THERMOELECTRIC PROPERTIES OF RARE-EARTH LEAD SELENIDE ALLOYS AND LEAD CHALCOGENIDE NANOCOMPOSITES

A Thesis

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Thermoelectric technology offers a reliable, environmentally clean, and maintenance-free method for power generation and temperature control applications. The main drawback traditionally has been its low efficiency in comparison with conventional heat engines. The developments in the last two decades in the understanding of nanoscale effects on thermoelectric properties of materials and new ways of enhancing the thermoelectric properties have led to resurgence in the interest in thermoelectricity. The efficiency of a thermoelectric device is a function of the dimensionless figure of merit of the material $ZT$ whose value has been limited to a low value of about 1 in bulk materials at all temperature ranges. Large values of $ZT$ require high thermopower, high electrical conductivity and low thermal conductivity, an intrinsically contradictory requirement. Since all the three quantities of the material are interconnected, it has not proven possible, in practice, to increase the $ZT$ of bulk materials higher than a certain limit. To enable a more widespread usage of thermoelectric technology power generation and heating/cooling applications, $ZT$ of at least 2-3 is required.

The three properties that make up the figure of merit can be decoupled by the use of certain techniques. In this work, we investigate the effect of two such methods on the thermoelectric properties: (1) Use of rare earth dopants with $f$-orbitals situated
close to the Fermi level, thus resulting in a high thermopower, and (2) use of nanos-structured bulk materials with size quantization effects that would affect transport properties of the material.

In the first part, we examine the effect of rare-earth dopant in PbSe by using a sequence of samples of pure PbSe (for reference), and PbSe doped with Ce, Pr, Nd, Eu, Gd and Yb. We report the magnetic susceptibility data, as well as a full set of galvanomagnetic and thermomagnetic measurements, from which we deduce the carriers transport properties, specifically density, mobility, density-of-states effective mass and scattering exponent. In short, the trivalent rare earth atoms act as donors; the mobility of the rare-earth alloys is decreased by mechanisms that we will discuss, while the scattering exponent is not affected. The effective mass is increased, but not sufficiently to overcome the mobility decrease and increase the weighted mobility or improve the thermoelectric performance of the material, except potentially for Pb$_{1-x}$Nd$_x$Se alloys.

In the second part, we developed a nanocomposite of PbTe and PbSe, made from nanoparticles with a core-shell structure and sintered together. At a core size of $\sim 20$ nm, the core is expected to show size-quantization effects, and confine energy levels at discrete values. Such a confinement would lead to an enhancement in the Seebeck coefficient through the interaction of the discrete energy levels with the host density of states. Moreover, the presence of the nanostructure in the matrix should lead to a reduction in the lattice thermal conductivity. In the nanocomposite samples, we did not find any enhancement in the Seebeck coefficient as expected, presumably due to the wide distribution in the size of the core (quantum dots) leading to very little size-quantization. However, we found a favorable reduction in the lattice thermal
conductivity, lower than an alloy of the same composition. Unfortunately, this gain by the thermal conductivity reduction comes at the cost of the carrier mobility, which were determined to be between 50 and 200 W/mK for most samples, considerably lower than a target value of at least 400 cm$^2$/Vs.
This is dedicated to my father and mother
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CHAPTER 1

INTRODUCTION

The term “thermoelectricity” refers to the phenomenon of interconnected transport of electrical charge and thermal energy, i.e., the transport of charge carriers under a temperature gradient, and the transport of thermal energy under a potential gradient. It collectively refers to the three effects: Seebeck effect, Peltier effect and Thomson effect. In the following, we discuss these effects, and also several other allied effects that are useful in the characterization of material properties.

1.1 Thermoelectric and allied effects

1.1.1 Seebeck effect

When a temperature gradient is maintained in a material, and the flow of electric current is disallowed, a steady-state electric potential difference develops between the two ends of the material maintained at different temperatures. The voltage difference appears due to the diffusion of high energy (“hot”) charge carriers from the hot side to the cold side of the conductor. The voltage developed $\Delta V$ is proportional to the temperature difference $\Delta T$, and the constant of proportionality is variously termed the Seebeck coefficient or thermoelectric power or just thermopower, and it is an intrinsic property of the material. This effect was discovered by Thomas Seebeck in 1821.
1821, originally through the development of an e.m.f. between the junctions of two dissimilar conductors, when the junctions were maintained at different temperatures.

\[ \Delta V = -S \Delta T. \tag{1.1} \]

Intrinsically for a homogeneous material, it may also be described as the generation of an electric field between the hot and cold sides of a conductor:

\[ E = SV T. \tag{1.2} \]

It may be noted that absent effects due to scattering of charge carriers, the Seebeck coefficient of the material is really a measure of the entropy of the charge carriers.

### 1.1.2 Peltier effect

The Peltier effect is the reverse of the Seebeck effect, and refers to the creation of temperature difference across the ends of a conductor when there is a flow of current through it at a uniform temperature. This is best observed when a uniform current \( I \) is made to flow through a circuit made of two dissimilar conductors, and temperature at the two junctions is measured. It is found that the heat is released at one junction and absorbed at the other. The quantity of heat released/absorbed, \( q \) is proportional to current through the circuit, and the constant of proportionality is called the Peltier coefficient \( \Pi \),

\[ q = \Pi I. \tag{1.3} \]

Peltier effect is due to the fact that a thermal current accompanies an isothermal current through the circuit, and the difference in heat flow in the two materials (due to their different \( \Pi \)'s) is released/absorbed at the junctions. The Seebeck coefficient
and the Peltier coefficient of a material are related as follows

\[ \Pi = ST, \]  

(1.4)

where \( T \) is the temperature of the material, measured in kelvin. Equation (1.4) is known as the first Thomson relation, and can be rigorously proved using Onsager’s relations [6].

1.1.3 Thomson effect

When a current flows through a homogeneous conductor that is subjected to a temperature gradient, heat is generated at a rate proportional to the electric current and the temperature gradient:

\[ q_{Thomson} = \tau I (-\nabla T), \]  

(1.5)

where \( \tau \) is the Thomson coefficient. Thomson heat is a reversible effect, and is in addition to the irreversible Joule heating. Thus heat can be absorbed by reversing the direction of current or the temperature gradient. Thomson coefficient originates in the temperature dependence of the Seebeck coefficient (which alters the entropy of the carriers at different points in the conductor leading to a change in the heat transported by the carrier). The relation is

\[ \tau = T(dS/dT), \]  

(1.6)

and is known as the second Thomson relation. In reality, there is only one thermoelectric cross-effect, and the Seebeck, Peltier, and Thomson effects are merely different manifestations of the same phenomenon.

The effects discussed so far are “longitudinal” in the sense that they are measured in the same direction as the heat/current flux, and are defined in the absence of
magnetic field. In the following, we discuss a few other effects that are defined in the presence of a magnetic field. The two other (longitudinal) material coefficients that are more commonly known are the resistivity and thermal conductivity, and we shall not discuss them here.

1.1.4 Hall effect

When a magnetic field is applied in at right angles to the current flow through a conductor, an electric field is set up in a direction perpendicular to the current and the magnetic field. If the current density is \( j_x \), the magnetic field is \( B_z \), and the Hall electric field is \( E_y \), then the Hall coefficient \( R_H \) is defined by the equation

\[ E_y = R_H j_x B_z. \]  

(1.7)

The physical significance of the Hall effect lies in the fact it is a direct measurement of the sign and the density of the charge carriers in a semiconductor.

1.1.5 Transverse Nernst-Ettingshausen effect

When a magnetic field is applied in at right angles to the heat flow through a conductor, an electric field is set up in a direction transverse to the heat flux and the magnetic field. If the temperature gradient is \( \nabla_x T \), the magnetic field is \( B_z \), and the Nernst electric field is \( E_y \), then the transverse Nernst-Ettingshausen coefficient \( N \) is defined by the equation

\[ E_y = -N \nabla_x TB_z. \]  

(1.8)

For the sake of brevity, we shall refer to this as the Nernst effect and the coefficient as the Nernst coefficient henceforth. The Nernst effect is the transverse counterpart of the Seebeck coefficient, much like the Hall coefficient is to electric conductivity.
Figure 1.1: A simple thermoelectric power generation circuit composed of two materials, $a$ and $b$, and a load resistor $R_L$. The regions shown in circles are isothermal with the temperatures shown.

The Nernst coefficient is the easiest to measure of all the transverse coefficients, and is related to the scattering mechanism in the sample.

The exact manner in which each of these coefficients is related to the material properties like carrier density, scattering mechanism, effective mass, and mobility is described in Chapter 3.

1.2 Theory of thermoelectric devices

As an illustration of the calculation of device performance, we consider the case of power generation in this section. For a detailed discussion, the reader may refer to textbooks in the field [6, 10].

Consider Figure 1.1 which shows a Seebeck power generation circuit composed of two dissimilar materials having their junctions at temperature $T_h$ and $T_c$, sending current across a load resistor $R_L$. The efficiency $\eta$ of the circuit may be defined as

$$\eta = P/q = I^2 R_L/q$$  \hspace{1cm} (1.9)
where \( P \) is the electrical power output to the load, and \( q \) is the input heat required at the hot junction in order to maintain the junction at \( T_h \). In order to evaluate \( q \) it is necessary to examine the heat flow at the hot junction. For the case of homogeneous materials with Seebeck coefficient \( S \), resistivity \( \rho \) and thermal conductivity \( \kappa \) independent of temperature, there are three effects that must be considered: (1) a Peltier heat \( q_1 \) will be absorbed at the hot junction, (2) a portion of the Joule heat \( q_2 \) generated in the elements go to the hot junction, and finally, (3) heat \( q_3 \) will be conducted away from the hot junction by the process of thermal conduction. It can be easily shown that

\[
q = q_1 + q_2 + q_3
\]

where

\[
q_1 = -\Pi I \\
q_2 = -(I^2/2)[\rho_a + \rho_b/A]L \\
q_3 = (\kappa_a + A\kappa_b)\Delta T/L
\]

where \( L \) is the length of the elements (assumed equal), and \( A \) is cross-section of element \( b \) (with cross-section of \( a \) set to unity). Using these expressions

\[
\eta = I^2 R_L/[(\kappa_a + A\kappa_b)\Delta T/L - (I^2/2)\{(\rho_a + \rho_b/A)L - \Pi I\}] \quad (1.10)
\]

where \( I = -S_{ab}\Delta T/[R_L + \{(\rho_a + \rho_b/A)L\}] \) with \( S_{ab} \) being the difference of the absolute Seebeck coefficients, \( S_b - S_a \). Equation\( (1.10) \) can be now maximized with respect to the two adjustable parameters \( A \) and \( R_L \). Doing this we find

\[
\eta = \frac{\Delta T}{T_h} \left[ \frac{(1 + Z\tilde{T})^{1/2} - 1}{(1 + ZT)^{1/2} + T_c/T_h} \right] \quad (1.11)
\]
where $\bar{T} = (T_h + T_c)/2$ and

$$Z = \frac{S^2_{ab}}{[(\rho_a \kappa_a)^{1/2} + (\rho_b \kappa_b)^{1/2}]}$$

is called the device figure of merit. It can be seen that the efficiency of the device is limited by the Carnot efficiency ($\Delta T/T_h$) and depends on the material parameters only through the combination $Z$. Although the overall $Z$ of the device depends on the material properties of both the legs, it is useful to have a measure of usefulness of each leg separately. Considering the fact that positive and negative thermoelectric materials are similar in performance, it is legitimate to define the figure of merit $Z$ for each of the two branches,

$$ZT = \frac{S^2 \kappa}{\kappa_L + \kappa_e} T$$

where the figure of merit has been made non-dimensional by multiplying both sides by the mean temperature, and the relation $\sigma = 1/\rho$ between electrical conductivity and resistivity has been used. Equation (1.13) is thus the definition of the figure of merit of the material. Similar analysis carried out for the refrigeration problem reveals that again $Z$ is the most important material factor entering into the performance of the refrigeration device. Thus the problem of developing good thermoelectric material is essentially one of developing materials with high $ZT$, with $T$ being the mean operating temperature.

A good thermoelectric material is one that has high Seebeck coefficient and electrical conductivity and low thermal conductivity. Due to the fact that all the three quantities are inherently inter-related, it has not been possible to increase the $Z$ beyond a certain extent by conventional means. This is because increasing the $S$ in materials leads to a decrease in the $\sigma$. An increase in the $\sigma$ on the other hand leads
to a concomitant decrease in $S$ and an increase in the electronic contribution to the thermal conductivity, $\kappa$ (through the Wiedemann-Franz law), thus leading to a net reduction in the $ZT$. Thus, the value of the dimensionless figure of merit $ZT$ has been limited to around 1 for the best thermoelectric materials. With this value, the coefficient of performance of thermoelectric coolers is only a third of conventional vapor compression systems. To be competitive with conventional systems, and replace them, thermoelectric materials with $ZT \approx 3$ need to be found. However even a small increase in the $ZT$ is certain to spawn many new applications.

One common method of increasing the $ZT$ is to reduce the lattice thermal conductivity $\kappa_L$ without significantly decreasing the electronic coefficients $S$ and $\sigma$. Low $\kappa_L$ is obtained by (i) using compounds made of heavy atoms and (ii) preferentially enhancing the scattering of phonons without scattering the electrons as much, for example, by alloying electronically similar compounds or by introducing scattering of phonons on grain boundaries. Unfortunately, the gain obtained in the $ZT$ by reduction of $\kappa_L$ is usually limited due to the reduction in the electron mobility also. The other way of increasing the $ZT$ is by maximizing the power factor, $S^2 \sigma$, by optimizing the doping level (and hence the carrier density). It is with the best of these approaches that we obtain a $ZT \approx 1$ in p-type $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$ for use at room temperature. Thus the classical approach is limited to a low $ZT$.

1.3 New approaches to increase material $ZT$

Starting from the 1990s there have been a few new methods discovered that have led to the development of materials with higher $ZT$s than ever. We briefly describe the various approaches undertaken toward the goal of high $ZT$ thermoelectrics.
Several bulk materials systems such as filled skutterudites [38], clathrate compounds [25], and half-Heusler alloys [2, 39] have been shown to have very favorable thermoelectric properties.

An interesting theoretical approach to high $ZT$ is the use of materials containing rare-earth ions. Mahan and Sofo [23] have shown that an electron density of states in the form of a delta-function distribution gives rise to the highest $ZT$ and that this is most closely realized in nature by the $f$-electron level of the rare-earth ion in a solid. Some experimental support for this concept is provided by the intermetallic alloy YbAl$_3$, which exhibits [40] a thermoelectric power factor $S^2\sigma$ larger than any known material—in fact, some five to ten times larger than the best thermoelectric materials known today. However due to high thermal conductivity, the $ZT$ of the material is very low. An alternative approach is to introduce $f$-electron levels into a thermoelectric material that would hybridize with the band of the host materials and be situated close to the Fermi level.

Hicks and Dresselhaus predicted in 1993 that the Seebeck coefficient, and consequently the figure of merit, should be enhanced in quantum well [17] and quantum wire structures [18] over that of an equivalent bulk material. The idea is that an enhanced density of states, such as demonstrated in quantum-confined structures, can increase the energy dependence of the carrier density if the Fermi energy is appropriately situated, similar to the introduction of an $f$-orbital in the band structure. Such an enhancement results in a higher density-of-states effective mass, which in turn increases the thermopower. Further, due to the increased scattering of the thermal phonons by the nanoscale inclusions, thermal conductivity of the material is also
reduced in comparison with that of the bulk material. These two effects will result in the enhancement of the figure of merit of the low-dimensional materials.

In this thesis, we experimentally study the effect of doping lead selenide with rare-earth atoms on the thermoelectric properties on the one hand, and that of introducing nanoscale features of lead selenide on the properties of lead telluride on the other.

1.4 State-of-the-art

Figure 1.2 shows the highest figure of merit of different classes of materials at various operating temperatures. Established thermoelectric materials can be conveniently divided into three groupings with each dependent upon the temperature range of operation. Alloys based on bismuth in combinations with antimony, tellurium, and selenium are referred to as low-temperature materials and can be used at temperatures up to around 450 K. These are the materials universally employed
in thermoelectric refrigeration. The intermediate temperature range up to around 850 K is the regime of materials based on lead telluride, while thermoelements employed at the highest temperatures are fabricated from silicon germanium alloys and operate up to 1300 K. New materials based on the quantum low dimensional effects and the concept of ‘phonon glass-electronic crystals’ (PGECs) have shown promising performances at each temperature range comparable to and often much better than conventional materials.

1.5 Organization of this thesis

The rest of this thesis is organized as follows.

In Chapter 2 we discuss a new mechanism for the enhancement of the figure of merit in the quantum dot superlattices. We suggest that the quantization of energy levels in the quantum dot nanocomposites can lead to an increased dependence of the relaxation time on the energy level and lead to a higher Seebeck coefficient.

Chapter 3 describes the experimental technique and data analysis procedure that is used to study the thermoelectric properties of different materials.

Chapter 4 summarizes the results of doping of lead selenide with different rare-earth atoms on the thermoelectric properties.

Chapter 5 describes and summarizes the study of the thermoelectric properties of a lead selenide-lead telluride core-shell nanocomposites.
CHAPTER 2

ENHANCEMENT OF FIGURE OF MERIT IN LOW DIMENSIONAL MATERIALS

2.1 Introduction

The efficiency of a thermoelectric device is a function of the dimensionless figure of merit of the material $ZT$, defined as

$$ZT = \frac{S^2 \sigma}{\kappa} T.$$  \hspace{1cm} (2.1)

Here $S$ stands for the thermopower, $\sigma$ for the electric conductivity, $\kappa$ for the total thermal conductivity and $T$ for temperature. As discussed in Chapter 1, Hicks and Dresselhaus predicted in 1993 that the thermopower, and consequently the figure of merit, should be enhanced in quantum well [17] and quantum wire structures [17] over that of an equivalent bulk material. The increase was experimentally observed on bismuth nanowires where, along with the expected semiconductor-to-semimetal transition predicted for this system, the nanowires were also shown to have thermopower in excess of 1 mV/K (as compared to the bulk value of about 50 $\mu$V/K [16]). In 2002, a $ZT$ value of 2 [8], and later 3 [9], were demonstrated in quantum dot superlattices (QDSLs). The basis for the original idea [17, 18, 23] is that an enhanced density of
states, such as demonstrated in quantum-confined structures, can increase the energy dependence of the carrier density if the Fermi energy is appropriately situated. Such an enhancement results in a higher density-of-states effective mass, which in turn increases the thermopower. Further, due to the increased scattering of the thermal phonons by the nanoscale inclusions, thermal conductivity of the material is also reduced in comparison with that of the bulk material. These two effects will result in the enhancement of the figure of merit of the QDSLs. Here $S$ stands for the thermopower, $\sigma$ for the electric conductivity, $\kappa$ for the total thermal conductivity and $T$ for temperature. As discussed in Chapter 1, Hicks and Dresselhaus predicted in 1993 that the thermopower, and consequently the figure of merit, should be enhanced in quantum well [17] and quantum wire structures [18] over that of an equivalent bulk material. The increase was experimentally observed on bismuth nanowires where, along with the expected semiconductor-to-semimetal transition predicted for this system, the nanowires were also shown to have thermopower in excess of 1 mV/K (as compared to the bulk value of about 50 $\mu$V/K [16]). In 2002, a ZT value of 2 [8], and later 3 [9], were demonstrated in quantum dot superlattices (QDSLs). The basis for the original idea [17, 18, 23] is that an enhanced density of states, such as demonstrated in quantum-confined structures, can increase the energy dependence of the carrier density if the Fermi energy is appropriately situated. Such an enhancement results in a higher density-of-states effective mass, which in turn increases the thermopower. Further, due to the increased scattering of the thermal phonons by the nanoscale inclusions, thermal conductivity of the material is also reduced in comparison with that of the bulk material. These two effects will result in the enhancement of the figure of merit of the QDSLs.
However, unlike the case of a quantum wire or quantum well superlattice, in a quantum dot nanocomposite system (such as the QDSLs), the effects of size-quantization may only be present inside the quantum dots as there is no conductive pathway through the dots. This would result in no increase in the thermopower throughout the sample. So far no theory has satisfactorily explained the increase of thermopower observed in the QDSLs. In this chapter, we discuss a possible mechanism by means of which the nanoscale inclusions can increase the energy dependence of scattering, which in turn, would result in the increase of the thermopower and hence, the figure of merit.

2.2 Comparison of QDSL with bulk

Table 2.1 shows a comparison between the different transport properties of QDSLs [8] and of bulk PbTe doped to the same carrier density \( n \) [30]. The thermopower values in Table 2.1 for bulk PbTe doped to a density \( n \) are calculated using the Pisharenko expression \( S(n) \) [19], which for bulk PbTe at 300 K with acoustic phonon scattering reads [7]:

\[
S(\mu\text{V/K}) = -477 + 175 \log_{10}(n/10^{17}\text{cm}^{-3}).
\]  

(2.2)

The thermal conductivity \( \kappa \) of the bulk samples is the sum of the lattice (2.3 W/mK) and electronic contributions, the latter calculated using a Lorenz number of 0.6\( \mathcal{L}_0 \) for lead telluride [30], where \( \mathcal{L}_0 \) is the free electron value. The \( \kappa \) for the QDSL samples was calculated from \( ZT, S, n \) and \( \mu \). There are two ways to look at the published data.

\footnote{A part of this chapter is published in ref [36].}
<table>
<thead>
<tr>
<th>Sample</th>
<th>$ZT$</th>
<th>$P = S^2\sigma$</th>
<th>$\kappa$</th>
<th>$\mu$</th>
<th>$n$</th>
<th>$\sigma = pq\mu$</th>
<th>$S$</th>
<th>$\kappa/\mu$</th>
<th>$S^2n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(µW/cmK²)</td>
<td>(W/mK)</td>
<td>(cm²/Vs)</td>
<td>(cm⁻³)</td>
<td>(1/Ωm)</td>
<td>(µV/K)</td>
<td>(JV/Km³)</td>
<td>(V²/K²m³)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-QDSL A</td>
<td>1.6</td>
<td>34.05</td>
<td>0.64</td>
<td>370</td>
<td>$1.2 \times 10^{19}$</td>
<td>$7.1 \times 10^{4}$</td>
<td>−219</td>
<td>17.3</td>
<td>$5.76 \times 10^{17}$</td>
</tr>
<tr>
<td>Bulk n-PbTe</td>
<td>0.29</td>
<td>41.16</td>
<td>3.49</td>
<td>1400</td>
<td>$1.2 \times 10^{19}$</td>
<td>$2.69 \times 10^{5}$</td>
<td>−123.7</td>
<td>24.9</td>
<td>$1.84 \times 10^{17}$</td>
</tr>
<tr>
<td>n-QDSL B</td>
<td>1.3</td>
<td>22.84</td>
<td>0.53</td>
<td>300</td>
<td>$1.1 \times 10^{19}$</td>
<td>$5.28 \times 10^{4}$</td>
<td>−208</td>
<td>17.6</td>
<td>$4.76 \times 10^{17}$</td>
</tr>
<tr>
<td>Bulk n-PbTe</td>
<td>0.3</td>
<td>41.13</td>
<td>3.39</td>
<td>1400</td>
<td>$1.1 \times 10^{19}$</td>
<td>$2.46 \times 10^{5}$</td>
<td>−129.3</td>
<td>24.2</td>
<td>$1.84 \times 10^{17}$</td>
</tr>
<tr>
<td>n-Qua B</td>
<td>2</td>
<td>44.66</td>
<td>0.67</td>
<td>340</td>
<td>$8.9 \times 10^{18}$</td>
<td>$7.69 \times 10^{4}$</td>
<td>−241</td>
<td>12.4</td>
<td>$5.17 \times 10^{17}$</td>
</tr>
<tr>
<td>Bulk n-PbTe</td>
<td>0.34</td>
<td>44.07</td>
<td>3.24</td>
<td>1500</td>
<td>$8.9 \times 10^{18}$</td>
<td>$2.14 \times 10^{5}$</td>
<td>−143.5</td>
<td>21.6</td>
<td>$1.83 \times 10^{17}$</td>
</tr>
<tr>
<td>n-Qua A</td>
<td>1.6</td>
<td>34.6</td>
<td>0.65</td>
<td>320</td>
<td>$1.3 \times 10^{19}$</td>
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<td>−228</td>
<td>20.3</td>
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<tr>
<td>Bulk n-PbTe</td>
<td>0.28</td>
<td>40.86</td>
<td>3.58</td>
<td>1400</td>
<td>$1.3 \times 10^{19}$</td>
<td>$2.91 \times 10^{5}$</td>
<td>−118.5</td>
<td>25.6</td>
<td>$1.83 \times 10^{17}$</td>
</tr>
</tbody>
</table>

Table 2.1: Comparison between the properties of equivalent bulk PbTe and QDSL samples from Harman et al. [8] at 300 K.
Figure 2.1: Pisarenko plot showing the absolute value of the Seebeck coefficient of various samples in comparison with that of bulk PbTe at different doping levels. The latter is calculated assuming acoustic phonon scattering. The data of QDSL samples are from [8], and PbTe:nanoPb samples are from [15].

Conventionally, one separates \( Z \) into the power factor \( P = S^2 \sigma \), and the total thermal conductivity \( \kappa \). From this perspective, we conclude from Table 2.1 that the \( ZT \) enhancement is almost entirely due to the reduction in the \( \kappa \) (by a factor of 5 - 7), as the change in the \( P \) is small, and adversely affects the \( ZT \) in most of the samples shown.

We now present an alternative viewpoint. The electrical conductivity \( \sigma \) can be expressed in terms of \( m^* \), the average effective mass along the direction of the current density vector, the electronic mean free path \( l_e \) and the Fermi energy \( E_F \) by \( \sigma = nq^2l_e/(2m^*E_F)^{1/2} \). Considering now the phonon properties, the classical kinetic equation can be used to express the lattice thermal conductivity \( \kappa_L \) as a function of \( C_V \), the specific heat per unit volume at constant volume, and the phonon velocity \( V_\phi \) and mean free path \( l_\phi \): \( \kappa_L = \frac{1}{3}C_V V_\phi l_\phi \). The thermoelectric figure of merit becomes,
with $\mathcal{L}$ being the appropriate Lorenz number,

$$
ZT \approx (S^2 n) \left( \frac{\mu}{\kappa} \right) qT = (S^2 n) \frac{1}{\left( \frac{l_\phi}{l_e} \right) \frac{C_v v_\phi}{3q^2 T} (2m^* E_F)^{1/2} + \mathcal{L} n}.
$$

(2.3)

In this framework, we can divide $ZT$ into three factors, (1) $S^2 n$, (2) $l_\phi/l_e$, (3) $\mathcal{L} n$.

As is evident from the Table 2.1, $S^2 n$ for the QDSL is increased by a factor of 3. We consider two cases for $\kappa$. (a) $\kappa_L$ dominates over $\kappa_e$, in which case the third term is small. Then we see that the $S^2 n$ increase is much higher compared to a smaller (but still advantageous) change in in both the samples ($\kappa_L \sim 0.33 \text{ W/mK for these samples}$). This implies that the quantum dots in the QDSL reduce the mobility of the charge carriers almost as much as the thermal conductivity, with a limited benefit to Z. (b) $\kappa_e$ dominates over $\kappa_L$, in which case, $ZT$ is mostly decided by $S$ only, as $\mathcal{L} n$ changes little with scattering parameter at high doping levels. Thus using this viewpoint, we would conclude that an important contribution to the increase in the $ZT$ in the quantum dot samples is the increase in $S$ at a given value of $n$ over the value for the bulk, equation (2.1), the magnitude of which is evident from Figure 2.1. Clearly both viewpoints are valid, though not equivalent, and it is the combination of the parameters that determines the $ZT$ value.

### 2.3 Effect of relaxation time on the thermopower

Further investigation is now justified as to why the $S(n)$ of these samples is increased in low-dimensional materials. From the Mott equation for thermopower of a degenerately doped solid we obtain,

$$
S = \frac{\pi^2 k_B}{3 q} \frac{k_B T}{q} \left\{ \frac{1}{n} \frac{dn(E)}{dE} + \frac{1}{\tau} \frac{d\tau(E)}{dE} - \frac{1}{m^*} \frac{dm^*(E)}{dE} \right\}_{E=E_F}.
$$

(2.4)
Figure 2.2: Density of states in a (a) 3-D bulk material, (b) ideal quantum dot and (c) quantum dot nanocomposite. (d) shows a Lorentzian curve enveloping the the nanocomposite DOS.

As discussed previously in Chapter 1, there are two mechanisms leading to an increase in $S$ when the density of states $g(E)$ is in the shape of a Dirac $\delta$-function, induced either by means of low dimensionality [17, 18] or by the introduction of hybridized $4f$ levels [23]. The previously identified mechanism [17, 18, 23], affects $(1/n)[dn(E)/dE]$ and $(1/m^*)[dm^*(E)/dE]$. Here, we point out that in a nanocomposite consisting of a matrix in which there is a multiplicity of embedded quantum dots, such as a QDSL, quantum confinement effects in the dots increase $d\tau(E)/dE$ in the ensemble. The density of energy states $g(E)$ in a single quantum dot is a series of Dirac $\delta$-functions at finite energies $E_{ijk}$ where $i$, $j$ and $k$ are quantum numbers as shown in Figure 2.2. In a single quantum wire, $g(E)$ is a series of Landau discontinuities of the form $g(E) \propto (E - E_{ij})^{-1/2}$ [12]. A bulk-like nanocomposite such as the QDSLs, contains a multiplicity of quantum dots or wires dispersed in a semiconducting matrix. Despite the quantization of the energy levels inside the dots, it is evident from the rather high values of $\mu$ in the QDSLs in Table 2.1 that the
Figure 2.3: Energy dependence of the density of states of a bulk solid (dashed line) and of a multi-quantum-dot system broadened by a distribution in dot size and by the presence of impurities. Scattering is inhibited by the absence of available states in the quantum dot system, resulting in a strong energy dependence of the relaxation time.

matrix provides band-like conduction and not just hopping between the dots. The quantized energy levels of the quantum dots in the QDSLs, as calculated using a simple parabolic model, are spaced within a few $k_B T$ of one another. Thus the dots act more like weak (compared to $k_B T$) potential barriers. We show schematically in Figure 2.3 what the $g(E)$ in such an ensemble would look like: on top of a background of 3-D like representing the matrix, is superimposed a series of discrete levels from the dots. These levels have a certain broadening $a$. Indeed, there is a distribution in the sizes of the multiple quantum structures. There are also impurities in the wires and dots, with an accompanying distribution in effective masses. Both effects lead to a distribution in quantization energies, and thus in the positions of the available states at energies $E_{ij}$ or $E_{ijk}$. The $g(E)$ of the ensemble of dots becomes a broadened
peak following a Lorentzian distribution function [21]:

\[ g(E) = \frac{a}{\pi a^2 + E^2}, \]

(2.5)

where \( a \) is the full width at half max of the Lorentzian, and \( E \) is measured from the center of the distribution. The simplest commonly used expression for the collision frequency, the inverse of the relaxation time, is [31]:

\[ \tau^{-1}(E) = |M|^2 g(E), \]

(2.6)

where \( M \) is the average matrix element of the interaction of an electron with a scatterer and is assumed to depend on the value of the crystal momentum independently of the details of the band structure. It gives the probability of transition between two quantum states of the same energy, and is taken to be independent of the dimensionality of the system. It is also usual to assign a power law to energy-dependence of the matrix element, where the power is called the scattering parameter \( \lambda \), a function of the type of dominant electron scattering mechanism in the material:

\[ |M|^2 \propto E^{-\lambda}. \]

(2.7)

The analysis is limited to elastic collisions, acoustic phonon scattering \((\lambda = 0)\), neutral impurity scattering \((\lambda = 1/2)\), ionized impurity scattering \((\lambda = 2)\) and scattering on polar optical phonons at high temperatures. From this we derive an expression for the relaxation time that is also a power law:

\[ \tau(E) = \tau_0 E^{\lambda + \chi} = \tau_0 E^\Lambda, \]

(2.8)

where \( \tau_0 \) is a proportionality constant determined experimentally. The key observation here is that both in the bulk and QDSLs, the density of states is, or can...
be approximated by a power function of energy, with the exponent $\lambda$ depending on the dimensionality of the material. For instance, in a 3-dimensional bulk material, $g(E) \propto E^{1/2}$ and $\chi = -1/2$, leading to the classical expression $\tau(E) = \tau_0 E^{-1/2}$. Using equations (2.5) to (2.8), we obtain for quantum wire and quantum dot ensembles, or for nanocomposites:

$$\tau(E) \propto a E^\lambda + \frac{1}{a} E^{\lambda+2}. \tag{2.9}$$

If the system is relatively uniform and clean, $a \ll k_B T$, and the second term dominates. The relaxation time becomes a function of $E^{\lambda+2}$ ($\Lambda = \lambda + 2$) as compared to ($\Lambda = \lambda - 1/2$) for bulk materials, a much stronger function of energy. A similar conclusion holds even when there is a rather large amount of disorder, in which case the first term in equation (2.9) dominates and thus $\tau \propto E^\lambda (\Lambda = \lambda)$, still a stronger function of energy than in bulk. This can be intuitively understood by considering Figure 2.3. An electron at a state 1 can get scattered to a nearby state 2 in a bulk material. Such a transition will be inhibited in a system consisting of distributed quantum dots, because there are fewer states available to scatter into, thereby making the relaxation time a stronger function of energy than in a uniform three-dimensional material. Thus the scattering exponent $\Lambda$ can have values of up to 4 when the scattering is due to ionized impurities which is expected to be predominant at high carrier concentrations (for PbTe, $n > 10^{19} / cm^3$ at 77K and $n > 10^{20} / cm^3$ at 300K) [30]. This results in an enhanced thermopower, as illustrated in the equation for a degenerately doped semiconductor with a parabolic band,

$$S = \pm \frac{\pi^2}{3} \left( \Lambda + \frac{3}{2} \right) \frac{k_B}{q} \frac{k_B T}{E_F}. \tag{2.10}$$
We suggest that this mechanism is responsible for the very high values of the total scattering exponent $\Lambda$ that were observed in PbTe containing nanoprecipitates of Pb [13, 15], where, as for the QDSLs Table 2.1, the thermopower $S(n)$ is enhanced above that given by equation (2.2) for the equivalent bulk material. It was experimentally shown by using the method to be described in Chapter 3 that it is a strong increase in $\lambda$ that resulted in higher $S(n)$ than in bulk, and not an increase in effective mass as would be expected from size-quantization effects. The origin of this enhancement was not clear at the time, and we suggest that the mechanism described here might be responsible. Perhaps such conclusion can be extended to the behaviour of the QDSLs though no data are published yet on their scattering exponent.
CHAPTER 3

EXPERIMENTAL METHOD

3.1 Introduction

At each temperature, assuming single band carrier conduction, there are essentially four unknown quantities for a given sample: the carrier density $n$ or $p$, the carrier mobility $\mu$, the density-of-states effective mass $m_d^*$, and the energy dependence of the relaxation time, which we choose to represent by the scattering exponent $\lambda$ in

$$\tau(E) = \tau_0 E^{\lambda - 1/2}$$

(3.1)

The value of the scattering parameter varies with the kind of predominant scattering mechanism in a given sample as follows:

- for acoustic phonon scattering, $\lambda = 0$,
- for neutral impurity scattering, $\lambda = 1/2$,
- for ionic impurity scattering, $\lambda = 2$.

In order to solve this system uniquely without fitting some parameters, we need experimental data for four electronic coefficients, and these we choose to be the resistivity,
the thermopower (Seebeck coefficient), the Hall coefficient, and the transverse Nernst-Ettingshausen coefficient. The thermoelectric power $S$, the carrier concentration $p$, and the electrical conductivity $\sigma$ are functions of the Fermi energy $E_F$ in the system, the carrier effective mass $m^*$ and the carrier scattering relaxation time $\tau$ for simple parabolic bands.

### 3.2 Experimental setup

All the four electronic coefficients, along with the total thermal conductivity are measured on the same sample, cut into a cuboid. The dimensions of the sample are kept small to ensure homogeneity of material properties. A schematic is shown in Figure 3.1. The transport properties are measured in a conventional flow cryostat in the temperature range 80 K-420 K at discrete values of magnetic field ranging from $-2$ T to 2 T. Galvanomagnetic measurements were taken using static D.C. method and inverting both current and magnetic field [14]. Electrical resistivity is measured as the average value between both directions of current and magnetic fields thus canceling out possible errors due to the geometric magnetoresistance. The length ($L$, distance between the top and bottom thermocouples) to width ($W$, distance between the transverse contacts) is kept high so as to minimize error [29] in the transverse measurements (Hall and Nernst) which increase with decreasing ratio. With an $L/W$ value of over 2, the Hall coefficient is more than 95% accurate. Slight misalignment in the transverse contacts leads to picking up longitudinal resistive voltage in the Hall voltage measurement leading to error in the measurement. However, in view of the cubic crystal symmetry of the PbTe system, this can be compensated for by the use of positive and negative magnetic fields, and taking the slope of the Hall resistance.
Figure 3.1: Schematic of a mounted sample showing the various contacts. TC stands for thermocouples. The subscripts T and B stand for top and bottom respectively. The direction of the magnetic field is perpendicular to the sample electric and heat current as indicated. The longitudinal measurements (Seebeck coefficient, thermal conductivity, and resistivity) are made between the thermocouples TC\(_T\) and TC\(_B\) for temperatures, and the Cu wires of the thermocouples for the voltages. A second set of the voltage data is obtained from the Cu voltage wires V\(_T\) and V\(_B\). The transverse measurements (Nernst and Hall coefficients) are made between the Cu wires of the TC\(_T\) and V\(_T\). The bottom wires give a second set of data for comparison.
vs. B-field about the zero field which this will give the low-field Hall coefficient for the sample. Similar argument applies for the Nernst measurement also. One further correction needs to be applied to the Nernst measurement, as the measured coefficient is the adiabatic coefficient ($N_a$, measured with heat flux in the transverse direction = 0), and not the isothermal coefficient ($N_{iso}$ as measured with temperature difference along the transverse direction = 0) as used in the data treatment. Assuming that the scattering parameter $\lambda = 0$, $N_{iso}$ is determined by multiplying $N_a$ by the following factor [37]:

$$NiNa = \left(1 + \frac{7e}{4k_B} \frac{|S|}{}\rho_k T \right)^{-1}$$  \hspace{1cm} (3.2)

### 3.3 Data treatment

The assumption that the bands are parabolic does not hold for the valence band of PbTe, for which the Fermi surfaces are ellipsoids of revolution, and the energy dispersion relation is given by

$$\frac{\hbar^2 k_l^2}{2m_l^*} + \frac{\hbar^2 k_t^2}{2m_t^*} = \gamma(E) = E(1 + \frac{E}{E_g})$$  \hspace{1cm} (3.3)

where $E_g$ is the direct energy gap of PbTe, and $k$ and $m$ are the electron wave vector and effective mass (at $k = 0$) along the longitudinal (suffix $l$) and transverse (suffix $t$) directions of the ellipsoids. The density of states:

$$g(E) = \frac{\sqrt{2m_d^*}^{3/2}}{\pi^2 \hbar^3} \gamma'(E) \sqrt{\gamma(E)},$$  \hspace{1cm} (3.4)

where $\gamma'$ is the derivative of $\gamma$ with respect to $E$, $\hbar$ is the Dirac constant, and $m_d^*$ is the density of states effective mass in which we include the degeneracy number when the Fermi surface contains more than one pocket. We saw that equation (2.6) contained two factors, the density of states and the transition matrix element; for
non-parabolic bands it follows that the energy dependence of the relaxation time is given by:

\[ \tau_e(E) = \tau_0 \frac{\gamma(E)^{\lambda-1/2}}{\gamma'(E)}. \]  

(3.5)

The carrier density is now:

\[ p = \frac{(2m^*_a k_B T)^{3/2}}{3\pi^2 \hbar^3} \int_0^\infty \frac{\gamma(z)^{3/2}}{\gamma'(z)} \tau(z) \left( -\frac{df_0}{dz} \right) dz, \]  

(3.6)

where \( z = E/k_B T \) is the reduced energy, so that \( \gamma(z) \) is given by equation (3.3) but with \( z \) replacing \( E \), and \( f_0 \) is the Fermi-Dirac distribution function. The electrical conductivity is given by

\[ \sigma = \frac{(2m^*_a k_B T)^{3/2} e^2}{3\pi^2 \hbar^3} \frac{m^*_a}{m^*_\alpha} \int_0^\infty \frac{\gamma(z)^{3/2}}{\gamma'(z)} \tau(z) \left( -\frac{df_0}{dz} \right) dz, \]  

(3.7)

where \( e \) is the carrier charge, \( m^*_\alpha \) is the effective mass along the crystallographic direction of the sample studied, or the appropriate average mass for polycrystals.

The low-field Hall coefficient is \((\mu B \ll 1)\):

\[ R_H = \frac{3K(K+2)}{(2K+1)^2} \frac{1}{pe} \frac{\int_0^\infty \frac{\gamma(z)^{3/2}}{\gamma'(z)} \tau^2(z) \left( -\frac{df_0}{dz} \right) dz \int_0^\infty \gamma(z)^{3/2} \left( -\frac{df_0}{dz} \right) dz}{\int_0^\infty \frac{\gamma(z)^{3/2}}{\gamma'(z)} \tau(z) \left( -\frac{df_0}{dz} \right) dz}, \]  

(3.8)

where \( K \) is the effective mass anisotropy coefficient \( K = m_l/m_t \). The thermopower is

\[ S = \frac{k_B}{e} \left[ \frac{\int_0^\infty \frac{\gamma(z)^{3/2}}{\gamma'(z)} \frac{z}{\gamma'(z)} \tau(z) \left( -\frac{df_0}{dz} \right) dz}{\int_0^\infty \frac{\gamma(z)^{3/2}}{\gamma'(z)} \tau(z) \left( -\frac{df_0}{dz} \right) dz} - \frac{E_F}{k_B T} \right], \]  

(3.9)

and the low-field isothermal Nernst-Ettingshausen coefficient is:

\[ N_{iso} = R_H \sigma \frac{k_B}{e} \left[ \frac{\int_0^\infty \frac{\gamma(z)^{3/2}}{\gamma'(z)^2} \tau^2(z) \left( -\frac{df_0}{dz} \right) dz}{\int_0^\infty \frac{\gamma(z)^{3/2}}{\gamma'(z)^2} \tau(z) \left( -\frac{df_0}{dz} \right) dz} - \frac{\int_0^\infty \frac{\gamma(z)^{3/2}}{\gamma'(z)^2} \tau(z) \left( -\frac{df_0}{dz} \right) dz}{\int_0^\infty \frac{\gamma(z)^{3/2}}{\gamma'(z)^2} \tau(z) \left( -\frac{df_0}{dz} \right) dz} \right], \]  

(3.10)
Solving these equations are each temperature with experimental values measured for the resistivity, thermopower, low-field Hall and low-field isothermal Nernst coefficients, we can deduce the density-of-states effective mass and the scattering parameter.

3.4 Degenerate Case

When the carrier density is not too high (and the $E_F \lesssim k_B T$), the above equations need to be solved numerically, and spontaneously making it a computationally intensive and slow process. In the special case of semiconductors where the Fermi level lies deep in the band (the degenerate case), it is possible to expand equations (3.6) through (3.10) using the Bethe-Sommerfeld expansion:

$$\int_0^\infty \Psi(E) f_0(E) dE = \int_0^{E_F} \Psi(E) dE + \frac{\pi^2}{6} (k_B T)^2 \frac{d\Psi(E)}{dE} + \ldots. \quad (3.11)$$

By performing integration-by-parts on each of the above integrals, and then applying Bethe-Sommerfeld expansion, we obtain the following simplified equations for a degenerate case:

$$p = \frac{(2m_d^* \gamma(E))^{3/2}}{3\pi^2 k^3}, \quad (3.12)$$

$$\sigma = p e \mu(E_F), \quad (3.13)$$

$$R_H = \frac{3K(K+2)}{(2K+1)^2} \frac{1}{pe}, \quad (3.14)$$

$$S = \frac{\pi^2 k_B}{3} e k_B T \left[ \Lambda \left( \frac{3}{2} \right) \frac{\gamma'(E_F)}{\gamma(E_F)} \gamma''(E_F) - 2 \frac{\gamma''(E_F)}{\gamma'(E_F)} \right], \quad (3.15)$$

$$N_{iso} = R_H \frac{\pi^2 k_B}{3} e k_B T \left[ \Lambda \frac{\gamma'(E_F)}{\gamma(E_F)} \gamma''(E_F) - 2 \frac{\gamma''(E_F)}{\gamma'(E_F)} \right]. \quad (3.16)$$

The degenerate equations as presented here agree well with the full equations if the Fermi energy is large enough ($> 6k_B T$) and the scattering parameter close to or less than 1.
The equations relating the transport coefficients to the materials parameters are shown for a p-type conductor. For an n-type conductor, they remain the same, except thermopower and Hall coefficient take a $'-'$ sign. It is to be noted that the equations shown here are valid only for a conductor with a single-band carriers.
CHAPTER 4

RARE-EARTH – LEAD SELENIDE ALLOYS

4.1 Introduction

Rare-earth alloys with the IV-VI compound semiconductors have a long history, starting with the discovery and use of Pb$_{1-x}$Eu$_x$Se alloys [28] which were developed as a larger-gap semiconductor almost lattice-matched to PbTe and used in heterojunctions, for instance in quantum-well infra-red diode lasers [26]. Many interesting magnetic [11] and magnetoresistive effects [27] were discovered. One possible application for alloys of rare-earth elements with lead salts therefore resides in the emerging field of spintronics. Another potential application arises from a suggestion of Mahan and Sofo, discussed in Chapter 1: a material with a delta-shaped density of states is calculated to have an enhanced thermoelectric figure of merit. A possible realization of this concept could use the 4$f$ levels of rare-earth elements, which have a quite heavy effective mass, embedded in a conventional thermoelectric material such as the lead salts, provided that the 4$f$ level hybridizes with the bands and that the Fermi energy of the alloy reaches the 4$f$ level. We study here a number of alloys in order to determine where this condition might be achieved.

$^1$The results of this study are published in ref [20].
We notice first that the rare-earth monoselenides crystallize in the NaCl structure [43], as does PbSe, and that their lattice constants match within a +0.1% (SmSe) to –7% (HoSe) bracket. Except for Eu, the rare-earths studied here are mostly trivalent atoms; since Pb is divalent in PbSe, we expect that those rare-earths will act as donors if they substitute for lead, as is likely. On the other hand, the Pauling electronegativity $X$ of the rare-earth atoms, as given by Allred is very different from that of Pb. Electronegativity difference $\Delta X = X_{\text{RareEarth}} - X_{\text{Pb}}$ dominates alloys scattering, following a formula

$$\mu_{\text{Alloy}} = \frac{C}{4\Delta X^2 x(1-x)} \sqrt{\frac{300}{T}}$$

(4.1)

where $x$ is the atomic concentration of the rare-earth element, $T$ is in K, and $C$ is a constant that depends on the dielectric constant of the material and the resulting electrostatic screening of the rare-earth atoms dipole moment in the lattice. For lead salts which have very high dielectric constants, $C \approx 7.5 \text{cm}^2/\text{Vs}$, while for group IV or III-V semiconductors $C \approx 2 \text{cm}^2/\text{Vs}$. Alloy scattering must be added to the other scattering mechanisms, specifically phonon and ionized impurity scattering. In view of the very large electronegativity differences ($0.6 < \Delta X < 0.8$), one expects the rare-earth PbSe alloys to have mobilities that are decreased by alloy scattering. On the other hand, in thermoelectric applications, it is the weighted mobility $U = \mu(m^*)^{3/2}$ that determines the figure of merit [33]: if the $4f$ level of the rare-earth atoms is near the Fermi energy, following the argument of Mahan and Sofo, one might hope that the increase in local density-of-states effective mass $m^*$ would partially overcome the decrease in $\mu$.

In this chapter, we examine these possibilities experimentally, using a sequence of samples of pure PbSe (for reference), and Pb$_{1-x}$Ce$_x$Se, Pb$_{1-x}$Pr$_x$Se, Pb$_{1-x}$Nd$_x$Se,
Pb$_{1-x}$Eu$_x$Se, Pb$_{1-x}$Gd$_x$Se, and Pb$_{1-x}$Yb$_x$Se alloys. We report magnetic susceptibility data, as well as a full set of galvanomagnetic and thermomagnetic measurements, from which we deduce the carriers transport properties, specifically density, mobility, density-of-states effective mass and scattering exponent. In short, the trivalent rare earth atoms act as donors; the mobility of the rare-earth alloys is decreased by mechanisms that we will discuss, while the scattering exponent is not affected. The effective mass is increased, but not sufficiently to overcome the mobility decrease and increase the weighted mobility or improve the thermoelectric performance of the material, except potentially for Pb$_{1-x}$Nd$_x$Se alloys.

4.2 Experiment

The different polycrystalline alloys studied are summarized in Table 4.1. The alloys were prepared by the Bridgman method. Analysis by X-ray diffraction revealed a rock-salt crystal lattice for all alloys. The presence of second phase inclusions in trace amounts was detected in the PbCeSe and PbPrSe crystals. One piece of 6N-pure polycrystalline PbSe was used as a reference, as prepared by Alfa-Aesar. All samples are n-type, except for the Pb$_{1-x}$Eu$_x$Se alloy and the reference PbSe sample, which are p-type.

In a first experiment, the magnetization $M$ was studied by SQUID magnetometry applying a dc magnetic field of 400 Oe. The ideally linear $M(H)$ dependence was checked in the range 0-1 kOe in all crystals, as expected for standard paramagnetic samples, which one expects dilute rare-earth alloys to be. The magnetic susceptibility $\chi$ was deduced. The temperature range was 5 to 120 K, except for the Ce alloy which was measured up to 200 K. The data are presented in Figure 4.1 after correction for
the diamagnetic susceptibility of the PbSe lattice, which was assumed temperature-independent.

In a second experiment, small parallelepipeds were cut from the samples and their transport properties were measured in a conventional flow cryostat from 80 up to 380 K, in magnetic fields of -1.3 to 1.3 Tesla, using the experimental technique described in Chapter 3. Magnetothermal conductivity was not observed in the alloys, as the thermal conductivity is mostly dominated by the lattice (except for Pb$_{1-x}$Ce$_x$Se and Pb$_{1-x}$Nd$_x$Se) and the magnetoresistance is small. The transverse Nernst-Ettingshausen voltages are measured by reversing the sign of the magnetic field and taking differences in transverse voltages, a procedure again justified by the cubic symmetry of the samples. The low-field condition $\mu B \ll 1$ is fulfilled throughout the measurement range, and the slopes of the Hall and Nernst voltages were plotted against the magnetic field to yield the Hall ($R_H$) and Nernst ($N_a$) coefficients. The measured Nernst coefficient $N_a$ is the adiabatic one; the data reported are the isothermal transverse Nernst coefficient $N$ which is calculated from the adiabatic one as in reference [37]. The galvanomagnetic and thermomagnetic data are presented in Figure 4.2; the thermal conductivity in Figure 4.3.

A detailed discussion firstly of the magnetic susceptibility, secondly of the galvanomagnetic and thermomagnetic data, and finally of the thermal conductivity follows in the next section.
Table 4.1: Properties of alloys studied at 300 K. The density of the rare-earth atoms as determined from the susceptibility is given in column 2, then the carrier density \((n \text{ or } p)\), mobility \(\mu\), resistivity \(\rho\), Seebeck coefficient \(S\), thermal conductivity \(\kappa\), Nernst coefficient \(N\), scattering parameter \(\lambda\), density-of-states effective mass \(m^*\) and thermoelectric figure of merit \(ZT\). The samples are not optimally doped to maximize the \(ZT\).
4.3 Discussion

Discussing now first the magnetic susceptibility measurements of each alloy individually, we see that:

- Pb$_{1-x}$Eu$_x$Se has a pure Curie-Weiss (C-W) behavior with a small Curie-Weiss temperature as expected for Eu$^{2+}$ atoms. The concentration of Eu atoms distributed in the lattice is given in Table 4.1, column 2; it corresponds to the composition given in column 1.

- Pb$_{1-x}$Gd$_x$Se and Pb$_{1-x}$Nd$_x$Se also have a pure C-W behavior and the concentrations are reported in Table 4.1.

- Pb$_{1-x}$Yb$_x$Se has a less clear C-W-like behavior, so that a determination of the concentration of Yb atoms is only possible with a very large error, on the order of 50%. For Pb$_{1-x}$Ce$_x$Se we observe a non-C-W behavior, indicating that the Ce$^{3+}$ atoms undergo the effect of a cubic crystal field, with a crystal

Figure 4.1: Inverse magnetic susceptibility as a function of temperature for the different alloys prepared. A straight line indicates Curie-Weiss behavior.
field splitting energy of 360K. This is consistent with earlier work. At higher temperatures (not shown in Figure 4.1), the sample shows a tendency toward a C-W behavior with a strongly antiferromagnetic C-W temperature, the origin of which is unclear. Measurements taken on different samples show a non-uniform Ce concentration, the average of which is given in Table 4.1.

- Pb$_{1-x}$Pr$_x$Se shows a C-W behavior, also with a high antiferromagnetic C-W temperature; X-ray diffraction studies show the presence of a second crystal phase. No estimate of the composition was possible for this non-uniform sample.

Secondly, we discuss the thermomagnetic measurements. As discussed in Chapter 3, by the use of the four galvanomagnetic and thermomagnetic coefficients it is possible to deduce, at each temperature, four independent parameters. In this method, we choose as independent parameters for the charge carriers their density $n$ or $p$, mobility $\mu$, scattering parameter $\lambda$ and density-of-states effective mass $m^*$ at each temperature.

The results are given in Figure 4.4, with room-temperature values also given in Table 4.1, and are described hereunder. For completion, we also report in Table 4.1 the thermoelectric figure of merit $ZT$. Thermoelectric materials need to be optimally doped to maximize $ZT$, and the samples used here are not. Therefore this cannot be used as technologically relevant data.

The only sample that is p-type (besides the reference PbSe) is the PbEuSe sample, in which Eu is divalent. The PbEuSe is close to intrinsic, and the effect of Eu is to increase the band gap, as previously established [22]. All the other rare-earth elements (Ce, Pr, Nd, and Gd) act as donors, as expected. The efficiency of the rare-earths as dopants (the ratio of the extrinsic electron concentration to the atomic concentration of rare-earths) is shown in Figure 4.5. Ce and Nd are somewhat less than monovalent.
Figure 4.2: Galvanomagnetic (resistivity $\rho$ and Hall coefficient $R_H$) and thermomagnetic (Seebeck $S$ and isothermal transverse Nernst-Ettingshausen $N$ coefficients) data as a function of temperature for the samples studied. The symbols are ($\triangledown$)PbSe, ($\circ$)Pb$_{1-x}$Ce$_x$Se, ($\blacktriangle$)Pb$_{1-x}$Pr$_x$Se, ($\circ$)Pb$_{1-x}$Nd$_x$Se, ($\bullet$)Pb$_{1-x}$Eu$_x$Se, ($\times$)Pb$_{1-x}$Gd$_x$Se, and (+)Pb$_{1-x}$Yb$_x$Se. Solid lines have been added to guide the eye.
The symbols are (▽)PbSe, (○)Pb₁₋ₓCeₓSe, (▲) Pb₁₋ₓPrₓSe, (◊) Pb₁₋ₓNdₓSe, (●)Pb₁₋ₓEuₓSe, (×)Pb₁₋ₓGdₓSe, and (+)Pb₁₋ₓYbxSe. Solid lines have been added to guide the eye.

 donors at the concentrations in which they are in the samples. Since most donors exhibit a decrease in doping efficiency at high concentrations, this is not surprising. The doping efficiency of Gd, and especially that of Yb, are much lower, and indication of possible mixed-valence behavior.

Gd is usually found in semiconductors in its 3+ charge state. There exists, however, experimental evidence that the 5d¹ orbital of Gd can be occupied is SnGdTe and PbSnGdTe crystals forming a state resonant with either a valence band (SnGdTe) or a conduction band (PbGdTe) [35].

PbYbSe appears to have a different behavior. In IV-VI semiconductors Yb is observed in both 3+ (4f¹³, paramagnetic) and 2+ (4f¹⁴, diamagnetic) configuration with a resonant donor state formed e.g. in PbTe and PbGeTe [32]. Magnetization
Figure 4.4: Results of fitting data of Figure 4.2 to the carrier density $n$ or $p$, mobility $\mu$, scattering parameter $\lambda$, and density-of-states effective mass $m^*$ at each temperature. The symbols are (▽)$\text{PbSe}$, (○)$\text{Pb}_{1-x}\text{Ce}_x\text{Se}$, (▲)$\text{Pb}_{1-x}\text{Pr}_x\text{Se}$, (⋄)$\text{Pb}_{1-x}\text{Nd}_x\text{Se}$, (●)$\text{Pb}_{1-x}\text{Eu}_x\text{Se}$, (×)$\text{Pb}_{1-x}\text{Gd}_x\text{Se}$, and (+)$\text{Pb}_{1-x}\text{Yb}_x\text{Se}$. Solid lines have been added to guide the eye.
measurements permit the determination of the concentration of Yb$^{3+}$ ions in our sample. We suggest that a possible mixed valence 2+/3+ state of Yb ions in PbSe:Yb crystal could exist, based on the following arguments. (1) The high Yb$^{3+}$ ions concentration observed in magnetic susceptibility analysis should have resulted in a much higher electron concentration as both substitutional and interstitial single Yb$^{3+}$ atoms should have been electrically active. (2) The sample has a surprisingly high electron mobility, a phenomenon known to occur in mixed valence type resonant donor states like HgSe:Fe or PbTe:In. (3) YbSe has a lattice constant that is not aligned with that of the trivalent rare-earth monoselenides, in which the lattice constant decreases with increasing atomic number. We have to admit, however, that a fully consistent physical picture is still lacking. A possible alternative explanation is that a part of total concentration of Yb ions might be chemically bound in Yb$_2$Sb$_3$-like micro precipitates (active magnetically because of 3+ charge state of Yb ions but neutral electrically), though X-ray diffraction does not reveal the presence of such compound.

The mobility of all rare-earth doped samples is reduced. Plots of the mobility at 300 K versus carrier concentration exist for PbTe [31], but we were unable to find the equivalent for PbSe. Comparing the mobility of the Ce, Gd, and Nd containing samples to that of heavily doped PbTe [30], we can conclude that the mobility levels for these samples are not unexpected for ionized impurity scattering at that doping level. We do not need to invoke alloy scattering for these samples, possibly because the mobility is already low. The Yb containing sample has a much higher mobility, but it is more reduced than expected from ionized impurity scattering alone. Alloy scattering may be a contributor, or so might the presence of electrically neutral Yb$^{3+}$ ions. The mobilities of the Pr-containing sample may reflect the presence of a second
Figure 4.5: Carrier density (●) and dopant efficiency (□) of the various rare-earth atoms as a function of the atomic number.

phase. It is well known that the mobility in Pb$_{1-x}$Eu$_x$Se and telluride decreases dramatically with $x$, and the present result is consistent with that.

Interestingly, the scattering parameter of all samples (except for the Pr-containing sample at lower temperatures, which may be non-uniform) remains between 0.5 and 1, which is what is expected in ordinary doped semiconductors. The fact that the dopants in the present samples are paramagnetic ions has no obvious effect on the scattering mechanisms.

The measured density-of-states hole effective mass at the band edge at 300 K reported here is 0.24$m_e$ for the pure PbSe sample, while a calculation using the hole masses of Preier gives 0.23$m_e$, illustrating the quality of the measurements and fits. The electron density-of-states mass calculated at 300 K from reference is 0.30$m_e$. We see in Figure 4.2 that the electrons in the Ce and Yb alloys have similar masses. The hole mass in Pb$_{1-x}$Eu$_x$Se is similar to that in PbSe, though it has a different temperature dependence. From the spectroscopy data of Kanazawa et al. we expect
the energy gap of Pb$_{1-x}$Eu$_x$Se to increase roughly as $E_g(x) = E_g(\text{PbSe}) + 2.16x$ (this dependence is only valid for concentrations $x < 0.07$, as in samples with higher Eu content, the 4$f$ levels of the Eu$^{2+}$ ions become located in the energy gap. See [4]).

For our sample at 300 K, $E_g \approx 0.50\text{eV}$, and we might intuitively have expected a proportional increase in mass, which is not observed. The measurement reported here is consistent with the magneto-optical data of Geist et al. which contrast the behavior of Pb$_{1-x}$Eu$_x$Se with that of Pb$_{1-x}$Eu$_x$Te: the band parameters of the selenide are practically unaffected by the Eu content, whereas in the telluride the matrix element and the masses show a clear increase with $x$. It is suggested that this is due to the different band-edge symmetries of the bands in the two chalcogenides. We observe a different temperature dependence presumably due to the fact that the energy gap of Pb$_{1-x}$Eu$_x$Se may have a different temperature dependence than that of PbSe. The data on the Pr sample are again affected by the inhomogeneities in the sample and are unreliable. The electron density-of-states mass of the Gd containing sample is similar to that of PbSe at 300 K, but increased at low temperature. The Nd-containing sample has a much heavier electron mass than PbSe. It can be concluded that, except perhaps for Pb$_{1-x}$Nd$_x$Se, the Fermi level is not near the 4$f$ level of the rare-earth donor, or that the 4$f$ level of the rare-earths does not hybridize with the bands of PbSe.

Turning now to the thermoelectric properties, we plot the Seebeck coefficient $S$ as a function of carrier density for both n and p-type samples (a Pisarenko plot) in Figure 4.6. The full line is calculated with the band parameters for PbSe; there is little difference between the calculations for electrons or holes. The experimental data point for pure p-type PbSe falls on that line; the data points for the rare-earth alloys
Figure 4.6: Absolute value of the Seebeck coefficient of $n$ and $p$-type PbSe and Pb$_{1-x}$RE$_x$Se alloys as a function of carrier density at 300 K. The full line is calculated using acoustic phonon scattering, and the data points are identified by the chemical symbol for the rare-earth atom.

systematically exceed the line, due to a slight increase in effective mass. As pointed out in the previous paragraph, Pb$_{1-x}$Nd$_x$Se stands out. However, the decrease in mobility outweighs the modest increase in Seebeck coefficient seen in Figure 4.6 in the calculation of the thermoelectric figure of merit.

Finally, the thermal conductivity is dominated by the lattice, except, as mentioned above, for Pb$_{1-x}$Ce$_x$Se and Pb$_{1-x}$Nd$_x$Se, and to a lesser extent Pb$_{1-x}$Gd$_x$Se, where the electrical conductivity is large. From a crude estimate of the Wiedemann-Franz law using the free electron Lorenz number, we can estimate the lattice thermal conductivity for these samples, and it is not significantly different from that of the other samples or from the literature values for the lattice thermal conductivity of PbSe. The increase in thermal conductivity with temperature is completely attributable to the Wiedemann-Franz law. One conclusion is that, in spite of the presence of crystal field
splitting in Pb$_{1-x}$Ce$_x$Se, the lattice thermal conductivity is not reduced as predicted by the theory of Morelli et al. [24] because the crystal field splitting energy (360 K) is too high compared to both the Debye temperature (for PbSe: 144-156 K [1]) and the measurement temperature range.

### 4.4 Conclusions

We have investigated the magnetic, galvanomagnetic and thermomagnetic properties of dilute Pb$_{1-x}$Ce$_x$Se, Pb$_{1-x}$Pr$_x$Se, Pb$_{1-x}$Nd$_x$Se, Pb$_{1-x}$Eu$_x$Se, Pb$_{1-x}$Gd$_x$Se, and Pb$_{1-x}$Yb$_x$Se alloys, and compared them to pure PbSe for reference. The resistivity, Hall, Seebeck and transverse Nernst-Ettingshausen coefficients for each sample at each temperature yield, through a 4-parameter fit, the samples carrier density, mobility, density-of-states effective mass and scattering exponent. The trivalent rare-earths act as donors in PbSe, suggesting that the rare-earth atom substitutes for Pb$^{2+}$; the Eu$^{2+}$ ion in PbEuSe alloys does not change the charge balance but increases the energy gap without increasing the effective mass. The doping efficiency appears to decrease for the heavier rare-earths. For most samples, the mobility is decreased compared to pure PbSe, but not much more than predicted from ionized impurity scattering: even though the electronegativity difference between the rare-earth atoms and Pb is quite large, we see only a moderate effect of alloy scattering. As far as thermoelectric applications of these alloys go, the most promising rare earth element is Nd, as its alloy shows the largest increase in effective mass, and the accompanying largest relative increase in Seebeck coefficient.
NANOCOMPOSITES OF LEAD TELLURIDE AND LEAD SELENIDE

5.1 Introduction

Quantum dots represent the ultimate in reduced dimensionality, i.e. zero dimensionality. The energy of an electron confined in a small volume by a potential barrier as in a QD is strongly quantized. For QDs the conduction band offset and/or strain between the QD and the matrix act as the confining potential. As discussed previously in Chapter 2, the quantization of energy is reflected in the dependence of the density of states on energy.

Following the prediction of high figure of merit in low dimensional materials, Springholz et al. [34] grew PbSe/PbEuTe superlattices in which a three-dimensional array of islands formed spontaneously, with dimensions small enough that they can be considered as quantum dots. Harman and co-workers later developed MBE-grown PbTe/PbTe$_{1-x}$Se$_x$ quantum dot superlattices, in which small quantum dots with a higher Se content grew at the interface between the PbTe regions and the alloy regions. When viewed from a 3D standpoint, these quantum dot superlattices can be interpreted as a PbTe host into which quantum dots are introduced in a periodic way.
in all three \((x, y, z)\) directions. With demonstrated \(ZTs\) as high as 2 at room temperature and even higher at elevated temperatures, the thin film QDSLs are a proof of the principle that low dimensionality can be used to obtain high figures of merit. There is now a recognized need for developing inexpensive processes for producing bulk materials incorporating the favorable effects of the nanostructures. The \(ZT\) is improved in the QDSLs through a combination of two factors: a strong decrease in lattice thermal conductivity, and an increase in the Seebeck coefficient over that of bulk PbTe for a given carrier concentration. In fact, the lattice thermal conductivity of the QDSLs as determined to be of the order of 0.33 W/mK, close to the theoretical minimum of PbTe.

In view of the fact that thermal conductivity reduction is a major mechanism behind the enhanced figure of merit in superlattices, and as past studies on the heat-conduction mechanisms in superlattices have shown that periodic structures are not necessary for thermal conductivity reduction [44], nanocomposites are a natural step for extending the success in superlattices to more scalable materials. Such nanocomposites can be in the form of nanoparticles and nanowires embedded in a host matrix material, or mixtures of two different kinds of nanoparticles.

To reduce the thermal conductivity without degrading the electron transport properties, one should work with constituent materials that have significant differences in lattice properties, but negligible differences in electronic properties. Recent experimental results on Bi\textsubscript{2}Te\textsubscript{3}/Sb\textsubscript{2}Te\textsubscript{3} superlattices [41] and PbTe/PbSeTe QDSL shows no significant reduction in the electrical conductivity was observed for current flow perpendicular to the interface of Bi\textsubscript{2}Te\textsubscript{3}/Sb\textsubscript{2}Te\textsubscript{3} superlattices and along the interface of

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PbTe/PbSeTe quantum-dot superlattices. This demonstrates that by properly choosing the mismatch in electronic properties, the electron transport properties can be maintained at a level comparable to bulk materials or even enhanced using interfaces as energy filters or energy quantization barriers.

5.2 Why Pb-Se-Te?

Some of the requirements that must be satisfied by the two components in the nanocomposite to enable high $ZT$ are listed below. A composite of PbTe and PbSe satisfies these requirements and therefore expected to be a good thermoelectric.

1. To prevent alloy scattering, the electronegativities ($X$) of the atoms in the composite must be comparable. Se and Te have electronegativities of 2.55 and 2.4 respectively ($\Delta X$ is only 0.15), thus reducing alloy scattering.

2. To enable high mobility of the carriers, it is necessary to have the energy gap mismatch within a few $k_B T$, i.e., $E_{g1} \approx E_{g2} \pm k_B T$. The room temperature band gaps of PbTe and PbSe are 0.312 eV and 0.297 eV respectively, satisfying this condition.

3. The valence and conduction band edges close to the chemical potential of the components should show a type I or type II alignment. This helps to confine the holes and/or electrons in the core atoms (that make the quantum dots), without introducing additional barriers to the transport of charge carriers. PbTe and PbSe have very similar band structures, with very little offset as shown in Figure 5.1: (a) shows a type I alignment determined experimentally at 77 K (from [5]). In fact, there is almost no offset between the conduction bands,
while a small offset of about 40 meV exists in the valence band. This implies that electrons may not exhibit any confinement at all, while holes may show a slight confinement; (b) shows a type II the alignment of the band edges as calculate by Wei and Zunger [42] at 4 K. In this case, either electrons or holes are can be confined, by making the quantum dot of either PbTe in matrix of PbSe or of PbSe in matrix of PbTe respectively.

![Diagram](image)

Figure 5.1: The band offsets between PbTe and PbSe (a) determined experimentally at 77 K and (b) calculated, at 4 K.

4. An alloy formed by both components of the composite should have a low lattice thermal conductivity. An alloy of PbTe:PbSe at 13% PbSe composition has a lattice thermal conductivity of about 1.5 W/mK, lower than PbTe by a factor of about 1.5. At a higher PbSe content (50%), the lattice conductivity reduces to about 0.84 W/mK.

It may further be added that although PbTe and PbSe form a completely miscible solution, the coefficient of the interdiffusion is much lower than the diffusion of Se in PbSe which in turn is lower than that of Te in PbTe [3]. This suggests that it is best
<table>
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<th>Atom</th>
<th>Pre-exponential factor</th>
<th>Activation energy</th>
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<td>Te in PbTe</td>
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</tr>
<tr>
<td>Se in PbSe</td>
<td>$2.1 \times 10^{-5}$</td>
<td>1.2</td>
</tr>
<tr>
<td>Interdiffusion</td>
<td>$1.61 \times 10^{-6}$</td>
<td>1.5</td>
</tr>
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</table>

Table 5.1: Pre-exponential factors and activation energies for the diffusion of Se and Te in PbSe and PbTe.

To have a core of PbSe and a shell of PbTe, as we desire high amount of diffusion of Te in PbTe to ensure high mobility, while the core may stay intact during the annealing. The diffusion coefficients at different temperature are calculated from the values given in Table 5.1. The diffusion length of each atom may then be calculated using the relationship $l = \sqrt{D(T)\tau}$, where $l$ is the diffusion length, $D(T)$ is the diffusion coefficient at temperature $T$, and $\tau$ is the annealing time at that temperature. Based on this argument, we infer that for an annealing duration of an hour, the temperature should be limited to utmost 450 °C to preserve the nanostructure.

### 5.3 Fabrication of the composite

The objective is to fabricate a composite comprising a matrix of PbTe, with nanoscale grains of PbSe embedded in it. We obtain the samples from Metamateria Partners, LLC, Columbus, made by a proprietary technique, using the following two step procedure:
Figure 5.2: Schematic diagram of the core-shell structure of the PbTe-PbSe composite. The second figure shows the nanoparticles after sintering. By sintering the nanoparticles in such a way as to keep the core particles separated from each other, it is possible to make a nanocomposite of PbTe.

1. PbSe/PbTe core-shell nanoparticles are prepared by sonochemical technique. The reactant solution (a mixture of lead precursor, tellurium precursor and selenium precursor) is sonicated in a closed container under nitrogen atmosphere for 5-25 minutes using a power supply capable of delivering 750 watts. The nanoparticles are centrifuged and then washed with various solvents and dried before pressing. A core size of about 20 nm and particle size (with coating) of 40 nm gives core-shell volume ratio 13:87, which corresponds to the typical value of the alloying ratio of high quality thermoelectric materials. A schematic of the nanoparticle geometry is shown in Figure 5.2. Also shown is a TEM image of the nanoparticles in Figure 5.4.

2. The particles are thereafter sintered into circular pellets measuring about 13 mm in diameter, and 3 mm in thickness. They are first compacted under a pressure of 275 - 350 MPa and temperature of 250 - 350 °C, and then pre-annealed at around a medium high temperature of about 200 °C for 24 hours. Subsequently,
Figure 5.3: Flow chart of the sequence of steps to make nanocomposite sample of PbTe-PbSe.

the pellets are annealed at a temperature between 350 and 400 °C for about an hour to improve mobility of the charge carriers. After the sintering process is complete, the nanocomposite as shown in Figure 5.2(b) is obtained.

In the following sections, we will discuss the properties of the nanocomposites.

5.4 Discussion of results

5.4.1 Description of samples

We measured the thermoelectric properties of samples made from nanoparticles synthesized by different methods, and then sintered and annealed in different conditions. The properties of the samples were found to be very sensitive to the preparation conditions, and even the slightest change in the conditions led to different properties. The samples and their preparation conditions are listed in Table 5.2.
Figure 5.4: TEM image of the nanoparticles showing the core-shell structure.

Figure 5.5: X-ray diffraction of the nanoparticles showing separate PbTe and PbSe-rich phases before compaction.
<table>
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<th>Sample</th>
<th>Composition (PbTe:PbSe)</th>
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<th>Hot press condition</th>
<th>Anneal condition</th>
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<td>A</td>
<td>275 MPa 350 °C 1hr</td>
<td>260 °C 6hrs</td>
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<td>A</td>
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<td>B</td>
<td>300 MPa 400 °C 1hr</td>
<td>375 °C 16hrs</td>
</tr>
<tr>
<td>PC4A10</td>
<td>87:13</td>
<td>B</td>
<td>300 MPa 400 °C 1hr</td>
<td>425 °C 16hrs</td>
</tr>
<tr>
<td>PC4A052</td>
<td>87:13</td>
<td>C</td>
<td>300 MPa 400 °C 1hr</td>
<td>–</td>
</tr>
<tr>
<td>PC4A083</td>
<td>87:13</td>
<td>C</td>
<td>300 MPa 400 °C 1hr</td>
<td>400 °C 1hr</td>
</tr>
</tbody>
</table>

A - Group I based precursor  
B - Group I based precursor with improved filtering technique  
C - Group II based precursor to facilitate controlled doping  

Table 5.2: Sample process conditions.
5.4.2 Samples MM095, MM268 and MM319

Sample MM095 was made from nanoparticles with a PbTe-core : PbSe-shell (13:87), the inverse of all the other samples. Also it is the only n-type sample studied. The Hall coefficient is weakly dependent on the temperature, similar to the bulk PbX behavior at temperatures below 500 K. The Seebeck coefficient is slightly above the bulk value, but this could be due to error in the measurement of the Hall coefficient. The mobility was found to be extremely low, and could not be improved with annealing.

Sample MM268 was made of nanoparticles with equal proportions of PbTe and PbSe, with PbSe as the core. This resulted in a higher mobility of about 100 cm$^2$/Vs at room temperature. However, the Seebeck coefficient was found to be far below that of bulk PbTe/PbSe. Annealing the sample at 300°C for 6 hours did not result in the improvement of the mobility.

Sample MM319 was made of nanoparticles for PbTe-shell : PbSe-core (87:13). The mobility was found to be not much better than MM268, but the Seebeck coefficient showed an enhancement over the bulk value (of about 25%). Based on this encouraging result, more samples were made using the same composition and similar preparation conditions. To address the issue of low mobility in the samples, a new filtering technique was used to clean the nanoparticles before sintering. The results of this method is discussed next.
Figure 5.6: Galvanomagnetic and thermomagnetic data of samples MM095, MM268 and MM319. The Hall and Seebeck coefficient of sample MM095 are the negative of the values shown.
5.4.3 Samples PC4A07 and PC4A10

Based on the previous measurements, it was found that the hot pressing condition of 300 MPa at 400 °C for 1hr gave the best results as far as the physical and thermoelectric properties are concerned. Two samples made using these conditions from different set of nanoparticles were studied. Both samples were made using Group I precursor B, with a composition of 87% PbTe and 13% PbSe. Sample PC4A07 was annealed at 375 K for a long time (16 hrs) while sample PC4A10 was annealed at 425 K for the same duration. The results of the measurements are shown in Figures 5.7 and 5.8.

Due to the doping effect of the precursor, both samples are found to be heavily doped to more than $1 \times 10^{19}$/cm$^3$ at room temperature and therefore result in very low values of the Seebeck coefficient, with no enhancement over bulk. Moreover, the mobilities are very low, limited to $\sim 150$cm$^2$/Vs at 300 K. Also attempts trying to dope it to lower values of the carrier density failed. Therefore this approach using the Group I precursor was replaced with one starting with a Group II precursor.

5.4.4 Samples PC4A052 and PC4A083

The doping level of the samples discussed so far was found to be rather uncontrollable, primarily due to the Group I alkali precursor that was used in the synthesis of the nanoparticles. This automatically dopes the samples p-type leading to unpredictable amounts of doping seen, for instance, in samples PC4A07 and PC4A10. To counter this problem, a Group II precursor was later used. This, being of the same valency as Pb and the chalcogenides, would not dope the material. We studied two samples made using this precursor. The first sample with no deliberate doping is
Figure 5.7: Galvanomagnetic and thermomagnetic data of samples PC4A07 (○) and PC4A10 (+).

Figure 5.8: Carrier density and mobility of samples PC4A07 (○) and PC4A10 (+).
called PC4A052, and the second one doped with 0.3% Na is designated PC4A083. The results of the measurements are shown in Figure 5.9. As the two samples are made using the same conditions with PC4A083 being different only due to the doping and annealing, it is helpful to compare their properties side-by-side.

As expected, the doped sample shows much lower resistivity values (about 22 mΩ-cm, vis-à-vis 800 mΩ-cm of the undoped one, at room temperature). The excitation of intrinsic carriers will be seen if the carrier density is low to begin with ($< 10^{18}/\text{cm}^3$) which indeed is the case here. The Hall coefficient is positive in the entire range shown for the doped sample, whereas in the undoped sample, it is positive at 80 K, but decreases with temperature and finally becomes negative at around 360 K. In the doped sample, the Hall stays flat in the range 180 K - 370 K, i.e., the hole density is nearly constant in this range (at $6 \times 10^{17}/\text{cm}^3$), after an initial dip possibly due to release of carrier from a trap that gets activated at 100 K. This is an order of magnitude lower than the predicted value of about $4 \times 10^{18}/\text{cm}^3$ based on the amount of Na$_2$Te added to the powder, implying that very little of the Na dopant has stayed in the sample. The Hall coefficient then starts to decrease after 370 K showing that there is excitation of secondary carriers (electrons), which should lead to a decrease in the Seebeck coefficient also. Thus, the sample has absorbed very little Na dopant. Therefore to dope to the desired level, the amount of dopant to be added is much higher than what is determined theoretically assuming a 100% doping efficiency. Sample 052 has a bipolar conduction at all temperatures, and therefore it is not possible to calculate its density and mobility assuming single carrier conduction. As the magnetoresistance of the sample was found to be very small (due to small mobility), and we were unable to calculated the properties of the undoped sample.
Figure 5.9: Galvanomagnetic and thermomagnetic data of samples PC4A052 (⋄) and PC4A083 (+) shown in the first four plots. The last two show the mobility and carrier density of the sample PC4A083 calculated assuming single-band conduction. This assumption is not valid in treating the sample PC4A052 due to the significant presence of minority electrons at all temperatures.
Figure 5.10: Pisarenko plot of the Seebeck coefficient of the different samples vs. carrier density at 300 K. The curve represents the baseline case of bulk PbTe.

The mobility of the sample 083 at room temperature ($\sim 500 \text{ cm}^2/\text{Vs}$) is found to be considerably higher than that of any other sample measured previously. Thus, sample 083 if appropriately doped is expected to result in a sample with a high $ZT$, comparable to or even higher than that of bulk PbTe.

### 5.5 Seebeck vs. carrier density

The room temperature Seebeck coefficient of the the samples at their carrier density, vs. that of bulk PbTe is shown in Figure 5.10. No significant increase in the Seebeck coefficient over that of the bulk was observed for any of the samples. This is probably due to the fact that the quantum dot size is not uniform, implying that the discretization of the energy levels is not complete and/or the size itself is large. Hence, new methods to make nanoparticles more uniform in size need to be developed.
Figure 5.11: Total thermal conductivity of the samples PC4A05 (⋄) and PC1B01 (+) measured by flash laser diffusivity method. The thermal conductivity is lower than that of an alloy of equivalent composition, $\kappa \approx 1.5$ W/mK at room temperature.

5.6 Mobility vs. thermal conductivity

The total thermal conductivity of the samples were measured using laser diffusivity method at TPRL. Samples prepared using conditions similar to those discussed here show a $\kappa$ of about 1 W/mK to 1.2 W/mK, which represents a reduction of the thermal conductivity by a factor of at least 2. This is lower than the lattice thermal conductivity of an alloy of PbTe-PbSe of the same composition [31], which is 1.5 W/mK. Thus nanostructuring of the composite indeed is helpful in scattering of the acoustic phonons leading to a reduction in the thermal conductivity. However, the $\mu$ reduction is much higher than that of $\kappa$ leading to a net decrease of the $\mu/\kappa$ ratio.
5.7 Conclusion

We made nanocomposites of PbTe and PbSe from nanoparticles with a core-shell structure and doped to different carrier densities, with the objective of enhancing the figure of merit above that of the bulk material. The nanocomposites exhibit a low lattice thermal conductivity value of about 1 W/mK at room temperature (which is lower than that of an alloy of the same composition) presumably driven by the enhanced scattering of the acoustic phonons by the nanostructure. However, this gain in the thermal conductivity reduction comes at the cost of the carrier mobility, which was determined to be between 50 and 200 cm$^2$/Vs for most samples, much lower than a target value of at least 400 cm$^2$/Vs. Moreover, the Seebeck coefficient of the samples was found to be not much enhanced as compared to bulk PbTe as expected, implying that no quantum confinement effects were at operating in the samples. This is possibly due to the rather large size of the core particles (∼20 nm), and a wide distribution in the size of the nanoparticles, that would nullify any discretization in the energy levels in each nanoparticle. This, coupled with the low mobility, limits the power factor to about $4 \times 10^{-4}$ W/mK$^2$ at room temperature.

It is observed that the properties (esp. resistivity and Hall coefficients) of the various samples do not show a monotonic dependence on the temperature. This leads to the conclusion that there may be residual impurities present in the nanoparticles from the chemicals used for their synthesis that may act as charge carrier traps and release carriers with certain activation energies.

The sample PC4A083, prepared with a precursor that does not dope the nanoparticles, with additional doping to about $5 \times 10^{17}$/cm$^3$ exhibits the highest mobility of all samples in the temperature range studied here, and also the highest
powerfactor at room temperature. Based on these results, we conclude that further
development should be made starting with the method used for making this sample
as the cue. Given the high mobility and low thermal conductivity of this sample, it is
expected that an enhanced figure of merit than bulk can be attained with this sample
if it is optimally doped.
BIBLIOGRAPHY


