Ethiopian International Journal of Multidisciplinary Research

pISSN:2349-5707 Volume:13,Issue 4, April -2026 eISSN:2349-5715

THERMOELECTRIC COMPLEX MATERIALS

Khojimatov Islombek Turg‘unboy o‘g‘li

e-mail: ixojimatov0420@gmail.com

Abstract

Thermoelectric materials, which can be utilized as solid-state Peltier coolers or to produce power from waste heat, may be crucial to a worldwide sustainable energy solution. Finding materials with greater thermoelectric efficiency than those now on the market is necessary for such a development, but this is difficult due to the contradictory combination of material properties needed. However, a new era of complicated thermoelectric materials is emerging due to contemporary synthesis and characterization methods, especially for nanoscale materials. We examine current developments in the sector, emphasizing methods for enhancing thermopower and lowering thermal conductivity.

Key words

thermopower, coolers, energy, thermoelectric generators, efficiency.

Introduction. Social and political turmoil is dramatically increasing due to the world's energy demand. Similarly, the effects of fossil fuel burning on the ecosystem as a result of global climate change are growing more concerning [1]. Using thermoelectric generators to scavenge waste heat is one option to increase the sustainability of our electrical base. Thermoelectrics could be used to turn the massive amounts of waste heat produced by industrial processes, automobile exhaust, and home heating into energy [2-4]. Thermoelectric generators are perfect for tiny, dispersed power generation because they are silent, dependable, and scalable solid-state devices with no moving components. In order to increase fuel efficiency, efforts are already being made to replace the alternator in automobiles with a thermoelectric generator installed on the exhaust stream. Similar developments in thermoelectrics may make it possible to switch from compression-based refrigeration to solid-state Peltier coolers.

Thermoelectrics have historically been too inefficient to be cost-effective in the majority of applications. However, in the mid-1990s, theoretical predictions suggested that thermoelectric effciency could be greatly enhanced through nanostructural engineering, which led to experimental efforts to demonstrate the proof-of-principle and high-effciency materials [5,6]. At the same time, complex bulk materials (like skutterudites, clathrates, and Zintl phases) were investigated and it was discovered that high efficiencies could be achieved. Is survey allows us to and common traits in these materials, and distill rational design strategies for the discovery of materials with high thermoelectric effciency.

Conflicting thermoelectric material properties. Optimizing a range of conflicting qualities is essential to the study of thermoelectric materials. A material must have high electrical conductivity, low thermal conductivity, and a substantial thermopower (absolute value of the Seebeck coefficient) [7] in order to maximize its thermoelectric figure of merit (zT). To increase zT, a variety of factors must be tuned because these transport characteristics rely on interconnected material properties.

Effective mass. Another tension arises from the charge carrier's effective mass, since higher effective masses result in high thermopower but low electrical conductivity. The density-of-states effective mass (m*) in equation [1] is a small band with a high density of states at the Fermi surface that rises with heat. However, heavy carriers would travel at slower speeds and so have smaller mobilities because the inertial effective mass is similarly correlated with m*, which results in reduced electrical conductivity [2]. Effective mass and mobility have a complicated relationship that is influenced by anisotropy, scattering processes, and electronic structure. In principle, these effective mass terms can be decoupled in anisotropic crystal structures.

A balance must be found for the effective mass (or bandwidth) for the dominant charge carrier, forming a compromise between high effective mass and high mobility. High mobility and low effective mass is typically found in materials made from elements with small electronegativity differences, whereas high effective masses and low mobilities are found in materials with narrow bands such as ionic compounds. It is not obvious which effective mass is optimum; good thermoelectric materials can be found within a wide range of effective masses and mobilities: from low-mobility, high-effective-mass polaron conductors (oxides14, chalcogenides21) to high-mobility, low-effective-mass semiconductors (SiGe, GaAs) [8].

Complexity through disorder in the unit cell. There is a long history of using atomic disorder to reduce the lattice thermal conductivity in thermoelectrics. Early work by

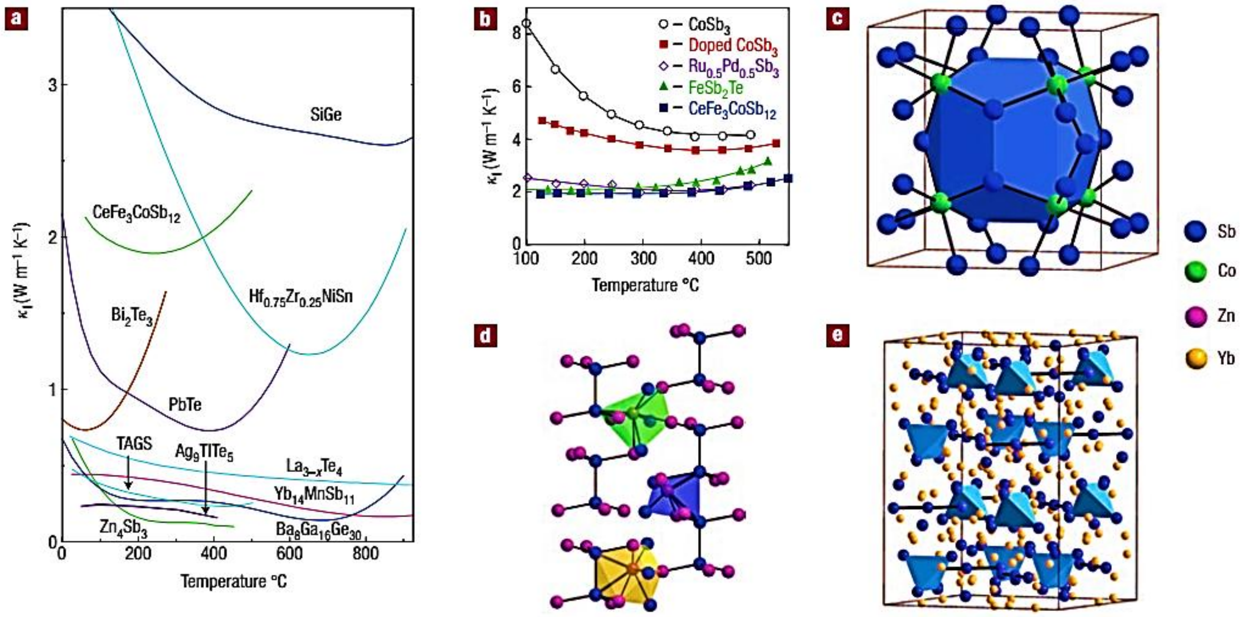

Figure 1. *Complex crystal structures that yield low lattice thermal conductivity.*

Complex nanostructured materials.

Reduced thermal conductivity in thin-film superlattices was studied in the 1980s, but it has only recently been applied to enhanced thermoelectric materials. Recent efforts on Bi2Te3-Sb2Te3 and PbTe–PbSe films and Si nanowires have demonstrated how phonon scattering can reduce lattice thermal conductivity to near κmin values (0.2–0.5 W m–1 K–1). Theoretical and experimental evidence of significantly increased zT in nanostructured thin-films and wires. Thin films containing randomly embedded quantum dots likewise achieve exceptionally low lattice thermal conductivities. Very high zT values (>2) have been reported in thin films but the difficulty of measurements makes them a challenge to reproduce in independent labs. It is clear however that nanostructured thin-films and wires do exhibit lattice thermal conductivities near κ_{min}, which results in higher material zT, but improvements of electrical and thermal contacts to these materials in a device are needed before higher device ZT is achieved [9]. The use of bulk mm^3 nanostructured materials would avoid detrimental electrical and thermal losses and use the existing fabrication routes. The challenge for any nanostructured bulk material system is electron scattering at interfaces between randomly oriented grains leading to a concurrent reduction of both the electrical and thermal conductivities. The effect of grain-boundary scattering in a silicon–germanium system has been extensively studied, as the system possesses excellent electron-crystal properties but very high thermal conductivities. In 1981, the synthesis of polycrystalline silicon germanium alloys were described, and the decrease in thermal conductivity with smaller grain size was tracked. Compared with single crystals of SiGe alloys, polycrystalline materials with grains on the order of 1 μm show an enhanced zT. However, later experiments on materials with grains between 1–100 μm found that the increased phonon scattering was offset by the decrease in electrical conductivity. Nevertheless, recent work suggests that truly nanostructured SiGe enhances zT. The results on epitaxial thin-films suggests that the ideal nanostructured material would have thermodynamically stable, coherent, epitaxy-like, interfaces between the constituent phases to prevent grain-boundary scattering of electrons. Thus, a promising route to nanostructured bulk thermoelectric materials relies on the spontaneous partitioning of a precursor phase into thermodynamically stable phases. The growth and characterization of such composite microsctructures have been studied in metals for decades because of their ability to greatly improve mechanical strength.

Conclusion. Over the past 50 years, researchers have struggled with the conflicting material qualities needed to create a high-efficiency (phonon-glass electron-crystal) thermoelectric material. The development of sophisticated high-efficiency materials that are able to decouple these features has led to a recent resurgence in the subject. High-efficiency materials are the result of a wide range of innovative techniques, from nanostructured bulk and thin-film materials to complexity inside the unit cell. All of these methods benefit from cooperation amongst chemists, physicists, and materials scientists because of the complexity of these systems. The global need for sustainable energy coupled with the recent advances in thermoelectrics inspires a growing excitement in this field.

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