Overview on High Potential Material for Thermoelectric and their Structure

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Abstract:- **This report will review the most promising material for thermoelectric application (thermoelectric refrigerator and thermoelectric generator). Here we are concerned on the material selection with emphasizing on their structure in order to achieve high thermoelectric figure of merit. Four kinds of material structure with Phonon Glass Electron Crystal (PGEC) approach are highlighted here, those are skutterudite structure, clathrate structure, half – Heusler structure and chalcogenide phase. They are established materials for thermoelectric and intensively studied by many researchers related to thermoelectric area.**

Keyword: Seebeck effect, Peltier effect, Phonon glass electron crystal, Skutterudite, Half - Heusler, Clathrate, Chalcogenide,

I. INTRODUCTION

Thermoelectricity today is receiving renewed attention spurred by recent theoretical and experimental developments, as well as by growth in niche markets for current technology [1].They are solid-state devices that convert electrical energy into a temperature gradient, known as the "Peltier effect" or convert thermal energy from a temperature gradient into electrical energy, the "Seebeck effect"[2]. The efficiency of thermoelectric energy converters depends on the transport coefficients of the constituent materials through the figure of merit, *ZT* [3]:

$$ZT = \left(\frac{S^2 \sigma}{\kappa} \right) T \qquad \ldots\ldots\ldots\ldots \text{Equation 1}$$

Where σ is the electrical conductivity and *S* is the Seebeck coefficient. The quantity in the denominator is the thermal conductivity; it is given by the sum of contributions from the electronic carriers κ_e and the lattice κ_l. The efficiency is increased by making *ZT* as large as possible, where *T* is the mean operating temperature of the device.

Over 40 years of history, thermoelectric materials research had been expand to various kinds of materials with a different kind of material structures. However, the aims of the research still remain same; to attain higher thermoelectric figure of merit - ZT values, where *Z* is a measure of a material's thermoelectric properties and *T* is the absolute temperature [4]. From the definition of the figure of merit given in Equation 1, it is clear that, to increase *Z*, we have to decrease the thermal conductivity of the material and/or increase the thermo power and electrical conductivity.

Among the four quantities involved in Eq. 1, three of them are mainly related to the electronic structure of the material (σ, *S*, and κ_e) and one is mainly related to the lattice (κ_l). One possible way to improve the figure of merit is to reduce the lattice thermal conductivity without significantly altering the electronic properties of the material. This approach has been explored extensively in the past through the enhancement of phonon scattering [5, 6]. However, a very comprehensive review done by Spitzer [7] shows that (2 mW/cm.K) is the practical lower limit for the lattice thermal conductivity of semiconductors. Another traditional way to improve the thermoelectric properties of a material is to maximize $S^2\sigma$ by varying the doping concentration, which varies the electron density.

A further understanding of thermoelectric materials awaited the development of quantum theory and its application to the electronic and thermal properties of semiconductors. Taking advantage of that groundwork, thermoelectric research teams focused on the physics and materials science of the semiconductors known at that time. As for the current work, there are two unifying themes drawn from physics and materials science: the discovery of new materials with greater chemical complexity and fabrication of known materials in submicron formats.

A Seebeck effect

The Seebeck effect is the first fundamental that come describing the conversion of heat differences directly into electricity. This effect was first discovered, accidentally, by the German physicist Thomas Seebeck in 1821 . The voltage difference, dV, produced across the terminals of an open circuit made up of a pair of dissimilar metals, A and B, whose two junctions are held at different temperatures. The Seebeck effect has two major applications: temperature measurement and power generation.
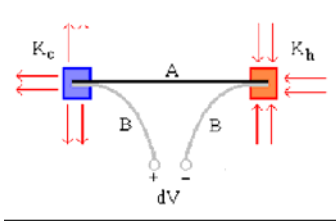
Figure 1: Simple illustration on phenomenon of Seebeck effect.

B Peltier effect

Peltier Effect is reversing the Seebeck Effect. It occurs when two members of the thermoelectric series were connected with the wires to form a circuit with two junctions (Fig. 1). In the presence of a current a temperature difference between the junctions is produced. In other words, Peltier effect occurs when an electric current magnitude I across the two junction of different conductors A and B.

The Peltier effect is caused by the fact that an electric current is accompanied by the heat current in a homogeneous conductor even at the constant temperature works in the opposite direction called the Seebeck effect. Peltier effect in physics, it is a changes in temperature at the junction of two conductor produced when an electric current flows through them. The extent of the change depends on what the conducting metals are, and the nature of change (rise or fall in temperature) depends on the direction of current flow.
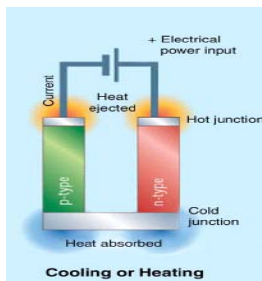

Figure 2: Peltier effect model

II CRITERIA FOR HIGH POTENTIAL THERMOELECTRIC MATERIAL

A good thermoelectric material must combine a large Seebeck coefficient, S with low electrical resistivity, ρ and low thermal conductivity, λ. But two irreversible processes which are thermal conduction and Joule heating lower the performance of thermoelectric devices to less than the thermodynamic limit. Further, because Joule heating is proportional to the square of the electric current and the Peltier effect is only linear in current, one cannot increase the

temperature gradient indefinitely simply by increasing the current.

Looking to the behavior of electron in material structure, in an isotropic conductor, the electrical conductivity σ is the reciprocal of ρ, but in anisotropic materials, for which the E and I vectors may not aligned, $\sigma \neq 1/\rho$. The application of a magnetic field application of a magnetic field in one direction makes all the materials anisotropic to some extent.

The combination of the thermal conduction and electron conduction inside the materials structure give the roughly idea in struggling higher ZT value for thermoelectrics.

It is said the requirements for semiconductor materials suitable for thermoelectric cooling and power generation applications at and above ambient temperatures [8].
a. High crystal symmetry with the electronic bands near the Fermi level and many valleys.
b. Heavy element compounds with small electro negativity differences between constituent elements.
c. Energy gap of about 10 $k_B T$, where T is the temperature of operation and k_B is Boltzmann's constant.

This approach give the idea to the concept of "Phonon Glass Electron Single Crystal" (PGEC). The concept was first introduced by Slack and given in detail in his review [9], is the heart of the investigation into semiconductors that posses "glass like" thermal conductivity values and may prove superior for thermoelectric applications.

As first pointed out by Slack [9], if atoms that are trapped inside the polyhedra, or atomic "cages", are smaller than the "cages", they may "rattle" about and interact randomly with the lattice phonons, resulting in substantial phonon scattering. This is one of the most conspicuous aspects of these compounds and directly determines many of their interesting and unique properties.

The type of "open structure" compound that may possess PGEC properties would contain at least three, perhaps more than three distinct crystallographic sites so that there is possibility of obtaining good electronic properties. At least one of the sites may reside inside an atomic cage formed by the constituent atoms at the other sites. The disorder caused by the rattling motion of this atom would scatter the heat-carrying phonons. The other sites would form the framework of the cage-like open structure. These framework atoms would presumably dominate the band structure that defines electronic transport properties. In this chapter we review two material systems that have received enormous attention for the thermoelectric applications.

Cahill et al.[10] enumerated a number of crystalline systems that possess low, glass-like lattice thermal conductivity (λ_L) values. The thermal conductivities measured in these systems indicate that the lattice vibrations are similar to those of

material was pointed out by Slack [11]. The main features of all of the research by Cahill et al. [10] indicate that

a. They posses loose atoms or molecules whose translational or rotational positions are not well defined and possess two or more metastable positions.
b. There is no long range correlation between the positions of the loose atoms or molecules.
c. The mass of these loose atoms or molecules is at least 3% of the total mass of the crystal.
d. Disorder produced by point defect scattering cannot lead to glass like lattice vibrations; this approach will not lead to λ_{min}.

This approach has resulted in solids with very low thermal conductivities and giving a great impact to thermoelectric research. Among the material that applying this concept is skutterudite structure, clathrate, half-heusler and chalcogenide phase that will be explain in this paper.

III SKUTTERUDITE STRUCTURE

The name skutterudite derives from a naturally occurring mineral, $CoAs_3$, first found in Skutterud, Norway. This mineral possess a cubic crystal structure and contains thirty-two atoms per unit cell [8]. A schematic of the basic structure is shown in fig. 3. Binary skutterudite compounds, such as $CoSb_3$, have interesting properties useful for thermoelectrics. Skutterudites possess a large unit cell, heavy constituent atom masses, low electronegativity differences between the constituent atoms and large carrier mobilities. They form covalent structures with low coordination numbers for the constituent atoms and so can incorporate atoms in the relatively large voids formed. Therefore, compounds can be formed where atoms fill the voids of the skutterudite structure.

As first predicted by Slack and Tsoukala [12], interstitially placing atoms in the voids of such compounds would substantially reduce the thermal conductivity λ by introducing phonon scattering centers. Thus, these atomic "void fillers" may "rattle" about in their oversized cages and thereby provide an approach to drastically reducing λ in the high-λ binary compound. Another advantage of the cubic material system is that single crystals are not necessary to investigate the electrical and thermal transport properties of skutterudites. This also makes their promise for thermoelectric applications more feasible, if the appropriate material parameters are achieved. In addition, these materials are hard and have a relatively low coefficient of thermal expansion.
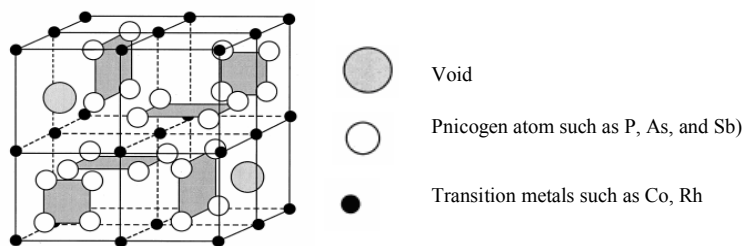
The basic family binary semiconducting compounds that form the skutterudite structure can be represented by MX_3 where M = Co, Rh or Ir and X = P, As or Sb. There are eight formula units per crystallographic cubic unit cell in the space froup *Im3*, eight M atoms occupy the c crystallographic sites, and twenty four X atoms are situated at the g sites. The structure can be uniquely specified from the lattice parameter, and the two positional parameters y and z specify the g site. One of the salient features that characterize the skutterudite structure is the nearly square X_4 rings that run parallel to the cubic crystallographic axes. From structural analysis of the binary skutterudites, the void radii of these compounds, it has been estimated, range from 1.763 to 2.040 for CoP_3 and $IrSb_3$, respectively [13].

Applying the "electron crystal-phonon glass" concept to the skutterudite system requires adding a ternary cation to the void in the skutterudite structure. While this reduces the thermal conductivity, the addition of ternary cation adds valence electrons to the conduction band degrading the electronic properties. The electronic properties can be improved by readjusting the valence electron count back towards that found in $CoSb^3$ through substitution of Fe for Co or Sn for Sb. While this readjusts the electron count, these substitution result in reduced carrier mobility due to impurity scattering.

A prominent feature of the skutterudite material system is the fact that it has an "open structure" lattice; two restively large voids exist at the *a* positions of the unit cell which can be interstitially filled with atoms. Its enough to accommodate large metal atoms like Ba and lanthanoids, resulting in the formation of 'filled-skutterudite' structures with the general formula MT_4X_{12} (M = Ba, Ln; T = Fe, Ru, Os; X = P, As, Sb) [2–7]. The crystal structures of skutterudite and filled-skutterudite are shown in Fig. 1. Both skutterudite-type TX_3 and filled-skutterudite-type MT_4X_{12} are transition metal pnictides (phosphides, arsenides, and antimonides); the former are compounds with nine-group elements (T = Co, Rh, Ir), while the latter are compounds with eight-group elements (T = Fe, Ru, Os) in the periodic table. This difference is well explained by the classical valence theory [14]

Void

Pnicogen atom such as P, As, and Sb)

Transition metals such as Co, Rh

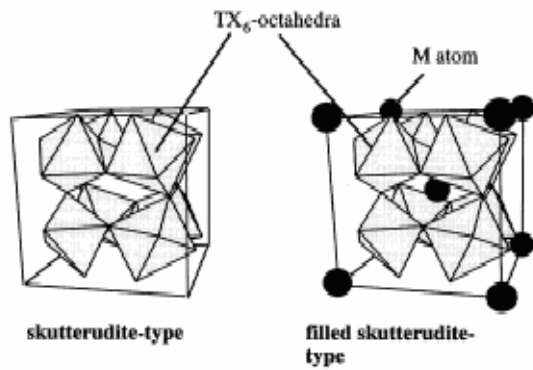Fig . 3: Basic Structure of skutterudite structure.

Figure 4: Skutterudite with unfilled and filled structure.

Filled skutterudites have been formed where group-III, group-IV, lanthanide actinide and alkaline-earth ions interstitially occupy these voids [6.12]. The interstitial ion in this structure is sixfold coordinated by the X-atom planar groups and is thereby enclosed in an irregular dodecahedral (12 fold coordinated) "cage" of X atoms.

Larger X-ray atomic displacement parameters (ADP) have been reported for the "guest" ions, indicating that they may "rattle" or participate in soft phonon modes in the voids of this crystal structure [16-18]. The ADPs of these ions increase with decreasing ionic size. It appears these ions "caged" in the voids of this structure and, if smaller than void in which they are caged, may "rattle" and thus interact randomly with the lattice phonons resulting in substantial phonon scattering. This is most evident from temperature-dependent structural data.

Table 1: Some of thermoelectric material for skutterudite structure [59,60]

Sample	Rattling atoms	ZT Value at 60
$Ca_{0.05}Co_4Sb_{12.43}$	Ca	0.06
$La_{0.75}Fe_3CoSb_{12}$	La	0.13

IV CLATHATE STRUCTURE

A clathrate compound is usually defined as an inclusion complex in which particles of one substance are completely enclosed in cavities formed by the crystal lattice or present in large molecules of another substance. Clathrates are periodic solids in which tetrahedrally coordinated atoms form cages that surround a metal atom. We examine Slack's suggestion [10,11] that the metal atoms scatter phonons but not electrons, thus lowering the thermal but not the electric conductivity [19]. Clathrates, in particular have received much attention recently because of their potential as thermoelectric materials.

The two most common forms of clathrates are known as type I and type II. Figure 6.10 illustrates the polyhedral "building blocks" that form type I and type II clathrates.
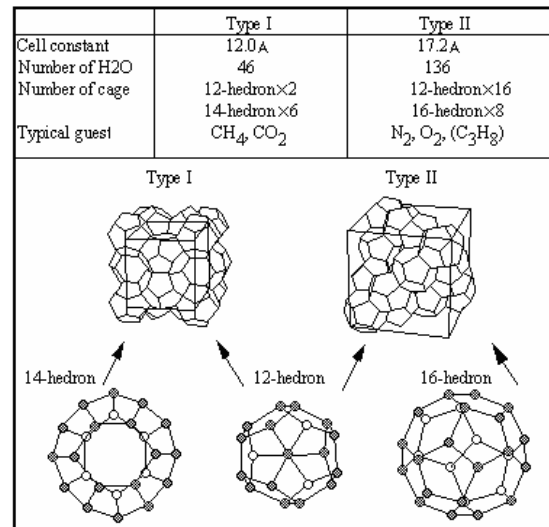

Fig. 5: Construction of type I and type II clathrate structure.

The type I structure has a cubic cell and holds forty six group IV atoms (i.e. Si, Ge or Sn) in the unit cell. There are comprised of two pentagonal dodecahedra, E_{20} , creating a center with $\bar{3}m$ symmetry and six tetrakaidecahedra formed by twelve pentagonal and two hexagonal faces, E_{24}, creating a center with $4m2$ symmetry. The corresponding unit cell is cubic with space group $Pm\bar{3}n$. Two types of cavities in the unit cell; two smaller pentagonal dodecahedra (12-hedron), where twenty water molecules are arranged to form twelve pentagonal faces, and six tetrakaidecahedra (14-hedron), where twenty four atoms are arranged by forming twelve pentagons and two hexagons. There are eight cavities, or atomic "cages" (M), in total in the cubic unit cell, and the general formula is 8M-46(IV).

The type II clathrate also has a cubic cell (space group of $Fd\bar{3}$ m), and there are 136 atoms per unit cell. These atoms are arranged in sixteen pentagonal dodecahedra and eight hexakaidecahedra (16-hedron), where the cage walls are twelve pentagons and four hexagons, E_{28}, are formed from twenty eight water molecules which creating a center with $\bar{4}3m$ symmetry. There are twenty four cavities in total per unit cell and the general formula is 24M-136 (IV). The type II compound can be formed nonstoichiometrically, without all the "cages" filled. In the general, the average interatomic distances are slightly larger than that of the analogous diamond structured compounds. The average IV-IV-IV bond angles range from 105° to 126°, and average close 109.5° that is characteristic of the tetrahedral angle in the diamond structure . The volume per fourth column atom of these two clathrate

compounds, however, is larger than those of their analogous diamond-structured compounds (~15%). This is good indication of the openness of these "open structure".

The majority of work thus far on clathrates for thermoelectric research has been focus on the two structural types that are isotropic with the clathrate hydrate crystal structures type I and II [20]. The type I structure can be represented by the general formula X_8E_{46} and that of the type II structure by the formula $X_8Y_{16}E_{136}$, where X and Y are typically alkali-metal or alkaline-earth atoms. E represents a group-IV element Si, Ge, or Sn, although Zn, Cd, Al, Ga, In, As, Sb or Bi can also be substituted to some degree for these elements. The key characteristic of both structural type is that the framework is formed by covalent, tetrahedrally bonded E atoms comprised of two different face-sharing polyhedra. These compounds display an exceedingly rich number of physical properties that result directly from the nature of their structure and bonding.

The highest frequency optic phonons in the clathrate structure have very low or zero group velocity and contribute little to the total thermal conductivity, whereas the low frequency acoustic phonons have the highest group velocity and contribute most to λ. The scattering of these low frequency acoustic phonons by the encaged ions results in low thermal conductivities.

The fact that clathrate compounds can possess "glass like" thermal conductivity, have the ability to vary the electronic properties with doping level, and the relatively good electronic properties obtained in these semiconductor materials indicate why this material system continues to be of interest for thermoelectric applications. Besides the possibility of thermoelectric applications, these clathrate systems have many other interesting properties that might lead to entirely different range of applications from superconductivity [21, 22] to large band gap semiconductor clathrates have been formed with crystal structures other than those of type I and II.

Table 2: Recent thermoelectric material for clathrate structure [23]

Sample	Rattling atoms	ZT Value
$Ba_8Al_{16}Si_{30}$	Ba	0.012

V HALF – HEUSLER STRUCTURE

Half - Heusler structure was first discovered by Heusler [24]. The unit cell of the Heusler X_2YZ structure with space group *Fm*. 3*m* consists of four inter-penetrating f.c.c. lattices at offsets A = (0, 0, 0), B = (1/4, 1/4, 1/4), C = (1/2, 1/2, 1/2), and D = (3/4, 3/4, 3/4), with site occupancies A = Y, B = D = X, and C = Z. This is closely related to the half-Heusler compounds XYZ. If one of the two equivalent sites (1/4, 1/4, 1/4) or (3/4, 3/4, 3/4) is empty, the half-Heusler XYZ structure with space group *F* . 43*m* appears. Many compounds have a half-Heusler structure, for instance TiCo(Sn,Sb) [25,26],

NiMn(Ga,Sb,Sn) [27,28], NiZrSn [29], and NiUSn [30–32]. Fig. 1 shows the crystal structure of half-Heusler compounds XYZ.
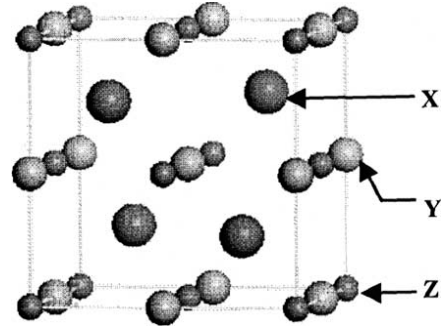

Fig. 6: Crystal structure of the half-Heusler type compounds.

Half-Heusler compounds have been actively studied by their magnetic properties, residual resistivity, and Curie temperature. At present, 18 electron half-Heusler compounds have been attracting increasing attention as new thermoelectric materials because of their semiconductor like band structure [33–37], and their high thermoelectric power (TEP). It is to be promising candidates for thermoelectric applications, due to its narrow band gap at the Fermi level in some of these compounds with 18 valence electron counts (VEC) per formula unit [38] and voids in the crystal structure. There is the concomitant large slope of the electron density of states around the Fermi surface.

These compounds have a narrow band gap of the order of 0.1–0.2 eV at the Fermi level [39–44]. But the problems of the half-Heusler compounds for thermoelectric application is their relatively high lattice thermal conductivity; as high as $10 Wm^{-1} K^{-1}$. In an effort to reduce the lattice thermal conductivity, Hohl et al. reported that the mass disorder in the A-site lattice of the solid solutions causes additional phonon scattering, thereby reducing the lattice thermal conductivity, and obtained $3.6–4.9 Wm^{-1} K^{-1}$ at room temperature for the composition of A0.5A_0.5NiSn (A, A_ = Ti, Zr, Hf) [44,45]. Hohl et al. [45] also reported the thermal conductivity of $5.4 Wm^{-1} K^{-1}$ for the Ta-doped Zr0.5Hf0.5NiSn and $ZT = 0.5$ was achieved at 700K for the composition of (Zr0.5Hf0.5)0.99Ta0.01NiSn. On the other hand, Uher et al. [46] reported that Sb is an efficient dopant for Sn sites of Zr0.5Hf0.5NiSn and that the resistivity and thermal conductivity of Zr0.5Hf0.5NiSn0.99Sb0.01 at room temperature were 0.8m_cm and $6.6 Wm^{-1} K^{-1}$, respectively. Recently, Shen et al. [47,48] investigated the effect of the partial substitution of Ni by Pd on the thermoelectric properties of ZrNiSn-based compounds and obtained $3.1 Wm^{-1} K^{-1}$ at room temperature for the composition of Zr0.5Hf0.5Ni0.8Pd0.2Sn0.99Sb0.01. Shen et al. also reported that $ZT = 0.7$ was achieved at about 800K for this composition.

Table 3: Thermoelectric material for clathrate structure [62-67]

Sample	Rattling atoms	ZT Value at 60
CoNb0.90Hf0.10Sn0.90Sb0.10	Hf	0.015
TiCo0.9Ni*0.1*Sb	Ni	0.030
Ti0.8Hf0.2NiSn0.99Sb0.01	Hf	0.030
Ti0.5(Zr0.5Hf0.5)0.5NiSn0.994Sb0.006	Hf,Zr	0.45
Zr0.5Hf0.5Ni0.8Pd0.2Sn0.99Sb0.01.	Hf,Zr	0.7 (at room temperature)

5.0 Chalcogenide Phase

Chalcogenide compounds have received considerable attention, due to their potential application as nonlinear optical materials, photoelectrics, and thermoelectrics. Chalcogenide are made of two or three dimensional bismuth chalcogenide, group IV chalcogenide or chalcogenide frameworks stabilized by weakly bonded alkali metal atoms which reside in cavities or tunnels in the framework. These electropositive atoms almost always possess the highest atomic displacement parameters (ADPs) in the structure, which is evidence that a certain degree of disorder may be present. This future is very important in substantially suppressing λ in these materials. These materials also incorporate other interesting features such as large unit cells and complex compositions that are beneficial for potentially improving thermoelectric properties

Chalcogenide phases with structural and compositional complexity because these characteristics are likely to lead to materials with low thermal conductivities and high thermo powers. These compounds have unusual structures with tunnels in them, for instance the structures which are hybrid between the Bi_2Se_3 and La_2S_3 structure types. In all compounds substantial site occupancy disorder between the alkali (or alkaline earth), the bismuth and lanthanide elements is observed, leading to stoichiometric deviations from the ideal formula. These material are investigated for large carrier effective masses, high carrier mobility, large degeneracy of the conduction and valence band extreme, and low lattice thermal conductivity to enhance the thermoelectric in good thermoelectric materials the energy distribution of carriers should be narrow and have a high carrier velocity in the direction of the applied field, which is possible in a highly anisotropic system. Consequently, nanofabrication of one-dimensional and two-dimensional arrays of materials have been attempted, and high values of *ZT* have been reported in PbTe-PbSeTe quantum-dot superlattices by Harman *et al.* and in p-type Bi_2Te_3 and Sb_2Te_3 superlattice films by Venkatasubramanian. The major reason governing the observed enhanced *ZT* in these superlattice systems appears to be in their reduced thermal conductivity rather than an increase in the power.

Chalcogenide compounds with the skutterudite structure ($CoAs_3$) have attracted of thermoelectric materials. Due to their structure, containing two large voids in the unit cell which could be "filled" with foreign ions acting here as effective phonon-scattering centres, skutterudites serve as a very typical example of "an ideal thermoelectric material"

defined according to PGEC (phonon-glass electron-single-crystal). The material of chalcogenide is of cubic structure but unlike the most of skutterudite materials (space group *Im*3) one of with the lower symmetry. N-type electrical conductivity was ascribed to the existence either of tellurium vacancies or incorporation of surplus Ge into voids presented in the skutterudite structure. The activation energies corresponding to extrinsic electrons transitions and those of corresponding to activation of the charge carriers across the intrinsic energy gap were identified in temperature dependence of electrical conductivity. The possibility to change content of incorporated Ge and Te in wide range around stoichiometric composition ($CoGe_{1.5}Te_{1.5}$) together with possibility to influence its thermoelectric properties by proper doping and void filling could lead to enhancement of thermoelectric properties of the compounds.

The most common application that is unique to group IV chalcogenides is in the area of thermoelectric cooling materials. The most investigated systems over the past 30 years are various solid solutions of M_2Q_3 (M) As, Sb, Bi; (Q) S, Se, Te compounds. These materials possess high electrical conductivity and thermoelectric power (TEP) and low thermal conductivity and are excellent materials for thermoelectric applications near room temperature. Whether the lone pair is stereochemically active or not affects the lattice structure, the electronic structure, and thus the properties of the resulting compounds.

Table 3: Thermoelectric material for clathrate structure [49]

Sample	Rattling atoms	ZT Value
20% Bi2Te3–80 % Sb2 Te3	-	3.0 (at room temperature)

7.0 Conclusion:

Four types of thermoelectric materials had been reviewed which is skutterudite structure, half-Heusler structure, clathrate structure, chalcogenide phase. This is because there are able to achieve high ZT values due to the anisotropic structure. Interesting in these materials are, they posses same behavior that can be explain by PGEC approach.

PGEC is the concept that certain materials can conduct electricity like a crystalline solid but heat like a glass. In such materials, a weakly bound atom or molecule can create localized dynamic order, or "rattle", thereby resulting in low λ value for the solid without severely affecting electronic conduction and potentially leading to improved thermoelectric materials (i.e. skutterudite structure, clathrate, half-Heusler and chalcogenide phase). This introduction of the PGEC concept makes more significant innovations in the field of thermoelectrics. This approach has resulted in solids with very low thermal conductivities. However, in practice such a material may be very difficult to engineer if not identify.

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