## Spark Plasma Sintering Nanostructured Thermoelectric Sulphides

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Thermoelectric (TE) power generation, which offers potential for converting waste industrial heat into useful electricity, is foreseen to become increasingly important in the near future because of the need for alternative energy sources. How big this role is likely to be depends not only on the efficiency of TE materials but also on the earths crustal abundance and toxicity of their raw materials. The main objective of this project was to develop high performance nanostructured TE sulphides to replace current commercial materials that use costly, scarce and toxic elements. This project has helped to clarify the physical mechanisms behinds the ultralow lattice thermal conductivity of the Cu-Sb-S system with nominal trivalent Sb atoms. New synthesis routes for nanostructured sulphides and silicides were also developed.

IB-VA-VIA compounds with intrinsically low lattice thermal conductivity have attracted considerable attention because of their potential for thermoelectric application. The anharmonicity in the lattice vibrations produced by the lone-pair electrons of nominally trivalent group VA elements may significantly reduce their thermal conductivity to a very low value (< 1Wm-1K-1). We designed two types of material systems, AgLa*x*Sb1-*x*Te2 (*x* = 0 - 0.05) and Cu12Sb4S16-*x* (*x* = 0 - 3) composites, to investigate the effect of electronic bonding at the Sb site on thermal conductivity. In both cases the experimental results support our hypothesis that the anharmonicity introduced by lone pair electrons significantly reduces thermal conductivity. The results indicated that the discovery and design of compounds with intrinsically low thermal conductivity is a new direction to broaden the scope of potential TE materials, especially compounds with special bonding nature and stable crystal structure.

To quantify the impact of lone-pair electrons on trivalent Sb3+ sites on the lattice thermal conductivity in the Cu-Sb-S system, we purposely introduced alloy phonon scattering by selecting chalcostibite CuSbS2 as a model system and set it up as a benchmark. By substitution of Sb by transition metal Fe and IIIA element Ga without s2 electrons, lone-pair electrons on some of the Sb sites were removed, which created a scenario with opposite influences on lattice thermal conductivity from the loss of lone-pair electrons and the gain of alloy scattering. A significant deviation from the classic alloy model was observed. Along with the impact of the lone-pair electrons on the bonding arrangement and crystal structure, the role of lone-pair electrons in the phonon transport of thermoelectric compound CuSbS2 was well demonstrated and quantified. We also disclosed unambiguously the origin of the role of the lone pair electrons by correlated special bonding on Sb sites with the phonon dispersion spectrum and density of state.

Most of the TE materials of current interest possess stable crystal structure and no phase transition in their working temperature range. However, recently materials with phase transitions have been identified with very promising TE figure-of-merits, such as SnSe, Cu2-xSe, and provide a new direction in the search for low thermal conductivity and high performance TE materials. Cu3SbS3 is a copper-based sulfide with three well defined temperature dependent polymorphs. It may also form an additional high temperature cubic structure similar to that of tetrahedrite (Cu3SbS3.25), with the S atom at the center of the unit cell missing. We successfully stabilized the cubic structure by incorporation of Fe atoms into Cu3SbS3. The improved TE performance and the electron band structure were also identified and correlated. Our results firmly demonstrate the possibility of stabilising the cubic structure of Cu3SbS3 material and highlight it as a strong candidate for high performance TE materials.

To broaden the synthesis route for TE materials and clarify the impact of local Joule heating during SPS processing, we investigated the feasibility and influences of flash-sintering (with the strongest local Joule heating) on both sulphides and silicide using a SPS furnace. The direct heating was so efficient that a heating rate of ~1000 oC was achieved and the sample was fully sintered in less than 45 sec. Due to the strong local Joule heating at the contacts of the particles, the onset densification temperature of MgSiSn was much lower than that in convectional SPS. Importantly, it was possible to produce dense samples in a wide sintering window of ~6 sec and the flash-sintering was controllable and repeatable. These preliminary results suggested that the flash sintering with strong local Joule heating could be a potential die-less rapid densification route for thermoelectric materials, especially, for maintaining the nanostructure and optimisation the distribution or removal of the grain surface oxidation.

Both sulphides and silicides materials were sent to our industrial collaborators to evaluate the materials and to make demonstration modules and devices.We have been discussing these results with a collaborating company. They are interested in the preliminary results. We plan to continue this work in collaborative projects with them.