

Influence of periodic table in designing solid-state metal chalcogenides for thermoelectric energy conversion

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Abstract. With the apparent burgeoning energy crisis, alternative sources of energies are in a greater need for a sustainable future. Thermoelectrics which can convert waste heat arising from industries, power plants and automobiles into a usable form, electricity; have the potential to be a game-changer in this critical energy shortage. The efficiency of thermoelectric materials which is given by the figure of merit is tricky to manipulate due to the complicated interrelationships of its parameters. But with proper understanding of a material and with the aid of periodic table, one can manoeuvre the shortcomings which hinder its efficiency. In this perspective, we discuss how the properties of materials can be manipulated just by understanding the elements of the periodic table and how each element in their respective position in the periodic table influences the outcome of high performing thermoelectric material.

Keywords. Periodic trends; Metal chalcogenides; Thermoelectrics; Chemical bonding; Solid state chemistry.

1. Introduction

The growing demand for energy has given rise to a tremendous scope for research in thermoelectrics. Thermoelectric materials can convert waste heat into electricity. High thermoelectric (TE) performance is observed in materials with high Seebeck coefficient, S , low electrical resistivity, ρ (high electrical conductivity, σ) and low thermal conductivity, κ_{tot} .¹⁻⁵ The thermoelectric figure of merit couples these necessary attributes of good TE material into one factor as given by

$$ZT = \frac{\sigma S^2 T}{(\kappa_{ele} + \kappa_{lat})} \quad (1)$$

where κ_{ele} and κ_{lat} correspond to electrical and lattice contributions respectively, of the total thermal conductivity, κ_{tot} . These physical properties are strongly interdependent on each other and thus makes it challenging to design high-performance TE materials. To understand the fundamental material

properties, assuming carrier concentration, a more prominent term called the TE quality factor, β is preferred.¹

$$\beta = \frac{N_v}{m_i^* \kappa_{lat}} \quad (2)$$

Large valley degeneracy, N_v which essentially relates to the number of similar energy states around conduction band minima or valence band maxima, contributes to a large number of conduction pathways for charge carriers for electronic transport and low inertial effective mass, m_i^* along the direction of conduction pathway. Effective mass is defined as the relative mass of the charge carriers with respect to the mass of free electron. Thus, effective mass being closer to the mass of free electron means the electrical conduction is much greater and can hence improve the mobility ($\mu = e\tau/m_i^*$). For single valley, $m_{band}^* = m_i^*$ and the contribution of m_i^* is related to density of states effective mass m_{DOS}^* via m_{band}^* as⁵

$$m_{DOS}^* = m_{band}^* N_v^{2/3} \quad (3)$$

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High Seebeck coefficient can either be due to large m_{band}^* or large N_v . However, large m_{band}^* increases scattering and decrease the mobility of electrons as it is related to m_i^* .

The band gap between the valence and conduction band plays an important role in TE performance of a material. When the temperature increases, the electronic carriers are thermally excited across the band gap and the minority carriers start to neutralize the majority carriers, leading to origin of low thermo-power and high thermal conductivity due to bipolar conduction. Thus, bandgap regulates the maximum suitable operating temperature and figure of merit of TE material.^{1,6} Figure 1 describes the band gap of a crystalline solid with hypothetical composition AB by Molecular Orbital Theory (MOT). The band gap, bonding energy or strength of bonding interactions, energy difference between atomic orbitals, width of valence and conduction band is given by E_g , B^* , $2A^*$, W_{VB} , W_{CB} , respectively. In simple MO of solid with composition AB, B^* is the subsequent energy from stabilization of molecular bonding orbitals and destabilization of antibonding orbital compared to atomic orbitals. B^* can be expressed in terms of orbital overlap interaction, V and A^* as^{7,8}:

$$B^* = \sqrt{V^2 + A^{*2}} - A^* \quad (4)$$

Larger A^* will lead to weaker covalent bonding energy, B^* . V is indirectly proportional to the square of the distance, d which can describe the valence shell interactions. According to Koopman's theorem, higher is the electronegativity, lower is A^* .⁹ Large difference in electronegativity (χ) between element A with small χ and B with large χ results in larger band gap. The orbital character of bands is also influenced by χ difference. In

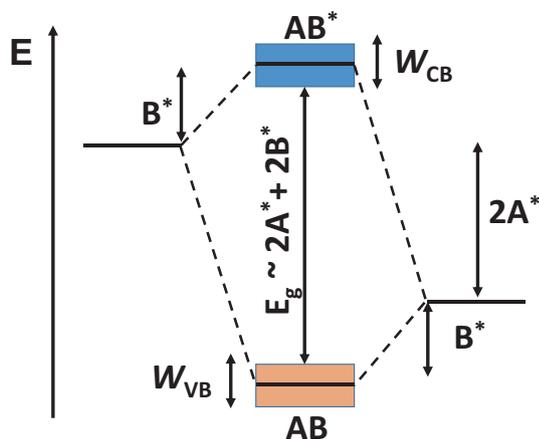


Figure 1. Molecular orbital (MO) diagram of solid with composition AB, where E_g is bandgap, A^* is energy difference of atomic orbitals, W is the width of conduction and valence band, B^* is the strength of bonding interactions.

ionic solids with large A^* , the valence band states will have anion B character and conduction band states will have cation A element character.

The electronic properties in semiconductors are governed by the width of an electronic band W .² Figure 1 shows that increased width W can lead to the reduction of the band gap and it is possible to tune the electronic properties. If $W > B^* + A^*$, AB and AB^* MO orbitals of AB will merge to form an overlapping band and result into metal or semimetal. For polar compounds ($A^* \neq 0$), W tends to drop with an increase in A^* as the overlap, V becomes less effective due to the rise in the energy difference between the neighboring orbitals leading to large band gaps in ionic compounds. Smaller dispersion (narrow band) arises from factors like longer bonds, high degree of polarity or dispersed f-orbitals which have lower overlap than p- or s-interactions. Narrow band in energy space corresponds to wide parabola in k-space, a large DOS and a high m_{band}^* which is expected in large electronegative difference ionic compounds.⁸

Arguably the most important parameter in the thermoelectric figure of merit is that of thermal conductivity. The total thermal conductivity (κ_{tot}) is a summation of two types of heat propagators. One of the heat propagators are the free charge carriers (electron or hole), and the amount of heat propagation by them is given by κ_{ele} ; while the other is heat transport via lattice vibration (or phonons) which is denoted as κ_{lat} . Since high κ_{ele} is a resultant of high σ by virtue of their relation using Wiedemann-Franz law (i.e., $\kappa_{ele} = L\sigma T$, $L =$ Lorentz number), reducing κ_{ele} is not a popular choice and thus reducing κ_{lat} is seen as an important avenue to achieving high performance in thermoelectrics. As a matter of fact, almost all high performing thermoelectric materials possess low thermal conductive parent compound and is often considered to be the backbone in designing superior, highly efficient thermoelectric material.¹⁰⁻¹² Periodic table more often than not dictates how the material will transport heat and along with keen chemical intuition, one often designs compounds showing low thermal conductive materials. For example, the tellurides of Ge to Pb in group 14 (i.e., GeTe, SnTe and PbTe), we see a decreasing trend in the thermal conductivity of the material. We have discussed the influence of periodic table in generating low thermal conductive materials in more detail in later part of our review.

Thus, we can say that the electronic and thermal transport are linked to bonding character, band gap, bonding strength, bond length, effective mass, orbital overlap and lone-pair anharmonicity; all of them can be understood by a thorough understanding of the

elements and their position on the periodic table. In this review, we will discuss the importance that the periodic table plays in shaping the thermoelectric properties of materials.

2. Periodic trends in electronic properties

2.1 Band gap

Band gap is one of the contributing factors in determining the electrical conductivity (σ) of a semiconductor. Generally, materials with low band gap show high σ and decrease with increasing band gap. In case of PbQ (Q = chalcogenides, S, Se and Te), the band gap for PbSe (0.27 eV) < PbTe (0.31 eV) < PbS (0.40 eV). The electrical conductivity too shows the same trend as ($\sigma(\text{PbSe}) > \sigma(\text{PbTe}) > \sigma(\text{PbS})$).¹³ For thermoelectrics, the materials should possess band gap which falls in the semi-conducting region in terms of band edge (i.e., neither very low metallic gap or high band gap as that of an insulator). Often σ is governed by the mobility of the major carriers in the material. Carrier mobility, μ is low for bands with heavy mass m_{band}^* , leading to low electrical conductivity ($\sigma = ne\mu$). This difference between the valence band and conduction band relies upon several factors like electronegativity, presence of stereochemical lone pairs and temperature, etc., and are known to play a crucial role in determining the electrical conductivity of a material.

2.2 Role of electronegativity

The difference in electronegativity can be helpful in tuning the band gaps and thereby the electronic mobility as $E_g \sim 2A^* + 2B^*$ and A^* depends on electronegativity. Larger is the electronegativity difference more will be band gap. For example, in $\text{AgBiSe}_{2-x}\text{X}_x$ (X = Cl, Br, I) the electrical conductivity for pristine AgBiSe_2 is around 63 S cm^{-1} . On doping aliovalent halogens, the band gap is seen to widen up (from $\sim 0.6 \text{ eV}$) due to higher electronegativity of halogens ($\chi_{\text{Cl}} (3.16) > \chi_{\text{Br}} (2.96) > \chi_{\text{I}} (2.66)$) as compared to selenium ($\chi_{\text{Se}} = 2.55$) which causes more ionic character in M-X bond than that of M-Se bond.¹⁴ As a result, the σ increases to 376 S cm^{-1} at room temperature for 4 mol% Cl doped AgBiSe_2 . For 4 mol% Br and I doped AgBiSe_2 , σ value is 337 S cm^{-1} and 196 S cm^{-1} respectively at room temperature.¹⁴ The σ trend for aliovalent halogen doped AgBiSe_2 mirrors the electronegativity trend down the Group 17 of the periodic table (Figure 2a). Thus, proper knowledge of periodic table and their corresponding electronegativity aids in

realizing high thermoelectric performance in n-type AgBiSe_2 .¹⁴ Similarly for PbSe, ongoing down Group 13, (i.e., B, Al, Ga), σ is seen to increase from $8.72 (10^2 \text{ S cm}^{-1})$ in case of B doped PbSe to around $38.5 (10^2 \text{ S cm}^{-1})$ for Ga doped PbSe.¹⁵ Here too, the periodic trend is observed; as we go down the group, the electronegativity decreases which increases the propensity of Group 13 elements to donate excess electrons and thereby increases the carrier concentration which in turn increases the σ of n-type PbSe.

2.3 Effect of lone-pairs

In the elements of group 13, 14 and 15, the lone pair of electrons play an important role in the electronic properties of thermoelectric materials. As we move down the group in p-block elements, the ns^2 lone pair experiences a greater effective nuclear force, and as a result tends to become inert in nature. In group 13, as the element becomes heavier from Ga to Tl, the lone pair becomes more stabilized in In^+ than in Ga^+ . In case of group 14 and 15, Pb^{2+} and Bi^{3+} have very stable lone pair and it is difficult to form Pb^{4+} and Bi^{5+} . This enormous stability of ns^2 lone pairs is due to relativistic effects which reduce the size of s-orbital and bring the electron near to nucleus. In semiconductors, containing Tl, Ge, Sn, Pb, Sb and Bi, the stereochemical expression of ns^2 lone pair, increases the band gap as it stabilizes in energy.² Depending upon the chalcogenides bonded to these metal ions, the lone pair is either stereochemically expressed or quenched. Down the group, there is a tendency to quench the lone pair and adopt high local symmetry. This concept can be realized in many examples and these are listed in Table 1. In Bi_2S_3 , SnSe , Sb_2Se_3 , GeS the lone pair stereochemically expressed, causes strong distortion and lowering of structural symmetry which lowers the energy of the orbitals significantly and thereby increasing the bandgap. Thus, the lone pairs become the contributing factor in estimating the band gap of a system and its influence on the electrical conductivity.

2.4 Seebeck coefficient

Seebeck coefficient is related to electrical conductivity by Mott equation (Eq. 5). S is the measure of variation of $\sigma(E)$ above and below the Fermi surfaces. $\sigma(E)$ is proportional to the DOS at E if the scattering of electrons is independent of energy. A larger slope ($d \ln \sigma(E)/dE$) where DOS changes rapidly, will contribute to larger thermopower.¹

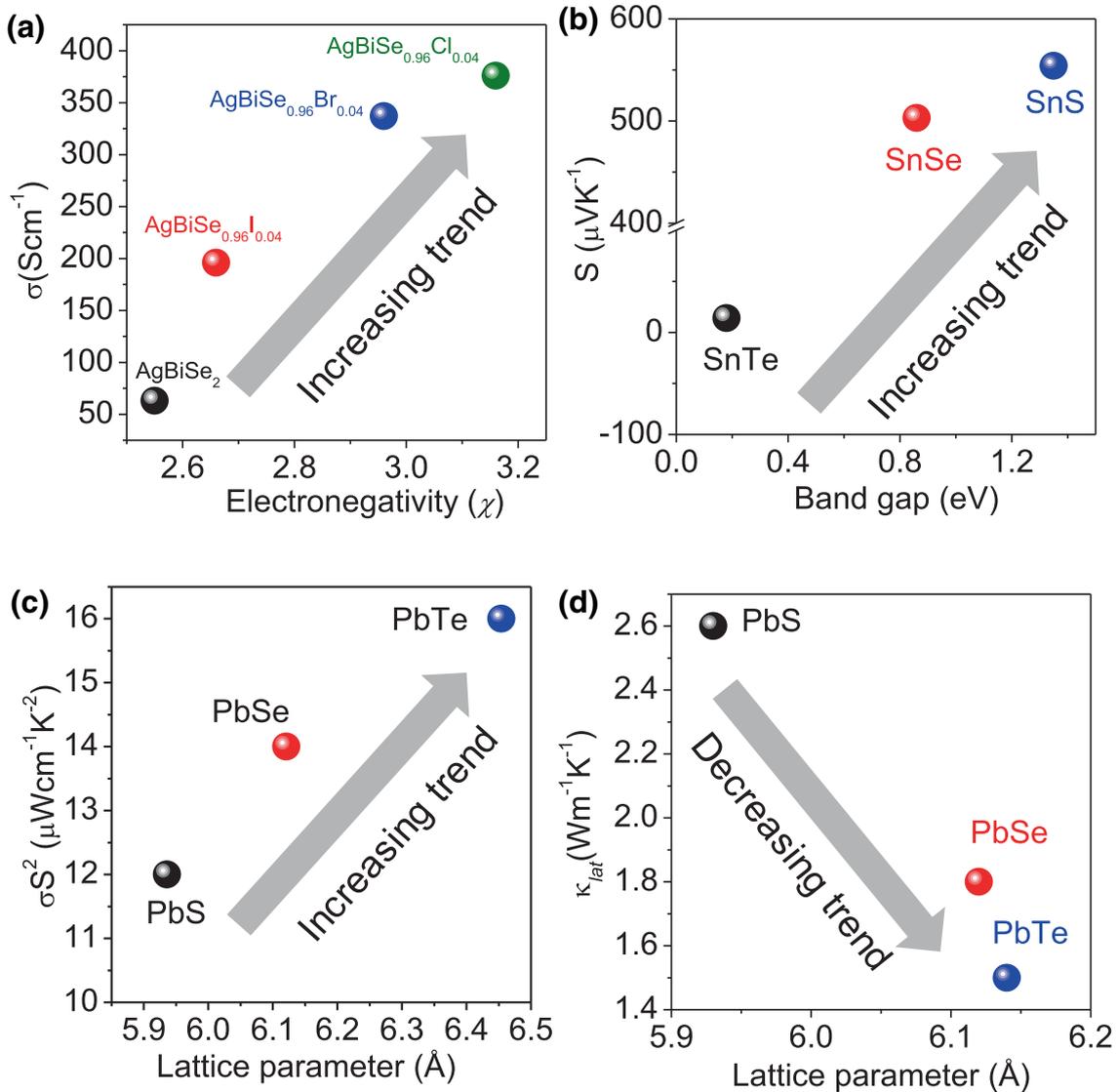


Figure 2. Periodic trends of (a) electrical conductivity (σ), (b) Seebeck coefficient (S), (c) Power factor (σ^2) and (d) lattice thermal conductivity (κ_{lat}) for some metal chalcogenides.

Table 1. Comparison of band gaps of chalcogenide based semiconductors down the group.

Semiconductor	Crystal structure (symmetry)	Band gap (eV)
Bi_2S_3	Orthorhombic (low)	1.30
Bi_2Se_3	Rhombohedral (high)	0.30
SnSe	Orthorhombic (low)	0.80
SnTe	Cubic (high)	0.18
Sb_2Se_3	Orthorhombic (low)	1.10
Sb_2Te_3	Rhombohedral (high)	0.11
GeSe	Orthorhombic (low)	1.07
GeTe	Rhombohedral (high)	0.6

$$S = \frac{\pi k^2 T}{3 e} \left[\frac{d \ln(E)}{dE} \right]_{E=E_f} \quad (5)$$

$$S = \frac{8\pi^2 k_B^2 T}{3 e h^2} m_{DOS}^* \left[\frac{\pi}{3n} \right]^{2/3} \quad (6)$$

Also, S is expressed in relation to density of state effective mass (m^*) of the carrier by the equation below:¹⁶ and density of states is given by:

$$g(E) = \frac{[m_{DOS}^*]^{3/2} \sqrt{2E}}{\hbar^3 \pi^2} \quad (7)$$

In SnQ (Q = S/Se/Te), down the Group 16, the band edge decreases, SnS having a band gap of 1.35 eV¹⁷ decreases to 0.86 eV for SnSe¹⁸ to around 0.18 eV for SnTe.¹⁹ This band edge decrease is also seen to increase the S value for SnQ. SnTe having S value of $\sim 14 \mu\text{VK}^{-1}$ is much lower than SnSe ($\sim 503 \mu\text{VK}^{-1}$) or SnS ($554 \mu\text{VK}^{-1}$) at ambient temperatures and the trend is continuous and in line with the periodic table trend (Figure 2b).^{19,20} Thus, here also, periodic table shows a tremendous influence in monitoring the Seebeck coefficient of thermoelectric materials. It is to be noted that PbQ (Q = S/Se/Te) does not follow the trend of decreasing band gap with increasing atomic number. Chalcogenides of Sn and Ge which resides on the same Group 14 follows the normal trend. This anomaly in PbQ may have to do with relativistic effects and an extensive spin-orbit coupling which renders it impossible to predict the band gap just from a simplified MO model and general trends.

2.5 Power factor

In PbQ, (Q = S, Se, Te), the room temperature power factor increases from $\sim 12 \mu\text{W cm}^{-1} \text{K}^{-2}$ for PbS to $\sim 14 \mu\text{W cm}^{-1} \text{K}^{-2}$ for PbSe and $\sim 16 \mu\text{W cm}^{-1} \text{K}^{-2}$ for PbTe. This is directly related to the size of the anion going down the group and the lattice parameter (Figure 2c).¹³ A similar trend is observed in MSe (M = Pb, Sn, Ge) series, where the room temperature power factor increases from $\sim 1.2 \times 10^{11} \text{ W mK}^{-2} \text{ s}^{-1}$ for PbSe to $\sim 4 \times 10^{11} \text{ W mK}^{-2} \text{ s}^{-1}$ for SnSe and $\sim 8 \times 10^{11} \text{ W mK}^{-2} \text{ s}^{-1}$ for GeSe due more overlapping factor.¹⁶

3. Periodic trends in thermal conductivity

Achieving a high thermoelectric figure of merit often relies on materials having low κ_{lat} .^{3,10,21} Often an overlooked parameter in the figure of merit equation, but with recent developments in the field of thermoelectrics κ_{lat} is often regarded as the defining parameter to achieve superior thermoelectric performance. SnSe, for example, has achieved ultrahigh ZT (> 2.5) in both n- and p-type conduction owing to the impressively low κ_{lat} values (κ_{lat} 0.2–0.3 $\text{Wm}^{-1} \text{K}^{-1}$ at 773 K) in both single-crystalline and polycrystalline forms.^{10,21–23} The most extensive work on achieving κ_{lat} in materials is *via* introducing micro and/or nanostructuring in the matrix,^{3,11} while recent

scientific explorations focus on looking at the intrinsic bonding inhomogeneity^{24–26} and enhanced anharmonicity^{27,28} to lower the phonon propagation in materials. Here, however, we will focus on the influence of chemical bonds and nature of phonon propagation trending with periodic table and will develop an understanding of how the periodic table shapes up the κ_{lat} of certain high performing materials.

Kinetic theory predicts that the κ_{lat} of material can be quantified approximately using the equation $\kappa_{lat} = \frac{1}{3} C_v v_m l$; where C_v is the specific heat at constant volume, l is the mean free path length for phonons and v_m is the mean speed of sound. v_m depicts the speed of phonon waves propagating through a lattice and is given by $v_m \sim \sqrt{k/M}$, where k is the spring constant and M is its molar mass. Thus, high bond strength results in high spring constant and eventually a higher κ_{lat} as envisaged earlier by Ioffe and Spitzer.¹

Pb based chalcogenides, PbQ (i.e., Q = Te, Se and S) adopt a rock-salt type structure, on going down Group 16, the v_m decreases. As a result, the κ_{lat} trend also depicts this periodic trend of decreasing v_m . PbS have a κ_{lat} of $\sim 2.6 \text{ Wm}^{-1} \text{K}^{-1}$ at room temperature and going down the group it decreases to $\sim 1.8 \text{ Wm}^{-1} \text{K}^{-1}$ and $\sim 1.5 \text{ Wm}^{-1} \text{K}^{-1}$ for PbSe and PbTe, respectively at room temperature (Figure 2d).¹³ However, for Ge based chalcogenides, we don't observe such trend in κ_{lat} values. GeTe have a κ_{lat} value of $\sim 3.0 \text{ Wm}^{-1} \text{K}^{-1}$ at room temperature, while GeSe possesses much lower κ_{lat} values of 1.76 $\text{Wm}^{-1} \text{K}^{-1}$ at room temperature. GeS possesses slightly higher κ_{lat} than that of GeSe but lower than GeTe.²⁹ The difference in trend here can be understood in terms of understanding the structure and the energy of the valence electrons of Ge 4p and 4s orbitals relative to the chalcogenides np orbitals (Figure 3). On going down the Group 16, the electronegativity of the Q decreases (i.e., χ_S (2.58) $>$ χ_{Se} (2.55) $>$ χ_{Te} (2.1)) and as a result, the energy of the p orbitals on the Q increases (Figure 3). For GeTe, the difference in energy between 4s of Ge and 5p of Te is high enough for any significant overlap between them, and hence remains in relatively higher symmetry as compared to GeSe and GeS. Se and S whose 4p and 3p, respectively are lower in energy can form significant bonding interaction with the Ge 4s and as a result the lone pairs on Ge stereochemically express themselves, which drive the structure to a lower symmetric layered structure (Figure 3). These stereochemically active lone pairs induce lattice anharmonicity which in turn lowers the κ_{lat} of GeSe and GeS as compared to GeTe. For SnQ, Sn-based

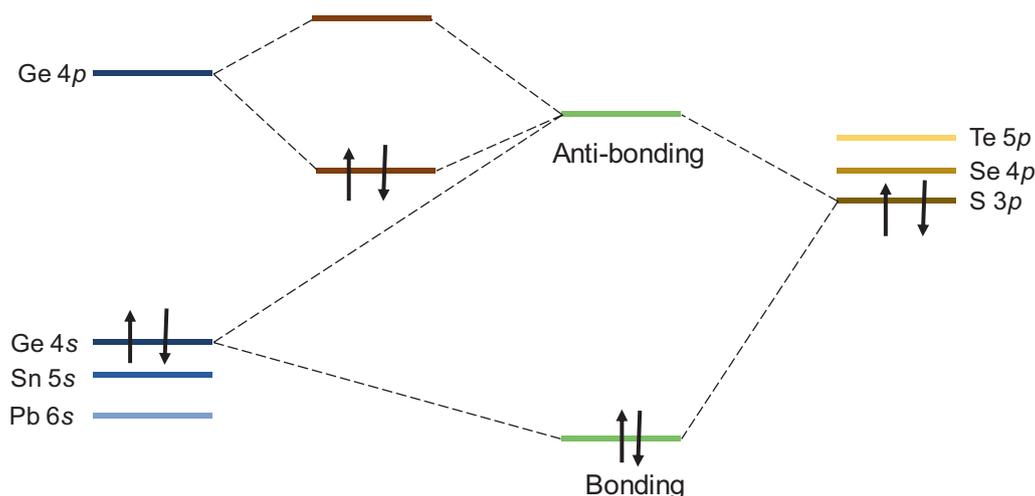


Figure 3. Modified MO diagram showing the interaction of *ns* orbitals of Ge (Sn, Pb) with *np* orbitals of S (Se, Te). The corresponding interaction results in an opening of band gap as the anti-bonding orbital interacts with *4p* orbital of Ge.

chalcogenides show similar trend as that of GeQ. SnTe has κ_{lat} of $\sim 3.1 \text{ Wm}^{-1} \text{ K}^{-1}$ at room temperature which is significantly higher than that of SnSe ($0.46 \text{ Wm}^{-1} \text{ K}^{-1}$) and SnS ($\sim 0.9 \text{ Wm}^{-1} \text{ K}^{-1}$) at room temperature.¹⁹ The reason for such trend is in line with the GeQ. However, SnTe at room temperature procures rock-salt structure contrary to GeTe which is rhombohedral in nature. The reason being the different energy states of *4s* for Ge and *5s* in case of Sn. The energy gap between *5s* of Sn and *5p* of Te is too much to have any meaningful interaction and thus the stereochemical nature of *5s*² lone pairs are suppressed and the structural distortion does not take place (Figure 3), unlike GeTe. Comparing MTe compounds now (M = Ge, Sn, Pb), we observe that the structure changes from rhombohedral in case of GeTe, to cubic in case of SnTe and PbTe. This is a direct result of the amount of interaction between *ns* orbitals of M and *5p* of Te. The trend here directly relates to the interaction between anion *p* and cation *s* and their corresponding distortion from the rocksalt structure.³⁰ PbQ, on the other hand, all resides as rock-salt type structure. That is due to the relativistic effect on *6s*² lone pairs which stabilizes them to a much greater extent.³¹ Although in case of PbQ and SnTe, the bonding interaction among them is not significant, there remains a substantial quantity of *s* character in the anti-bonding state. As a result, the structure although attains a globally cubic structure, but locally distorts due to trivial but finite contribution from the *ns*² lone pairs on Sn and Pb which is observed from the local structure determining technique Pair Distribution Function.^{32,33} This results in local off-centring of cation in these materials (i.e., PbQ and SnTe) which lowers their thermal conductivity from the ideal one

and also gives rise to lone pair induced anharmonicity in the lattice which is also responsible for scattering of phonons in the lattice and lowering of κ_{lat} . Thus, periodic table enables a chemist to logically intuit the outcome of κ_{lat} in a material and thereby enhances the probability for furnishing high performing thermoelectric materials.

4. Figure of merit

The thermoelectric figure of merit (ZT) which accounts for both the aforementioned properties (i.e., electronic and thermal) leads to efficient values for heavier elements (i.e., Pb and Te). As seen from the above discussions, this is how the periodic properties optimize the TE parameters which show PbTe with high electronic properties, yet surprisingly low thermal conductivity. The factors influencing such high efficiency in PbTe directly arise from the optimal band gap of $\sim 0.3 \text{ eV}$ and low κ_{lat} of $1.5 \text{ Wm}^{-1} \text{ K}^{-1}$. As a result, PbTe shows unmatched thermoelectric ZT values (ZT ~ 2.2) with very high device efficiencies using appropriate dopants.^{3,34–36} The use of dopants to stimulate higher thermoelectric properties are directly governed by the position in the periodic table and one can easily engineer the properties influencing the ZT value by proper intuition and knowledge of the periodic table.

5. Cost of materials

Apart from the low thermal conductivity and good thermoelectric performance, there is also a need for earth-abundant, non-toxic, and low-cost constituent

elements. The leading advanced thermoelectric materials are mainly based on Pb, Ge, Se, Te. There is a need to explore attractive potential alternatives due to the toxicity of Pb, extreme scarcity of Te, cost issues related to Ge. Extensive research on inexpensive sulfur which has long-price stability and abundance is required. Down the group, as the element becomes heavier, it becomes less abundant and costly.

6. Conclusions

In conclusion, the advances in thermoelectric materials have come a long way since its inception in the late 1940s. A plethora of new techniques like the formation of resonant level, band convergence, formation of hierarchical nano/meso-architectures skyrocketed the development in this field. A $ZT > 2$ which was inconceivable in the past have been achieved and now with the aid of theoretical guidance and materials genome project, a vast plethora of new materials with potential to furnish efficient thermoelectric materials are being generated. But, even all these new techniques rely on the periodic table to dictate their performance. Without the periodic table, attaining such high ZT values would not have been possible. It guides a scientist to look into the right direction and with proper knowledge and keen understanding of the periodic properties, one can easily attain a right dopant to improve on the already known thermoelectric materials or even better, furnish a new and high performing one. But one must keep in mind that even with all the prowess of the periodic table, it alone is not enough to cater to the scientific query for high performing thermoelectric materials. Integrating the knowledge obtained from periodic table with theoretical calculations and the chemical intuition to apply the required techniques like nano-structuring will pave a long way to develop materials having superior thermoelectric performances.

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