 1.7) can be obtained.

(3) low-cost and nontoxic sulphide system

In digenite Cu_xS, atomic-scale percolation phenomena of electric and thermal conductivity were found as copper ions are randomly located between the closely packed sulphur ions and jump to another position via unoccupied interstices. Near the threshold value (f_c ~ 0.3) in the conductive region, a 60% enhancement of zT value can be obtained. This indicates the effect of percolation phenomena produces a new strategy to optimize the properties of thermoelectric materials, especially for quasi disordered materials(as shown in Fig. 3).

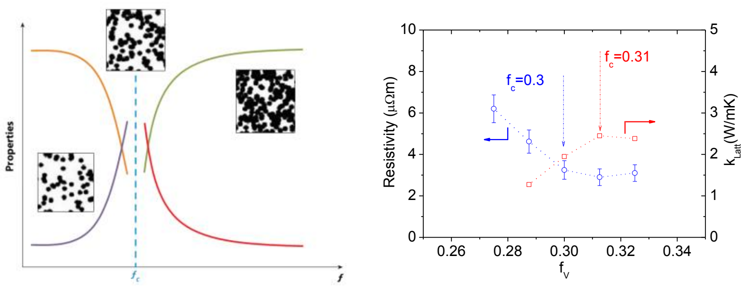

Fig. 3 Schematic of nonlinear changes in the properties of composites near the percolation threshold (left) and Dependence of the resistivity and lattice thermal conductivity of Cu_xS on the unoccupied interstices fraction f_V =(18-6x)/24 at 200 °C (right)

However, the zT value of Cu_xS is only about 0.1 at 350 °C. CuZnSnS solid solution was select because of its unique crystal structure. Its crystal structure has two functional units: Cu2S4 units are helpful for electrically conducting and other Cu_2ZnSnS_4 units act as insulating units. As a result, by the control of the content of Cu and Zn, the maximum value of about 0.6 was obtained. Hot forging process can further enhance zT value (0.8). This will reduce the cost of thermoelectric elements.

References:

[1] B. Poudel, Q. Hao, Y. M, et al, *Science*, 2008, **320**, 634-638.
[2] D. L. Medlin and G. J. Snyder, *Current Opinion in Colloid & Interface Science*, 2009, **14**, 226-235.
[3] H. Alam, and S. Ramakrishna, *Nano Energy*, 2013, **2**, 190-212.