

*Review Article***Advances in Thermoelectric Materials and Devices for Energy Harnessing and Utilization**

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The emerging global need for energy generation, conservation, and utilization has intensified interest in more efficient, cost-effective and pollution-free means of power generation. Thermoelectric materials can generate electrical energy from waste heat and can play an important role in a global alternative energy solution. Recently, there have been significant advances in direct thermal-to-electrical energy conversion materials development and this has generated increased interest in the field of chemistry, physics and materials engineering. This article highlights a combination of new high performance materials, new device concepts and future directions to improve material efficiencies and cost effectiveness. Here, I have first presented a brief introduction to thermoelectrics followed by the reason for the importance of the research and development in this field for India. I have discussed about the main criteria for good thermoelectric materials and provided important examples of state-of-the-art materials followed by future direction and conclusions.

Keywords: Energy Conversion; Waste Heat Recovery; Thermoelectrics; Thermal Conductivity; Seebeck Coefficient; Earth Abundant Materials

Introduction

Driven by the demand for clean and sustainable energy sources, thermoelectricity has become a significant part of research portfolio seeking to identify new and efficient energy materials for power generation (Snyder and Toberer, 2008; Sootsman *et al.*, 2009; Chen *et al.*, 2003). Thermoelectric materials can directly and reversibly convert heat energy into electrical energy (Snyder and Toberer, 2008; Sootsman *et al.*, 2009; Chen *et al.*, 2003). The heat can be generated from the combustion of fossil fuels, from sunlight, or as a byproduct of various processes (e.g. combustion of coal and petroleum, chemical reactions, nuclear decay, etc.). Therefore, thermoelectric materials can play a pivotal role in both primary power generation and energy conservation (i.e., waste-heat harvesting). An important topic of discussion is how big this role is likely to be and the answer to this

question depends exclusively on how efficient these materials are. It is hoped and expected however that thermoelectrics will play a more increasing role than it has in the past and will be one of the several technologies working together to address energy efficiency issues.

Thermoelectric modules are solid-state devices that directly convert thermal energy into electrical energy (Fig. 1). This process is based on the Seebeck effect, which is the appearance of an electrical voltage caused by a temperature gradient across a material. The inverse of this, that is the appearance of a temperature gradient upon the application of voltage is known as the Peltier effect. For power generation, the thermoelectric efficiency (η) is defined by combining the Carnot efficiency ($\Delta T/T_{\text{hot}}$) and the figure of merit (ZT) as shown in the equation (Snyder and Toberer, 2008; Sootsman *et al.*, 2009; Chen *et al.*, 2003).

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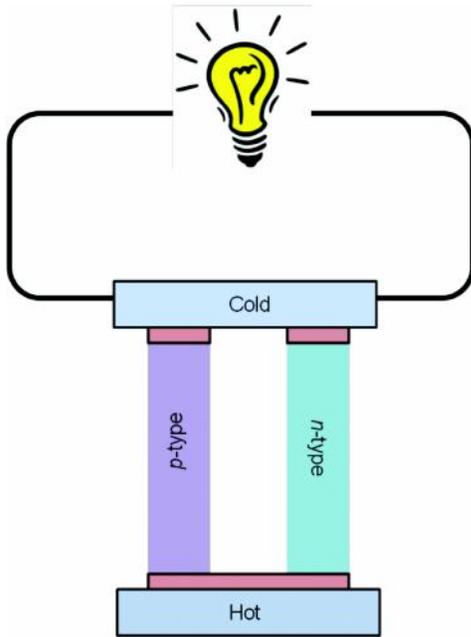


Fig. 1: Generic module diagram of a thermoelectric couple made of *n*-type and *p*-type materials in power generation mode

$$\eta = \frac{\Delta T}{T_{\text{hot}}} \frac{(\sqrt{1 + ZT_{\text{av}}} - 1)}{(\sqrt{1 + ZT_{\text{av}}} + \frac{T_{\text{cold}}}{T_{\text{hot}}})}$$

where T_{hot} and T_{cold} are the temperatures of the hot and cold ends in a thermoelectric device and ΔT their difference. This equation indicates that increasing efficiency requires both high ZT values and a large temperature difference across the thermoelectric materials. Market-based thermoelectric devices currently available have a ZT of ~ 1 and operate at an efficiency of only around 6-8%. By increasing ZT by a factor of 4, and depending on ΔT , the predicted efficiency increases to 30%, a highly attractive prospect. The challenge to create high ZT thermoelectric materials lies in achieving simultaneously high electronic conductivity (σ), high Seebeck coefficient (S) and low thermal conductivity (κ) in the same solid. These properties define the dimensionless thermoelectric figure of merit $ZT = (S^2\sigma/\kappa)T$, where T is the temperature (Snyder and Toberer, 2008; Sootsman *et al.*, 2009; Chen *et al.*, 2003; DiSalvo, 1999; Trit, 2011; Li *et al.*, 2010; Biswas *et*

al., 2011; Biswas *et al.*, 2012). The quantity $S^2\sigma$ is called the power factor and is the key to achieving high performance. A large power factor means that a large voltage and a high current are generated. The thermal conductivity κ has a contribution from lattice vibrations, κ_{latt} , called the lattice thermal conductivity. Thus, $\kappa = \kappa_{\text{el}} + \kappa_{\text{latt}}$, where κ_{el} is the electronic thermal conductivity. Naturally, the thermal conductivity must be low as a large temperature gradient must be maintained; a large thermal conductivity will short the thermal circuit.

The field of thermoelectrics presents an important challenge to synthetic chemists, physicists, as well as the materials scientists. The main challenge in this field is to develop highly efficient, stable, environment-friendly and inexpensive solid state materials. The discovery of new promising materials requires a combination of theoretical direction, intense chemical intuition, synthetic chemistry skill, materials processing, and good measurement expertise. This powerful combination can be effectively achieved by reaching across scientific disciplines.

Why is Thermoelectrics Important to India?

In the last decade, Indian economy has shown incredible growth. Steadily and slowly, India is gaining strategic importance globally owing to the impressive economic growth pattern and market attractiveness. With growing economy, there will be more energy consumption in the country. India is the world's 5th largest energy consumer accounting for about 4.1% of the world's total annual energy consumption and moving fast enough to become the third largest consumer by 2025 after USA and China (Source: India Energy Book, 2012). The per capita energy consumption of India is 0.5 toe (tonnes of oil equivalent) as compared to the world average of 1.9 toe, and this indicates a high potential for energy consumption (Source, 2012). Fig. 2A shows the graph of total energy consumption by type for India in 2011 (Source: US Energy Information Administration, 2012). It can be seen that major percentage of the energy was consumed in terms of the use of coal, petroleum and gas. In general, main share of the electricity is generated from coal, hydro and nuclear fuel. On the

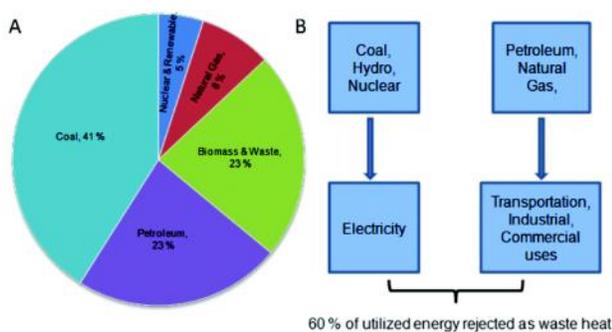


Fig. 2: (A) Total energy consumption by type for India in 2011. Source: U.S. Energy Information Administration, International Energy Statics, Indian Central Electricity Authority (2012). (B) Schematic shows partly the utilized energy being lost as waste heat

other hand, combustions of petroleum and gas are used to run the industrial and transportation sector in India. If we carefully observe that after the use of this enormous amount of energy in terms of electricity or combustion process, $\sim 60\%$ of the utilized energy is being lost as waste heat (Fig. 2B) (Biswas *et al.*, 2012). Could it be possible to make use of this untapped heat energy? The answer is yes, and 10-20% conversion to the useful form can have significant impact on overall energy. Thermoelectric materials allow the direct conversion between thermal and electrical energy. Different sectors of application include automobiles, heavy trucks and vehicles, coal burning electric utilities, and nuclear reactor facilities. Anything that uses an internal combustion engine (moving or stationary) can use these thermoelectric materials to convert waste heat to electrical energy for enhanced energy-efficiency. Basic research and extensive academic-industrial collaboration are essential to improve the existing thermoelectric efficiencies further to make it usable for major applications.

Criteria for a Good Thermoelectric Material

Primary object to the field of thermoelectric materials is the need to optimize a variety of interdependent properties. To maximize the thermoelectric figure of merit (ZT) of a material, a large Seebeck coefficient, high electrical conductivity, and low thermal conductivity are required. As these transport

characteristics depend on interrelated material properties, a number of parameters need to be optimized to maximize ZT . As high ZT requires high electrical conductivity but low thermal conductivity, the Wiedemann-Franz law reveals an inherent materials conflict for achieving high thermoelectric efficiency. Electrical part of the thermal conductivity (κ_{el}) is directly related to electrical conductivity (σ) by the relation, $\kappa_{el} = L\sigma T$, where L is the Lorenz number (Snyder and Toberer, 2008; Sootsman *et al.*, 2009). Ideally, a good thermoelectric material should have low thermal conductivity (property of glass), high electrical conductivity (property of metal) and large Seebeck (property of semiconductor). Challenge lies in the field to optimize all these important properties to achieve high thermoelectric performances.

Reduction of the Thermal Conductivity

A successful approach to increase the ZT value has been introduced to modify an already promising compound by introducing point defects through the synthesis of solid solutions. The solid solution provides an environment of the atomic mass fluctuation throughout the crystal lattice (disorder), which gives rise to strong phonon scattering and generally can lead to the significantly lower thermal conductivity and a high ZT value. For example, solid solutions of $PbTe_{1-x}Se_x$ and $Pb_{1-x}Sn_xTe$ have lower thermal conductivity than that of pure $PbTe$ (see Fig. 3) (Kanatidis, 2010). Nanoscale inclusions in bulk materials can dramatically suppress lattice thermal conductivity by scattering the longer mean free path

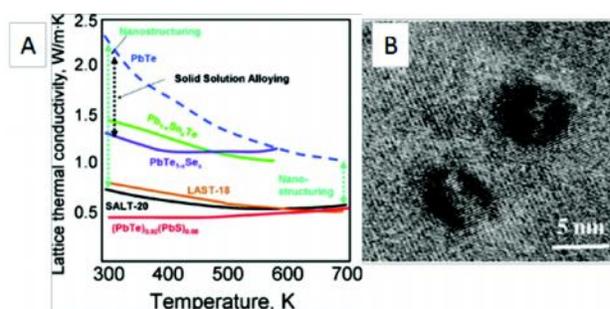


Fig. 3: (A) Lattice thermal conductivity as a function of temperature for various PbTe-based alloys and nanostructured samples. (B) High resolution transmission electron microscopy of a LAST-m sample. Source: Kanatidis (2010)

heat-carrying phonons, as in $\text{AgPb}_m\text{SbTe}_{m+2}$ (LAST-m) (Fig. 3), which resulted in high ZT of 1.8 (Hsu *et al.*, 2004). Calculations predict that a wide size distribution of nanoparticles is preferable since it can effectively scatter different phonon modes and reduce thermal conductivity. However, the power factor is also reduced because the nanoprecipitates increase carrier scattering, which in turn unfavourably affects the carrier mobilities.

An interesting idea to achieve high ZT was proposed by Slack and is referred to as the “phonon glass electron crystal” (PGEC) approach (Slack, 1995). A PGEC material features cages in its crystal structure inside which massive atoms can reside. These big atoms are small enough relative to the cage to rattle. This situation produces a phonon damping that can result in significant reduction of the lattice thermal conductivity. In the PGEC picture, a glass-like thermal conductivity can in principle coexist with charge carriers of high mobility. The PGEC approach has inspired a significant amount of new research and has led to significant increases in ZT for several compounds such as the multiple filled skutterudites (Shi *et al.*, 2011).

Cubic AgSbTe_2 and AgBiSe_2 compounds are renowned for their intrinsically low κ_{lat} due to the strong anharmonicity of the bonding arrangements in these compounds (Morelli *et al.*, 2008). Recent theoretical and experimental studies on a series of cubic bulk I-V-VI₂ compounds have shown that the lone pair on the group V element plays an important role in deforming the lattice vibration, which results in strong bond anharmonicity (Nielsen *et al.*, 2012). Valence electronic configuration of Bi/Sb is ns^2np^3 , where only np^3 electrons are involved in the bond formation with chalcogen valence electrons while the beguiling ns^2 electrons of Bi/Sb form a lone pair. The origin of strong anharmonicity in Bi/Sb-X (X = S/Se/Te) bond is the electrostatic repulsion between the stereochemically active lone pair of Bi/Sb and the valence bonding charge of the chalcogen (Guin *et al.*, 2013).

Increment of the Power Factor

The important challenges in current thermoelectric

research are how to increase the thermoelectric power (S) of a material without depressing the electrical conductivity (σ) and to predict precisely which materials will have a high power factor ($S^2\sigma$). Generally, the thermoelectric power and electrical conductivity change in opposite directions with doping (Sootsman *et al.*, 2009) and thus there is a compromised set of values that must be achieved. Generally, multiple pockets in valence or conduction band extrema give rise to high Seebeck coefficient (Snyder and Toberer, 2008). When the system is highly doped, more valleys are populated, thus resulting in high power factor. Convergence of multiple charges carrying electronic band valleys has virtually no detrimental effects on the carrier mobility (μ). Multiple degenerate valleys (separate pockets of Fermi surface with the same energy) have the effect of producing large effective mass (m^*) without explicitly reducing μ (Pei *et al.*, 2012). Flat/broad valence band maximum also gives rise to high m^* (Guin *et al.*, 2013, 2014a, b), thus resulting in enhanced S as:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{3/2},$$

where k_B is the Boltzmann constant, e is the electron charge, h is the Planck constant and n is carrier concentration.

Boltzmann transport theory describes both electronic and thermal transport in the vast majority of solids. This theory provides a general understanding of the thermopower (S) that is expressed by the Mott equation (Sootsman *et al.*, 2009):

$$\left[S = \frac{\pi}{3} \frac{k_B T}{e} \frac{d \ln \sigma(E)}{dE} \right]_{E=E_f},$$

$\sigma(E)$ is the electronic conductivity determined as a function of the band filling of Fermi energy, E_F . If electronic scattering is independent of energy, then $\sigma(E)$ is just proportional to the density of states (DOS) at E . Fig. 4 shows two hypothetical electronic DOS diagrams; one in which the DOS varies rapidly near E_F , and the other in which it does not. Based on the above equation, the system in Fig. 4A with sharp

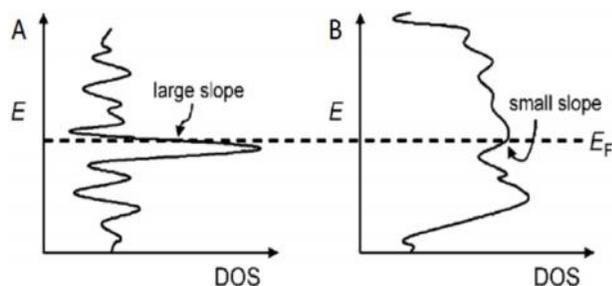


Fig. 4: Hypothetical density of state (DOS) with (A) a large slope and (B) a small slope near Fermi energy (E_F). Source: Sootsman *et al.* (2009)

changing DOS is expected to have a larger thermoelectric power (Sootsman *et al.*, 2009).

Thus, important parameters to consider when selecting or designing material systems are the band gap values, the shape and width of the bands near the Fermi level (E_F), and the carrier effective masses and carrier mobilities. The band gap is important because, in general, it is the temperature at which the ZT maximizes scales with band-gap size (Snyder and Toberer, 2008). This is because for a given band gap energy (E_g), there is a temperature at which thermally induced cross-gap carrier excitations occur to generate carriers of opposite sign which decrease the thermopower. Thus, for cooling applications, lower band-gap (0.1-0.2 eV) materials are best; whereas for high-temperature power generation, slightly larger band gaps (0.3-1 eV) are well-suited.

State-of-the-art Thermoelectric Materials

Various thermoelectric materials have been prepared and are present as device form in the mass market. My goal herein is to provide a brief overview about the most recent progress in thermoelectric materials. The thermoelectric figure of merit of the best recent thermoelectric materials is compared in Fig. 5 (Kanatzidis, 2010). Here onwards, a few of them are discussed case-by-case.

Bismuth Chalcogenides

Bi_2Te_3 is a narrow-gap semiconductor with an indirect gap of ~ 0.15 eV (Sootsman *et al.*, 2009). Bi_2Te_3 crystallizes in the rhombohedral space group $R\bar{3}m$ and the structure is made up of quintuple layers (Te1-

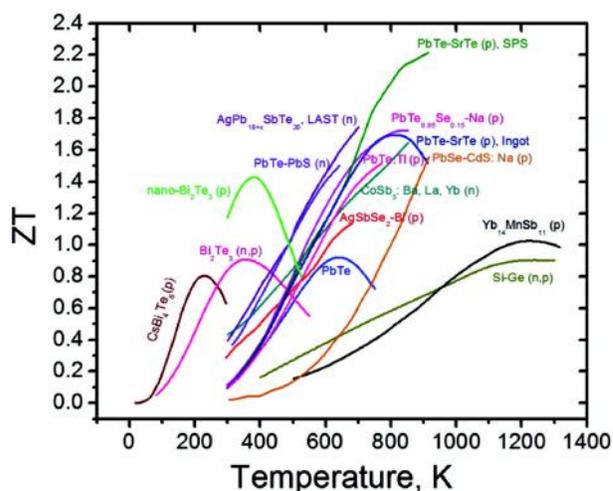


Fig. 5: Current state-of-the-art in bulk thermoelectric materials. Plot shows the temperature-dependent thermoelectric figure of merit (ZT) vs T. Note: Data obtained from recent literature and Kanatzidis (2010)

$Bi_2Te_2-Bi_2Te_1$), stacked by van der Waals interactions along the c -axis in the unit cell (Fig. 6A). The state-of-the-art Bi_2Te_3 materials with $ZT = 1$ are synthesized by alloying with Sb for p -type and Se for n-type materials. In actual devices, the p -type “legs” are

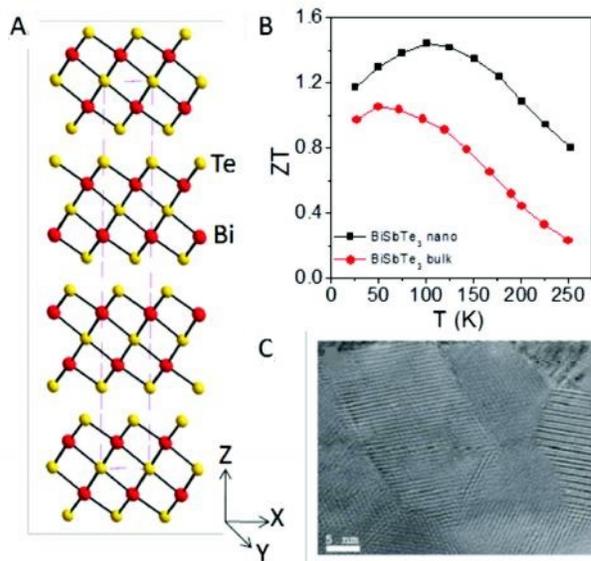


Fig. 6: (A) Layered crystal structure of Bi_2Te_3 . (B) Temperature-dependent ZT of hot-pressed nanostructured and market-based ingot bismuth antimony telluride. (C) Transmission electron microscope (TEM) image showing nanocrystalline grain of high performance bismuth antimony telluride. Note: (B) and (C) from Poudel *et al.* (2008)

generally hot-pressed and annealed pellets of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$, which have good mechanical properties. The *n*-type counterpart is typically an ingot form of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ grown by zone melting techniques. Melt spinning followed by spark plasma sintering (SPS) yielded *p*-type Bi_2Te_3 ingots with a *ZT* value of 1.35 at 300 K (Tang *et al.*, 2007). This material features 25 nm wide ribbons composed of nanostructured layers of Bi_2Te_3 crystals with 1 nm interplanar distance. The highest *ZT* value for a bulk *p*-type Bi_2Te_3 material was reported recently (Poudel *et al.*, 2008). The material with *ZT*~1.4 at 100°C was prepared by ball milling followed by hot pressing (see Fig. 6B) (Poudel *et al.*, 2008). The *ZT* enhancement for this system arises from reducing the lattice thermal conductivity while maintaining a comparable power factor to that of the bulk *p*-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$. This material is called “nanobulk” $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ and it is a single-phase material composed of nanograins and micrograins mixed together (see Fig. 6C). Devices made of these nanostructured materials have shown superior thermoelectric efficiency than that of the devices from commercially available *p*-type Bi_2Te_3 . Promising thermoelectric performance has been achieved in nanostructured Bi_2Te_3 , Sb_2Te_3 and their alloys synthesized by bottom-up solution-based microwave-assisted synthesis (Mehta *et al.*, 2012).

CsBi_4Te_6 is a promising material for low-temperature thermoelectric applications (Chung *et al.*, 2000). The presence of Bi-Bi bonds in the structure is responsible for the very narrow energy gap (~0.08 eV), nearly half of that of Bi_2Te_3 . The narrower band gap is responsible for the maximum *ZT* value in CsBi_4Te_6 being at lower temperature than that of Bi_2Te_3 . A *ZT* value of 0.8 at 225 K was obtained for 0.06% SbI_3 -doped CsBi_4Te_6 .

Lead Chalcogenides

PbTe is the champion thermoelectric material for mid-range temperature (600–800 K) applications. It crystallizes in the NaCl crystal structure with Pb atoms occupying the cation sites and Te forming the anionic lattice. A band gap of 0.32 eV allows it to be optimized for power-generation applications and can be doped in either *n*- or *p*-type with appropriate

dopants.

Significant enhancement of the Seebeck coefficient was achieved by introducing resonance level (sharp changes in density of states) in the valence band of PbTe by doping 2 mol% thallium, which resulted in the doubling of *ZT* to 1.5 at 773 K (Heremans *et al.*, 2008). The *p*-type Na-doped $\text{PbTe}_{1-x}\text{Se}_x$ also exhibits high performance thermoelectric properties (*ZT*~1.8 at 850 K) arising from convergence of the multiple valence bands (Pei *et al.*, 2011).

Nanoscale inclusions in bulk materials can dramatically suppress the lattice thermal conductivity (κ_{latt}) by scattering the longer wavelength heat-carrying phonons, as shown for the first time in $\text{AgPb}_m\text{SbTe}_{m+2}$ (Hsu *et al.*, 2004). In all these cases, however, the power factor ($S^2\sigma$) is also reduced because the nano-inclusions increase carrier scattering which in turn adversely affects the carrier mobilities. Recently, it was observed that by embedding endotaxial SrTe nanocrystals at a concentration as low as 2% in *p*-type bulk PbTe, the heat flow can be greatly inhibited without affecting the carrier mobility, thereby allowing a large power factor to be maintained (Biswas *et al.*, 2011). The insensitivity of carrier scattering was attributed to valence band alignment of SrTe and PbTe allowing facile hole transport. The crystallographic alignment of SrTe and PbTe lattices and associated strain at interfaces decouples phonon and hole transport leading to a thermoelectric figure of merit of 1.7 at ~800 K (Biswas *et al.*, 2011). Later, similar research has been extended to PbTe–MgTe/CaTe/BaTe (matrix–nanoprecipitate) system, where promising thermoelectric performances have also been achieved (Biswas, He *et al.*, 2011; Ohta *et al.*, 2012; Lo *et al.*, 2012). Recently, Biswas and Kantzidis have demonstrated the substantial suppression of lattice thermal conductivity at high temperature in the PbTe–SrTe system that leads to a record high *ZT* of ~2.2 at 915 K in spark plasma sintered-processed samples (Biswas *et al.*, 2012). This is the result of introducing phonon scattering at all-length scales in a hierarchical fashion from atomic scale doping and endotaxial nanostructuring to mesoscale grain boundary engineering (Fig. 7). With this new advance in the maximum *ZT*, average ZT_{avg} values of ~1.2 and

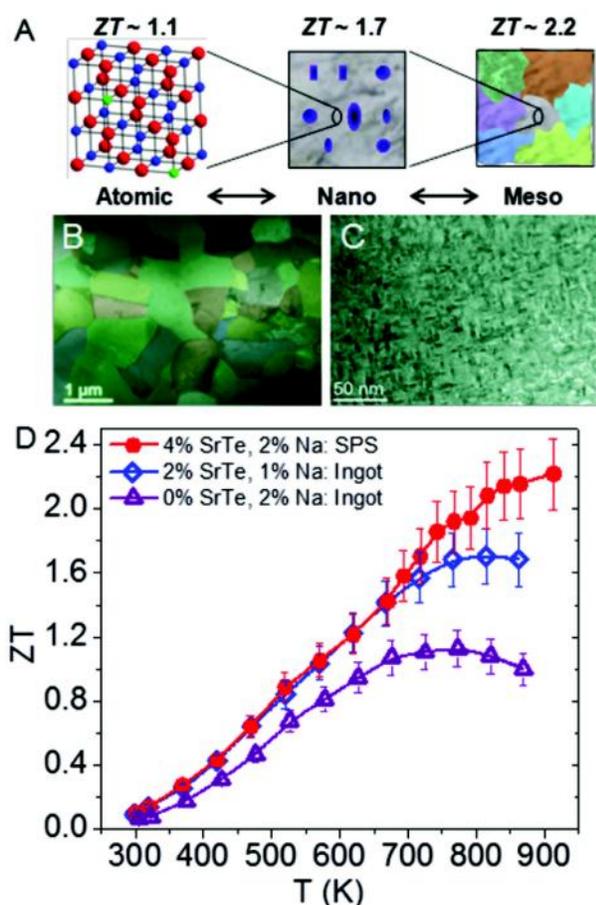


Fig. 7: (A) Maximum achievable ZT values for the respective length scales: the atomic scale (alloy scattering), the nanoscale (PbTe matrix, grey; SrTe nanocrystals, blue) to the mesoscale (grain-boundary scattering). (B) and (C) TEM images show the micro and nanostructures in spark-plasma-sintered PbTe-SrTe doped with Na. (D) Temperature-dependent ZT for an ingot (atomic scale), endotaxial nanostructured PbTe (atomic plus nanoscale) and spark-plasma-sintered PbTe (atomic + nano + mesoscale). Source: Biswas *et al.* (2012)

~1.7 were obtained for non-segmented and segmented thermoelectric devices, respectively (segmentation with BiSbTe, $ZT \sim 1.2$ at 350 K). Considering a cold side temperature of 350 K and hot side temperature of 950 K for such devices, waste heat conversion efficiencies, respectively of ~16.5% and ~20% were predicted (Biswas *et al.*, 2012).

Silver Antimony Chalcogenides

Fifty years earlier, Rosi (Rosi *et al.*, 1961) recognized AgSbTe₂ to be an efficient p -type thermoelectric

material with ZT of 1.3 at 720 K. In the recent years, AgSbTe₂ compound has been repeatedly studied to improve performance further by optimization carrier concentration through various doping. Interestingly, AgSbTe₂ alloys with GeTe (TAGS) (Lee *et al.*, 2014; Salvador *et al.*, 2009; Zhang *et al.*, 2013) and PbTe (LAST-m) (Hsu *et al.*, 2004) showed extraordinary ZT values ~1.5 at 750 K and ~1.8 at 800 K, respectively. Recently, we have shown from India that enhanced electrical transport and ultra low thermal conductivity resulted in high thermoelectric performance of Pb or Bi doped bulk p -type AgSbSe₂ which is Se analogue of AgSbTe₂ (Guin *et al.*, 2013). The maximum ZT achieved is 1.2 at 685 K for 2 mol% Bi-doped sample, which is 190% higher than pristine AgSbSe₂ sample (Fig. 8). With this advance in the maximum ZT values of this Te-free material, we can expect an average ZT value of ~0.75 (considering a hot side temperature of 700 K and cold side temperature of 350 K), which is higher than leading metal selenide-based thermoelectric systems reported recently in literature (Fig. 8) (Guin *et al.*, 2013). Considering a cold side temperature of 350 K and hot side 700 K for such devices, waste heat conversion efficiencies, respectively of ~9% was predicted, which is comparable to market-based metal telluride devices. We have also shown that by introducing second phase nanostructures and proper carrier engineering, high ZT can be achieved in AgSbSe₂ (Guin *et al.*, 2014a, b).

Skutterudites

Skutterudites are an extremely promising class of compounds for thermoelectric power generation (Shi *et al.*, 2011). They crystallize in the cubic CoAs₃-type structure with the space group $Im\bar{3}$. The structure is composed of eight-corner-shared XY₆ (X=Co, Rh, Ir; Y=P, As, Sb) octahedra. Linked octahedra gives rise to a void at the centre of the (XY₆)₈ cluster, where the void space occupies a body-centered position of the cubic lattice. This void is large enough to accommodate large metal atoms to form filled skutterudites. Since the void-filling atoms can act as electron donors or acceptors, partially filling the void space of skutterudites could lead to an optimum electron concentration. At the same time,

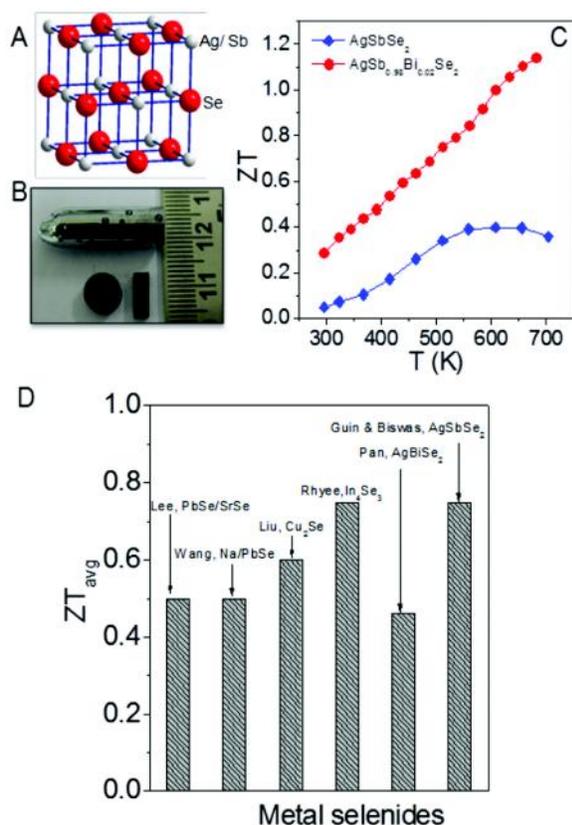


Fig. 8: (A) Crystal structure of cubic rocksalt AgSbSe_2 with disordered Ag/Sb positions. (B) Photograph of as-synthesized ingot. Bar- and coin-shaped samples are used for electrical and thermal transport measurements, respectively. (C) Temperature-dependent ZT of Bi-doped and pristine AgSbSe_2 . (D) Average ZT of present $\text{AgSb}_{0.98}\text{Bi}_{0.02}\text{Se}_2$ and leading metal selenides reported in recent literature, considering a hot side temperature of 690 K and cold side temperature of 350 K. Source: Guin *et al.* (2013)

these atoms can also act as strong phonon-scattering centres to greatly reduce the lattice thermal conductivity. The “rattling” effect of these void-filling atoms has resulted in improvements in the thermoelectric properties of skutterudite. High ZT values of partially filled skutterudites with a small amount of Ni doping for Co, $\text{Ba}_{0.30}\text{Ni}_{0.05}\text{Co}_{3.95}\text{Sb}_{12}$ ($ZT \sim 1.25$ at 900 K) were reported (Tang *et al.*, 2005). Further improvement in the ZT was achieved by filling up multiple atoms in the void of CoSb_3 (Shi *et al.*, 2011).

Half-Heusler Compounds

Another class of compounds of considerable interest

as potential thermoelectric materials for high-temperature applications are the half-Heusler (HH) compounds (Snyder and Toberer, 2008; Sootsman *et al.*, 2009), given by the composition MNiSn ($\text{M}=\text{Ti}, \text{Hf}, \text{Zr}$). HH phases have the MgAgAs crystal structure which consists of three filled interpenetrating face centered cubic sublattices and one vacant sublattice. The general formula is XYZ , where X and Y are transition metals and Z is a main-group element. Another advantage of these compounds is their high melting points of 1100-1300°C as well as their chemical stability with essentially zero sublimation at temperatures near 1000°C. The Heusler intermetallic compounds with fully filled sublattices are metals (full-Heusler alloys), whereas the vacant Ni atom sites in half-Heusler compounds give rise to narrow bands resulting in d-orbital hybridization and substantial semiconducting character of the compounds. Notable progress was reported with $ZT \sim 0.7$ at 800 K for n -type $\text{Zr}_{0.5}\text{Hf}_{0.5}\text{Ni}_{0.8}\text{Pd}_{0.2}\text{Sn}_{0.99}\text{Sb}_{0.01}$ (Shen *et al.*, 2001). Sakurada and Shutoh (2005) reported a ZT value near 1.4 at 700 K for n -type $(\text{Zr}_{0.5}\text{Hf}_{0.5})_{0.5}\text{Ti}_{0.5}\text{NiSn}_{1-y}\text{Sb}_y$. A study by Indian researchers shows enhanced thermoelectric performance ($ZT \sim 1.1$ at 773 K) in nanostructured $\text{Zr}_{0.25}\text{Hf}_{0.75}\text{NiSn}$ was prepared by ball milling followed by spark plasma sintering (Bathula *et al.*, 2012).

Future Outlook and Conclusions

The development of new materials and complex composites over the last 5-10 years has significantly increased the ZT values. It has been occurred through better theoretical understanding, development of new synthesis techniques, and state-of-the-art measurements that the field has progressed so far and promises to move forward further. For a long time, it was thought that there was a practical barrier at $ZT = 1$; however, new mechanisms for increasing the power factor and reducing the thermal conductivity in thermoelectric materials continue to emerge and increase the ZT value. The newest generation of bulk materials has $ZT \sim 1.6$ -2.2 at approximately 700-900 K (Biswas *et al.*, 2011, 2012; Pei *et al.*, 2011). It is hoped that $ZT \sim 3$ will soon be achieved, which will provide a new generation of thermoelectric power generators with thermoelectric efficiency of $\sim 25\%$.

Future efforts in understanding these mechanisms promise to increase the ZT value further and enable more practical application. The discovery of advanced thermoelectrics poses a challenge to chemists, physicists, materials scientists and engineers.

Further reductions in the thermal conductivity alone may be sufficient to raise ZT values to 2.5; however, to reach values of 3-3.5 or greater, we also need dramatic enhancement in the power factor. This can be achieved with innovation of some new and unexpected single-phase materials. What is needed now are new physical concepts on how the power factor can be enhanced 2-4-fold in the existing leading materials.

For realistic applications, the cost of power generation – as governed by material, manufacturing, and heat exchanger costs – is also a critical factor which is not captured in ZT alone (Yee *et al.*, 2013). Among the high performance materials, PbTe is the most efficient for power generation application at high temperature, whereas Bi_2Te_3 -based materials are well-known for refrigeration near room temperature. These leading high performance materials are mainly

based on tellurium which is enormously scarce in the earth's crust (Hu *et al.*, 2008). Hence, the cost of Te is likely to rise sharply if Te-based thermoelectric materials reach the mass markets. Therefore, it would be desirable to develop alternative materials which minimize the use of rare and toxic elements such as Te and involve cheaper and abundant elements. S and Se are much more earth abundant and less expensive than Te. Highly promising thermoelectric performance was observed in optimized bulk PbS (Zhao *et al.*, 2012), PbSe (Zhao *et al.*, 2013) and Bi_2S_3 (Biswas, Zhao *et al.*, 2012), which can replace expensive PbTe and Bi_2Te_3 based thermoelectric materials. We have also observed high thermoelectric performance in Te-free bulk AgSbSe_2 (Guin *et al.*, 2013, 2014a, b).

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References

- Bathula S, Jayasimhadri M, Singh N, Srivastava A K, Pulikkotil J, Dhar A and Bhudhani R C (2012) Enhanced thermoelectric figure-of-merit in spark plasma sintered nanostructured n-type SiGe alloys *Appl Phys Lett* **101** 213902 1-5
- Biswas K, He J, Blum I D, Wu C I, Hogan T P, Seidman D N, Dravid V P and Kanatzidis M G (2012) High-performance bulk thermoelectrics with all-scale hierarchical architectures *Nature* **489** 414-418
- Biswas K, He J Q, Wang G, Lo S H, Uher C, Dravid V P and Kanatzidis M G (2011) High thermoelectric figure of merit in nanostructured p-type PbTe-MTe (M = Ca, Ba) *Energy Environ Sci* **4** 4675-4684
- Biswas K, He J, Zhang Q, Wang G, Uher C, Dravid V P and Kanatzidis M G (2011) Strained endotaxial nanostructures with high thermoelectric figure of merit *Nat Chem* **3** 160-166
- Biswas K, Zhao L-D and Kanatzidis M G (2012) Tellurium-free thermoelectric: The anisotropic n-type semiconductor Bi_2S_3 *Adv Energy Mater* **2** 634-638
- Chen G, Dresselhaus M S, Dresselhaus G, Fleurial J P and Caillat T (2003) Recent developments in thermoelectric materials *Int Mater Rev* **48** 45-66
- Chung D Y, Hogan T, Brazis P, Rocci-Lane M, Kannewurf C, Bastea M, Uher C and Kanatzidis M G (2000) CsBi_4Te_6 : A high-performance thermoelectric material for low-temperature applications *Science* **287** 1024-1027
- DiSalvo F J (1999) *Thermoelectric cooling and power generation Science* **285** 703-706
- Guin S N and Biswas K (2013) Cation disorder and bond anharmonicity optimize the thermoelectric properties in kinetically stabilized rocksalt AgBiS_2 nanocrystals *Chem Mater* **25** (15) 3225-3231
- Guin S N, Chatterjee A and Biswas K (2014a) Enhanced thermoelectric performance in p-type AgSbSe_2 by Cd-doping *RSC Adv* **4** 11811-11815
- Guin S N, Chatterjee A, Negi D S, Datta R and Biswas K (2013) High thermoelectric performance in tellurium free p-type AgSbSe_2 *Energy Environ Sci* **6** 2603-2608

- Guin S N, Negi D S, Datta R and Biswas K (2014b) Nanostructuring, carrier engineering and bond anharmonicity synergistically boost the thermoelectric performance of p-type $\text{AgSbSe}_2\text{-ZnSe}$ *J Mater Chem A* **2** 4324-4331
- Heremans J P, Jovovic V, Toberer E S, Saramat A, Kurosaki K, Charoenphakdee A, Yamanaka S and Snyder G J (2008) Enhancement of thermoelectric efficiency in PbTe by distortion of the electronic density of states *Science* **321** 554-557
- Hu, Z and Gao C S (2008) Upper crustal abundances of trace elements: A revision and update *Chem Geol* **253** 205-221
- Hsu K F, Loo S, Guo F, Chen W, Dyck J S, Uher C, Hogan T, Polychroniadis E K and Kanatzidis M G (2004) Cubic $\text{AgPb}_m\text{SbTe}_{2+m}$: Bulk thermoelectric materials with high figure of merit *Science* **303** 818-821
- Kanatzidis M G (2010) Nanostructured thermoelectrics: The new paradigm? *Chem Mater* **22** 648-659
- Lee J K, Oh M W, Kim B S, Min B K, Lee H W and Park S D (2014) Influence of Mn on crystal structure and thermoelectric properties of GeTe compounds *Electron Mater Lett* **10** 813-817
- Li J-F, Liu W-S, Zhao L-D and Zhou M (2010) High-performance nanostructured thermoelectric materials *NPG Asia Mater* **2** 152-158
- Lo S-H, He J Q, Biswas K, Kanatzidis M G and Dravid V P (2012) Phonon scattering and thermal conductivity in p-type nanostructured PbTe-BaTe bulk thermoelectric materials *Adv Func Mater* **22** 5175-5185
- Mehta R J, Zhang Y, Karthik C, Singh B, Siegel R W, Tasciuc T B and Ramanath G (2012) A new class of doped nanobulk high-figure-of-merit thermoelectrics by scalable bottom-up assembly *Nat Mater* **11** 233-240
- Morelli D T, Jovovic V and Heremans J P (2008) Intrinsically minimal thermal conductivity in cubic I-V-VI₂ semiconductors *Phys Rev Lett* **101** 035901 1-4
- Nielsen M D, Ozolins V and Heremans J P (2012) Lone pair electrons minimize lattice thermal conductivity *Energy Environ Sci* **6** 570-578
- Ohta M, Biswas K, Lo S-H, He J, Chung D -Y, Dravid V P and Kanatzidis M G (2012) Enhancement of thermoelectric figure of merit by the insertion of MgTe nanostructures in p-type PbTe doped with Na₂Te *Adv Energy Mater* **2** 1117-1123
- Pei Y, Shi X, La Londe A, Wang H, Chen L and Snyder G J (2011) Convergence of electronic bands for high performance bulk thermoelectric *Nature* **473** 66-69
- Pei Y, Wang H and Snyder G J (2012) Band engineering of thermoelectric materials *Adv Mater* **24** 6125-6135
- Poudel B, Hao Q, Ma Y, Lan Y, Minnich A, Yu B, Yan X, Wang D, Muto A, Vashaee D, Chen X, Liu J, Dresselhaus M. S, Chen G and Ren Z (2008) High-thermoelectric performance of nanostructured bismuth antimony telluride bulk alloys *Science* **320** 634-638
- Rosi F D, Hockings E F and Lindenblad N E (1961) Semiconducting materials for thermoelectric power generation *RCA Rev* **22** 82-121
- Sakurada S and Shutoh N (2005) Effect of Ti substitution on the thermoelectric properties of (Zr,Hf)NiSn half-Heusler compounds *Appl Phys Lett* **86** 082105 1-3
- Salvador J R, Yang J, Shi X, Wang H and Wereszczak A A (2009) Transport and mechanical property evaluation of $(\text{AgSbTe})_{1-x}(\text{GeTe})_x$ (x=0.80, 0.82, 0.85, 0.87, 0.90) *J Solid State Chem* **182** 2088-2095
- Shen Q, Chen L, Goto T, Hirai T, Yang J, Meisner G P and Uher C (2001) Effects of partial substitution of Ni by Pd on the thermoelectric properties of ZrNiSn-based half-Heusler compounds *Appl Phys Lett* **79** 4165-4167
- Shi X, Yang J, Salvador J R, Chi M, Cho J Y, Wang H, Bai S, Yang J, Zhang W and Chen L (2011) Multiple-filled skutterudites: High thermoelectric figure of merit through separately optimizing electrical and thermal transports *J Am Chem Soc* **133** 7837-7846
- Slack G A (1995) Title In: CRC Hand Book of Thermoelectrics (Ed: Rowe D M) pp 407-440, CRC Press, Boca Raton
- Snyder G J and Toberer E S (2008) Complex thermoelectric materials *Nat Mater* **7** 105-114
- Sootsman J, Chung D Y and Kanatzidis M G (2009) New and old concepts in thermoelectric materials *Angew Chem Int Ed* **48** 8616-8639
- Source: India Energy Book 2012, World Energy Council
- Source: U.S. Energy Information Administration 2012, International Energy Statics, Indian Central Electricity Authority
- Tang X, Xie W, Li H, Zhao W and Zhang Q (2007) Preparation and thermoelectric transport properties of high-performance p-type Bi₂Te₃ with layered nanostructure *Appl Phys Lett* **90** 012102 1-3
- Tang X, Zhang Q, Chen L, Goto T and Hirai T (2005) Synthesis and thermoelectric properties of p-type- and n-type-filled skutterudite $\text{R}_y\text{M}_x\text{Co}_{4-x}\text{Sb}_{12}$ (R:Ce,Ba,Y;M:Fe,Ni) *J Appl Phys* **97** 093712 1-10
- Tritt T M (2011) Thermoelectric phenomena, materials, and applications *Annu Rev Mater Res* **41** 433-448

Yee S K, LeBlanc S, Goodson K E and Dames C (2013) \$ per W metrics for thermoelectric power generation: beyond ZT *Energy Environ Sci* **6** 2561-2571

Zhang L, Wang W, Ren B and Guo J The effect of adding nano-Bi₂Te₃ on properties of GeTe-based thermoelectric material *J. Electron Mater* 2013 **42** 1303-1306

Zhao L-D, He J, Hao S, Wu C-I, Hogan T P, Wolverton C, Dravid V P and Kanatzidis M G (2012) Raising the thermoelectric

performance of p-Type PbS with endotaxial nanostructuring and valence-band offset engineering using CdS and ZnS *J Am Chem Soc* **134** 16327-16336

Zhao L-D, Hao S, Lo S H, Wu C-I, Zhou X, Lee Y, Li H, Biswas K, Hogan T P, Uher C, Wolverton C, Dravid V P and Kanatzidis M G (2013) High thermoelectric performance via hierarchical compositionally alloyed nanostructures *J Am Chem Soc* **135** 7364-7370.