

# Trend for Thermoelectric Materials and Their Earth Abundance

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The low crustal abundance of materials such as tellurium (Te) (0.001 ppm by weight), antimony (Sb) (0.2 ppm), and germanium (Ge) (1.4 ppm) contributes to their price volatility as applications (competing with thermoelectrics) continue to grow, for example, cadmium telluride photovoltaics, antimony-lead alloy for batteries, and Ge for fiber optics and infrared optical technologies. Previous consideration of material scarcity has focused on Te-based thermoelectrics. Here, we broaden the analysis to include recent high-figure-of-merit ( $ZT$ ) materials such as skutterudites, Zintl phase compounds, and clathrates that employ Sb, ytterbium (2.8 ppm), and Ge. The maximum demonstrated  $ZT$  for each particular alloy exhibits an empirical dependence on the crustal abundance,  $A$ , such that  $ZT = A^{-b}$ , where  $b$  is in the range from 0.05 to 0.10. This analysis shows that no material with crustal abundance of 30 ppm ( $\sim 4 \times 10^{18}$  metric tons) has  $ZT$  greater than 0.8.

**Key words:** Thermoelectric, earth abundance, figure-of-merit

## INTRODUCTION

In the past two decades, there has been a surge in research of new thermoelectric materials, driven partly by the need for clean and sustainable power generation technology. A good thermoelectric material has high Seebeck coefficient ( $\alpha$ ), large electrical conductivity ( $\sigma$ ), and low thermal conductivity ( $\kappa$ ), giving a large dimensionless figure of merit ( $ZT = \alpha^2 \sigma T / \kappa$ , where  $T$  is absolute temperature).<sup>1</sup> Until the 1980s, the figure of merit of state-of-the-art thermoelectric material was approximately 1,<sup>2</sup> which limited the thermal-to-electrical conversion efficiency to below 5% with a temperature gradient of  $\sim 200$  K, at an average temperature of 350 K. Thus, application of thermoelectrics was only in niche markets such as power sources for deep-space probes and small thermoelectric coolers for electronics.<sup>1,3,4</sup> Recently, with the development of new materials and fabrication technologies, there have been continuous reports of materials with  $ZT > 1$ ; some of the highest  $ZT$  (bulk) materials are listed in Table I. The advancement in material technology has helped grow the application space for

thermoelectrics. Waste heat recovery in automobiles,<sup>5,6</sup> industrial waste heat recovery,<sup>7</sup> and solar thermoelectrics<sup>8,9</sup> are some of the applications that become feasible with high- $ZT$  materials.

As the scope of thermoelectrics increases, material usage and environmental conservation issues start to become of importance when choosing elements for thermoelectrics. Some of the key constituent elements in recent high- $ZT$  materials are not abundant in the Earth's crust, such as tellurium (Te) (0.001 ppm by weight), antimony (Sb) (0.2 ppm), germanium (Ge) (1.4 ppm), ytterbium (Yb) (2.8 ppm), and gallium (Ga) (19 ppm).<sup>10</sup> The low crustal abundance of materials contributes to their price volatility as applications (competing with thermoelectrics) continue to grow, for example, cadmium telluride photovoltaics (PV), antimony-lead alloy for batteries, antimony tin oxide for display panels and capacitors, Ge for fiber optics and infrared optical technologies, Ga for PV films and integrated circuits, and cobalt for high-strength permanent magnets for wind turbines and hybrid automobiles. Previous consideration of material scarcity has focused on Te-based thermoelectrics,<sup>11</sup> as Te is one of the most commonly used elements in thermoelectrics, and it also happens to be one of the rarest elements in the Earth's crust. In this paper,

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**Table I. High- $ZT$  (bulk) thermoelectric materials**

Material	$ZT$	Weighted Crustal Abundance (Metric Tons)	Competing Applications	Comments
$\text{Bi}_2\text{Te}_3$	1 (300 K) <sup>1</sup>	$2.8 \times 10^{14}$	Te—CdTe PV	Used in commercial modules
SiGe	0.8 (1000 K) <sup>12</sup>	$2.6 \times 10^{17}$	Ge—fiber optics, infrared technologies	Used in deep-space probes
PbTe	0.9 (750 K) <sup>1</sup>	$3.5 \times 10^{14}$	Te—CdTe PV	Natural nanostructure and grain boundaries suppress thermal conductivity
$\text{AgPb}_{18}\text{SbTe}_{20}$ (LAST)	1.72 (800 K) <sup>13</sup>	$3.4 \times 10^{14}$	Te—CdTe PV Sb—batteries, capacitors, displays	
$(\text{GeTe})_{75}(\text{AgSbTe}_2)_{25}$ (TAGS-75)	1.75 (700 K) <sup>14</sup>	$2.3 \times 10^{14}$	Ge—fiber optics and infrared technologies Te—CdTe PV Sb—batteries, capacitors, displays	Small features ( $\sim 10$ nm) cause phonon scattering to suppress thermal conductivity
$\text{Sr}_{0.16}\text{Yb}_{0.03}\text{Co}_4\text{Sb}_{12}$ (skutterudite)	1.32 (850 K) <sup>15</sup>	$3.2 \times 10^{16}$	Co—permanent magnets for wind turbines, hybrid automobiles Sb—batteries, capacitors, displays	$p$ -Type: $(\text{Ce}_y\text{Co}_{4-x}\text{Fe}_x\text{Sb}_{12})$ $ZT \approx 1$ <sup>16</sup>
$\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ (clathrate)	1.35 (900 K) <sup>17</sup>	$3.8 \times 10^{17}$	Ge—fiber optics and infrared technologies	$p$ -Type: $(\text{Ba}_8\text{Ga}_{16}\text{Al}_3\text{Ge}_{27})$ $ZT = 0.61$ <sup>18</sup>
$\text{Yb}_{14}\text{Mn}_{1-x}\text{Al}_x\text{Sb}_{11}$ (Zintl phase)	1 (1200 K) <sup>19</sup>	$7.7 \times 10^{16}$	Sb—batteries, capacitors, displays	(No Sb) $\text{Zr}_{0.5}\text{Hf}_{0.5}\text{NiSn}$ $ZT = 0.5$ <sup>22,23</sup>
$\beta\text{-Zn}_4\text{Sb}_3$	1.3 (670 K) <sup>20</sup>	$4.6 \times 10^{16}$	Sb—batteries, capacitors, displays	
$\text{Hf}_{0.75}\text{Zr}_{0.25}\text{NiSn}_{0.975}\text{Sb}_{0.025}$ (half-Heusler)	0.8 (1025 K) <sup>21</sup>	$3 \times 10^{18}$		$n$ -Type material ( $\text{SrTiO}_3$ ) $ZT = 0.37$ <sup>25</sup>
$\text{NaCo}_2\text{O}_4$ (oxide)	0.8 (1050 K) <sup>24</sup>	$7.1 \times 10^{18}$		(No Sb) $\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$ $ZT < 0.1$ <sup>26</sup>
$\text{Mg}_2\text{Si}_{0.4-0.015}\text{Sn}_{0.6}\text{Sb}_{0.015}$ (silicide)	1.1 (800 K) <sup>26</sup>	$0.5 \times 10^{18}$		

we broaden the analysis to include new materials such as skutterudites, Zintl phase compounds, and clathrates that employ Sb, Yb, and Ge.

In “ [\$ZT\$  Versus Crustal Abundance](#)” section, the recent trend in  $ZT$  and material abundance is analyzed for bulk thermoelectric materials. The crustal abundance of several important elements in today’s thermoelectrics is explored in this section. Detailed discussion on some of the recent high- $ZT$  materials, namely skutterudite, clathrate, and Zintl phase, is presented in “[High- \$ZT\$  Materials](#)” section. Some new Earth-abundant, benign thermoelectrics (half-Heusler, oxides, and silicides) are described in “[Earth-Abundant Thermoelectric Materials](#)” section. Observations and guidelines for a good thermoelectric material are discussed in “[Guideline for Good Thermoelectrics](#)” section. In this work, only bulk thermoelectric materials are analyzed. Analysis of thermoelectric properties of other materials and technologies, namely low-dimensional materials and nanostructuring (nanocomposite), can be found elsewhere.<sup>27–29</sup>

## $ZT$ VERSUS CRUSTAL ABUNDANCE

Figure 1 shows the solar (a) and the crustal (b) abundance of the elements with respect to their atomic number. There is a general trend of decreasing abundance for heavier elements. In the universe, all elements after iron (Fe), which is the most stable nucleus, are formed by a slow neutron capture process called the S-process.<sup>30</sup> This nucleosynthesis process occurs in stars where a stable isotope captures a neutron and forms a radioactive isotope, which decays to its stable daughter before the next neutron is captured to form a heavier isotope.<sup>30,31</sup> Bismuth is the last and the heaviest of the stable atoms created by the S-process.<sup>31</sup> Atoms produced by such neutron capture are less stable than Fe.<sup>31</sup> Another noticeable trend is that elements with even atomic number are slightly more abundant than the odd-numbered elements. This has to do with the stability of neutrons and protons in the nuclei which form “closed shells” configuration (similar to shells in atomic structure) in

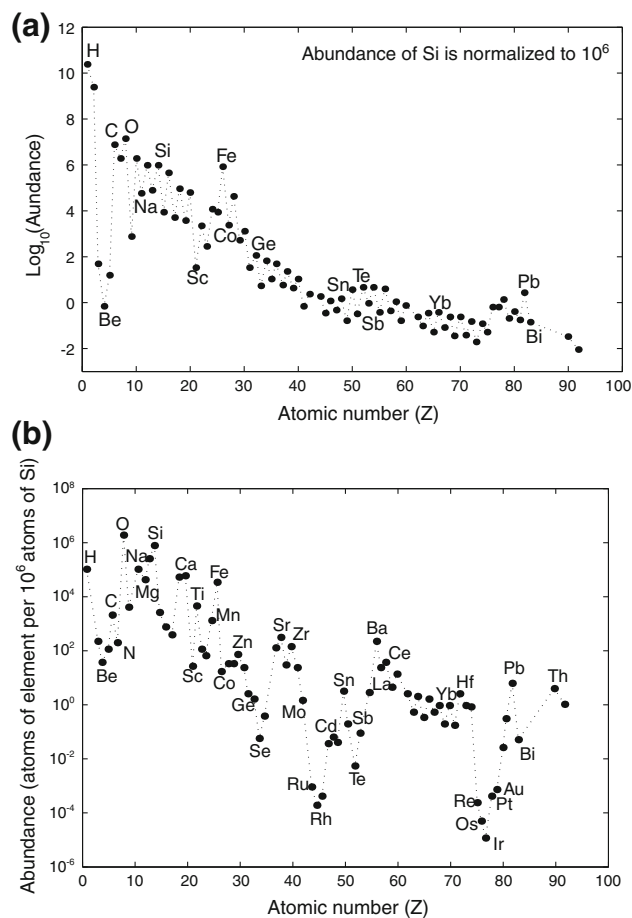


Fig. 1. Solar (a) and crustal (b) abundance of elements according to their atomic number (adapted from Refs. 33, 34).

even-atomic-numbered elements (Oddo–Harkins rule).<sup>32</sup> Crustal abundance (Fig. 1b) does not follow this simple trend with atomic number. The rarest elements are not the heaviest stable atoms. Ruthenium (Ru), rhodium (Rh), palladium (Pd), and Te with atomic numbers between 40 and 55 are rarer than the heavier rare-earth elements. The crustal abundance is determined not only by the overall solar abundance (Fig. 1a) but also by the element's affinity to ore-forming chemicals such as oxygen (O), sulfur (S), and Fe. The oxides and the silicates form the lightest mineral ores, which are found easily in the Earth's crust. Elements which have higher affinity for Fe tend to be denser and closer to the core, thus limiting their distribution in the Earth's crust. Crustal abundance of some of the thermoelectric elements is discussed in detail here.

Even though knowledge of crustal abundance can provide guidance in terms of environmental sustainability and scarcity of elements, the major factor influencing a material's usage for any technology is going to be its price. Determining an element's price for comparison can be a tricky topic, as it is a dynamic function of economic (demand/supply chain), engineering, political, and environmental

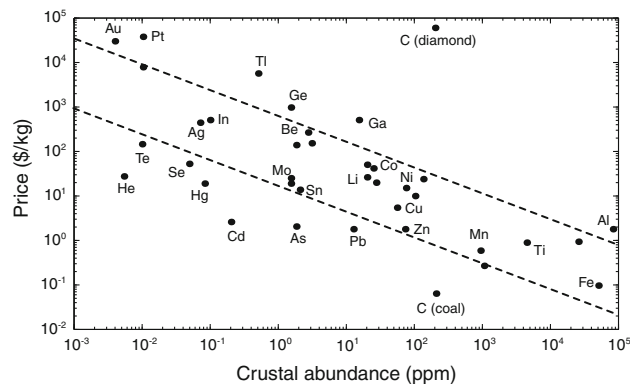


Fig. 2. Price (US \$/kg) versus crustal abundance [adapted from Ref. 35 (2009–2010 price)].

factors. Many economic geologists agree on a negatively sloped trend between price and crustal abundance for most of the elements (Fig. 2), which shows that, as elements become rarer, they are generally more expensive.<sup>35,36\*</sup> There are a few elements which deviate from this trend, such as Ge, Ga, gold (Au), and platinum (Pt), which are more expensive than other elements of similar crustal abundance.<sup>35</sup> Similarly, cadmium (Cd), arsenic (As), bismuth (Bi), and mercury (Hg) have lower market price relative to their abundance.<sup>35</sup> These deviations could be due to differences in demand for these elements; for example, Ge has similar crustal abundance to molybdenum (Mo), Yb, lanthanum (La), and tungsten (W). As the demand for Ge is higher compared with these other elements, it is natural that Ge has higher market price. Another important factor in the market price of an element is the homogeneity and concentration in which it is found in ores or minerals. This is important in determining mines which are economical for extraction. Many sulfide ores have high concentration of minable elements due to precipitation, compared with oxides or silicates, which can lower the price.<sup>37</sup> Elements such as Cd, Bi, and Hg are extracted in high concentration from sulfide ores.

As material demand increases with every new emerging technology competing with thermoelectrics, the price fluctuation will invariably affect the application scope of thermoelectrics. Many thermoelectric elements such as Sb, As, Bi, selenium (Se), and Te are mined as byproducts with primary metals such as lead (Pb), zinc (Zn), or copper (Cu) ores.<sup>38</sup> The production capacity of these mines chiefly depends on the market (demand and price) for the primary element. Looking at the high- $ZT$  thermoelectrics (Table I) and the crustal abundance (Fig. 1b), some elements that may be critical in terms of cost and sustainability are Te, Sb, Ge, and Yb.

\*The USGS report includes material purity for the price data (e.g., 99.6% purity for antimony price).

Even though Te is widely distributed in the solar system, having comparable solar abundance to tin (Sn), the low average abundance in the Earth's crust has to do with the fact that Te has low affinity for oxygen and prefers to bond with sulfur, forming heavier minerals.<sup>39,40</sup> These chalcophile (sulfur-loving) elements are much denser than lithophile elements (silicate minerals), and they accumulated below the lithophiles at the time of the first crystallization of the Earth's crust, which led to their depletion in the crust compared with the solar abundance.<sup>41</sup> Te does not occur in concentrations high enough to economically justify mining on its own.<sup>38,42</sup> The surge of new technologies has driven the price of Te in the last decade from less than US \$22/kg (2004) to nearly US \$440/kg at the beginning of 2011.<sup>38</sup> However, global production of Te has only increased by less than 25% in the last decade,<sup>43</sup> which may indicate the limitation in the accessible quantity of this element.

Sb is also a chalcophile element, mostly produced as a byproduct from a sulfide ore mineral called stibnite.<sup>44,45</sup> The primary use of Sb has been in flame retardants and lead-acid batteries. Increasing use in new technologies in the past decade has caused a sharp rise in the price for Sb. Recently, the price volatility has also been due to speculation of decline in mines in China, which is the world's largest Sb producer (>90%).<sup>42</sup> The Herfindahl index defines the measure of the degree of competition in an industry. A normalized index value of 0 indicates a highly competitive market with all involved firms/countries with equal share. An index value of 1 indicates full concentration in a single firm/country. For Sb, the normalized Herfindahl index is 0.77; for comparison, the index value for Cu is 0.16.<sup>46</sup>

As with Te, Ge is unevenly distributed in the Earth's crust; it forms more than 100 minerals, but only a few ores (usually chalcophiles) have enough concentration of Ge to allow for economic extraction.<sup>47</sup> Ge also has the tendency to alloy with Fe, which makes it denser and closer to the core.<sup>47</sup> Due to the small extractable quantities, there are many refining steps from mining to the actual element, which adds to the cost. The current market price of Ge (~US \$1000/kg) may make it prohibitive for use in any large-scale thermoelectric applications.<sup>38,42</sup> Another potential critical material used in thermoelectrics is Yb. The low annual production of Yb has more to do with its few commercial applications rather than the production capability given by the crustal abundance. However, the element is very expensive (US \$14,000/kg), primarily due to difficulties in isolation of rare-earth elements from each other as their chemical properties are very similar.<sup>42</sup>

Figure 3 shows a plot of  $ZT$  versus crustal abundance for some of the best, recent thermoelectric materials. The maximum demonstrated  $ZT$  for each particular compound exhibits an empirical dependence on the crustal abundance,  $A$ , such that

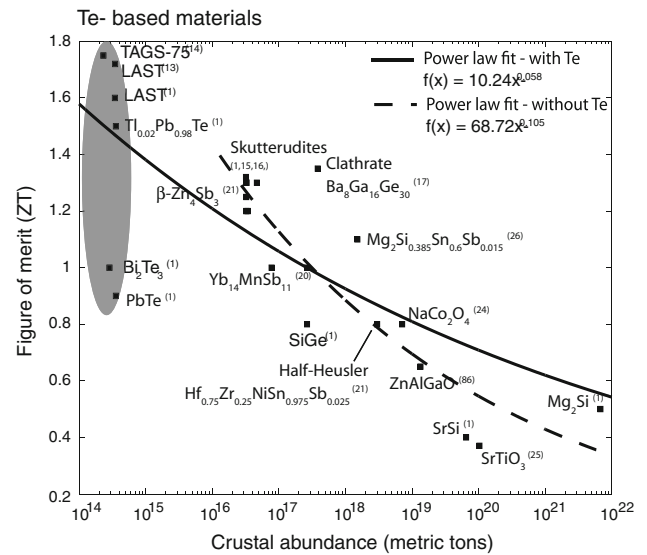


Fig. 3.  $ZT$  versus crustal abundance for bulk thermoelectric materials.

$ZT = A^{-b}$ , where  $b$  is in the range from 0.05 to 0.10, depending on inclusion of the Te-based materials. Here,  $A$  is the weighted crustal abundance of the rarest element in the composition of each thermoelectric material. In an alloy ( $M_xN_y$ ), the variable  $A$  is given by

$$A = \begin{cases} xC_M & \text{if } C_M < C_N \\ yC_N & \text{if } C_M > C_N \end{cases},$$

where  $C_M$  and  $C_N$  are the crustal abundances of the constituent elements [conversion from ppm to kg is done by estimating the crust's mass ( $\sim 1.3 \times 10^{23}$  kg) from the rock density and the total volume of the crust];  $x$  and  $y$  are the percentage weights of the individual component.

Careful consideration has to be applied when researching new thermoelectric materials, keeping in mind such factors as element scarcity, toxicity, and price, especially if the end goal is high-volume application of thermoelectrics. In the remaining sections, individual thermoelectric elements utilizing these trace and rare elements will be analyzed to understand the role of rare elements in enhancing the thermoelectric properties.

## HIGH- $ZT$ MATERIALS

### Skutterudites

Based on Slack's phonon-glass electron-crystal (PGEC) concept, skutterudites are some of the most researched thermoelectric materials of the last decade.<sup>48</sup> Occurring naturally in  $\text{CoAs}_3$ -type structure, skutterudites are formed by transition metals (TM) [Co, Rh, iridium (Ir)] and group V elements [phosphorus (P), As, Sb]. Among the choices, Rh (0.0007 ppm) and Ir (0.0004 ppm) are two of the rarest elements in the Earth's crust,<sup>10</sup> leaving Co

and Sb as the pair with the smallest electronegativity difference (0.17). Small electronegativity difference ( $\leq 0.3$ ) gives nonpolar covalent bonds between elements, which improves the electrical transport properties; namely, large electrical conductivity is possible due to high carrier mobility.<sup>1</sup> Original skutterudite,  $\text{CoSb}_3$ , has high power factor but also relatively high thermal conductivity (10 W/m K).<sup>49</sup> The conduction and valence bands near the Fermi level are derived from the hybridized combination of TM  $3d$ -states and pnictogen (group V elements)  $p$ -states.<sup>50</sup> The interactions between  $d$ - and  $p$ -orbitals lead to nonbonding orbitals.<sup>51,52</sup> The nonbonding orbitals in molecular orbital theory are equivalent to lone pairs in Lewis structure. These states have little overlap with the  $d$ -orbitals of the neighboring TM sites, which results in low dispersion curve near the Fermi energy and high effective mass,<sup>53,54</sup> thus giving a large Seebeck coefficient. The relatively large lattice thermal conductivity of the compound can be suppressed by partially filling the voids in the structure with small, heavy ions that produce large disorder for phonon scattering. The filler element should satisfy the electronegativity ( $\chi$ ) relation to Sb ( $\chi_{\text{Sb}} - \chi_{\text{filler}} > 0.8$ ).<sup>55</sup> These filler atoms essentially form loose bonds with Sb atoms, and their displacement parameter is responsible for the reduction of the lattice thermal conductivity. Yb has been shown to be a successful filler element, with thermal conductivity reduced to nearly 2 W/m K.<sup>56</sup> Other substituents can be La, cesium (Ce), or more abundant barium (Ba).<sup>57,58</sup> Recent advances in material development have been looking at multiple elements as fillers in the voids. A combination of alkaline-earth and rare-earth elements as fillers is better for thermal conductivity suppression, as they have different masses and different vibrational frequencies to scatter a wide range of phonons.<sup>15,59,60</sup> Skutterudite development is at the stage of research where it has good potential for industrial production and application, as both  $n$ - and  $p$ -type legs can be obtained with good  $ZT$  at high temperature by changing the filler ions and TM doping. In terms of the abundance of elements used in making common skutterudite, Sb (0.2 ppm) is the least abundant in the Earth's crust. Even though it is not a rare element such as Te, increased demand, usage in new emerging technology other than thermoelectrics, and a single-country production monopoly (China) may limit the market size and its sustainability.

### Clathrate

Clathrates are some of the best examples of phonon-glass thermoelectric materials, as they have shown a thermal conductivity trend similar to that of glass ( $\text{SiO}_2$ ), with measured values below 0.5 W/m K.<sup>61</sup> These compounds have an open framework of tetrahedrally coordinated group IV semiconductor/metalloids (Si, Ge, Sn) as host atoms

with “guest” atoms from group I [sodium (Na), potassium (K)] and II [strontium (Sr), Ba] that are encapsulated in two different polyhedral cages of the host atoms.<sup>18,61</sup> The loose bond between the guest atoms and the host lattice cage causes vibration of the guest atoms, which interacts with a wide range of low-frequency phonons, causing flattening of the phonon bands and lowering of the phonon velocity that leads to lower lattice thermal conductivity.<sup>1,61</sup> Group IV elements form the host matrix, which contributes to most of the electronic transport properties of the thermoelectric material. The highest  $ZT$  for clathrate has been measured for Ge-based material. Instead of Ge, if more abundant silicon (Si) is used, the thermoelectric properties have been slightly lower.<sup>62</sup> This could be primarily due to the fact that Ge is heavier than Si and could contribute to lower thermal conductivity. Sn compounds have slightly lower melting point compared with Ge- and Si-based clathrates.<sup>18</sup> As mentioned earlier, the high cost of Ge may make these types of thermoelectrics cost prohibitive for any application in the current market scenario.

### Zintl Phase/ $\beta$ - $\text{Zn}_4\text{Sb}_3$

Another PGEC thermoelectric material that has shown  $ZT > 1$  is Zintl phase material ( $\text{Yb}_{14}\text{MnSb}_{11}$ ). It has low thermal conductivity, most likely due to structure complexity (limiting the phonon mean free path) and heavy constituent elements (reducing the fraction of atomic vibrational modes that carry heat efficiently).<sup>63,64</sup> Zintl phases have elements with relatively large electronegativity difference (0.40) to form the anionic and cationic parts. The existence of polyanionic bonds (Sb-chain) is responsible for the complexity of the crystal structure.<sup>63,65</sup> The exceptionally low thermal conductivity ( $\sim 1$  W/m K) is also due to this ionic nature of the bonds. The tradeoff is that the ionic bond formation leads to relatively poor electrical properties. However, Zintl phase complex structures often have cationic sites (alkaline/heavy elements) that allow addition of disordered scattering and carrier concentration tuning by doping. This allows fine adjustment of the Fermi level, which can enhance the electrical transport properties.<sup>66</sup>

$\beta$ - $\text{Zn}_4\text{Sb}_3$  is another thermoelectric compound with low thermal conductivity at room temperature (0.9 W/m K to 1.1 W/m K).<sup>67,68</sup> The low thermal conductivity is likely due to highly disordered Zn sites. In the crystalline structure, some Zn atoms occupy interstitial sites that give rise to significant local lattice disorientation to reduce the thermal conductivity.<sup>69</sup> Sb pairs also form a linear chain in the structure, which contributes to large vibration along the chain direction to suppress the thermal conductivity. An ordered Sb framework provides the electron-crystal component of the PGEC with decent power factor.<sup>63,70</sup> Thermoelectric module-level development has been hard due to the phase

transition around 670 K which changes the thermal and electrical properties; its brittle character is also problematic.<sup>69</sup> Usage of trace Sb and expensive Yb in these Zintl phase compounds may also hinder their utilization in any large-scale thermoelectric systems.

### TAGS/LAST

Both of these materials have shown some of the highest  $ZT$  values measured for thermoelectric material (TAGS-75:  $ZT = 1.75$  at 700 K<sup>14</sup>;  $\text{AgPb}_m\text{SbTe}_{2+m}$ :  $ZT = 1.72$  at 700 K<sup>13</sup>). A considerable number of nanoscale ( $\sim 10$  nm) domains have been seen in the samples, which reduces the lattice thermal conductivity due to enhanced grain boundary scattering.<sup>14</sup> The boundary defects and nanoscale microstructures occur naturally when the material is grown in bulk form. The LAST compound is roughly Sb/Ag-codoped PbTe.<sup>13</sup> These compounds have shown difficulties in handling and stability at high temperatures, and the material properties are highly sensitive to the chemical composition. Due to toxicity of Pb compounds, usage of TAGS/LAST may be limited for terrestrial applications.

Even though the above-mentioned materials have been studied heavily for the past two decades and have consistently shown  $ZT > 1$ , module development and utilization has not yet been significant. There are challenges of stability and handling. However, use of some critical elements such as Te, Ge, and Sb could prevent these materials from scaling. In the next section, we look at some of the more recent Earth-abundant thermoelectrics with promising potential.

## EARTH-ABUNDANT THERMOELECTRIC MATERIALS

### Half-Heusler

The interest in these intermetallic compounds as potential thermoelectrics started because of their high melting point, chemical and thermal stability, mechanical robustness, nontoxicity, and potential low-cost elements.<sup>21,55,71</sup> Half-Heusler structures are of  $\text{MgAgAs}$  format, and the most promising of all material combinations is  $\text{M}(=\text{Ti,Zr,Hf})\text{NiSn}$ .<sup>72-74</sup> The large Seebeck coefficient of these compounds is primarily due to the TM  $d$ -orbital, which can induce a large density-of-state (DOS) peak near the Fermi level.<sup>75</sup> The energy positions of the  $d$ -orbital-induced DOS peaks are element sensitive. The relatively flat band structure near the Fermi level is due to hybridization between  $d$ -band states of the primary TM [Co/nickel (Ni)] and  $d$ -band states of neighboring zirconium (Zr)/hafnium (Hf) atoms.<sup>75,76</sup>  $\text{TiCo}(\text{Sn,Sb})$ ,  $\text{NiMn}(\text{Ga,Sb,Sn})$ , and  $\text{NiZrSn}$  are a few example half-Heusler structures that are being investigated for their thermoelectric properties.<sup>22,77</sup> Currently, the limit on  $ZT$  values is mostly due to

high thermal conductivity (5 W/m K to 10 W/m K).<sup>22</sup> Half-Heusler materials have voids in the crystal structures which can be engineered to decrease the thermal conductivity. The best  $ZT$  values are for  $\text{Zr}_{0.5}\text{Hf}_{0.5}\text{NiSn}$  with  $ZT = 0.5$  at 700 K.<sup>22,23</sup> Substitution and doping of Ni and Sn with Pd and Sb has given  $ZT \approx 0.8$  at 800 K.<sup>23</sup> The usage of Sb as a dopant requires a relatively small quantity compared with that in skutterudites or Zintl phase compounds (Fig. 3). The other constituent elements of half-Heusler compounds are moderately abundant in the Earth's crust.

### Oxide

The recent discovery of high Seebeck coefficient (100  $\mu\text{V/K}$ ) in  $\text{NaCo}_2\text{O}_4$  has opened a new direction in the search for thermoelectric materials.<sup>78</sup> Oxides are very promising thermoelectric materials due to their high temperature stability, high oxidation resistance, and usage of environmentally benign elements.<sup>79</sup> The origin of the good thermoelectric properties in these TM oxides is a large peak in the DOS, which comes from the narrow  $3d$ -orbital of the TM at the valence band.<sup>79</sup> The relatively large Seebeck value for  $\text{NaCo}_2\text{O}_4$  is attributed to the spin-induced entropy from the possibility of large degeneracies in different valence states of Co (i.e.,  $\text{Co}^{4+}$ ,  $\text{Co}^{3+}$ ).<sup>80</sup> These different valence states of Co in the low spin state carry large entropy, which is transported by the charge carriers to increase the Seebeck coefficient.<sup>80</sup> Co-O forms the metallic layer with high carrier mobility and electrical conductivity.<sup>81</sup> This compound has very high carrier concentration ( $10^{21}$   $\text{cm}^{-3}$  to  $10^{22}$   $\text{cm}^{-3}$ ). These oxides form a natural two-dimensional layered structure, and the reduction in the thermal conductivity (3 W/m K to 4 W/m K) is due to misfit structures of Na-ion nanoblock layer between  $\text{CoO}_2$  layers.<sup>78,79</sup> Substitution of Co with other TMs (Rh, Ti, and Pd) can reduce the thermal conductivity, as they act as phonon scattering sites. Ni instead of Co has low electrical conductivity due to small charge carrier density.<sup>82</sup>  $\text{SrTiO}_3$  is another example of a potential good thermoelectric material which is found in layered structure.<sup>25,83</sup> High electrical conductivity and high Seebeck coefficient are due to high effective mass, where the band structure is mostly influenced by Ti  $3d$ -orbitals.<sup>84</sup> This compound has relatively high thermal conductivity of 8 W/m K at room temperature. At higher temperature, the conductivity goes down to 3 W/m K with doping.<sup>85</sup> Zn-based oxides have good power factors (comparable effective mass to  $\text{Bi}_2\text{Te}_3$ , PbTe) but very high thermal conductivity of  $\sim 40$  W/m K at room temperature and 5 W/m K at 1000°C.<sup>86,87</sup> Doping with heavier elements can decrease the thermal conductivity, but it will also reduce the carrier mobility and the electrical conductivity. Nevertheless,  $ZT \approx 0.8$  has been achieved for the oxides, which is comparable to the high-temperature state-of-the-art

thermoelectric material (SiGe) but without using expensive and scarce materials. The constituent elements of the oxide-based thermoelectrics are some of the most abundant crustal elements such as Na, Zn, Ti, and Sr.

### Silicide

Another interesting and benign compound with potential as thermoelectric material is metal silicide, which was initially studied in the late 1950s.<sup>88</sup> Most heavy metal silicides are mechanically and chemically stable Nowotny chimney-ladder compounds.<sup>88</sup> The good Seebeck coefficient (150  $\mu\text{V/K}$  to 200  $\mu\text{V/K}$ ) can be associated with the *d*-band states of TM in materials such as  $\text{FeSi}_2$  and  $\text{MnSi}_x$ .<sup>89–91</sup> Other silicides ( $\text{Ru}_2\text{Si}_3$ ,  $\text{Ru}_2\text{Ge}_3$ , and  $\text{Os}_2\text{Si}_3$ ) are also semiconductors with narrow band gap and could potentially have good thermoelectric properties;<sup>92</sup> especially,  $\text{Ru}_2\text{Si}_3$  can potentially be better than SiGe at high temperature, but the main difficulty has been finding suitable dopants for optimum doping.<sup>92</sup> However, the material choices in these examples are some of the rarest elements in the Earth's crust. A potential problem with alkali/alkaline-earth silicides ( $\text{Mg}_2\text{Si}$ ,  $\text{Ca}_2\text{Si}$ , and  $\text{Sr}_2\text{Si}$ ) is their chemical reactivity and low melting point. Tertiary compounds based on magnesium silicide have recently shown great promise as thermoelectric material with  $ZT \approx 1$ . Bi-doped  $\text{Mg}_2\text{Si}_{0.6}\text{Ge}_{0.4}$  was reported with measured  $ZT \approx 1$  at 800 K.<sup>93</sup> The most favorable system to date has been  $\text{Mg}_2\text{Si}_{0.4-x}\text{Sn}_{0.6}\text{Sb}_x$  with measured  $ZT = 1.1$  at 800 K.<sup>26</sup> High  $ZT$  has been due to low thermal conductivity given by the maximum mass difference between components.<sup>26</sup> Utilization of Ge and Sb in both of these compounds limits the abundance of this material. However, the average weight percentage usage of these trace elements (as dopants) is lower than that in clathrates and skutterudites (Fig. 3). Some of the metal silicides, even though they have small  $ZT$  values ( $\text{FeSi}_2$ : *n*-type  $\sim 0.4$ ; *p*-type  $\sim 0.2$ <sup>88</sup>), could be very useful as they make very inexpensive thermoelectric materials.

### GUIDELINE FOR GOOD THERMOELECTRICS

There are some general observations that can be used as guides when considering elements and compounds that could give good  $ZT$  values. These “selection criteria”<sup>94–96</sup> lead to either lower thermal conductivity ( $\kappa$ ) or higher power factor ( $\alpha^2\sigma$ ) necessary to increase  $ZT$ . The well-known criteria for good thermoelectric materials are listed below:<sup>94–96</sup>

1. Optimum carrier concentration in the range from  $10^{19} \text{ cm}^{-3}$  to  $10^{20} \text{ cm}^{-3}$  is needed to maximize the power factor, leading to usage of mostly semiconductor-based material for thermoelectrics.
2. Most thermoelectric materials have covalent bonds (i.e., elements with low electronegativity

difference  $\leq 0.3$ ) and high atomic coordination, which gives large electrical conductivity due to high carrier mobility.<sup>1</sup>

3. Heavy elements make good thermoelectric material, as large atomic mass contributes to low lattice thermal conductivity.<sup>1,94,95</sup> Ge, Sn, Sb, Te, Pb, Bi, As, and Se are the heaviest stable elements that show semiconductor/semimetal properties (i.e., group IV, V, and VI).<sup>94</sup> Within the above-listed elements, many are toxic (Pb and As) and less abundant in the crust (Te, Sb, and Ge). Elements such as Sn, Zn, Sr, Hf, and Zr are Earth-abundant heavy elements (atomic weight  $> 50$ ) which may be utilized to make good thermoelectrics.
4. Alloys with atoms of similar electric potentials but different masses can scatter phonons more effectively, where scattering is due to difference in mass and/or bond stiffness.
5. Large number of valleys in the band structure gives rise to a higher effective mass and a large change in the DOS near the Fermi level, giving high Seebeck coefficient.<sup>1</sup>

On the basis of the materials discussed in this work, we can add several more observations to this guideline for good thermoelectrics:

- Complex/open cage structure can give very low lattice thermal conductivity. Structures with large empty cage where fillers/guest atoms are introduced can scatter acoustic phonons, as these atoms have large atomic displacement parameter (ADP), which is interpreted as the rattling effect causing decrease in the lattice thermal conductivity. ADP is the measure of the mean-square displacement amplitude of an atom about its equilibrium lattice site.<sup>1,63</sup> In skutterudite, Sb is an important element in making this type of cage structure, whereas in clathrates, Ge or Si form the host matrix. In terms of abundance, Si will be an ideal choice for making Earth-abundant thermoelectrics.
- Use of TM with partially filled *d*-band states can give high Seebeck coefficient even for large carrier concentration,<sup>97</sup> due to low dispersion curve near the Fermi energy and high effective mass.<sup>54</sup> Earth-abundant TMs such as manganese, Fe, Ni, Zr, and scandium could provide benefits of partially filled *d*-band for high thermoelectric performance.

Most thermoelectric materials discussed in this work have good thermoelectric properties, and they follow one or more of the guidelines mentioned above.

### CONCLUSIONS

The primary material found in today's commercial thermoelectric modules is  $\text{Bi}_2\text{Te}_3$ , which has the highest  $ZT \approx 1$  at 350 K. As a generator, these modules can be used with low-grade heat for waste heat recovery applications. Knowing the crustal abundance, the limiting material in terms of

availability in  $\text{Bi}_2\text{Te}_3$  thermoelectrics will be Te. Annual production of Te is on the order of 200 metric tons, of which nearly 70% is used for industrial metallurgical applications.<sup>38,98</sup> The current demand from Te thermoelectrics has been less than 10%, due to the small application space.<sup>98</sup> However, with growth in emerging new technologies such as photovoltaics (CdTe), the supply/demand balance and eventually the price have become very volatile.<sup>99,100</sup> In such a scenario, the increase in demand from thermoelectrics with Te will only add to the scarcity and rising cost of the element.<sup>38</sup>

The current limitation in the availability of other material options as modules is mainly due to low module performance and low  $ZT$ , which does not encourage many applications to use thermoelectrics. As the material  $ZT$  and the module performance are improved, and new applications are explored, the demand for modules will also rise. Earth-abundant thermoelectric materials (i.e., lower right-hand-side materials in Fig. 3) hold the promise of potential high thermoelectric performance without the risk of material scarcity. Annual production of some of the key elements such as Na (200 kilotons), Co (17 kilotons), Zn (12.5 megatons), Al (30 megatons), Zr (7 kilotons), Ni (1.3 megatons), Sn (165 kilotons), Mg (350 kilotons), Si (3.88 megatons), Sr (137 kilotons), and Ti (99 kilotons) is very high.<sup>10</sup> The reserve base, which is the predetermined/known economically viable concentration for mining, for these elements is also high, as these are mostly elements with high crustal abundance.<sup>36</sup> Even though the current  $ZT$  for these material is low compared with most of the high- $ZT$  thermoelectrics (i.e., skutterudites, clathrates, LAST, and TAGS), new material development technology such as nanostructuring and nanocomposite synthesis can potentially enhance the performance without changing the key constituent elements.<sup>29,101</sup> Such technological improvement will be a key factor in developing thermoelectric materials with Earth-abundant constituents for high-volume applications.

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