Introduction

A thermoelectric material converts a difference in temperature to an electric potential or, conversely, an applied voltage to a difference in temperature [1]. This phenomenon has made these materials attractive for their potential in applications from microprocessor cooling to power generation. The most notable application is power generation in spacecraft too far away from the sun for solar cells to operate [2]. However, in general, applications for this technology have been limited. With energy conservation becoming more and more critical, engineers would like to convert waste heat into electricity. However, the technology has not progressed far enough to make this a reality.

The fundamental problem is that to generate thermoelectricity efficiently, a material needs to be a good conductor of electricity, but not of heat. Otherwise, the device will reach thermal equilibrium and the generation of electricity will cease. Unfortunately, in most materials, thermal and electrical conductivity tend to go hand in hand. However, in recent years, researchers are finding ways to modify materials to separate the thermal and electrical conductivity. This has lead to an increase in potential thermoelectric applications [3, 4].

As with most material properties, controlling the microstructure is key to optimizing thermoelectric performance. Two specific areas being researched to improve efficiency are crystallographic texture and the arrangement and types of grain boundaries. Medlin and Snyder [5] have reviewed the current state of understanding of interfaces in bulk thermoelectric materials. This review shows some results obtained by EBSD on thermoelectric materials. EBSD in the scanning electron microscope is an established tool for characterizing both texture and grain boundaries in polycrystalline materials.

Texture

Many material properties are anisotropic at the level of individual grains. A prime example is the high temperature superconductor \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8 \). Single crystals of this material show electrical conductivity \( 10^4 \) times stronger along the \( c \)-axis than in the \( ab \)-plane [6]. As the constituent grains of a polycrystal are essentially single crystals, any material that exhibits anisotropy of properties in the single crystal lends itself to properties optimization through alignment of constituent crystals along favorable crystal directions. This alignment is termed crystallographic texture. As thermoelectric materials tend to be highly anisotropic in their thermal and electronic transport properties, they are candidates for improved performance through texture control during processing. In fact, improvements as much as 6-7 times over randomly textured materials have been achieved [7] and are comparable to those of single crystals [8].

Texture control can be achieved through several different processes in these types of materials. For example, if the starting powder in a sintered material is composed of particles with anisotropic shapes coupled to specific crystallographic directions, then the individual grains can be aligned under compression to form strongly textured compacts as shown schematically in Figure 2a. Another method is through plastic deformation. Crystalline materials accommodate deformation through slip on specific crystal planes in specific crystalline directions. This results in lattice rotations of the constituent grains in the polycrystal relative to the external axes of the sample. Thus, it is possible to control texture through extensive plastic deformation with the additional benefit of grain
refinement. For instance, texture control of thermoelectric materials has been achieved through hot extrusion. Nonmechanical techniques for controlling texture are also being considered. For example, magnetically anisotropic thermoelectric materials can be crystallographically aligned by processing the material under a high magnetic field as shown schematically in Figure 2b.

Textured materials generally exhibit non-random distributions of grain boundary types. Controlling both the crystallographic texture, as well as the grain boundary texture leads to optimal performance.

**Grain Boundaries**

In a material with columnar grains where a specific crystallographic axis is aligned with the column axis (as shown in Figure 3), the grain boundary population tends to be dominated by tilt boundaries. In a material with plate-like grains where the plate normals are aligned with a specific crystallographic direction (as shown in Figure 3), the grain boundary distributions are dominated by twist boundaries. The interfacial structure between tilt and twist boundaries are quite different. Thus, the electronic and thermal transport properties differ as well. This variance is not restricted to tilt and twist boundaries but varies with boundary type in general. For example, well ordered interfaces like coherent twin boundaries tend to scatter phonons reducing the heat conductivity without a corresponding reduction in electrical conductivity. Increasing the fraction of these types of boundaries relative to random boundaries will improve thermoelectric performance. Grain boundary engineering in metals has been achieved through repeated strain–anneal cycles. These techniques may be applicable to thermoelectric materials as well. Solid-state phase transformations can also be used to increase the fraction of beneficial boundary types. In some phase transformations, as the material transforms several distinct orientation variants are produced in the transformed material. Often the interfaces between these variants are well-ordered and a grain boundary distribution tending towards these types of boundaries will be well suited for electronic transport.

**Case Study**

Several different types of materials are currently being researched for implementation in thermoelectric devices [1]. The thermoelectric properties tend to derive from superlattices

![Figure 2](image-url) 2D schematic of a textured material formed by (a) compaction of anisotropic shapes and (b) magnetic alignment of magnetically anisotropic shapes.

![Figure 3](image-url) Schematic of two microstructures exhibiting the same fiber texture (i.e. a specific crystal direction aligned with the sample normal). One with columnar grains (top) and the other with plate-like grains (bottom). (Adapted from [5]).
formed by layered nanostructures. For example, bismuth chalcogenides composed of alternating layers of Bi$_2$Te$_3$ and Bi$_2$Se$_3$ produce devices that perform very well at room temperature. Natural superlattices formed by layered structures in oxide compounds are under consideration for high-temperature thermoelectric applications. Nanostructured thin films such as PbTe/PbSeTe have also shown promise.

A thermoelectric material of recent interest is skutterudite (cobalt arsenide). Skutterudite is a mineral where variable amounts of nickel and iron substitute for cobalt with a general formula: (Co,Ni,Fe)(P,Sb,As)$_3$. Filled skutterudites are of particular interest for their thermoelectric properties. The skutterudite crystal structure (see Figure 4) contains voids. Filling the voids with ions (typically rare earth elements) produces phonon scattering, which reduces thermal conductivity without reducing electrical conductivity [9].

EBSD results have been obtained on a skutterudite sample prior to complete compaction [10]. Of particular note in the EBSD map shown in Figure 5, is the smooth variation in orientation within individual grains. This is further reflected in the grain boundary distribution shown in Figure 6. The large peak on the left side of the distribution arises from the small angle boundaries that arise because of the texture gradients within the particles. The material exhibits some texture as shown in Figure 7. The inverse pole figure in Figure 7 shows some alignment of the (001) planes with the sample surface.
Conclusions
EBSD is well suited to assist researchers in investigating both the evolution of microstructure in the processing of thermoelectrics, and the relationship between microstructure and performance. This understanding will ultimately lead to devices with improved performance. The ability of EBSD to make spatially specific orientation measurements within a sample enables EBSD to measure both texture and grain boundary character. With automated EBSD, it is possible to characterize these elements of the microstructure with statistical reliability in the scanning electron microscope.

Bibliography