Atlas of Science
another view on science
https://atlasofscience.org

Anion exchange in water: a simple way to complex and greener thermoelectrics

The need to convert and store energy in an efficient and sustainable way has already become one of the highest priorities of the new millennium. One possible solution to this challenge is the thermoelectric, which can be utilised to harvest electricity from waste heat. Tin selenide, SnSe, has an excellent thermoelectric conversion efficiency, as evaluated by the so-called figure of merit, "*ZT*". Single crystals of SnSe can demonstrate *ZT* above 2, which is exceptional, but it has proven difficult to achieve comparable performance in the polycrystalline bulk materials that would be required for practical applications. Moreover, bulk materials are primarily fabricated by high-temperature, energy-intensive processes.

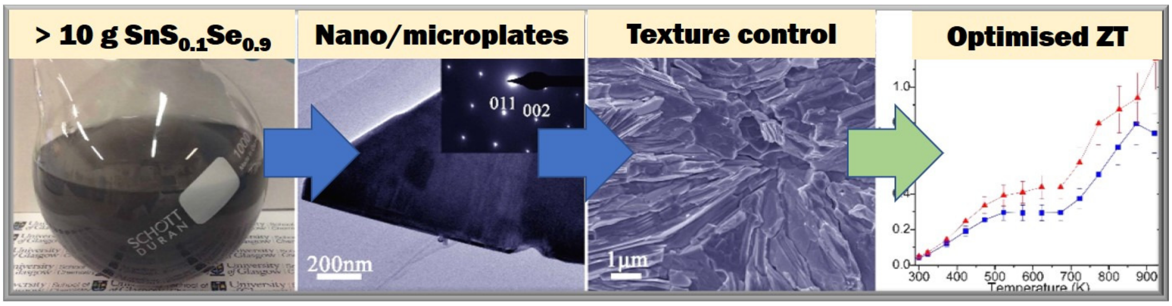

Fig. 1. From left to right: SnS0.1Se0.9 solution after a typical anion-exchange synthesis; Transmission electron microscopy image of a SnS0.1Se0.9 plate and its corresponding selected area diffraction pattern (inset); Scanning electron microscopy image of a cross section of a SnS0.1Se0.9 pellet; ZT values of pellets vs. temperature.

Although the component elements of SnSe are more abundant and less toxic than bismuth or tellurium, for example (which are used in other thermoelectrics), it would be highly advantageous if the amount of selenium required in the material could be reduced. (For example, the World Health Organisation recommends 50-55 µg/day Se in the human diet but ingestion of > 400 µg can be acutely toxic). Sulfur is considerably less toxic (LD_{50} of 5000 mg Kg^{-1}) and *ca.* four orders of magnitude more Earth-abundant. There would be major economic, health and environmental benefits in removing Se and replacing it by S in SnSe. A scalable and cost-effective approach to synthesise ternary Sn(Se,S) materials with tuneable composition and consistently excellent performance could deliver these benefits.

To address this, we have developed a new "soft chemical" aqueous solution method to synthesise these materials on a 10 g-scale. The key stage of the synthesis involves anion exchange. Initially, SnS nano/microplates are made in water without any need for surfactants or organic solvents. The anion exchange process can then be implemented and exchange of sulfur and selenium takes place in solution to give birth to substituted tin selenides without changing the original structure of the SnS. We can easily tailor the composition of these $SnS_{1-x}Se_x$ powders on a 10 g-scale while keeping the physical property benefits of nanostructuring (Fig. 1).

The $SnS_{0.1}Se_{0.9}$ nanoplates can be made into phase-pure, textured, dense pellets by spark plasma sintering. At this stage, we can tune the texture of the pellets and the *ZT* can be increased from 0.74 to 1.16 at 650 °C by making these microstructural modifications (Fig. 1). The *ZT* values of our sulfur-containing nanoplates compare very favourably with an array of doped p-type SnSe materials. This reinforces our thinking that a nanostructuring/anion exchange strategy can give thermoelectrics where the selenium content can be reduced without loss of performance.

This simple approach has recently been extended to the anion exchange synthesis of even more complex chalcogenides, $SnS_{0.1}Se_{0.9-x}Te_x$, with similar nano/microstructures and enhanced electrical performance (L. Huang, G. Han, B. Zhang, D. H. Gregory, *J. Mater. Chem. C*, 2019, *7*, 7572-7579). We expect that the method can be extended to make a host of other main group metal chalcogenides with even better thermoelectric performance.

Guang Han, Duncan H. Gregory
WestCHEM, School of Chemistry, University of Glasgow, United Kingdom

Publication

Topotactic anion-exchange in thermoelectric nanostructured layered tin chalcogenides with reduced selenium content.
Han G, Popuri SR, Greer HF, Zhang R, Ferre-Llin L, Bos JG, Zhou W, Reece MJ, Paul DJ, Knox AR, Gregory DH
Chem Sci. 2018 Mar 23