A Primer On Phonon Glass Electrical Crystal Material

Stefan Bringuier
Materials Science and Engineering,
University of Arizona
stefanb@email.arizona.edu
http://u.arizona.edu/~stefanb

May 7, 2012

Abstract

In this term paper an overview of thermoelectric materials is given with insight into thermal conductivity of crystals and glasses. This every expanding field is becoming more and more important and thus the need for new materials continues to be in demand. In the past 10 years there has been an effort to look at phonon glass electric crystals (PGEC), which are materials that exhibit thermal conductivities of glasses but electrical conductivity of single crystals. This concept was first pushed by G.A. Slack et al. [1].
Contents

1 Thermoelectric Materials 3

2 Thermal Conductivity 5
   2.1 Thermal Conductivity of Crystals 5
   2.2 Thermal conductivity of Glass 6

3 Phonon Glass 7
   3.1 Skutterudites 7

4 Recent Thermoelectric Material 9

5 Summary 11

6 References 11
1 Thermoelectric Materials

The relationship between temperature and electrical current was first observed in the 1800’s by Thomas Johann Seebeck, a German physicist. What Seebeck observed is when two dissimilar materials are joined together and placed within a thermal gradient, a voltage difference is produced. The ratio between these two quantities, that is, $\frac{\Delta V}{\Delta T}$ is now referred to as the Seebeck coefficient, $\alpha$. The Seebeck coefficient is an intrinsic property and for metals ranges between $1 - 10 \mu V/K$, whereas for semiconductors the value is much higher, $10^2 - 10^3 \mu V/K$. An interesting fact is that insulators have very high Seebeck coefficients but due to their lack of electrical conductivity are of no use in thermoelectric devices.

A similar effect was later observed by J.C. A. Peltier, a French physicist. In Peltier’s experiments the reverse was detected, that is when a voltage is applied between two dissimilar materials heat is reversibly absorbed (i.e. rejected) at the junction. This is the fundamental physics for modern day thermoelectric cooling devices and a schematic can be seen in Fig. 1. What is being demonstrated is when an applied voltage induces current flow, heat is lost at the interface between the two materials. This is in response to the thermal gradient generated which drives heat flow from the external surface it is attached to.

Figure 1: Demonstration of the thermoelectric effect used in cooling [2]
The rate of heat production at the junction between the two materials is described by:

\[ \dot{Q}_p = \frac{dQ_p}{dt} \]  

(1)

where the heat produced is given by \( Q_p = \alpha IT \), \( I \) and \( T \) are the current and temperature (in Kelvin), respectively. **Equation 1** is sometimes written in terms of the peltier coefficient, \( \Pi \). The peltier coefficient is related to the seebeck coefficient by:

\[ \Pi = \alpha T \]  

(2)

The advantages of thermoelectric materials is the ability to design a compact, quiet, and localized heating or cooling devices. In areas such as as temperature sensitive sensors and nano/micro electronics, these kind of materials can and are becoming essential. An example is the use of thermoelectric materials in the NASA Cassini and Voyager missions. In both these missions thermoelectric materials where used to capture the heat produced by radioactive decay of plutonium and convert it into electricity to power the space crafts [3]. In both missions the devices operated beyond their intended life cycle. Other areas of use are in refrigeration and localized heating and cooling.

One way to understand how effective a material is in regards to thermoelectric behavior, is to employ the use of a figure of merit. This is given in **Eq. 3**

\[ Z = \frac{\alpha^2 \sigma}{\kappa} \]  

(3)

Where \( \alpha \) is the Seebeck coefficient, \( \kappa \) the thermal conductivity, and \( \sigma \) the electrical conductivity. It some times is more convenient to report \( Z \) values as \( ZT \). It should be noted that the thermal conductivity has contributions from both phonons and electrons, that is, \( \kappa = \kappa_p + \kappa_e \). Some common thermoelectric materials are shown with the corresponding figure of merit values in **Table 1** and **Fig. 2**.

<table>
<thead>
<tr>
<th>Material</th>
<th>( ZT )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bismuth chalcogenides</td>
<td>0.8 – 1.0</td>
</tr>
<tr>
<td>Doped PbTe</td>
<td>1.4 – 1.8</td>
</tr>
<tr>
<td>Inorganic clathrates</td>
<td>0.5 – 1.7</td>
</tr>
<tr>
<td>Magnesium group IV compounds</td>
<td>0.9</td>
</tr>
<tr>
<td>Skutterudite thermoelectrics</td>
<td>( \geq 1.0 )</td>
</tr>
<tr>
<td>Nanostructured thermoelectrics</td>
<td>( \geq 1.0 )</td>
</tr>
</tbody>
</table>

**Table 1**: Common thermoelectric materials.

\(^1ZT\) is a dimensionless quantity and allows for the determining the figure of merit with respect to operating temperature.
2 Thermal Conductivity

2.1 Thermal Conductivity of Crystals

It is necessary to first investigate the thermal conductivity of crystals. Heat conduction can be understood as the propagation and interaction of quantized thermal energy wave modes, called phonons. The waves traveling within the crystal occur over a broad range of frequencies and the interaction between waves is a function of frequency. The thermal conductivity may be calculated with the use of the Callaway-Holland model which is given in Eq. (4).

\[
k = \frac{1}{6\pi^2} \sum_j \int c_j(q) \nu_j^2 \tau_j(q) \, d\mathbf{q}
\]  

where \(c_j(q)\) is the specific heat contributed by the wave mode (i.e. frequency \(\omega(q)\)), \(\nu_j\) is the phonon group velocity, \(\tau_j(q)\) is the phonon lifetime, and \(\mathbf{q}\) is the wave vector. It turns out that most of the heat conductivity in crystals is due to long-wavelength phonons, known as acoustic phonons. In addition, there are two modes that are responsible for the transverse and longitudinal polarizations. Typically the longitudinal acoustic phonons have larger velocities. One may ask then why does thermal conductivity have a limitation, on factor is the occurrence of phonon-phonon interactions which give rise to inelastic scattering. The presence of imperfections and interface boundaries in crystals, act as elastic scattering centers for phonons, also limiting the thermal conductivity. In all, what is reduced is the phonon mean free path or equally phonon lifetime\(^2\) which is directly related to thermal conductivity.

\(^2\)In this paper the terms phonon mean free path and phonon life time will be used synonymously, in the sense that they both directly effect thermal conductivity.
conductivity. A useful expression for this is known as Matthiessen’s rule, which states that the total phonon life time is the sum of all contributions of phonon life time for different events:

\[
\frac{1}{\tau} = \frac{1}{\tau_{impurities}} + \frac{1}{\tau_{lattice}} + \frac{1}{\tau_{defects}} + \ldots
\]  

(5)

The treatment above does not take into consideration the contribution to thermal conductivity by electrons. This is because in most non-metallic bonded solids electrons essential have a life time of zero [1]. With that said, in most metals the thermal conductivity is dictated by electrons since the life time is significantly larger than phonons.

### 2.2 Thermal conductivity of Glass

The first analysis of phonon mean free paths in glasses was carried out by Charles Kittel [4] and was demonstrated that the values are on the order of atomic dimensions (see Fig. 3). Thermal conductivity for glassy material tends to be much lower because the lack of long range order. The random distribution of atoms in a glass causes them to act as point scatters for incoming phonons and therefore reduce the overall life time of propagating phonons. As a result \(\tau(q)\) in Eq. 4 is constant. It is important to note that at higher temperatures glasses can actually lose a considerable amount of heat due to radiative processes; glasses are quite effective at this.

![Figure 3: Phonon mean free path for Quartz glass after Kittel [4].](image)

In Table 2 the various values for thermal conductivity of amorphous and crystalline materials is shown. In general amorphous materials (including glass) have much lower thermal conductivities than crystalline materials.
Since the figure of merit is given by Eq. 3, one way to tailor the properties is to adjust the thermal and electrical conductivities of a material systems. In the early 1990’s, it was proposed by Glenn Slack [1], that if one could design a material with the thermal conductivities of a glass but electrical conductivities of a single crystal, high values for $Z$ could be obtained. Again, this is due to the low thermal conductivity (or phonon mean free path) and high electrical conductivities of single crystals. We also know that the seebeck coefficient must be large to obtain a good figure of merit, semiconductors offer the most promise. In general the Seebeck coefficient is usually not affected very much by altering the electrical and thermal conductivities. One way to increase the electrical conductivity of semiconductors is to increase the total number of charge carries, this can be done by doping the material with n-type or p-type atoms. In regards to decreasing the thermal conductivity of these doped semiconducting materials, Glenn Slack [5] proposed that by selecting semiconducting materials with “open structures” and inserting massive atoms to act as phonon scatters, one could decrease the thermal conductivity. He coined the term Phonon Glass Electric Crystal (PGEC) to describe such materials.

### 3.1 Skutterudites

The specific structure that has come to dominate the concept of PGEC is known as Skutterudite. The name Skutterudites is derived from the place where the natural occurring mineral of the form CoAs$_3$ was found, that being the Skuterud Mines in Norway. The space group for this structure is $Im\bar{3}$. Other compounds in this family are CoP$_3$, CoSb$_3$, RhP$_3$, RhAs$_3$, RhSb$_3$, IrP$_3$, IrAs$_3$, and IrSb$_3$. What makes this structure unique is that it posses the qualities for high $ZT$ based on G.A. Slacks concept. This is due to the large unit cell (see Fig. 5), heavy constituent atomic masses, low electronegative differences between atoms, and large carrier mobility.

Researchers found that by inserting rare-earth ions into Skutterudite structure, they reside at the interstitial sites and are weakly bound to the host crystal, that is they occupy the voids as atoms within a cage. This unique attribute causes them to undergo large local anharmonic vibrations and as a result, vibrate independently from other atoms in the
Table 1  Structural parameters of known binary skutterudites

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice constant (Å)</th>
<th>Density (g cm⁻³)</th>
<th>y (Å)</th>
<th>z (Å)</th>
<th>Void radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoP₃</td>
<td>7.7073</td>
<td>4.41</td>
<td>0.348</td>
<td>0.145</td>
<td>1.763</td>
</tr>
<tr>
<td>CoAs₃</td>
<td>8.2055</td>
<td>6.82</td>
<td>0.344</td>
<td>0.151</td>
<td>1.825</td>
</tr>
<tr>
<td>CoSb₃</td>
<td>9.0385</td>
<td>7.64</td>
<td>0.335</td>
<td>0.160</td>
<td>1.892</td>
</tr>
<tr>
<td>RhP₃</td>
<td>7.9951</td>
<td>5.05</td>
<td>0.355</td>
<td>0.139</td>
<td>1.909</td>
</tr>
<tr>
<td>RhAs₃</td>
<td>8.4507</td>
<td>7.21</td>
<td>0.348</td>
<td>0.145</td>
<td>1.934</td>
</tr>
<tr>
<td>RhSb₃</td>
<td>9.2322</td>
<td>7.90</td>
<td>0.342</td>
<td>0.151</td>
<td>2.024</td>
</tr>
<tr>
<td>IrP₃</td>
<td>8.0151</td>
<td>7.36</td>
<td>0.354</td>
<td>0.139</td>
<td>1.906</td>
</tr>
<tr>
<td>IrAs₃</td>
<td>8.4673</td>
<td>9.12</td>
<td>0.347</td>
<td>0.145</td>
<td>1.931</td>
</tr>
<tr>
<td>IrSb₃</td>
<td>9.2503</td>
<td>9.35</td>
<td>0.340</td>
<td>0.153</td>
<td>2.040</td>
</tr>
</tbody>
</table>

Figure 5: Table of unit cell properties for compounds with Skutterudite structure.

If we recall from Eq. 5, the contribution from $\tau_{lattice}$ causes the life time (equally phonon mean free path) to decrease and therefore the thermal conductivity. An example of this can be seen in Fig. 6, where the results for IrAs₃ doped with germanium (p-type) and different rare-earth ions. The reduction of phonon propagation was found to be as low as 58% due to the large mass of the rare-earth ions [6].
Figure 6: The effect on thermal conductivity of doped IrAs$_3$ by inserting different rare-earth ions [11].

4 Recent Thermoelectric Material

Recent progress has shown that Selenium Copper structures, Cu$_{2-x}$Se, have unique properties that show promise for high $Z$ values [7]. The formal structure is an anti-Fluorite where the Se atoms occupy a FCC lattice and the Cu tetrahedron structure occupies the tetrahedral sites. What is interesting about this structure is the Cu sublattice behaves like a liquid and thus has subpar electrical conductivity and low thermal conductivity ($\sim 1$ W/mK). Even though the Cu has poor electrical conductivity the Se sublattice has excellent electrical conductivity and poor thermal conductivity. The combination gives rise to $ZT$ values of 1.6 at 900K, however the performance of Cu$_{2-x}$Se is dependent on the configuration of Cu ions.

Figure 7: Graphical rendering of the Cu$_{2-x}$Se structure [7].
Figure 8: Crystal structure of Cu$_{2-x}$Se at high temperatures ($\beta$-phase) with a cubic anti-fluorite structure. **a**, Unit cell where only the 8c and 32f interstitial positions are shown with Cu atoms. **b**, Projected plane representation of the crystal structure along the cubic [110] direction. The arrows indicate that the Cu ions can freely travel among the interstitial sites. There are two Cu layers between the neighbouring Se (111) planes. The structure changes to a monoclinic $\alpha$-phase by stacking the ordered Cu ions along the cubic [111] direction when cooled to room temperature.[7].

Figure 9: Thermoelectric properties of the low-temperature ($\alpha$) and high-temperature ($\beta$) phases in Cu$_{2-x}$Se. **a-d**, Temperature dependences of electrical resistivity $\rho$ (**a**), thermopower $S$ (**b**), thermal conductivity $\kappa$ (**c**) and dimensionless figure of merit $ZT$ (**d**) [7].
5 Summary

In this brief term paper, we have looked at thermoelectric materials, specifically the physics of them. It was shown in Sec. 1 that Seebeck and Peltier’s observations lead to the development of modern day devices that utilize thermoelectric materials. Subsequently in Sec. 2, the understanding of thermal conductivity in crystalline and glassy materials was compactly explained. This set the stage to discuss in Sec. 3 the idea of Glenn Slack to develop materials which exhibit the low thermal conductivity of glasses and the high electrical conductivity of single crystals. His idea has been manifested in the use of compounds which have the Skutterudite structure, which allows for doping of n-type and p-type elements as well as introducing rare-earth elements to occupy the open interstitial sites within this structure. This has lead to promising figure of merit values for a range of temperatures. Finally, new material which exhibits low thermal conductivity due to the liquid like behavior of the copper ions was briefly touched on in Sec. 4.

6 References


