Two Thermoelectric Materials:
Thermoelectric Properties of SnTe-SnSe and Synthesis of Skutterudite Na$_{1+x}$Fe$_4$P$_{12}$

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Abstract

This thesis examines two different types of thermoelectric materials, compounds that can convert heat energy into electrical energy. First, Stevens et al. synthesized a two-phase SnTe-SnSe system and analyzed its thermoelectric properties. It was determined that the two-phase nature of the system contributed to a reduced thermal conductivity and to enhanced thermoelectric performance over that of one-phase SnTe. Second, Liu et al. studied the effects of heating time and temperature on the synthesis of Na$_{1+x}$Fe$_4$P$_{12}$, a filled skutterudite. X-ray diffraction experiments revealed that the reaction conditions affect the directional growth of crystalline ‘whiskers.’ The x-ray spectra also gave insight into the possible reaction scheme for the formation of the crystal.

Introduction

As the world energy crisis intensifies, technologies that operate efficiently and with little to no CO$_2$ emissions are becoming increasingly important. Thermoelectric (TE) materials, solid state materials that convert heat energy to electricity and vice versa, address both of these issues. They are capable of scavenging and converting waste heat produced from other power generation methods. These materials have been utilized in military imaging systems for heat-seeking missiles and night-vision, medical instruments, car seat temperature regulators, and deep space NASA probes.\textsuperscript{1-3}

This thesis will present two topics that will help readers to further understand TE materials. First, the TE properties of the bulk material SnTe-SnSe will be examined. Then, the thesis will investigate the synthesis and crystal structure of another type of TE material, the skutterudite Na$_{1+x}$Fe$_4$P$_{12}$. 
Thermoelectric Properties and SnTe-SnSe

TE materials are capable of energy conversion by the Seebeck effect, where a temperature gradient in a material induces a voltage according to Equation 1.

\[ S = \frac{\Delta V}{\Delta T} \]  

Eq. 1

where \( S \) is the Seebeck coefficient, \( \Delta V \) is voltage, and \( \Delta T \) is the temperature difference across the material.

Most TE materials are semiconductors with an excess of one type of charge carrier, either negative electrons or positive holes. In n-type materials, electrons are excited from the valance band to the conduction band. In p-type materials, positive holes are excited from the valance band to the conduction band (Figure 1).

![Band diagram and the electron-hole distribution in semiconductors](image)

Figure 1. N- and P-type semiconductors. Excess electrons in n-type materials are excited to the conduction band and allowed to move through the material. In p-type materials, positive holes are excited to the conduction band.

When one side of a material is hotter than the other side, excess charge carriers move to the colder side. This movement creates a charge-buildup and induces a voltage. By placing both n- and p-type TE materials thermally in parallel and electrically in series as shown in Figure 2, that voltage can be used to generate a current.
Figure 2. TE power generation. A temperature gradient causes charge buildup and an induced voltage that can generate a current.

TE performance depends on both the temperature gradient and the figure of merit, $ZT$ (Equation 2).

$$ZT = \frac{S^2 \sigma T}{\kappa_{\text{tot}}},$$

where $\sigma$ is electrical conductivity, $T$ is temperature, and $\kappa_{\text{tot}}$ is total thermal conductivity of the material. $\kappa_{\text{tot}}$ is a combination of the thermal energy transported by charge carriers ($\kappa_{\text{el}}$) and the lattice thermal energy transported by quantum particles called phonons ($\kappa_{\text{latt}}$). The electrical transport $S^2 \sigma$ term is called the power factor.$^3$

A high $ZT$ can be obtained by increasing the power factor and decreasing the thermal conductivity. However, optimizing these properties can often be difficult because all of the properties except $\kappa_{\text{latt}}$ depend on the electronic structure of the material and are thus coupled. The $S$ and $\sigma$ variables are inversely coupled (so an increase in $\sigma$ will result in a decrease in $S$ and vice versa). To understand this coupling, it is helpful to examine the definition of electrical conductivity. Electrical conductivity is the inverse of resistivity. By examining the relationship between resistivity and voltage (Equation 3), it is possible to see the reason behind this coupling.

$$\Delta V = IR$$

Eq. 3
ΔV is voltage, I is current, and R is resistivity. As electrical conductivity increases, resistivity decreases by their inverse relationship. When resistivity decreases, ΔV must also decrease by Equation 3. The definition of the Seebeck coefficient (Equation 1) shows that if ΔV decreases, so does S.

Another pair of parameters is coupled: σ and κ_{el}. These properties are coupled directly (if one increases, the other does as well). High electrical conductivity means there are many charge carriers moving through the lattice. Each of these charge carriers brings with it a small amount of heat, which contributes to κ_{el}^{2,3}

Because κ_{latt} can be manipulated independently, much research has focused on reducing it through nanostructuring. Phonons, the heat-carrying quantum particles that contribute to κ_{latt}, have a range of wavelengths depending on temperature, but they are often on the order of about 1-100 nm.^{4} The wavelengths of electrons are generally smaller at the same temperatures so nanoscale interfaces inside the materials scatter phonons and decrease κ_{latt} without affecting electrical conductivity by scattering electrons.^{3}

To achieve the highest ZT, nanoscale inclusions should be incorporated into a bulk material that already presents good TE properties. Compounds made of metals and Group 16 elements (a class known as metal chalcogenides) have good TE properties in many cases. For example, PbTe, a material that has been proposed for commercial applications, has a ZT of 0.8 at 700 K.\(^5\) SnTe is another type of metal chalcogenide; however, its high thermal conductivity results in a relatively low ZT. Stevens et al. incorporated a SnSe second phase into SnTe to form SnTe-SnSe. It was suspected that this change would lower κ_{latt} because the second phase would introduce nanoscale interfaces and scatter phonons. The scattering would prevent heat from
diffusing evenly through the material and destroying the temperature gradient necessary for a voltage.

Another type of TE material: the skutterudite Na$_{1+x}$Fe$_4$P$_{12}$.

Some crystal structures present inherently good TE properties. Skutterudites have one such structure. These compounds feature a simple cubic space group where three of every four cubes contain a four-membered pnictide ring ('pnictogens' are elements in Group 15 of the periodic table). A skutterudite chemical formula is generally given as AB$_3$ where A can be Co, Ir, Fe, or Rh and B is As, P, or Sb. The A element makes up the simple cubic structure and the B element makes up the pnictide ring. The void that does not contain a pnictide ring can be filled with another atom (in many cases an alkali metal) to form a filled skutterudite. An AB$_3$ filled skutterudite is shown in Figure 3. The chemical formula for the space group shown is calculated in Equation 4.

\[
A = 8 \times \left( \frac{1}{8} \right) + 12 \times \left( \frac{1}{4} \right) + 2 \times \left( \frac{1}{2} \right) + 1 = 8 \quad B = 24 \text{ (totally enclosed atoms)} \quad \text{Eq. 4}
\]

\[
A_8B_{24} = \text{Empirical Formula AB}_3
\]

Figure 3. Filled skutterudite with AB$_3$ structure. A atoms are shown in red while B atoms are shown in blue. The yellow spheres represent filler atoms such as La or Ce.
Alkaline-filled skutterudites based on the FeP$_3$ structure have been difficult to synthesize by conventional methods. In 2001, Liu and colleagues presented a new hydrothermal synthesis method for Na$_{1+x}$Fe$_4$P$_{12}$ that overcame the difficulties of the previous method. In Liu’s reaction, hot NaOH, white phosphorus, and FeCl$_3$·H$_2$O were added to deionized water in an autoclave. The reaction mixture underwent several different heat treatments, each of which returned at least some yield of Na$_{1-x}$Fe$_4$P$_{12}$ as shown in Equation 5.\textsuperscript{6}

\[
\text{NaOH} + 3\text{P}_4 + 4\text{FeCl}_3 \rightarrow \text{Na}_{1-x}\text{Fe}_4\text{P}_{12} + \text{others}
\]  
\text{Eq. 5}

Results

The aim of this paper is to investigate two different TE materials: two-phase metal chalcogenides and skutterudites. Specifically, it examines the TE properties of SnTe combined with SnSe and the synthesis and crystal structure of the skutterudite Na$_{1+x}$Fe$_4$P$_{12}$.

\textit{Thermoelectric Properties of SnTe-SnSe}

In hopes of decreasing thermal conductivity in SnTe, Stevens et al. incorporated a SnSe second phase into bulk SnTe. To synthesize the two-phase material SnTe-SnSe, solid SnTe and SnSe binaries were combined and heated under vacuum to 970°C to allow mixing of the liquid phases. Only certain concentrations of SnSe will result in a two-phase system. These concentrations can be found by examining the phase diagram for the material. The ternary phase diagram for Se-Sn-Te is shown in Figure 4. The atomic percent of Te is shown on the x-axis and temperature is shown on the y-axis. In the white portions of the diagram, the system will form two immiscible phases while in the blue portions it will form one homogenous phase. Because the concentration of SnSe will be varied, it is helpful to look at the x-axis of the phase diagram.
backwards, starting at the right with 0 atomic percent Se and moving towards 50 atomic percent Se. To find the concentration of SnSe, multiply the atomic percent of Se by two (this adjustment accounts for the Sn in SnSe). From this standpoint, SnTe and SnSe will form two immiscible phases at SnSe concentrations of 30 to 75%. Samples of 20, 30, and 40% SnSe were synthesized to target the areas around this two-phase portion of the phase diagram.

Figure 4. The ternary phase diagram of Se-Sn-Te. The blue region shows temperatures and SnSe concentrations that will yield a solid solution (one phase) while the white indicates conditions for a distinctly two-phase system. Samples at 20, 30, and 40% SnSe were made.

Before any conclusions could be drawn about the TE benefits or disadvantages of a two-phase system, the presence of good phase-separation had to be confirmed. Phase separation can be determined through powder x-ray diffraction (PXRD), an x-ray scattering technique that gives insight into the crystal structure of a given sample. Each material has a unique x-ray spectrum, many of which are available through the literature. SnTe and SnSe have significantly different
spectra, so if the SnTe-SnSe material is two-phase, peaks from each crystal structure should be visible. PXRD spectra for 20, 30, and 40% SnTe-SnSe samples are shown in Figure 5. The intensity of a peak shows the relative abundance of the corresponding crystal structure. The 2θ values along the x-axis are related to the angle of incidence for the x-rays during the PXRD experiment. A peak’s location along the x-axis is characteristic of a specific crystal structure.

Figure 5. PXRD spectra for SnTe-SnSe 20, 30, and 40% samples. These spectra show that as the SnSe concentration is increased, peaks corresponding to the SnSe crystal structure become more prominent (* peaks in inset). The presence of distinct SnTe and SnSe peaks confirms the presence of two phases at 30 and 40% SnSe, which is consistent with the ternary phase diagram.

Nearly every peak for the 20% SnSe sample can be indexed according to cubic SnTe, which makes sense because that sample lies in the solid-solution portion of the phase diagram. Instead of two separate phases, Se atoms insert themselves into the cubic SnTe lattice by
replacing Te. As more SnSe is added and the composition moves to the two-phase portion of the phase diagram, separate peaks begin to emerge (Figure 5 inset). The SnSe peaks shown indicate a second phase with an orthorhombic crystal structure alongside the cubic SnTe structure (shown in Figure 6).

Figure 6. Crystal structures of SnTe and SnSe. SnTe has a face-centered cubic space group where Sn occupies the red cation position and Te occupies the blue anion position (a). SnSe has an orthorhombic space group (b). In the solid solution portion of the phase diagram, Se atoms are inserted into the SnTe cubic lattice by replacing Sn. In the two-phase portion of the phase diagram, each crystal structure is distinctly present.

Thermal and electrical transport properties were measured for each sample at temperatures from 300 to 700 K (Figure 7). The solid-solution SnTe-SnSe 20% sample shows a high power factor and low total thermal conductivity, leading to a ZT of 0.45 at 700 K. While not high enough for commercial applications, this ZT is high enough to attempt optimization of the material. Another interesting feature is the very low $\kappa_{\text{tot}}$ for each of the samples (e.g. 1.6 W/mK at 700 K for the 20% sample). The $\kappa_{\text{tot}}$ of SnTe alone is 7.9 W/mK at 700 K. These significant decreases in thermal conductivity could lead to higher ZT values with further optimization. Other transport properties will be reviewed in the discussion section of the paper.
Figure 7. Electrical and thermal transport properties for SnTe-SnSe 20, 30, and 40% samples.

The 20% sample exhibits a ZT of 0.45 at 700 K, which is high enough to consider optimization of the material. Of note are the low $\kappa_{\text{tot}}$ values for samples of each concentration (down to 1.6 W/mK at 700 K for the 40% sample).
Synthesis and characterization of $Na_{1+x}Fe_4P_{12}$

Skutterudites such as $Na_{1+x}Fe_4P_{12}$ are another class of materials with good TE properties. Because of its interesting crystal structure, the synthesis and characterization of this material will be discussed here as opposed to its TE properties. Liu et al. tested the effects of heating temperature, heating time, and reagent ratios during the synthesis of $Na_{1+x}Fe_4P_{12}$. FeCl$_3$·6H$_2$O, NaOH, and white phosphorus were heated in an autoclave according to different reaction conditions (shown in Table 1) to form the $Na_{1+x}Fe_4P_{12}$ product.\(^6\)

Table 1. Reaction conditions for $Na_{1+x}Fe_4P_{12}$ synthesis

<table>
<thead>
<tr>
<th>Setting</th>
<th>FeCl$_3$·6H$_2$O (g)</th>
<th>NaOH (g)</th>
<th>P$_4$ (g)</th>
<th>Heating Temp (°C)</th>
<th>Heating Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6</td>
<td>1</td>
<td>1</td>
<td>200</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
<td>1</td>
<td>1</td>
<td>200</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>0.6</td>
<td>1</td>
<td>1</td>
<td>200</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>0.6</td>
<td>1</td>
<td>1</td>
<td>210</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>0.6</td>
<td>1</td>
<td>1</td>
<td>220</td>
<td>24</td>
</tr>
<tr>
<td>6</td>
<td>0.6</td>
<td>1</td>
<td>1</td>
<td>230</td>
<td>24</td>
</tr>
<tr>
<td>7</td>
<td>0.6</td>
<td>1</td>
<td>1</td>
<td>240</td>
<td>24</td>
</tr>
<tr>
<td>8</td>
<td>0.2</td>
<td>1</td>
<td>1</td>
<td>200</td>
<td>24</td>
</tr>
<tr>
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<td>0.6</td>
<td>1</td>
<td>1</td>
<td>200</td>
<td>24</td>
</tr>
<tr>
<td>10</td>
<td>1.0</td>
<td>1</td>
<td>1</td>
<td>200</td>
<td>24</td>
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<tr>
<td>11</td>
<td>1.2</td>
<td>1</td>
<td>1</td>
<td>200</td>
<td>24</td>
</tr>
</tbody>
</table>

In the first three settings, the effects of heating time were tested as reagent ratios and heating temperatures were kept constant. Settings 4-7 vary heating temperature while keeping other variables constant. Finally, settings 8-11 vary the ratio of FeCl$_3$·6H$_2$O to phosphorus while heating time and temperature are kept constant.

After heat treatment, the products were washed twice: first with HCl to remove excess NaOH and second with CS$_2$ to remove excess phosphorus. The powders were then analyzed by PXRD.\(^6\) X-ray spectra from the products for different reaction conditions are shown in Figure 8. The column on the left compares reaction temperatures while the column on the right compares FeCl$_3$·6H$_2$O/phosphorus ratios.
Figure 8. PXRD patterns resulting from different reaction conditions. The left column shows reaction temperatures of (a) 200°C, (b) 210°C, (c) 220°C, (d) 230°C, and (e) 240°C for 24 hours each. The right column shows FeCl₃·6H₂O/phosphorus ratios of (a) 0.2/1, (b) 0.6/1, (c) 1.0/1,(d) 1.2/1. The numbers in parentheses are related to the growth of the crystal in a specific direction.
In general, at least six peaks from each spectrum correspond to a LaFe$_4$P$_{12}$ skutterudite structure. Na$_{1+x}$Fe$_4$P$_{12}$ has not been synthesized before and thus does not have a literature spectrum for comparison, but it should have a nearly identical crystal structure to LaFe$_4$P$_{12}$ because the only difference between the two structures is in the filler atom (La or Na). Peaks indicating additional products γ-Fe$_2$O$_3$ and FeP$_4$ are present in each pattern. Other iron-phosphide compounds (such as FeP or FeP$_2$) do not appear in any pattern. Changes in temperature and reagent ratios result in changing peak intensities. For instance, as heating temperature increases (Figure 8 left panel), the (211) skutterudite peak decreases and the (220) skutterudite peak increases, indicating that one direction of crystal growth is favored over the other. In addition, the Fe$_2$O$_3$ peak decreases as heating temperature increases. As the FeCl$_3$·6H$_2$O/phosphorus ratio increases, the peaks for the undesirable products Fe$_2$O$_3$ and FeP$_4$ become more pronounced.  

Both panels of PXRD results confirm that the crystal structure of the Fe$_4$P$_{12}$ is cubic skutterudite as pictured in Figure 3 of the introduction. The lattice parameters of the crystal structure change slightly with temperature, but all fall within the range of $a = 7.768$-7.803 Å. Na atoms do not appear in the PXRD spectra because they are filler atoms not directly incorporated into the crystal lattice. The presence of Na atoms had to be confirmed by elemental analysis, which was performed on the products with an x-ray fluorescence analyzer (Table 2).  

For each reaction condition, a small amount of Na was present in addition to Fe and P. Free Na$^+$ ions would have been washed away by the HCl and water washes, which means that the Na must be trapped into the skutterudite voids, making it a filled skutterudite.
Table 2. Elemental composition of product powders for 200 and 220°C reaction conditions

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Fe (mass %)</th>
<th>P (mass %)</th>
<th>Na (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 °C, 24 h</td>
<td>56.68</td>
<td>38.89</td>
<td>2.60</td>
</tr>
<tr>
<td>220 °C, 24 h</td>
<td>55.96</td>
<td>40.02</td>
<td>3.51</td>
</tr>
</tbody>
</table>

Figure 9 shows scanning electron microscopy (SEM) images of samples synthesized with different heating temperatures and times. At every reaction condition, the skutterudite crystals form preferentially into rod-like structures called ‘whiskers.’ These images further confirm what the PXRD results showed with changing intensities in the (211) and (220) peaks: the Na$_{1+x}$Fe$_4$P$_{12}$ crystals grow preferentially in one direction. The length and diameter of these whiskers are affected by heating time and temperature.\(^6\)

![SEM images of product powders](image-url)

Figure 9. SEM images of product powders obtained at different reaction conditions. (a) 200°C for 15 h, (b) 200°C for 24 h, (c) 200°C for 40 h, (d) 220°C for 24 h, (e) 240°C for 24 h. Heating time increases from a to b to c while temperature increases from d to b to e.\(^6\)
As the temperature of the reaction increased from 200°C to 240°C, the diameter of the crystals (as measured on the SEM images) increases. When heating temperature is kept constant and heating time is increased, the average length of the whiskers increases.\textsuperscript{6}

**Discussion**

*Thermoelectric properties of SnTe-SnSe*

Stevens et al. hypothesized that if two distinct phases were formed in a SnTe-SnSe material, it would have improved TE properties over SnTe alone. The PXRD shown in Figure 5 proves that for concentrations of 30 and 40% SnSe, a two phase system was formed. The TE properties of this two-phase system improve upon those of SnTe alone in some cases (Figure 7).

The electrical conductivity ($\sigma$) of these SnTe-SnSe samples will be examined first. This value is calculated with Equation 6.

$$\sigma = ne\mu$$

\text{Eq. 6}

where $n$ is the number of charge carriers, $e$ is the fundamental charge of an electron, and $\mu$ is electrical mobility. The electrical conductivity was very high at \(~5000\) S/cm for a SnTe-SnSe 20\% sample (Figure 7a). This high value is probably because of the natural p-type character of the material. According to Gelbstein et al., there is a slight excess of Te at room temperature in a SnTe binary. The extra Te creates cation vacancies and provides excess holes which contribute to a high electrical conductivity by increasing $n$.\textsuperscript{8}

As the concentration of SnSe increased, the electrical conductivity decreased significantly (from \(5000\) S/cm at 20\% SnSe to \(900\) S/cm at 40\% SnSe, Figure 7a). This decrease could either result from a decrease in charge carriers ($n$) or a lower electrical mobility ($\mu$). The Seebeck coefficient depends on $n$. Because it stays nearly constant for each SnSe concentration,
it is likely that \( n \) remains constant and \( \mu \) changes. It was shown previously that as the SnSe concentration increases, the material becomes more of a two-phase system. This decrease in electrical mobility as a result of larger SnSe concentrations makes sense because electrons traveling through the lattice will encounter two distinct crystal structures (cubic and orthorhombic). The interfaces between these crystal structures are not always completely coherent, so electrons traveling through the lattice might encounter cracks and be unable to continue along their original path.

The highest Seebeck coefficient obtained for these samples was 120 \( \mu V/K \) at 700 K for the 20\% sample (Figure 7b). In general, good TE materials have a Seebeck coefficient of at least 150 to 250 \( \mu V/K \).\(^2\) Therefore, this material could still be significantly improved, not only by decreasing the thermal conductivity but by increasing the Seebeck coefficient. A maximum Seebeck coefficient can be obtained through doping studies. As stated in the introduction, the Seebeck coefficient and electrical conductivity are inversely coupled. In order to get the best TE properties, doping must be used to find the optimal compromise between the two properties. In this case, it is likely that decreasing the number of holes (positive charge carriers) will increase the Seebeck coefficient. The number of holes could be decreased by adding n-type dopants, perhaps a material like SnI\(_2\) (the extra electrons will cancel out some of the holes).

Thermal conductivity is especially interesting in this material because for every concentration of SnSe, a significant decrease compared to SnTe alone was achieved (Figure 7d). SnTe has a \( \kappa_{\text{tot}} \) of 7.9 W/mK at 700 K.\(^8\) The lowest \( \kappa_{\text{tot}} \) obtained for the SnTe-SnSe samples was \(~1.4\) W/mK at 700 K for the SnTe-SnSe 40\% sample, an 82\% decrease.
This significant decrease in thermal conductivity leads to a ZT of 0.4 at 700 K for the SnTe-SnSe 20% sample (Figure 7f). Although not high enough for commercial applications, this material shows promise. The heating time, temperature, mixing strategies and cooling times could all be varied for optimization of this material. Dopants could also be added to maximize the electrical conductivity and Seebeck coefficients.

It is interesting to note that a negative \( \kappa_{\text{latt}} \) value was calculated for the SnTe-SnSe 20% sample (Figure 7e). This result does not imply that zero heat is traveling through the lattice, but rather it is the result of the way \( \kappa_{\text{latt}} \) is calculated. Total thermal conductivity results from the combination of thermal transport by charge carriers (\( \kappa_{\text{el}} \)) and thermal transport by phonons through the crystal lattice (\( \kappa_{\text{latt}} \)). \( \kappa_{\text{tot}} \) can be measured directly while \( \kappa_{\text{el}} \) and \( \kappa_{\text{latt}} \) are calculated. \( \kappa_{\text{el}} \) can be calculated with the Wiedemann-Franz Law (Equation 7).

\[
\kappa_{\text{el}} = L_0 \sigma T \tag{Eq. 7}
\]

where \( L_0 = 2.45 \times 10^{-8} \text{J}^2\text{K}^{-2}\text{C}^{-2} \) for free electrons. \( \kappa_{\text{el}} \) is then subtracted from \( \kappa_{\text{tot}} \) to obtain \( \kappa_{\text{latt}} \). \( L_0 \) is a constant known as the Lorenz factor, but depending on the charge carrier concentration it can vary up to 20\%. Because \( \kappa_{\text{el}} \) can have significant error and \( \kappa_{\text{latt}} \) is calculated with \( \kappa_{\text{el}} \), this sometimes results in inaccurate \( \kappa_{\text{latt}} \) values. The conductivity relative to other samples of the same carrier concentration should still hold true, so qualitative conclusions can still be drawn from these data.

**Synthesis and Characterization of Thermoelectric Material \( \text{Na}_{1+x}\text{Fe}_4\text{P}_{12} \)**

Liu et al. reacted NaOH, white phosphorus, and FeCl\(_3\)·H\(_2\)O to form the filled skutterudite, \( \text{Na}_{1+x}\text{Fe}_4\text{P}_{12} \). All reactants were mixed in distilled water and heated simultaneously, but it is likely that more than one step occurred during the reaction. Both PXRD analysis of the
products and logic concerning the intermediates that have to be formed give insight into the steps of this reaction.

Although no unreacted Fe(OH)\(_3\) was present in the product mixture, the authors of this article suspect that FeCl\(_3\) reacts with NaOH to form Fe(OH)\(_3\) in the first step of this reaction as shown in Equation 8.

\[
\text{FeCl}_3(s) + 3\text{NaOH} \rightarrow \text{Fe(OH)}_3 + 3\text{Na}^+(aq) + 3\text{Cl}^-(aq) \quad \text{Eq. 8}
\]

The iron remains in the +3 oxidation state throughout this portion of the reaction, which is a ligand transfer. Fe(OH)\(_3\) is insoluble in water and participates in further reactions while Na\(^+\) and Cl\(^-\) ions remain in solution.\(^6\)

PXRD analysis of the products shows a significant presence of \(\gamma\)-Fe\(_2\)O\(_3\), more commonly known as rust. \(\gamma\)-Fe\(_2\)O\(_3\) can be formed when Fe(OH)\(_3\) undergoes a dehydration reaction at high temperatures (Equation 9).

\[
2\text{Fe(OH)}_3 \rightarrow 3\text{H}_2\text{O} + \text{Fe}_2\text{O}_3 \quad \text{Eq. 9}
\]

Simultaneous to those reactions, white phosphorus (P\(_4\)) reacts with NaOH and water to form hydrogen phosphide (PH\(_3\)) and NaH\(_2\)PO\(_2\). This reaction is known as a disproportionation because the phosphorus is simultaneously reduced and oxidized to form two different products. It starts in the 0 oxidation state and goes to -3 in PH\(_3\) and +1 in NaH\(_2\)PO\(_4\). The half reactions for this reduction/oxidation reaction are shown in Equations 10 and 11. The Na\(^+\) counter-ions have been omitted because they do not participate in the reaction.

\[
12 \text{e}^- + P_4 + 12\text{H}_3\text{O}^+ \rightarrow 4\text{PH}_3 + 12\text{H}_2\text{O} \quad \text{Eq. 10}
\]

\[
3P_4 + 48\text{H}_2\text{O} \rightarrow 4\text{PH}_3 + 12\text{H}_2\text{PO}_2^- + 24\text{H}_3\text{O}^+ + 12 \text{e}^- \quad \text{Eq. 11}
\]
So under acidic conditions, the balanced reaction is shown in Equation 12.

$$4P_4 + 36H_2O \rightarrow 4PH_3 + 12H_2PO_2^- + 12H_3O^+$$  \hspace{1cm} \text{Eq. 12}

Under basic conditions, the reaction occurs as in Equation 13.

$$4P_4 + 12 \ H_2O + 12OH^- \rightarrow 4PH_3 + 12H_2PO_2^-$$  \hspace{1cm} \text{Eq. 13}

Simplifying and returning the Na$^+$ ions yields Equation 14.

$$P_4 + 3H_2O + 3NaOH \rightarrow PH_3 + 3NaH_2PO_2$$  \hspace{1cm} \text{Eq. 14}

The hydrogen phosphide with its low phosphorus oxidation state acts as a reducing agent in the next step, reducing Fe(III) to Fe(0). The half and full reduction/oxidation reactions are shown in Equations 15-17.

$$PH_3 + 9H_2O \rightarrow H_3PO_3 + 6H_3O^+ + 6e^-$$  \hspace{1cm} \text{Eq. 15}

$$6e^- + 2Fe(OH)_3 + 6H_3O^+ \rightarrow 2Fe + 12H_2O$$  \hspace{1cm} \text{Eq. 16}

$$PH_3 + 2Fe(OH)_3 \rightarrow 2Fe + 3H_2O + H_3PO_3$$  \hspace{1cm} \text{Eq. 17}

Not all of the PH$_3$ reacts with the Fe(III), however. Some of it decomposes at high temperature to form gaseous phosphorus and hydrogen (Equation 18). P is oxidized from the -3 oxidation state to the 0 oxidation state. H is reduced from a +1 oxidation state to a 0 oxidation state in H$_2$.

$$PH_3 \rightarrow P + 3/2H_2$$  \hspace{1cm} \text{Eq. 18}

Herms and colleagues report that phosphorus gas is mainly composed of P$_4$ with a small amount of P$_2$. This P$_4$ is necessary in the next step where it reacts with Fe(0) to form the skutterudite of interest, Fe$_4$P$_{12}$ (Equation 19).

$$4Fe + 3P_4 \rightarrow Fe_4P_{12}$$  \hspace{1cm} \text{Eq. 19}

The percent composition of the product powders was determined by x-ray fluorescence analysis. As shown in Table 2, there was a small percentage of Na present in all the product
powders. Because the products were washed thoroughly with aqueous HCl, any left over Na in the powders must be part of the crystal structure as opposed to being a free ion. The authors suggest, therefore, that the product is a filled skutterudite, Na$_{1+x}$Fe$_4$P$_{12}$ where at least one out of every four cubes in the lattice is filled with a Na$^{+}$ ion.$^6$

**Conclusion**

TE materials are becoming more important in many applications and will play a role in the world’s energy solution. Many materials present TE properties, including metal chalcogenides like SnTe-SnSe and skutterudites like Na$_{1+x}$Fe$_4$P$_{12}$. The two-phase material SnTe-SnSe had TE properties that showed promise. Further optimization studies through heat treatment and doping should be pursued to increase its ZT. The skutterudite Na$_{1+x}$Fe$_4$P$_{12}$ was successfully synthesized with a hydrothermal reduction method. It was found that heat treatment affected the direction of crystal growth and a mechanism for the multi-step synthesis reaction was proposed. A better understanding of this specific crystal structure may shed light on the class of compounds in general, which should help when designing high-efficiency skutterudite TE materials in the future.
References


