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Multiscale Microstructural Features in Thermoelectric Materials

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Thermoelectric materials provide a solution to recapturing energy lost to wasted heat through their ability to directly convert a temperature gradient into usable electrical energy. The industry's main challenge is to introduce microstructures into materials that will both conduct electrons while remaining thermally resistive. To optimize thermoelectric performance, defects of multiple dimensions (0-3D) and on multiple length scales must be utilized. Point defects (0D defects) decrease lattice thermal conductivity by scattering high frequency phonons (lattice vibrations) and affect electrical properties primarily through doping to manipulate electronic band structure [1][2]. 1D and 2D defects such as dislocations and grain boundaries scatter medium and low frequency phonons and can simultaneously be atomically thin in some dimensions while microns in length in others [1]. Finally, second phase precipitates and voids range from nanometres to micrometres in 3D. These are used as phonon scattering sites and aligning precipitate and matrix bands also allows for higher electrical conductivity [2][3].

Processing of thermoelectric materials is intimately tied to their microstructure, and subsequently their properties. Therefore, gaining an understanding of how processing affects microstructural development over multiple length scales, is important to enhancing thermoelectric performance. Because the features of interest in optimized thermoelectric materials vary over multiple length scales, it is important to utilize a variety of electron microscopy techniques to fully understand the material microstructure. In Figure 1. we use SEM to identify the porous platelet structure in a Bi-Sb-Te (BST) thermoelectric system. Additionally, TEM reveals 1D dislocations, indicating that thermal scattering sites exist in the system in the form of both 3D pores and 1D dislocations. Furthermore, Figure 2. illustrates, how ball milling and hot pressing the BST system can both reduce grain size and induce grain alignment (texturing) on the microscale. Texturing benefits polycrystalline thermoelectric materials with asymmetric crystal structures because grains can be aligned along their most electrically conductive axes. The smaller grain size will increase thermal scattering because of the increase in 2D grain boundaries.

In a study of the $NaPb_mSbTe_{m+2}$ (SALT) system, it was revealed that Spark Plasma Sintering (SPS) helps homogenize the material's microstructure and promote doping. SEM is used to show how 0D defects are introduced into the material matrix, via doping, after SPS. In this system, doping occurs because of elemental diffusion of Sb out of micron sized dendritic Sb-rich structures. Figure 3. illustrates the dendritic structures identified using SEM. In addition, we used simultaneous EDS-EBSD scans to show that the elemental segregation was pervasive throughout the grain and not relegated to the grain boundaries alone. Furthermore, EBSD reveals a change in grain size increasing the amount of 2D grain boundary interfaces for thermal scattering by orders of magnitude. This presentation will further examine the structure-property relationship of 1D and 2D microstructures in thermoelectric materials [4].

References:
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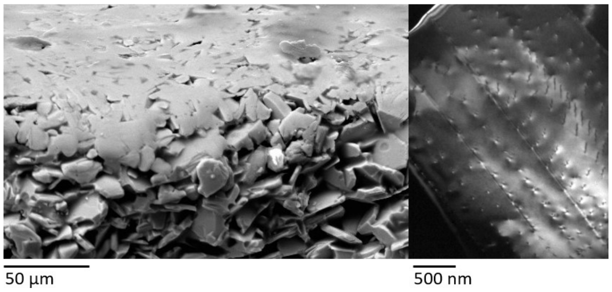

Figure 1. (Left) An SEM of the side profile of a BST system revealing the porous stacked platelet structure. (Right) Dark Field image revealing stacked dislocation arrays.

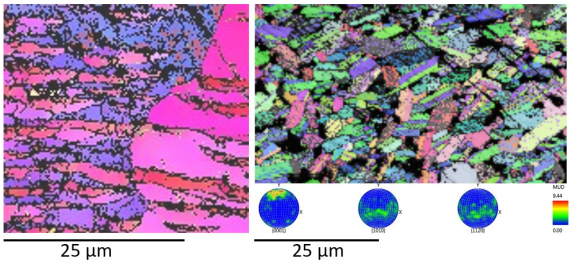

Figure 2. EBSD maps of (left) large grain ingot BST and (right) Ball milled and hot-pressed BST with pole projections indicating grain alignment.

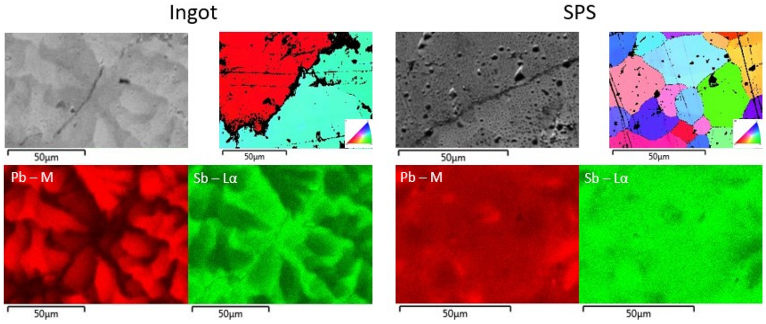

Figure 3. Secondary electron images alongside their corresponding EBSD and EDS maps of ingot and Spark Plasma Sintered (SPS) samples. The Ingot sample has a larger grain size and elemental segregation within the grain. After SPS the grain size is decreased, and the elemental distribution becomes more homogenous.