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Characterization of 3-phase (ternary-like) n-type and p-type thermoelectric materials fabricated by explosive (shock-wave) consolidation

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ABSTRACT

Three-phase powder mixtures of Bi–Te–Se and Bi–Te–Sb were prepared by cylindrical explosive consolidation to emulate traditional, melt-grown n-type and p-type doped Bi_2Te_3 thermoelectric materials. The powder diameters ranged from 40 μm to 3 μm, with starting Bi and Te particle Vickers microindentation hardnesses of 0.18 and 0.56 GPa, respectively, in contrast to average shocked n-type and p-type monolith microindentation hardnesses of 1.15 and 1.31 GPa, respectively. The values may also be contrasted to 0.72 and 0.68 GPa hardnesses for melt-grown n-type and p-type materials, respectively. Shock consolidated monolith microstructures were characterized by optical metallography, SEM and TEM along with EDS analysis and XRD of all materials, including the melt-grown materials which had measured thermoelectric parameters considerably in excess of the shock (explosively) consolidated monoliths. Notable shock microstructures were characterized by deformation twins, while the melt-grown materials contained considerable, fine eutectic microstructures. These shock-grown microstructures do not appear to be conducive to thermoelectric figure of merit optimization.

1. Introduction

Since electrons in solids are energy carriers as well as electric charge carriers, thermal effects can produce electrical effects and vice versa. Thermoelectric (TE) generation is the conversion of heat energy to electrical energy. When a temperature difference exists along a conductor, it causes mobile charge carriers (electrons and/or holes) to migrate from hot to cold. The resulting separation of charge creates an electric field potential known as the Seebeck voltage, that is given by $\Delta V = S\Delta T$, where S is a temperature-dependent material property known as the Seebeck coefficient and, by convention, ΔT represents the temperature of the cold side with respect to the hot side. The Seebeck coefficient for a material may be positive or negative, depending upon doping. When an external voltage is applied to a TE element, it will create a thermal gradient, yielding Peltier heating or cooling, depending upon the voltage polarity.

For thermoelectric generation, it is common to use doped alloys of tellurium as the active elements for converting thermal energy to electrical energy. Doped bismuth telluride alloys are the most popular for the temperature range of about 220 K to 420 K and have the attractive properties of a relatively high Seebeck coefficient, S, a relatively high electrical conductivity, σ, and a relatively low thermal conductivity, $K = K_{el} + K_{ph}$, where K_{el} is the electronic thermal conductivity and K_{ph} is

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Table 1 – Thermoelectric semiconductor precursor properties and composition

Element	Nominal particle size (μm)	Hardness (GPa)	Purity (%)	n-type composition (wt.%)	p-type composition (wt.%)
Bi	40	0.18	99.99	53	16
Te	30	0.56	99.70	44	57
Sb	6	–	99.99	–	27
Se	3	–	99.90	3	–

Note that 1 GPa = 100 VHN (Vickers Hardness Number).

the phonon (or lattice) thermal conductivity. These bulk material properties are often lumped into a single dimensionless figure of merit *ZT*, where *T* is temperature in degrees Kelvin and

$$ZT = \frac{T(S^2\sigma)}{(K_{el} + K_{ph})}.$$

The term $S^2\sigma$ is often referred to as the power factor, which characterizes the energy conversion ability of the material. *S*, σ, and K_{el} are essentially interrelated and all are determined by the electron transport properties, since K_{el} and σ are proportional to the mean free path (or scattering) of the electrons.

The better figures of merit range around unity for Bi_2Te_3 and variously doped Bi_2Te_3, nominal ternary compositions such as $Bi_2Te_{2.7}Se_{0.3}$ and $Bi_{0.5}Sb_{1.5}Te_3$: n-type and p-type, respectively; where $S = 220\ \mu V/K$ [1, 2]. But, for the conversion of waste heat to electricity to be efficient (>20%), or for a thermoelectric device to compete with traditional cooling technologies, $ZT \geq 3$ is required.. To raise the figure of merit requires σ (or $S^2\sigma$) to be large so energy is not wasted, and at the same time the thermal conductivity ($K_{e1} + K_{ph}$) must be small so that heat transported to the hot end (or temperature reference) of the device remains there. This manipulation of thermal transport in materials may allow for the development of high efficiency thermoelectric (solid-state) refrigerators and power generators [3].

Extremes of electrical conductivity (σ) in materials now span roughly 25 orders of magnitude (from $6.8 \times 10^7\ (\Omega\ m)^{-1}$ for Ag to $1.3 \times 10^{-18} (\Omega\ m)^{-1}$ for SiO_2-glass) in contrast to the thermal conductivity of solid-state materials at room temperature which spans only 4 orders of magnitude; the lowest thermal conductivities occur in alloys, especially semiconductor alloys, because the atomic substitutions significantly scatter phonons, leading to a short mean free path. These values range from 5 W/mK to 10 W/mK (at room temperature). Of course dislocations and other defects in crystalline materials which scatter electrons also scatter phonons, and scattering is therefore the key, or at least a key, to thermoelectric optimization; since on the one hand we require low scattering and large mean free path for electrons, and correspondingly large

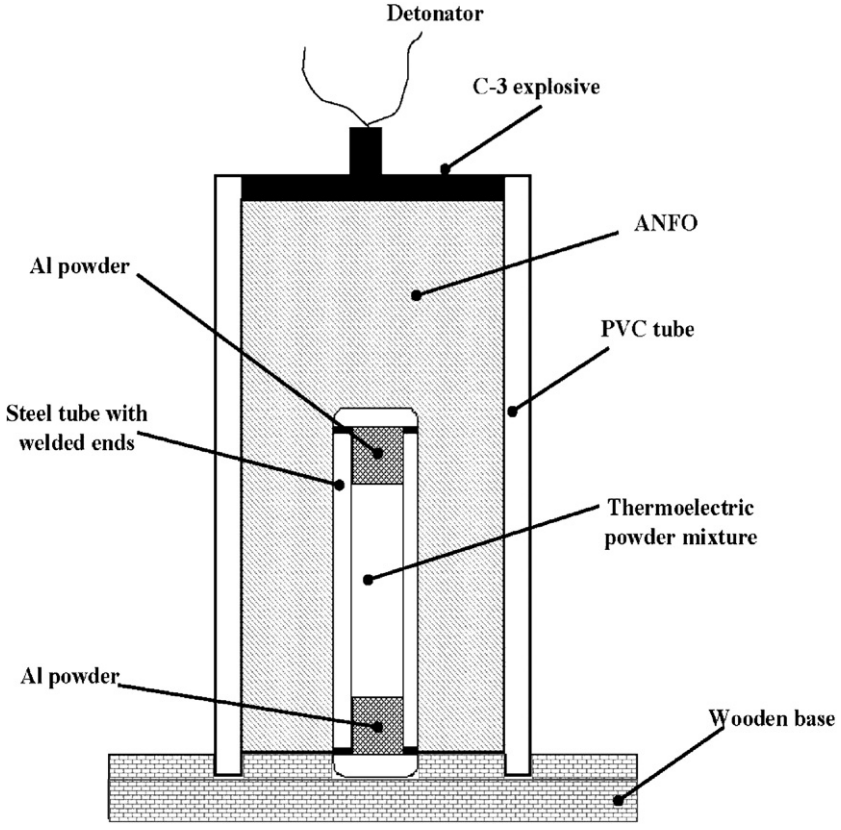

Fig. 1 – Schematic diagram illustrating cylindrical explosive powder consolidation arrangement.