Solution synthesis of nanostructured transition metal chalcogenides and their electrical and thermal properties

Wei Zheng
Iowa State University

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Solution synthesis of nanostructured transition metal chalcogenides and their electrical and thermal properties

by

Wei Zheng

A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

Program of Study Committee:
Yue Wu, Major Professor
   Xinwei Wang
   Zengyi Shao
   Jonathan Claussen
   Matthew G. Panthani

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University

Ames, Iowa

2019

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DEDICATION

To my parents

Wenping Zheng & Guiqin Xu
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<td>PCMs</td>
<td>Phase Change Materials</td>
</tr>
<tr>
<td>TES</td>
<td>Thermal Energy Storage</td>
</tr>
<tr>
<td>SH</td>
<td>Sensible Heat</td>
</tr>
<tr>
<td>LH</td>
<td>Latent Heat</td>
</tr>
<tr>
<td>RAM</td>
<td>Random Access Memory</td>
</tr>
<tr>
<td>PCRAM</td>
<td>Phase Change Random Access Memory</td>
</tr>
<tr>
<td>MCE</td>
<td>Magnetocaloric Effect</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium hydroxide</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene Glycol</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
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<tr>
<td>FFT</td>
<td>Fast Fourier Transform</td>
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<tr>
<td>HRTEM</td>
<td>High Resolution TEM</td>
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<tr>
<td>SPS</td>
<td>Spark Plasma Sintering</td>
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<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>EM</td>
<td>Electromagnetic</td>
</tr>
<tr>
<td>EMC</td>
<td>Electromagnetic compatibility</td>
</tr>
<tr>
<td>NHS</td>
<td>Nano-heterostructure</td>
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Firstly, I would like to thank my advisor, Professor Yue Wu, for his continuous guidance and support. I joined his group with no experience in nanomaterials. At the beginning of my research, professor Wu told me every step what I should do in experiments as well as professional writing and presentation. With his detailed guidance especially during the first two years of my graduate studies, I learned how to perform research and present the experiment results. After that, he gave me the freedom to design my own experiments and improved my own creativity and judgement. His insightful discussions and advice helped me to avoid many wrong ways and overcome a lot of obstacles. This thesis can not be finished without professor Wu’s continuous support.

I also want to thank my group members, Dr. Haiyu Fang, Dr. Scott Finefrock, Dr. Yanming Sun, Dr. Haoran Yang, Dr. Enzheng Shi, Dr. Linxiu Dai, Sungbum Hong, Victor Zhu, Bokki Min, Jiayang Wang. As a first-year graduate student, I received training from Dr. Haiyu Fang, Dr. Scott Finefrock, Dr. Yanming Sun. I enjoyed useful discussions during lunch time or spare time with my group members. I spent a really good time working with them.

In addition, I would like to thank my collaborators. Professor Xinwei Wang, Dr. Meng Han, Dr. Bowen Zhu, and Dr. Ridong Wang provided great help in thermal conductivity measurement. Professor Claussen and Bolin Chen helped me to printed thin film thermoelectric samples. Professor Jiming Song and Dr. Yang Bao assisted me to measure electromagnetic absorption parameters for my samples. Dr. Lin Zhou, Dr. Kewe Sun,
and Dr. Tao Ma helped me to take high quality TEM pictures. They filled gaps in my knowledge, and I benefited a lot from their great help.

Finally, I am so grateful to my parents and other family members with their unconditional love and support. I would also like to thank my friends, colleagues, the department faculty and staff for making my time at Iowa State University a wonderful experience.
ABSTRACT

With the development of electronic devices, more electrical units need to squeeze into small packages. As a result, more heat energy will be produced in the same area and thermal management has become more critical issue for the design of electrical devices. One protection method is to integrate thermal switch into electrical device, and it will cut off current when temperature is above the operation temperature range. There are significant gaps that must be overcome before thermal switch can be integrated into electrical device. The performance requirements include low resistance under normal operation to reduce power consumption while turn into high resistance at critical condition to cut off or reduce the current. It also should be self-recoverable after cooling down and have low production cost.

This dissertation first describes a solution-phase synthesis of iron telluride nanostructures with reversible and reproducible switching behavior between p- and n-type conduction. A proof-of-concept thermally triggered p-n diode has been demonstrated. This device has a large electrical conductivity during normal operation which can minimize power consumption. While at high temperature, it will be triggered to a p-n diode with a fast response time to temperature rising. Secondly, a large-scale solution-phase synthesis method to synthesize silver telluride based on tellurium nanowire template has also been developed. Its structural phase transition can be realized by temperature- or electrically-driven method. In addition, the threshold DC voltage is less than 1 V and can result in sharp drop in conductance. Lastly, A new electromagnetic sensor prototype is presented by sintering electromagnetic absorption material and phase change material together. The
electromagnetic absorption material will absorb electromagnetic wave in X band and increase temperature.
CHAPTER 1. INTRODUCTION

1.1 Motivation and Background

Phase change materials are characterized by a unique property that their electronic, thermal, or optical properties can be significantly changed depending upon their atomic arrangement. This property of phase change materials is attractive for applications in electronic switch devices, thermal switches, thermal sensors, chemical sensors, metamaterials, memristive devices, and optical modulators.

1.1.1 Application in thermal energy storage and short circuit protection

Thermal energy storage (TES) is an important aspect for energy management which can be realized by using phase change materials (PCMs) as the source of sensible heat (SH) and latent heat (LH). Solid-solid PCMs usually undergo small volume change and no phase separation during the phase transition, which are favorable for TES materials. With the development of electronic devices, more electrical units need to squeeze into small packages. As a result, thermal management has become more critical issue for the design of electrical devices. PCM-based heat sinks can maintain electronic devices temperature under the critical level.

1.1.2 Application in random access memory

Phase change materials (PCMs) such as GeSbTe can be rapidly switched between amorphous structure and crystalline structure, which makes them a good candidate for rewriteable optical data storage and random-access memory (RAM) devices. In phase change random access memory (PCRAM) devices, the reversible switch between amorphous and crystalline state can be triggered both optically and electrically. This transition is accompanied by a
change in optical, thermal, and electrical properties. A short high laser or current pulse will convert PCMs into amorphous state which is the write state and a long lower laser or current pulse will result in the formation of crystalline phase which is the erase step.

Figure 1-1 Schematic for phase change random access memory (Reprinted with permission from Ref 1. Copyright Nature Materials, 2007)
1.1.3 Application in magnetocaloric effect.

The magnetocaloric effect (MCE) is a phenomenon that the entropy and temperature of a material will be changed due to the variation of magnetic field, which is used to reach low temperatures in a condition of adiabatic demagnetization. Gd$_5$(Si$_2$Ge$_2$) will change from orthorhombic Sm$_5$Ge$_4$-type to a monoclinic Gd$_5$(Si$_2$Ge$_2$) -type structure when subjected to a change in the adiabatic magnetic field. This structure transformation will lead to an extremely large magnetic entropy$^2$. The entropy of an isolated system has a constant value and an increase in magnetic entropy will lead to a decrease in the lattice entropy. Therefore, this magnetocaloric effect can have potential application in refrigeration in the sub-room temperature (~250-290 K).

![Magnetocaloric Effect](image)

Figure 1-2 Magnetocaloric Effect (Reprinted with permission from Ref 2. Copyright Physical Review Letters, 1997)
1.1.4 Application in gas sensor

Single crystal VO$_2$ nanowires have an extremely sharp metal-insulator phase transition and it will responsive to small perturbation in pressure and temperature. Based on this property, the realization of gas sensor using PCMs has been approved$^3$. As shown in figure 3, the joule power (P) is dissipated in three ways: heat transfer to ambient gas, to the metal contacts, and via radiation losses. The joule power will have a linear relationship with gas pressure, which makes it a good candidate for gas sensor.

![Figure 1-3 Gas sensor based on phase change material VO$_2$](Reprinted with permission from Ref 3. Copyright Nano Letters, 2009)

1.1.5 Application in thermoelectric

High performance thermoelectric materials can convert waste heat into electricity without moving parts and release of greenhouse gases. The conversion efficiency can be expressed as thermoelectric figure of merit $zT = S^2\sigma T/\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is electrical conductivity, $T$ is the absolute temperature, and $\kappa$ is the thermal conductivity. A
high zT material should have high Seebeck coefficient and electrical conductivity, while keep low thermal conductivity. In 2012, Liu et al\textsuperscript{4} found phase change materials such as Cu\textsubscript{2}Se could be good candidates for thermoelectric materials. The phase transition step for Cu\textsubscript{2}Se will turned into a liquid-like state, which can inhibit the propagation of transverse waves phonons and directly reduce the phonon mean free path. As a result, phase transition materials can reduce the thermal conductivity directly and improve the thermoelectric figure of merit.

Figure 1.4 Phase change materials in thermoelectric field (Reprinted with permission from Ref 4. Copyright Nature Materials, 2012)
1.2 Research Objectives and Contributions

The main objective of this work is to investigate narrow bandgap phase change semiconductor materials as an integrated, active, and self-recoverable protector to prevent damage in integrated circuits. The performance requirements include:

(1) Low cost, scalable solution-phase synthesis methods to produce phase change materials;

(2) A prototype protection thermal switch based on self-recoverable phase change materials;

(3) Larger electrical conductivity during normal operation and ultrafast response to short circuit protection.

This research work to develop phase change materials for thermal switches and thermal sensors has achieved the following milestones:

(1) A solution-phase synthesis of iron telluride nanostructures with reversible and reproducible switching behavior between p- and n-type conduction is demonstrated by a simple change of temperature. A proof-of-concept thermally triggered p-n diode has been demonstrated. This device has a large electrical conductivity during normal operation which can minimize power consumption. While at high temperature, it will be triggered to a p-n diode with a fast response time to temperature rising.

(2) Development of a large-scale solution-phase synthesis method to synthesize silver telluride based on tellurium nanowire template. [1 1 0] axes is thermodynamic favorable growth direction for silver telluride nanowires and its structural phase transition can be realized by temperature- or electrically-driven method. In addition,
the threshold DC voltage is less than 1 V and can result in sharp drop in conductance. These results indicate the potential application of using silver telluride as a low cost, self-recoverable, and low power consumption nanoscale short circuit protection devices.

(3) A new electromagnetic sensor prototype is presented by sintering electromagnetic absorption material and phase change material together. The electromagnetic absorption material will absorb electromagnetic wave in X band and increase temperature. This rising temperature will drive the phase change and have the potential application in electromagnetic sensor and switch.

1.3 Organization of Dissertation

This dissertation is divided into six chapters. Chapter 1 provide an introduction of applications of phase change materials including in energy storage, short circuit protection, random accessory memory, magnetocaloric effect, gas sensor, and thermoelectric devices. The theory of phase change materials is discussed in Chapter 2. Solution-phase synthesized iron telluride nanostructures with controllable thermally triggered p-type to n-type transition project is presented in Chapter 3. Chapter 4 in this dissertation discusses electrically driven structural phase transition in single Ag₂Te nanowire devices project. Electromagnetic radiation driven phase transition in Ag₂Te-Fe₃O₄ nano-composites and FeTe₂ disks project is presented in Chapter 5. Chapter 6 included my effort to find applications for phase change materials in thermoelectric field.
CHAPTER 2. SWITCHING KINETICS THEORY OF PHASE CHANGE MATERIALS

The driving force for crystallization is the difference Gibbs free energy between the two phases. The first step for crystallization is the crystal nucleation and the second step of crystallization process is the growth of crystalline nuclei to macroscopic size. This chapter starts from the simplest case, which occurs in the interior of the parent phase without a foreign phase. This is homogeneous nucleation (Chapter 2.1). Another crystallization nucleation is heterogeneous nucleation, which is occurred at a foreign substance (Chapter 2.2). Chapter 2.3 will discuss the growth dynamics briefly. Chapter 2.4 will discuss the electrical properties of phase change materials

2.1 Homogeneous nucleation theory.

Figure 2-1 Scheme of the free energy as a function of different phase need copyright
Nucleation refers to the situation when a system (parent phase) is put into a nonequilibrium metastable state\(^5\). The simplest case is vapor-liquid transition. At metastable state, the chemical potential in the bulk liquid \(\mu^l\) is lower than in the bulk vapor chemical potential \(\mu^V\), which makes it thermodynamically favorable to transfer from parent phase (vapor) to daughter phase (liquid). The driving force for this transformation is the difference of chemical potential between metastable state (parent phase) and stable state (daughter phase).

The chemical potential difference \(\Delta \mu\) can be expressed as\(^6\)

\[
\Delta \mu = \mu_g - \mu_l = k_B T \ln S
\]  
(2.1)

where \(k_B\) is Boltzmann constant and \(T\) the temperature. \(S\) is called the supersaturation and can be approximated as\(^7\):

\[
S = \frac{p^V}{p^\text{sat}}
\]  
(2.2)

\(p^\text{sat}\) is saturation vapor pressure when vapor start to transform into liquid and \(p^V\) is the vapor pressure at metastable state. Equation (2.1) indicate that the driving force to nucleation can be pressure or temperature.

In parent phase, atoms collide with each other and forming new phase with statistically numbers. For simplicity, the clusters are assumed spherical and the cluster distribution is given by Boltzmann statistics\(^8,9\):

\[
N^{\text{equ}}(r) = N_0 \cdot \exp \left( - \frac{\Delta G_{\text{cluster}}(r)}{k_B T} \right)
\]  
(2.3)

where \(\Delta G_{\text{cluster}}(r)\) is the reversible work for crystal cluster formation, \(N_0\) the total number of atoms in the liquid and \(N^{\text{equ}}(r)\) the number of clusters of radii \(r\) at equilibrium. \(\Delta G_{\text{cluster}}(r)\) can be expressed as a sum of two contributions\(^10\):
\[ \Delta G_{\text{cluster}}(r) = -\Delta G_{lc,V} \cdot \frac{4}{3} \pi r^3 + \sigma \cdot 4\pi r^2 \] (2.4)

\( \Delta G_{lc,V} \) is the Gibbs free energy difference between the parent and the crystalline phase per unit volume. The second term in above equation results from the creation of an interface between the cluster and the gas. \( \sigma \) is the surface tension and this term is positive and therefore energetically it is not favorable\textsuperscript{11,12}.

As shown in figure 2.2, the curve passes through a maximum, which can be obtained by solving \( \frac{\partial \Delta G_{\text{cluster}}(r)}{\partial r} = 0 \). The maximum occurs because the surface-to-volume ratio is large for small clusters. The position of the maximum is \( r = \frac{2\sigma}{\Delta G_{lc,V}} \) and the height is \( \Delta G_c = \Delta G_{\text{cluster}}(r_c) = \frac{16\pi}{3} \frac{\sigma^3}{(\Delta G_{lc,V})^2} \). The quantity \( r_c \) is called the critical radius, which is on the order
of nanometers. A cluster of radii $r_c$ is called critical cluster and $\Delta G_c(T)$ the critical work for cluster formation. $\Delta G_{\text{cluster}}(r)$ increase for $r < r_c$. Hence, clusters of $r < r_c$ are energetically not favorable and spontaneously decay. However, for $r > r_c$, clusters grow due to a gain in free energy. Therefore, $\Delta G_c$ can be considered an activation barrier against crystallization.

Volmer and Weber$^{13}$ developed the first kinetic model for nucleation (equation 2.3). Their model becomes unphysical for $r > r_c$ (cluster number increase with increasing radius $r$), it was ignored and set to zero. For $r = r_c$,

$$N^{\text{equ}}(r_c) = N_0 \cdot \exp\left(\frac{-\Delta G_c}{k_B T}\right)$$ \hspace{1cm} (2.5)

The nucleation rate $I^{\text{equ}}$ (dimension: $1/m^3s$) is then give by

$$I^{\text{equ}} = S_c \cdot k \cdot N^{\text{equ}}(r_c) = S_c \cdot k \cdot N_0 \cdot \exp\left(\frac{-\Delta G_c}{k_B T}\right)$$ \hspace{1cm} (2.6)

where $k$ is the arrival rate of parent phase atoms to the critical crystalline cluster (number of arrivals per atom on the cluster surface per unit time, dimension: $1/s$). $S_c$ is the number of surface atoms in the critical cluster. The Volmer-Weber model (equation 2.3) assumes that a critical cluster grows to macroscopic size as soon as it becomes post-critical by the addition of one more parent phase atom. Its main deficiency is that it neglects that post-critical clusters ($r > r_c$) can still decay with a certain probability, and that critical cluster ($r = r_c$) grow or shrink with equal probability (since $\left.\frac{\partial \Delta G_{\text{cluster}}(r)}{\partial r}\right|_{r=r_c} = 0$). Becker and Döring$^{14}$ have argued that the true cluster distribution $N^{\text{ss}}(r)$ in steady state does not abruptly fall to zero at $r = r_c$ but takes a value of $N^{\text{ss}}(r_c) = 1/2N^{\text{equ}}(r_c)$ and decreases gradually to zero for large cluster sizes. After a few additional assumptions, Becker and Döring$^{13}$ obtain the following expression for the steady state nucleation rate $I^{\text{ss}}$
\[ I^{ss} = S_c \cdot k \cdot N_0 \cdot \frac{1}{i_c} \cdot \left( \frac{\Delta G_c}{3\pi k_B T} \right)^{\frac{1}{2}} \cdot \exp \left( -\frac{\Delta G_c}{k_B T} \right) \tag{2.7} \]

where \( i_c \) is the number of atoms in the critical cluster. Zeldovich\(^{15,16} \) factor \( I_z \), which only has a weak temperature dependence. As the nucleation rate is far more sensitive to slight changes in \( \Delta G_c \) than to the exact value of the pre-exponential factor, the importance of the Becker and Döring theory is that the kinetic problem has been treated correctly\(^{17} \).

Volmer, Weber, Becker and Döring originally developed their theories for the case of a gaseous parent phase (vapor condensation). For this case, the arrival rate \( k \) is readily obtained by the theory of gases. However, Turnbull and Fisher\(^{18} \) were the first to evaluate the pre-exponential factor in equation (2.7) for crystal nucleation in an undercooled liquid or an amorphous phase. They differentiated between two limiting cases: diffusion-limited and collision-limited crystallization kinetics.

For diffusion-limited crystallization, changes of neighbors and/or coordination number are necessary for crystallization. This usually applies to metallic alloys, ionic materials, covalent materials. The frequency of diffusive jumps \( k \) across the interface per interface atom is according to Turnbull and Fisher

\[ k = \frac{6D}{\lambda^2} \quad (\text{diffusion-limited}) \tag{2.8} \]

where \( D \) is associated with the diffusivity in the liquid or amorphous phase (not in the crystal). \( \lambda = \Omega^{1/3} \) is the average interatomic distance (\( \Omega = \text{atomic volume} \))
For collision-limited crystallization, atomic neighbors generally do not have to change by
diffusive rearrangements upon crystallization. Instead, atomic movement from the liquid to
the crystalline cluster can be accomplished by thermal vibration. Hence, crystallization is
governed by the collision of the atoms. This usually occurs only in pure metals and in van der
Waals bonded materials.

\[ k = \frac{u_{\text{sound}}}{\lambda} \quad (\text{collision} - \text{limited}) \]  

(2.9)

where \( u_{\text{sound}} \) is the sound velocity in the liquid or amorphous phase.

Substituting (2.8) into (2.7):

\[ I_{ss} = S_c \cdot \frac{6D}{\lambda^2} \cdot N_0 \cdot \frac{1}{i_c} \cdot \left( \frac{\Delta G_c}{3\pi k_B T} \right)^{\frac{1}{2}} \cdot \exp \left( -\frac{\Delta G_c}{k_B T} \right) \quad (\text{diffusion} - \text{limited}) \]  

(2.10)

Approximating the diffusivity \( D \) locally with an Arrhenius equation, \( D \propto \exp[-E_D/(k_B T)] \),

where \( E_D = -\frac{\partial \ln D}{\partial [1/(k_B T)]} \) is the (local) activation energy of the diffusivity, gives the (local)
activation energy \( E_{I_{ss}} \) of the steady-state nucleation rate \( I_{ss} \):

\[ E_{I_{ss}} = E_D + \Delta G_c \quad (\text{diffusion} - \text{limited}) \]  

(2.11)

It is often helpful to express \( I_{ss} \) in terms of the liquid shear viscosity \( \eta \), which is easier to
obtain experimentally than the liquid diffusivity \( D \). Using the Stokes-Einstein equation,

\[ \eta D = \frac{k_B T}{3\pi \lambda} \]  

(2.12)

inserting into (2.10)

\[ I_{ss} = S_c \cdot \frac{2k_B T}{\eta \pi \lambda^3} \cdot N_0 \cdot \frac{1}{i_c} \cdot \left( \frac{\Delta G_c}{3\pi k_B T} \right)^{\frac{1}{2}} \cdot \exp \left( -\frac{\Delta G_c}{k_B T} \right) \quad (\text{diffusion} - \text{limited}) \]  

(2.13)
2.2 Heterogeneous Crystal nucleation

Homogeneous nucleation is an intrinsic process. Heterogeneous nucleation is therefore an extrinsic process and can be influenced by the experimental conditions\textsuperscript{17}. The simplest model for heterogeneous nucleation is due to Volmer\textsuperscript{19}. The model is based on the Gibbs model but with a flat substrate, which acts as a heterogeneous nucleation site. The crystalline cluster grows on the flat substrate like a spherical cap of radius $r$. As a function of the wetting angle $\Theta$, the exposed volume fraction $0 \leq f(\Theta) \leq 1$ relative to a sphere of the same radius $r$ is

$$f(\Theta) = \frac{(2 + \cos\Theta)(1 - \cos\Theta)^2}{4}$$  \hfill (2.14)

Equation (2.4) will change to
\[ \Delta G_{\text{cluster}}^\text{het}(r) = -\Delta G_{lc,V} + \frac{4}{3} \pi r^3 f(\Theta) + \sigma_{lc} \cdot 4\pi r^2 \frac{1 - \cos \Theta}{2} + \pi(r \sin \Theta)^2 (\sigma_{cs} - \sigma_{lc}) \] (2.15)

because \( \sigma_{cs} - \sigma_{lc} = -\sigma_{lc} \cos \Theta \), the critical work for heterogeneous cluster formation is then reduced to

\[ \Delta G_c^\text{het} = \Delta G_{\text{cluster}}(r_c) \cdot f(\Theta) = \frac{16\pi}{3} \frac{\sigma^3}{(\Delta G_{lc,V})^2} \cdot f(\Theta) \] (2.16)

The only difference is the lower work for critical formation and the reduced number of parent phase atoms than can act as a nucleation site. If \( \varepsilon \) is the fraction of parent phase atoms in contact with the heterogeneity (usually \( \varepsilon \ll 1 \)), then the steady state nucleation rate for heterogeneous nucleation and diffusion-limited kinetics, \( I_{ss,het} \), is

\[ I_{ss,het} = \varepsilon \cdot S_c \cdot \frac{6D}{\lambda^2} \cdot N_0 \cdot \frac{1}{l_c} \cdot \left( \frac{\Delta G_c^\text{het}}{3\pi k_B T} \right)^{\frac{1}{2}} \cdot \exp \left( -\frac{\Delta G_c^\text{het}}{k_B T} \right) \cdot \frac{1}{m^3 s} \] (2.17)

with a (local) energy of

\[ E_{ps,het} = E_D + \Delta G_c^\text{het} \]

Since \( \Delta G_c^\text{het} < \Delta G_c \) for \( f(\Theta) < 1 \), it follows that \( E_{ps,het} < E_{ss} \). Usually, heterogeneous nucleation rates are observed to be far higher than homogeneous nucleation rates, which implies that \( \Theta \) must be small. Heterogeneous nucleation occurs in addition to homogeneous nucleation but with much higher nucleation rate\(^{20}\). The total nucleation rate is the \( I_{ss,total} = I_{ss,het} + I_{ss,hom} \).

3.3 Kinetics and Steady-State Nucleation Rate

![Figure 2-4 Scheme for kinetics of homogeneous nucleation](image)
2.3 Crystal Growth

Chapter 2.1 and 2.2 describes the formation of crystal clusters. The next step for nucleation theory is that those crystal clusters grow into macroscopic size. There are two possibilities for crystal growth: interface-controlled growth and growth controlled by a long-range diffusion field. For phase change materials, there is no phase separation upon crystallization. The composition of parent phase and crystal cluster are always the same. Therefore, growth is controlled by rearrangement process only and is called interface-controlled. Within the classical nucleation theory, the following assumptions are made:

- The elementary process which changes the size of a nucleus is the attachment to it or loss by it of one molecule
- If a monomer collides a cluster, it sticks to it with probability unity
- There is no correlation between successive events that change the number of particles in a cluster.

The last assumption means that nucleation is a Markov process. Its schematic illustration is presented in figure 2.4. The possible interactions that a cluster of n molecules can have are then

\[ n - 1 \leftrightarrow n \leftrightarrow n + 1 \]

Atoms move from the parent phase to the new cluster by diffusive jumps with the arrival rate \( k \) and are added to the cluster at a rate \( \nu_n^+ \) proportional to the surface atoms \( S_c = 4n^{2/3} \). They need to move over the energy barrier \( \Delta G_c \).

\[ \nu_n^+ = S_c \cdot k \cdot \exp \left( -\frac{\Delta G_c}{k_BT} \right) \]  \hspace{1cm} (2.18)
Similarly, the reverse process of removal atoms from a cluster with \(n+1\) atom is

\[
v_{n+1}^+ = S_c \cdot k \cdot \exp \left( - \frac{\Delta G_{c,n} - \Delta G_{c,n+1}}{k_B T} \right)
\]  

(2.19)

where \(\Delta G_{c,n}\) and \(\Delta G_{c,n+1}\) are the Gibbs free energies of clusters of size \(n\) and \(n+1\). Then the crystal growth velocity \(\mu\) can be written as

\[
\mu = \frac{\partial r}{\partial t} = \frac{\partial r}{\partial n} \frac{\partial n}{\partial t} = \frac{\Omega}{4\pi r^2} \left( v_n^+ - v_{n+1}^+ \right)
\]

(2.20)

and \(\Omega\) is the volume of the atom. Inserting \(\Delta G_{c,n}\) and \(\Delta G_{c,n+1}\), the growth velocity can be

\[
\mu = r_s \cdot \lambda \cdot k \left[ 1 - \exp \left( - \frac{\Delta G_c(T)}{k_B T} \right) \right] \quad T < T_m
\]

(2.21)

where \(\lambda = \Omega^{1/3}\) is the average interatomic distance. For diffusion-limited kinetics, rate constant \(k\) can also be replaced by equation (2.8) or (2.9)

\[
\mu = r_s \cdot \frac{6D}{\lambda} \cdot k \left[ 1 - \exp \left( - \frac{\Delta G_c(T)}{k_B T} \right) \right] = r_s \cdot \frac{2k_B T}{\eta \pi \lambda} \left[ 1 - \exp \left( - \frac{\Delta G_c(T)}{k_B T} \right) \right]
\]

(2.22)

Therefore, the growth velocity is proportional to diffusivity \(D\) or viscosity \(\eta\):

\[
\mu \propto D \propto \frac{1}{\eta}
\]

which implies that the (local) activation energies of the crystal growth velocity \(E_\mu\) and the diffusivity \(E_D\) are equal:

\[
E_\mu = E_D
\]

(2.23)

Inserting (2.23) into (2.11),

\[
E_{\mu}^{ss} - E_\mu = \Delta G_c
\]

which means the activation energies of nucleation rate and growth velocity differ by the critical work for cluster formation.
2.4 Electrical properties of phase change materials

According to quantum theory, the probability of an electron state is defined by Fermi distribution function

\[
f_0(E) = \left[ \exp\left(\frac{E - E_f}{kT}\right) + 1 \right]^{-1}
\]

(2.24)

where \(E_f\) and \(k\) are Fermi level and Boltzmann's constant.

Figure 2-5 Fermi distribution function (solid line) and its first derivative (dotted line). Reprinted with permission from Elsevier: Materials Science and Engineering: R: Reports (Pichanusakorn, P. & Bandaru, P. Nanostructured thermoelectrics. 67, 19-63), copyright 2010.

The Fermi distribution function (in Fig 2.5\(^2\)) shows that the probability is equal to 0 when \((E - E_f) \gg kT\) and that means there is no electron at this energy state and this state is empty.
Equation (2.24) indicates that only the electrons with energy near Fermi level can participate in transport. The total number of electrons\(^{23}\) is given by

\[
n = \int_{0}^{\infty} f_{0}(E)g(E)dE \tag{2.25}
\]

where \(g(E)dE\) is the density of electron state in the energy range between \(E\) and \(E + dE\).

The electric current density can be expressed as\(^{24}\):

\[
i = \mp \int_{0}^{\infty} e\mu f(E)g(E)dE \tag{2.26}
\]

where \(\mu\) is the velocity of the carriers in the \(x\) direction. The minus sign applies for electrons and plus sign apply for holes respectively. To calculate the current density, we first need to find the \(f(E)\). The simplest way is to consider one-direction transport model. The transport will occur only at nonequilibrium condition and \(f(E) = f_{0}(E)\) means equilibrium condition\(^{25}\). Then, equation (2.26) can turn into

\[
i = \mp \int_{0}^{\infty} e\mu [f(E) - f_{0}(E)]g(E)dE \tag{2.27}
\]

From Boltzmann equation, the disturbance of the distribution can be written as

\[
\frac{f(E) - f_{0}(E)}{\tau_{e}} = \mu \frac{\partial f_{0}(E)}{\partial E} \left(\frac{dE_{f}}{dx} + \frac{E - E_{f}}{T} \frac{dT}{dx}\right) \tag{2.28}
\]

\[
g(E)dE = \frac{1}{2\pi^{2}} \left(\frac{2m^{*}}{\hbar^{2}}\right)^{3/2}dE = \frac{4\pi(2m^{*})^{3/2}}{h^{3}}dE \tag{2.29}
\]

For electrical conductivity, assume there is no temperature gradient, \(\frac{dT}{dx} = 0\). The electrical conductivity is equal to the ratio of electrical current density to the electrical field. Inserting
(2.28) and (2.29) into (2.27) and set $\frac{dT}{dx} = 0$, $\mu^2 = 2E/m^*$, and $\tau_e = \tau_0E^r$. Then (2.27) will change into

$$\sigma = \frac{e^2}{T} K_1 \tag{2.30}$$

where

$$K_s = \frac{8\pi}{3} \left( \frac{2}{\hbar^2} \right)^{3/2} (m^*)^{1/2} \tau_0 (s + r + 3/2)(kT)^{s+r+3/2} F_{s+r+1/2} \tag{2.31}$$

$$F_n(\eta) = \int_0^\infty \frac{x^n}{1 + \exp(x - \eta)} dx \tag{2.32}$$

and $\eta$ is the reduced Fermi energy: $\eta = E_f/kT$, $\tau_0$ and $r$ are constants for a given scattering process, $m^*$ is effective mass of electron. Now as shown in (2.30), the electrical conductivity is a function of with $m^*$, $\tau_0$, $r$, and reduced Fermi energy. Solid-solid phase transition usually will lead to structure change and result in different band gap energy. According to equation (2.25), different band gap energy will affect carrier concentration, which will change electrical conductivity ($\sigma = n\mu$). Equation (2.30-2.32) show the insight relationship between electrical conductivity and reduced Fermi energy.

In conclusion, the driving force for phase transformation is the difference of chemical potential between metastable state (parent phase) and stable state (daughter phase). As shown in equation (2.1) and (2.2), the driving force can be temperature or pressure. External perturbation can disturb temperature or pressure will initiate phase transition. This external perturbation can be in the form of thermal$^{26}$, electrical$^{27-29}$, optical$^{30-32}$, magnetic field$^2$, or strain engineering$^{33,34}$. For solid-solid phase change materials, there is no phase separation
upon crystal growth. Therefore, crystal growth step is controlled by interface-controlled. The solid-solid phase transition will change the band gap energy, which will affect the carrier concentration and change the electrical conductivity.
CHAPTER 3. LARGE-SCALE SOLUTION-PHASE SYNTHESIS OF IRON TELLURIDE AND THERMALLY TRIGGERED P-N DIODE BEHAVIOR

This chapter is based on the manuscripts “Large-scale solution-phase synthesis of Iron Telluride and thermally triggered p-n diode behavior” This manuscript is accepted by nanoscale, which is co-authored by Sungbum Hong, Bokki Min, and Yue Wu.

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3.1 Introduction

Materials with switchable physical properties are attracting more interest due to the promising applications such as memories, sensors, and switches. For example, external stimuli such as light irradiation, electric field, temperature, and pressure can induce changes in their electronic, magnetic, optical and mechanical properties. Therefore, the ability to design and control the desired changes under external stimuli is the key prerequisite for the modern functional materials. Transition metal chalcogenides with non-stoichiometric ratios can easily switch their electrical properties from p-type (chalcogenides excess) to n-type (chalcogenides deficiency), which make them a good candidate for functional switching materials.

Recently, numerous transition metal chalcogenides exhibiting switching electronic properties under temperature stimulus have been reported. Tom Nilges et al reported Ag$_{10}$Te$_4$Br$_3$ can switch its electrical properties by a simple change of temperature due to high silver mobility,
a non-stoichiometric range, and an internal redox process. A reversible p-n-p type conduction switching property in AgCuS material caused by phase transition has been reported by Kanishka Biswas’s group\textsuperscript{8}. Thomas Palstra et al\textsuperscript{9} showed that the electrical property can be changed in marcasite FeSe\textsubscript{2-δ} by effect of vacancies. However, the commercialization is hampered by low scalability\textsuperscript{10,11} and high cost. More importantly, it is difficult to control the transition temperature for switching electrical properties intrigued by temperature.

This work shows a low-cost and large-scale solution-phase synthesis of FeTe\textsubscript{2} using a robust, one-pot approach at low temperature and atmospheric pressure. We also demonstrate that the switching temperature can be tuned by changing the original precursor ratio. The defect concentration can be controlled by changing the sintering time, which makes it possible to control the switching temperature. Additionally, we developed a thermally triggered p-n diode device based on the above results.

3.2 Experimental methods

All chemicals are used as received without further purification. Tellurium oxide (TeO\textsubscript{2}, 99.99%) was purchased from Alfa Aesar. Polyvinylpyrrolidone (PVP, average 40,000 g/mol), potassium hydroxide (KOH, 99.99%), hydrazine (anhydrous, 98%), and iron chloride (FeCl\textsubscript{3}, 97%) were purchased from Sigma-Aldrich. Hydrazine monohydrate (79%) was purchased from Tokyo Chemical Industry and Ethylene glycol (EG) was purchased from VWR.
For the synthesis of FeTe₂, 5.145 g TeO₂ (32.25 mmol), 14.625 g of KOH, and 450 ml of EG are added to 1 L three-neck flask with magnetic stirring initiated for continuous mixing. The reactor is heated to 70 °C and 9 g of PVP is added to the flask slowly. Then increase the temperature to 110 °C and 5.5 ml of hydrazine is rapidly injected into the reactor. The temperature is maintained at 110 °C for 1 hour under nitrogen gas protection. As the Te nanowires growing, an iron precursor solution is made in a nitrogen-filled glovebox. 2.6153 g of FeCl₃, and 50 ml of EG are added to a 100-ml beaker and heated to 80 °C. 26 ml hydrazine is slowly added. After 1-hour reaction for Te nanowires, setting the temperature to 120 °C. When the temperature reaches 120 °C, all the iron precursor is rapidly injected. 4 hours after iron precursor injection, stop heating and cool down the solution to room temperature. For the synthesis of FeTe₂-2xFe, the only difference is double the amount of FeCl₃ amount to 5.2306 g.

Then, the as-synthesized FeTe₂ are washed three times with deionized (DI) water. The sediment after water washing is then soaked into hydrazine hydrate (30% volume ratio) and ethanol solvent. The soaking procedure is also protected by nitrogen gas and stirred by a magnetic bar. The mixture is then centrifuged three times by ethanol and the supernatant is

![Figure 3-1](image)

Figure 3-1 (a) Schematic illustration of the synthesis of FeTe₂ and FeTe₂-2xFe. (b) XRD patterns of FeTe₂ disk. (c) XRD patterns of FeTe₂-2xFe disk.
discarded. The material is then dried overnight in the vacuum chamber at room temperature and brought directly into a nitrogen-filled glovebox for grinding with a mortar and pestle.

3.3 Results and discussions

The synthesis of Te nanowires is based on our previous reports\textsuperscript{12-14}. The schematic illustration of the synthesis of iron telluride is shown in Fig 3-1a. Iron telluride morphology will change a lot by adjusting the amount of iron precursor. The original stoichiometric ratio (Fe:Te=1:2) will form a flake structure, while doubling the amount of iron precursor (Fe:Te=2:2=1:1) form a necklace structure. The large-scale synthesis of FeTe\textsubscript{2} are first analysed using disk X-ray diffraction (XRD); the result in Fig 3-1b show that the products of Fe:Te=1:2 original ratio (which is denoted as FeTe\textsubscript{2} in this paper) can be indexed as pure-phase FeTe\textsubscript{2} (Red lines: JCPDS #14-0419). Fig 3-1c is the XRD pattern of Fe:Te=1:1 ratio (which is denoted as FeTe\textsubscript{2}-2xFe in this paper) and it can also be indexed as orthorhombic phase FeTe\textsubscript{2} (Red lines: JCPDS #14-0419). The XRD pattern indicate there is no impurity in our synthesized iron telluride.

The compositions of our products are further verified by our transmission electron microscope (TEM) study. Fig 3-2a and 3-2d are the low-magnification TEM image of FeTe\textsubscript{2} and FeTe\textsubscript{2}-2xFe, respectively. The FeTe\textsubscript{2} has flake structure while FeTe\textsubscript{2}-2xFe shows necklace structure. Fig 3-2b and Fig 3-2c are the high-resolution TEM (HRTEM) of FeTe\textsubscript{2} and its corresponding fast Fourier transform (FFT) image. The HRTEM of FeTe\textsubscript{2}-2xFe and its corresponding FFT image are shown in Fig 3-2e and Fig 3-2f. Both of FeTe\textsubscript{2} and FeTe\textsubscript{2}-2xFe can be indexed as orthorhombic phase of FeTe\textsubscript{2} (space group is 58). TEM results showed the morphology of FeTe\textsubscript{2} and FeTe\textsubscript{2}-2xFe can be controlled very well.
The only difference is the amount of iron precursor, while all other experimental conditions remain the same. It was found that the iron precursor concentration has a dramatic effect on the morphology of iron telluride. From kinetic analysis\textsuperscript{15-17}, with dilute iron precursor concentration (1:2 ratio), the iron precursor has a smaller diffusion rate from the solution phase to telluride phase. It is easy to form new iron telluride phase (orthorhombic structure) at the surface of tellurium nanowire (hexagonal structure). Strong structure stress breaks down the tellurium nanowires, ultimately forming flake structures. While in the higher iron precursor concentration case (double iron precursor), higher diffusion rate kept the iron precursor in the tellurium nanowires. Iron telluride can be synthesized both at the surface and interior of tellurium nanowires. The wire structure can be conserved while forming the necklace structure.

Figure 3-2 (a) TEM image of FeTe\textsubscript{2} (b) HRTEM image of FeTe\textsubscript{2} (c) FFT of Fig 2b (d) TEM image of FeTe\textsubscript{2}_\textsubscript{2xFe} (e) HRTEM image of FeTe\textsubscript{2}_\textsubscript{2xFe} (f) FFT of Fig 2e
Figure 3-3 (a) Seebeck coefficient of FeTe₂₋₂xFe@3mins (b) Seebeck coefficient of FeTe₂@3mins (c) Seebeck coefficient of FeTe₂@6mins (d) Seebeck coefficient of FeTe₂@30mins (e) Seebeck coefficient of FeTe₂@60mins (f) Transition temperature of FeTe₂ v.s. logarithm of sintering time
Large-scale (1 L per batch) and high yield (> 4 g per batch) synthesis of FeTe$_2$ allowed us to sinter several 10mm diameter FeTe$_2$ disks by Spark Plasma Sintering (SPS) and investigate their electrical properties. The Seebeck coefficient of FeTe$_2$$_{2x}$Fe have been measured from 70 °C to 320 °C and is shown in Fig 3-3a. The Seebeck coefficient decreases monotonically with temperature and switch from positive value (p-type) to negative value (n-type). Every sample was tested three times and this switching phenomenon is reproducible. The actual transition temperature for every cycle which was recorded by our LSR-3 system software and the calculated average transition temperature is shown in the insert table in Fig 3-3a. Fig 3-3b is the Seebeck coefficient of FeTe$_2$ and it also shows reproducible switching behaviour for FeTe$_2$. Compared to FeTe$_2$$_{2x}$Fe, FeTe$_2$ has a higher positive Seebeck coefficient value below 188.8 °C. The average transition temperature from p-type to n-type is 236.43 °C for FeTe$_2$ while is 188.8 °C for FeTe$_2$$_{2x}$Fe. At the range of 188.8 °C and 236.43 °C, FeTe$_2$ shows p-type behaviour and FeTe$_2$$_{2x}$Fe turns to n-type material. Both of FeTe$_2$ and FeTe$_2$$_{2x}$Fe switch to n-type when the temperature is higher than 236.43 °C while the absolute Seebeck coefficient value of FeTe$_2$ is smaller than FeTe$_2$$_{2x}$Fe.

The transport of matter in solid phase is directly dependent upon deviations from ideal crystalline order$^{17}$. For transition metal chalcogenide, usually, it will show p-type behaviour when chalcogenide excess while show n-type behaviour when chalcogenide deficiency$^4$. One possible reason is that during the temperature increasing, isolated tellurium from iron telluride structure will form polytelluride and the system have more tellurium vacancy defect, which will tune the electrical conductivity from p-type to n-type. This explanation can be expressed in equation (3.1) with Kröger symbolism.
\[
TeTe^{\text{heating}} \rightarrow V_{Te} + Te_i^{e}\tag{3.1}
\]

The subscript means lattice site while the superscript corresponds to electric charge of the relative to the site. The body indicates the species. According to electronegativity, iron will have positive charge while tellurium keeps negative charge. On the left of equation (3.1), one tellurium anion is sitting on a tellurium lattice site with negative charge. During heating, it will decompose into one vacancy in the tellurium lattice site with negative charge while tellurium atom is in the interstitial site with neutrality charge. The Fermi energy will be changed because of the change in volume of crystal during the formation of vacancy and because of the scattering of the electron waves at the defects\textsuperscript{19}. Therefore, an increasing of tellurium vacancies will affect the valence state and change the electrical conductivity type. From macroscopic view, the equation can be written as following:

\[
FeTe_2^{\text{heat}} \rightarrow FeTe_{2-\delta} + \delta Te\tag{3.2}
\]

where \(\delta\) indicates a very small number that won’t affect the stoichiometric ratio. Every sample has reproducible result which means equation (3.1) and (3.2) are reversible when the temperature is cooling down.

The Seebeck coefficient of FeTe\textsubscript{2} with different sintering times are also showed in Fig 3-3c (6 minutes; FeTe\textsubscript{2}@6 mins), Fig 3-3d (30 minutes; FeTe\textsubscript{2}@30 mins) and Fig 3-3e (60 minutes; FeTe\textsubscript{2}@60 mins). Compared to Fig 3-3b which is sintered for 3 minutes (FeTe\textsubscript{2}@3 mins), FeTe\textsubscript{2}@6 mins, FeTe\textsubscript{2}@30 mins and FeTe\textsubscript{2}@60 mins disks show lower transition temperatures. All the disks were tested 3 times and showed reproducible switch behaviour. The average transition temperature for FeTe\textsubscript{2}@6 mins, FeTe\textsubscript{2}@30 mins and FeTe\textsubscript{2}@60 mins
switch from p-type to n-type are 230.27 °C, 201.8 °C and 195.8 °C. The sintering temperature is 600 °C while the melting point of pure Tellurium is 445 °C\textsuperscript{18}. During sintering, the vacuum pump kept open all the time. Fig 3-3f is the plot of average transition temperature v.s. the logarithm of sintering time. There is a linear relationship between average transition temperature and logarithm of sintering time. The longer of the sintering time, the lower of the transition temperature.

The possible reason of this phenomenon is that the sintering temperature is higher than the melting point of tellurium. As shown in equation (3.3), tellurium will tune into gas phase and be vacuumed by the pump. Therefore, equation (3.3) is not reversible and the total concentration of tellurium vacancy is related to the sintering time.

\[FeTe_2 \xrightarrow{heat} FeTe_{2-\delta} + \delta Te (g)\]  \hspace{1cm} (3.3)

Compared to the whole tellurium atoms, the concentration of tellurium vacancies is very small, and the laws of dilute solution can be used to calculate the relationship between sintering time and concentration of tellurium vacancies\textsuperscript{13,15}. The reaction rate and sample thickness are assumed to be constant\textsuperscript{20-22}, then the concentration of tellurium vacancies model can be expressed as following:

\[
\frac{C_t - C_{t=0}}{C_\infty - C_{t=0}} = 1 - \exp\left(-\frac{kt}{L}\right) \]

\hspace{1cm} (3.4)

where \(t\) is the sintering time, \(k\) is the reaction rate, and \(L\) is the sample thickness. \(C_t\) is the concentration of tellurium vacancies at time \(t\). There will be more tellurium vacancies when the sintering time increased and the transition temperature will be decreased as a result. To our knowledge, it is difficult to tune the transition temperature in a large range of
temperature. For our FeTe$_2$ system, the transition temperature can be adjusted from 195.8 °C (FeTe$_2$@60 min) to 236.43 °C (FeTe$_2$@3 min). More importantly, the transition temperature has a linear relationship with the logarithm of sintering time. In other words, the transition temperature can be controlled by just changing the sintering time, which makes its switching behaviour more useful.

To understand the reason caused the switching behaviour, in-situ XRD of FeTe$_2$ is performed and shown in Fig 3-4a. The FeTe$_2$ sample is sealed in the heating holder with Argon gas protection. The FeTe$_2$ peaks keep unchanged at all the temperature range while pure Te peaks (JCPDS #36-1452) appeared with temperature rising. The crystalline structure will
expand when temperature increasing, which will increase the peak intensity. However, compared with FeTe$_2$ peaks, there should be a pure Tellurium phase occurred during temperature increasing. The differential scanning calorimetry (DSC) result of FeTe$_2$ is shown in Fig 3-4b, there are no peaks in the temperature range from 70 °C to 350 °C, which means
there is no phase change during this temperature range. The DSC result of FeTe$_2$-_2xFe also
didn’t show phase change during 70 °C to 350 °C.

Materials with switching physical properties are good candidates for sensors and memories. However, usually the thermally triggered switching behaviours change gradually with
temperature and the low switching speed hamper the applications for those materials$^4$. While through combining FeTe$_2$ and FeTe$_2$-_2xFe together, the thermally triggered p-n diode
behaviour is realized and show an abrupt change in the I-V curve. The schema is showed in
Fig 3-5a. Same amount of FeTe$_2$ powder and FeTe$_2$-_2xFe powder are loaded in one graphite
die and sintered together by SPS. Then the SPSed disk is fixed on the glass and connected to
copper wires by silver paste. The hot plate is placed under glass substrate as a heating source
and copper wire connected to Agilent 4156C to get the I-V curve. Below the transition
temperature of FeTe$_2$-_2xFe, both of FeTe$_2$ and FeTe$_2$-_2xFe are p-type semiconductors and
the I-V curve is straight lines which means an “On” state. The I-V curve will show p-n diode
behaviour when the temperature is higher than the transition temperature of FeTe$_2$-_2xFe (T$_1$)
while lower than the transition temperature of FeTe$_2$ (T$_2$), which means on “Off” state. The I-
V curve is shown in Fig 3-5b. While the I-V curves show p-n diode behaviour when the
temperature at the range between T$_1$ and T$_2$. It is like a thermal resistor, but it has one
advantage: the crystalline structure of FeTe$_2$ and FeTe$_2$-_2xFe are same and there is no
structure stress between the boundary, which makes the device more stable. The thermally
triggered p-n diode behaviour and the big change of system resistance make it a good
candidate for thermal sensor.
3.4 Conclusion

In summary, we have developed a large-scale solution-phase method of FeTe$_2$ synthesis at low temperature and atmospheric pressure. The transition temperature can be tuned by changing the amount of iron precursor. More importantly, the transition temperature has a linear relationship with the logarithm of sintering time, making it controllable by adjusting the sintering time. The in-situ XRD and DSC experiments showed the reason for switching is the valence change effect caused by tellurium deficiency. The successful thermally triggered p-n diode device indicates its potential application as a thermal sensor or thermal resistor.

The future work for this project can be optimization the idea factor of I-V curve. Synthesis thermally triggered p-n-p bipolar transistor based on FeTe$_2$-FeTe$_2$-2xFe-FeTe$_2$ structure.

References


7. Guin, S. N. *et al.* Temperature dependent reversible p–n–p type conduction switching with colossal change in thermopower of semiconducting AgCuS. *Journal of the...


CHOI, G. M. & Tuller, H. L. Defect structure and electrical properties of single -
crystal Ba0. 03Sr0. 97TiO3. *Journal of the American Ceramic Society* 71, 201-205
(1988).

Leonhardt, M., De Souza, R., Claus, J. & Maier, J. Surface kinetics of oxygen
incorporation into SrTiO3. *Journal of The Electrochemical Society* 149, J19-J26
(2002).
CHAPTER 4. ELECTRICALLY DRIVEN STRUCTURAL PHASE TRANSITION IN SINGLE $\text{Ag}_2\text{Te}$ NANOWIRE DEVICES

This chapter is based on the manuscript “Electrically Driven Structure Phase Transition in Single $\text{Ag}_2\text{Te}$ Nanowire Devices” accepted by *Nanoscale*, which is co-authored with Kasun Premasiri$^a$, Biao Xu$^b$, Tao Ma$^c$, Lin Zhou$^c$, Yue Wu$^b$, and Xuan P.A. Gao$^a$.

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4.1. Introduction

The ceaseless demand for electronic memory in the evolution of electronics makes phase–change materials a constitutive facet of research in solid state physics and devices. In modern electronics, miniaturizing electronic memory devices$^{1-4}$ is becoming ever so important where nanostructures that can host phase changes draw a lot of attention mainly due to their unrivalled room for miniaturization. It has already been demonstrated that two–dimensional materials$^{5-12}$ nanowires and nanoribbons$^{13-18}$ can be utilized as phase–change materials. Among different types of nanostructures, sub–lithographic dimensions combined with cylindrical shape add to the versatility of nanowires with structural phase changes as a potential class of materials for memory devices, specifically towards acquiring high storage density. However, utilizing
nanowires as phase-change materials still largely remains as a less-explored territory, especially with the dearth of new reliable materials.

Figure 4-1 (a) Schematic of the crystal structure of α–Ag$_2$Te. (b) An XRD analysis for Te nanowires. (c) An XRD analysis for Ag$_2$Te nanowires. (d) A TEM image of Te nanowires (scale bar: 500 nm). (e) An HRTEM image of Te nanowires (scale bar: 10 nm). (f) An FFT image of Te nanowires. (g) A TEM image of Ag$_2$Te nanowires (scale bar: 100 nm). (h) An HRTEM image of Ag$_2$Te nanowires (scale bar: 5 nm). (i) An FFT image of Ag$_2$Te nanowires
Germanium– and antimony–based tellurides serve as a benchmark for phase–change materials.\textsuperscript{19-21} And Ag$_2$Te belongs to the family of silver chalcogenides which are known for their reversible structural phase transitions.\textsuperscript{22} Ag$_2$Te is identified as Hessite in mineralogy. This material has two distinct phases, namely $\alpha$–Ag$_2$Te and $\beta$–Ag$_2$Te.\textsuperscript{24,25} Ag$_2$Te possesses an antifluorite structure in its $\alpha$ form which transits to a distorted antifluorite structure as the material switches to $\beta$–Ag$_2$Te. Fig. 4-1a illustrates the atomic structure of $\alpha$–Ag$_2$Te. Ag$_2$Te enters the $\alpha$–phase from its $\beta$–phase above 417 K. In its $\beta$ form, Ag$_2$Te is a narrow bandgap semiconductor with a bandgap of a few tens of meV,\textsuperscript{25} and has shown great promise as a thermoelectric material\textsuperscript{26,27}. Moreover, it has been demonstrated that $\beta$–Ag$_2$Te contains topological surface states\textsuperscript{28,29}.

There are various chemical and physical means such as pressure, temperature, chemical doping etc. that can be used to induce structural phase transitions. But most of those become incompetent in switching in memory devices either due to the inability to drive a phase transition reversibly and/or the necessity of extreme physical conditions that are unfavourable for applications. However, there are some materials that host structural phase transitions that can be triggered using a voltage. In this scenario, the voltage applied serves as an indirect way of bringing the required chemical or physical changes to trigger the phase change. There are basically two cases for which a voltage can be used to drive a phase change. Firstly, a voltage can be utilized to create an electric field via which strain can be applied to induce a pressure–driven phase change\textsuperscript{8,30-32}. Secondly, a voltage can be used to generate Joule heating that can trigger a temperature-driven phase change. These voltage-induced structural phase transitions provide ideal systems for switching, especially when the transition can be achieved within a
reasonably low voltage (low energy consumption). In this work, we demonstrate the voltage–induced phase transition in Ag$_2$Te nanowires for the first time.

4.2 Experimental Section

4.2.1 Nanowire Synthesis

Tellurium nanowires were synthesized first and then they were converted to Ag$_2$Te nanowires. For this, tellurium oxide (TeO$_2$, 99.99%) and silver nitrate (AgNO$_3$, 99.9%) were purchased from Alfa Aesar. Polyvinylpyrrolidone (PVP, with 40,000 g/mol on average), potassium hydroxide (KOH, 99.99%), L-Ascorbic acid (99%), and hydrazine (anhydrous, 98%) were purchased from Sigma Aldrich. Ethylene glycol (EG) was purchased from VWR International.

Tellurium Nanowires: 40.0 g of L-Ascorbic acid was dissolved in 120.0 ml of deionized water at 100 °C. Then, 6.4 g of TeO$_2$ (40 mmol), 20.0 g of PVP, 60.0 g of KOH and 600.0 ml of EG were added to a three-neck flask (1 L) and the temperature was set to 100 °C. Afterwards, the ascorbic acid solution was rapidly injected into the three-neck flask as the temperature reaches 100 °C. Then the system was allowed to react for 24 hours under nitrogen protection. Silver Telluride Nanowires: The as-synthesized tellurium nanowires were centrifuged three times with deionized water. Then, the tellurium nanowires were re-dispersed in 600.0 ml of EG. Alongside, 20.37 g of AgNO$_3$ (120 mmol) was added into 150.0 ml of EG, and then the mixture was dissolved with the aid of a sonicator, to prepare the silver precursor. Thereafter, the silver precursor was added dropwise to the tellurium nanowire solution and stirred at room temperature for an hour. This reaction converts tellurium into Ag$_2$Te. Then, the as-synthesized Ag$_2$Te nanowires was centrifuged two times with deionized water and washed in an ethanol
solution (6% of hydrazine) for 2 hours. Then, they were washed twice with ethanol, and vacuum-dried. The transmission electron microscope (TEM) images in Fig. 4-1 show that the Te and Ag₂Te nanowires synthesized using this method are highly crystalline.

4.2.2 Device Fabrication

To demonstrate the structural phase change in individual nanowires, two-probe Ag₂Te nanowire devices were fabricated on Si (degenerately-doped) substrates with 300 nm thick silicon oxide on surface. At the onset, Si/SiO₂ substrates were sonicated in acetone for 20 min. Then they were rinsed with isopropyl alcohol followed by deionized water and were blow-dried using compressed air. Afterwards, the cleaned SiO₂ surface was treated with ultraviolet-ozone at 150 °C for 10 min. Then, Ag₂Te nanowires (suspended in acetone) were drop-casted onto the cleaned SiO₂ surface. Thereafter, it was air-dried for a few min. A standard photolithography procedure (with a photomask of 2-micron minimum resolution) was used to pattern the SiO₂ surface with Ag₂Te nanowires embedded in the photoresist. Then the patterned chip was etched using an HF solution (1%) for 5 secs before depositing metal. This was to remove any possible native oxide that can build up on the surface of the Ag₂Te nanowires during the fabrication process. Removing the native oxide can help having good electrical contacts between the contact metal and the nanowire surface. Ni (60 nm) was evaporated (using an electron beam evaporator, Angstrom Evovac Deposition System). Afterwards, a standard photoresist remover was used to clear away the photoresist residue. Fig. 4-2a is a schematic of the device structure fabricated. All the devices used in this study had single nanowires confined between two Ni electrodes so that those two metal contacts can be used to apply a voltage across the nanowire. Moreover, the devices used for the study had Ohmic contacts, and thus
additional annealing was not required. Fig. 4-2b is an optical micrograph of one of the devices used in this study (Ni electrodes across which a voltage is applied are labeled).

4.2.3 Electrical Measurements

A probe station (Lakeshore) was utilized for the electrical measurements. Heating up the nanowires was carried out using the probe station's stage heater with the aid of a temperature controller (Lakeshore 332 Temperature Controller). Standard DC–techniques were used to obtain current–voltage (IV) and resistance measurements for the nanowires.

4.3 Results and Discussion

Figure 4-2 (a) Schematic of the device structure of the Ag$_2$Te nanowire devices. (b) Optical micrograph of an Ag$_2$Te nanowire device (Device A). Scale bar: 20 µm (white line). (c) Conductance vs temperature of single Ag$_2$Te nanowires (for Devices A, B, C and D) showing the transition at T$^*$.

Fig. 4-1b and c show X-ray diffraction (XRD) analysis for Te and Ag$_2$Te nanowires, respectively. This analysis clearly shows all the signature peaks corresponding to Te and Ag$_2$Te crystallographic phases suggesting that the synthesized Ag$_2$Te is highly crystalline and pure. Fig. 4-1d and g are transmission electron microscopy (TEM) images of Te and Ag$_2$Te phases; and Fig. 4-1e and h are high-resolution transmission electron microscopy (HRTEM) images of Te and Ag$_2$Te phases, respectively. Fig. 4-1f and i are the fast Fourier transform
(FFT) images corresponding to those HRTEM images. These synthesized Ag$_2$Te nanowires are single crystal. Since a solution phase method is utilized in synthesizing them, they may contain lattice defects. Moreover, as the TEM analysis reveals, the growth direction of the nanowires can vary. However, the HRTEM images clearly reveal the crystalline nature of the material. According to these results, Te nanowires can be indexed as in trigonal phase (space group: 152; P$_{3(1)21}$) and Ag$_2$Te nanowires can be indexed as in monoclinic phase (space group: 13; P$_{121}$).

Transition temperature ($T_{tr}$) between $\alpha$ and $\beta$ phases of bulk Ag$_2$Te is 417 K. Fig. 4-2c shows the change in conductance with temperature for four different nanowire devices (Device A, B, C and D). $T^*$ denotes the temperature reading of the sample stage of the probe station at the transition between $\alpha$ and $\beta$ phases of Ag$_2$Te. Conductance values in Fig. 4-2c were extracted from I vs V measurements (within $\pm$ 100 mV), and all those devices showed linear IV responses. Since a small voltage interval of mere $\pm$100 mV was used, the contribution from Joule heating to the conductance changes in Fig. 4-2c is negligible compared to the ambient temperature raising. In this analysis, Device B is close to the predicted value for the transition temperature ($T_{tr}$) in bulk Ag$_2$Te. Device A and D show positive deviations from $T_{tr}$, while Device C shows a substantial negative deviation from $T_{tr}$. These variations are presumably due to the structural distinctions and/or irregularities in individual nanowires (e.g. diameter, lattice defects etc.). More importantly, all four devices in Fig. 4-2c show sharp and significant changes in conductance near $T^*$, which are indicative of the phase change from conductive $\alpha$ phase to more resistive $\beta$ phase Ag$_2$Te.
In the aforementioned analysis (in Fig. 4-2c), the phase transition is triggered via elevating the temperature of the nanowire by heating up the surroundings. Joule heating can be used for the same purpose when the transition temperature for the phase transition is reasonably low. In this scenario, a voltage applied to the nanowire can be used to generate the required Joule heating. So, the contributions from both the Joule heating and the ambient heating can be quantified as follows.

\[ \Delta Q = \Delta Q_T + \Delta Q_J \]  

(4-1)

where, \( \Delta Q \) is the total thermal energy required to surpass the phase transition temperature, \( \Delta Q_T \) is the thermal energy supplied by the surroundings to heat up the nanowire and \( \Delta Q_J \) is the thermal energy provided via Joule self-heating. In Fig. 4-2c, the contribution from Joule heating was nullified \( (\Delta Q_J \sim 0) \) by confining the maximum applied voltage to a very small value so that the elevation of the temperature of the nanowire is almost due to the heating of the surroundings.

Figure 4-3 (a) I vs V responses (for Device E) at different temperatures. (b) Variation of conductance with temperature for Device E.
Equivalent to the situation in Fig. 4-2c, one can supply the energy to heat up the nanowire via self-Joule-heating ($\Delta Q_J > 0$). This becomes more convenient in controlling the phase change via a voltage applied across the nanowire, without the need to adjust the temperature of the environment; which can be very favourable in memory applications. The amount of Joule heating necessary to self-heat the nanowire above the transition temperature is proportional to the temperature difference between the transition temperature for the nanowire ($T^*$) and the ambient temperature, the specific heat of Ag$_2$Te, and the thermal conductance between the nanowire and the surroundings. Therefore, it is straightforward to see that the higher the ambient temperature of the nanowire is, the lesser the Joule heating power necessary to induce the phase transition.

This scenario is studied as the next step of this study (Fig. 4-3). For the IV curves in Fig. 4-3a, the ambient temperature of the nanowire and the maximum contribution from Joule heating are fixed, via fixing the temperature of the stage ($T$) and the maximum voltage applied (0.5 V), respectively (Device E shows a linear IV response). Moreover, the voltage sweeping rate was the same across all the IV responses in Fig. 4-3a (0.1 V/s). As illustrated in Fig. 4-3a, the $\Delta Q_J$ provided by 0.5 V at both $T$ = 293 and 380 K is not large enough to trigger the phase transition. This suggests that a higher voltage (> 0.5 V) is required to induce the phase change in the region up to 380 K. As $T$ is raised, the voltage corresponding to the required $\Delta Q_J$ drops below 0.5 V. According to Fig. 4-3a, this happens within the region of $T$ = 380 - 410 K. And the phase transition is triggered around 0.45 V at 410 K. Further elevating the temperature brings the required voltage sequentially down, and eventually becomes zero leading to the condition $T^* - T = 0$ which happens somewhere between 425 K to 445 K. Fig. 4-3b depicts the response of
the conductivity of Device E to the temperature of the stage ($T$) measured at low bias voltage (±100 mV), and it validates the T* inferred in the voltage–driven phase transition in Fig. 4-3a.

This structural phase transition in Ag$_2$Te becomes more appealing in memory devices’ perspective if it can be induced at room temperature over multiple cycles with the mere aid of a voltage. This aspect of Ag$_2$Te nanowire devices is studied in Fig. 4-4, in which the phase transition is electrically-induced at room temperature over three times (Device F shows a linear IV response). However, one important trend in Fig. 4-4 is that as more and more cycles are executed, the voltage required to surpass the phase change goes up in those subsequent cycles (Cycle#2 and Cycle#3 in Fig. 4-4 compared to Cycle#1). On the other hand, the conductance at a certain voltage drops sequentially with the cycles (with Cycle#1 being the highest). This reduced conductance demands higher power ($P$) to acquire the same temperature difference. This means the voltage required to impart the same power ($P = \frac{V^2}{R}$) increases for the subsequent cycles. But this trend of decreasing conductance is not that obvious in Fig. 4-3a. Compared to the IV responses in Fig. 4-3a, larger voltages are used in Fig. 4-4. And also, the voltage loops are run one after another without any lapse in between whereas in Fig. 4-3a, there is a relatively significant time interval between adjacent voltage loops due to the time it takes to heat up the nanowires using the stage heater. These point to the fact that this reduced conductance over cycles in Fig. 4-4 could be due to the persistent strain or degradation on the electrical contacts (between Ag$_2$Te and Ni electrodes). This could be due to the mismatch between Ag$_2$Te and Ni in thermal and mechanical properties. Further enhancement to the device structure is necessary to minimize this effect so that better stability and durability can be achieved.
4.4 Conclusion

This study shows that resistive switching of individual Ag₂Te nanowires due to the structural phase transition between α–Ag₂Te and β–Ag₂Te can be driven by either direct thermal heating or indirect Joule heating via an electrical voltage bias of less than one volt. This study covers the vital aspects of the properties of the structural phase change of Ag₂Te, and also opens up the opportunity for further development of electrically controlled Ag₂Te nanowire phase change devices (e.g. inducing the phase change via a voltage pulse for high frequency applications).

Figure 4-4 IV responses (Device F) at 296 K over multiple voltage loops.
References


CHAPTER 5. ELECTROMAGNETIC RADIATION DRIVEN PHASE TRANSITION IN Ag₂Te-Fe₃O₄ AND FeTe₂ NANOCOMPOSITES

This chapter is based on the manuscript “Electromagnetic radiation driven phase transition in Ag₂Te-Fe₃O₄ and FeTe₂ Nanocomposites”, which is co-authored with Yang Bao⁹, Praveen Gurrala⁹, Biao Xu⁹, Jiming Song⁹, and Yue Wu⁹. This article is pending for submission upon approval from Office of Naval Research.

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5.1 Introduction

As the rapid development of wireless communication, the increasing usage of electromagnetic wave devices results in the serious electromagnetic interference (EMI) and electromagnetic compatibility (EMC) problems¹-⁴. More seriously, the high density of electromagnetic (EM) radiation caused by the wireless communication has been confirmed as having a great effect on the health and safety of humans, such as sleep disturbance, headache, nausea, visual disorders, respiratory problems, and nervous excitation⁵.
In considering of the pollution and threat from EM radiation, great efforts have been proposed to prevent the radiation from being harmful to the humans and communities. EM sensors or switchers have since come out. There are some sensors or switchers based on amorphous semiconductor\(^6\), superconductor\(^7\), and high-pressure gas arresters\(^8\). However, the semiconductor has a limited number of operations when protecting circuits against high voltage transients, the superconductor has requirement of the low-temperature cooling, and gas arresters have complicated design with relatively large size\(^9\). After that, in recent years, significant progress has been achieved in microwave cryogenic electronics operating at liquid nitrogen temperatures\(^10\). Current-induced phase transitions from superconductor to normal state based symmetrical thin-film switchers\(^11\), and polycrystalline manganite films exhibiting the “electro-resistance” effect\(^12\) were proposed. However, the high speed of operation of these sensors is always accompanied with energy focusing in narrow channels of the film and damage to the protector\(^10\). To overcome the drawbacks mentioned above, we apply the property of the solution-phase synthesis of silver telluride and iron telluride nanostructures, which is based on converting the EM radiation induced Joule heats to rapid electrical property changes, potentially to develop the EM sensors.

In this article, the silver telluride nanowire, which has limited EM absorption, blend with the iron oxide powder, which has the abilities to absorb the EM radiation and convert the EM energy into heat or other forms of internal energy\(^13-17\), to improve the samples’ EM absorption while keeping the feature of rapid electrical property changes\(^18-26\). The EM absorption properties of three mixture samples with different percentages of silver telluride nanowire and iron oxide powder, and the nanodisk made of iron telluride are measured in X band, which is
in great demand\textsuperscript{27-30}. The good EM absorption properties of samples made of silver telluride nanowire and iron oxide powder, and the nanodisk made of the iron telluride lead to the temperature increase, which cause the rapid change of the electrical conductivity by $\alpha$-type to $\beta$-type phase transition\textsuperscript{31,32} and the triggered p-type to n-type transition\textsuperscript{33,34} that can be potentially applied to develop EM sensors.

5.2 Experiment details

All chemicals are used as received without further purification. Tellurium dioxide ($\geq$99.99%), polyvinylpyrrolidone (PVP, MW~ 40,000), potassium hydroxide, (KOH, $\geq$90%), hydrazine monohydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, 78\%~82\%), and iron oxide ($\text{Fe}_3\text{O}_4$, $\geq$99.99\%, 325 mesh) were purchased from Sigma Aldrich, while silver nitrate ($\text{AgNO}_3$, $\geq$99.9\%), ethylene glycol (EG, $\geq$99\%) and ethanol ($\geq$95\%) were purchased from VWR.

Synthesis of $\text{Ag}_2\text{Te}_{2x}\text{Ag}$ nanowires procedure was exactly followed our previous publication. Firstly, 9.576 g TeO$_2$, 12 g PVP, 44.484 g KOH, and 600 ml EG were added to a 1 L glass reactor with magnetic stirring initiated for continuous mixing. The glass reactor was heated to 120\degree C and 20 ml $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ was rapidly injected into the reactor. The temperature was maintained at 120\degree C for 1 hour under nitrogen gas protection. Then the reaction was stopped and cooled down to room temperature naturally. The tellurium nanowire was washed three times with deionized (DI) water and re-dispersed in 800 ml EG in a 2 L beaker for $\text{Ag}_2\text{Te}$ synthesis. Alongside, 40.769 g $\text{AgNO}_3$ was dissolved in 200 ml EG. Then, the $\text{AgNO}_3$/EG solution was added into the 2 L beaker and stirred at room temperature for 2 hours for the conversion from Te into $\text{Ag}_2\text{Te}$. The as-synthesized $\text{Ag}_2\text{Te}_{2x}\text{Ag}$ nanowires were centrifuged
two times with deionized water and washed in an ethanol solution (12.5% of N\textsubscript{2}H\textsubscript{4}•H\textsubscript{2}O) for 24 hours to remove the surfactant. The mixture was then washed twice with ethanol, and vacuum-dried.

\text{Ag\textsubscript{2}Te-Fe\textsubscript{3}O\textsubscript{4}} composite sintering: The Ag\textsubscript{2}Te nanowires was grounded into loose powder and griddled by a 325-mesh sieve in a nitrogen-filled glovebox. Ag\textsubscript{2}Te and Fe\textsubscript{3}O\textsubscript{4} powder were mixed evenly by mortar and loaded into graphite die for spark plasma sintering (SPS). The sintering condition was under 40 MPa at 850\degree C for 5 minutes and then cooled down to room temperature naturally.

The EM absorption property was measured by a programmable vector network analyzer (VNA, Agilent E8364) with calibration kit (Agilent 85052D) and cables (GORE Microwave). The samples were placed inside the X band waveguide (Aircom Microwave) to measure the S parameters.

![Figure 5-1 XRD of Te and Ag\textsubscript{2}Te nanowires](image-url)
5.3 Results and discussion

The Ag$_2$Te is analyzed by using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Figure 5-1a is the XRD result of telluride nanowires, which can be indexed as pure hexagonal phase telluride (red lines: JCPDS # 36-1452). The XRD result, Figure 5-1b, shows that our synthesized Ag$_2$Te can be indexed as pure monoclinic phase silver telluride (blue lines: JCPDS # 34-1042). Figure 5-2a is the low-magnification TEM image of Ag$_2$Te and Figure 5-2b is the high-resolution TEM (HRTEM) image of Ag$_2$Te with its fast Fourier transform (FFT) image. The synthesized Ag$_2$Te is further proved to be the same monoclinic phase of Ag$_2$Te (space group is 13).

![Figure 5-2 TEM images of Ag$_2$Te nanowires](image)

(a) Low magnification TEM image of Ag$_2$Te  (b) High resolution TEM image of Ag$_2$Te

This large-scale solution-synthesis method enables us to sinter several Ag$_2$Te-Fe$_3$O$_4$ composite disks with 1 cm diameter by Spark Plasma Sintering (SPS) and investigate their electrical properties. Figure 5-3a is the XRD results of Ag$_2$Te-Fe$_3$O$_4$ composites and all these
percentages are weight percent. There are both silver telluride peaks (JDCPS #34-1042) and iron oxide peaks (JCPDS #19-0692) in all three composite disks. With increasing Ag₂Te weight percent, Ag₂Te peaks increase while Fe₃O₄ peaks decrease. The Seebeck coefficient of Ag₂Te-Fe₃O₄ composites has been measured from 40°C to 220°C and is shown in Figure 5-3b.

Figure 5-3. (a) XRD results of Ag₂Te-Fe₃O₄ composites. All these percent numbers are weight percent. (b) Seebeck coefficient of Ag₂Te-Fe₃O₄ composites. (c) Electrical conductivity of Ag₂Te-Fe₃O₄ composites.
All these three samples have negative Seebeck coefficient values during the test temperature range which indicate they are n-type semiconductors. For 25% Ag$_2$Te-75% Fe$_3$O$_4$ and 50% Ag$_2$Te-50% Fe$_3$O$_4$ samples, the absolute Seebeck coefficient increase with the temperature rising. However, the absolute Seebeck coefficient of 75% Ag$_2$Te-25% Fe$_3$O$_4$ decrease first then increase after 125°C. Figure 5-3c is the electrical conductivity of Ag$_2$Te-Fe$_3$O$_4$ composites. 25% Ag$_2$Te-75% Fe$_3$O$_4$ sample has the highest electrical conductivity with the value between 140 S/cm to 160 S/cm. The electrical conductivity of all three samples have a dramatic decrease during 140°C to 160°C.

As we know Ag$_2$Te will change from low-temperature monoclinic phase ($\alpha$ phase) to high-temperature cubic phase ($\beta$ phase) at 150°C$^{35,36}$. During phase transition from $\alpha$ phase to $\beta$ phase, the energy band gap of Ag$_2$Te will be increased which will decrease the carrier concentration ($n$) while the electron mobility ($\mu$) fluctuates a little bit. As a result, the electrical

![Figure 5-4 EM absorption of samples in X band.](image-url)
conductivity will change from a highly conductive state (α phase) to a low conductive state (β phase) based on the equation \( \sigma = ne^3 \). This phase transition property may explain the dramatic changes in Figure 5-3b and 5-3c especially in the case of 75% Ag\(_2\)Te-25% Fe\(_3\)O\(_4\).

Figure 5-4 shows the EM absorption of three samples made of silver telluride nanowire and iron oxide powder with different mixture percentages in mass (75% Fe\(_3\)O\(_4\)-25% Ag\(_2\)Te, 50% Fe\(_3\)O\(_4\)-50% Ag\(_2\)Te, 25% Fe\(_3\)O\(_4\)-75% Ag\(_2\)Te), and the iron telluride nanodisk in X band. The input power \( p_0 \) is 0 dBm. The thickness of the samples and nanodisk is 1.6 mm. The EM absorption is achieved by measuring S parameters when placing the nanostructures in the X band waveguide. The EM absorption power is calculated by

\[
\left(1 - |S_{11}|^2 - |S_{21}|^2\right)p_0
\]

The maximum EM absorption power is 0.37 mW at 11.2 GHz with the sample made of 50% Fe\(_3\)O\(_4\)-50% Ag\(_2\)Te which also shows the better EM absorption performance over others with the frequency ranges from 8 GHz to 11.4 GHz. For the samples made of 25% Fe\(_3\)O\(_4\)-75% Ag\(_2\)Te, 75% Fe\(_3\)O\(_4\)-25% Ag\(_2\)Te, and the iron telluride, the maximum absorption power is 0.31 mW at 11.31 GHz, 0.32 mW at 11.29 GHz and 0.28 mW at 11.35 GHz, respectively. At least 30% power is absorbed by the samples at around 11 GHz. The potential sensors can absorb the high-power EM radiation and convert that to heat which results in the temperature change by

\[
\Delta T = \frac{Q}{C}
\]

where \( Q \) is the amount of the heat and \( C \) is the heat capacity. The temperature variation causes rapid changes of electrical conductivity by \( \alpha \)-type to \( \beta \)-type phase transition for Ag\(_2\)Te-Fe\(_3\)O\(_4\) samples as shown in Fig. 5-3, and the triggered p-type to n-type transition with reversible and reproducible switching behavior. The electromagnetic radiation driven...
phase transitions in Ag₂Te-Fe₃O₄ and FeTe₂ nano-composites can be potentially applied to develop EM sensors.

5.4 Conclusion

We show in this work that the mixture of silver telluride nanowire and the iron oxide powder, and the iron telluride nanodisk have good EM absorption in X band with the feature of rapid electrical property changes. The EM absorption properties of three mixture samples with different percentages of silver telluride nanowire and iron oxide powder, and the nanodisk made of iron telluride are measured in X band. The good EM absorption properties of samples made of silver telluride nanowire and iron oxide powder, and the nanodisk made of the iron telluride lead to the temperature increase, which causes the rapid change of the electrical conductivity by $\alpha$-type to $\beta$-type phase transition and the triggered p-type to n-type transition that can be potentially applied to develop EM sensors.

References


Aliev, F. Phase Transition of Ag-Enriched Ag2Te. *Inorganic materials* **38**, 995-997
CHAPTER 6. OBSERVATION OF TRANSIENT STRUCTURAL PHASE TRANSITION IN SINGLE COPPER TELLURIDE NANOWIRE

This chapter is based on the manuscript “Recent progress in thermoelectric nanocomposites based on solution-synthesized nanoheterostructures” accepted by Nano Research, which is co-authored by Biao Xu, Lin Zhou, Yilong Zhou, Haimei Zheng, Chenghan Sun, Enzheng Shi, Tanner Dale Fink, and Yue Wu.

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6.1 Introduction

As more than half of the world’s energy consumption is wasted as low-grade heat, thermoelectric materials have attracted tremendous interest of researchers during the last two decades owing to their quietness and portability, as well as low efficiency\(^1\). The heat recovery efficiency of thermoelectric materials is determined by the dimensionless figure of merit, \(ZT = S^2\sigma T/\kappa\). To enable the use of thermoelectrics in practical applications, several strategies have been developed recently. First, carrier concentration\(^2\) is found to be crucial to tune the peak temperature and the maximum value of power factor \((S^2\sigma)\). Moreover, band convergence\(^3,4\), resonant-level effects, and minority carrier blocking\(^5\) are efficient ways to enhance \(S\). To improve \(\sigma\), modulation doping\(^6\) offers an effective way without compromising
n and S. Contrarily, \( \kappa \) needs to be minimized. Several materials with intrinsically low thermal conductivity, such as Cu\(_2\)Se\(^7\), SnSe\(^8\), BiCuSeO\(^9\), and CsAg\(_5\)Te\(_3\)\(^{10}\) have been discovered based on the in-depth understanding of their atomic and electronic structures.

Nanostructuring and nanoprecipitation will further decrease the value of \( \kappa \)\(^{11-13}\), owing to the intensified scattering of phonons across the grain boundary.

Recent progress in thermoelectric materials is attributed to the decreased thermal conductivity realized by applying nanostructured materials\(^4\). Solution synthesis is becoming a promising alternative to produce thermoelectric nanomaterials because of the low cost and precise size control\(^{14,15}\) achieved. However, a lower limit of the lattice thermal conductivity does exist. Therefore, new progress must come from improving the power factor. One crucial way to achieve a higher power factor is by the adjustment of carrier concentration. However, owing to the self-purification mechanism\(^ {16,17}\), controlling charge carrier concentration by doping in semiconductor nanocrystals is difficult. Nanoheterostructure (NHS) materials can fill this gap because of their tunable electrical properties such as the energy-filtering effect.

An NHS material, combing multiple components in one nanoparticle\(^{18}\), enables the fine-tuning of the composition, grain microstructure (e.g., size, twinning, misfit, dislocation) and the solid–solid interface. Generally speaking, three types of NHSs exist: (1) heterostructures with core/shell geometries; (2) oligomer-like architectures based on isotropic material seeds; and (3) heterostructures based on anisotropically shaped material domains. The growth mechanisms include surface growth, surface growth and diffusion, simultaneous nucleation and growth of both components, etc. Detailed synthesis and growth mechanisms for colloidal NHS materials can be found in Ref. [18]. Further applications for NHS have been
summarized by Banin\textsuperscript{19,20} and Cozzoli\textsuperscript{21}. Usually, heterogeneous nucleation and growth are necessary. Solution-phase synthesis is a scalable and efficient way to produce NHSs, although gas-phase synthesis also can yield high-quality NHSs in a smaller quantity. A variety of NHSs have been developed by solution synthesis, especially for those based on metal chalcogenides, which are the dominating compounds in thermoelectrics.

The structural variability of an NHS will provide many opportunities in modifying its thermoelectric property. Composition tunability of the NHSs should allow for carrier concentration modulation. The solid–solid interface across the subunits can induce an energy-filtering effect of the electronic carrier and simultaneously enhance the scattering of phonon carriers. Grain microstructure can further diminish the thermal transport and improve the figure of merit. Albeit for the aforementioned advantages, NHSs have been seldom used in thermoelectrics. In this review article, we will discuss the existing and promising applications of NHSs in thermoelectrics. The discussion is categorized according to the mechanism that enhances the thermoelectric performance.

6.2 Tuning the power factor ($S^2\sigma$)

6.2.1 Tuning the carrier concentration $n$

As a multicomponent material, one unit of the NHS may be dissolved into the other, depending on the solubility at high temperatures. The solubility limit can be extracted from the phase diagram. If the valence electrons of them differ, there may be a doping effect, either in an acceptor (generating holes) or donor (generating electrons) style. The tuned carrier concentration will lead to a tunable power factor. Usually, the optimized carrier
concentration for most of the degenerated semiconductors is of the range $10^{18}$–$10^{21}$ cm$^{-3}$. A too low carrier concentration will lead to a too large Seebeck coefficient, according to the Pisarenko relationship$^2$, but a too low electrical conductivity. This is the behavior of an insulator or a wide-band-gap semiconductor. A too high carrier concentration will induce a too low Seebeck coefficient although the electrical conductivity is high. This indicates metal-like or degenerate-semiconductor electron transport. Usually, a good thermoelectric material is based on a narrow-band-gap (E$_g$ $\approx$ 0.1 – 1.0 eV) semiconductor, such as Bi$_2$Te$_3$ (0.15 eV), PbTe (0.31 eV), and SnSe (0.9 eV)$^8$. Using the NHS, one major component forms the matrix material, while the other component can be dissolved into the matrix and act as dopant upon the high-temperature processing. Yan et al. synthesized PbTe–PtTe$_2$ NHS in the solution phase$^{22}$. 

Figure 6-1. (a) SEM micrograph of PbTe-PtTe$_2$ nanoparticles with X$_{PbTe} = 0.5$. (b) TEM micrograph and (c) SAED pattern of the same sample. (d) and (e) phase contrast high resolution TEM micrographs highlight the detail structure of one multi-phased nanoparticle. Electrical properties of the PbTe-PtTe$_2$ particle films: (f) temperature dependence of electrical conductivity for samples with different X$_{PbTe}$, (g) charge carrier concentration of three types of samples measured at T = 300 K. Here, samples with X$_{PbTe} = 1$ are p-type and samples with X$_{PbTe} = 0.5$ and 0.67 are n-type. (h) Seebeck coefficients and (i) power factors of samples at different temperature. Reprinted with permission from Ref. 107. Copyright WILEY Publishing, 2009.
They characterized the product using X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) (Fig. 6-1). XRD indicated that both PbTe and PtTe$_2$ exist in the product. TEM revealed that the NHS is composed of 5–12 nm PbTe grains and 5* 10 nm PtTe$_2$ nanorods (Fig. 6-1(d)). They tuned the portion of PtTe$_2$ by tuning the feed ratio between Pb and Pt. The measured carrier concentration showed monotonic change with respect to the molar ratio of Pb:Pt. Pt acted as an n-type donor. As the portion of Pt increased, the electron concentration increased (Fig. 6-1(g)). The undoped PbTe was p-type with a very low n = 7 × 10$^{17}$ cm$^{-3}$. The 23 at. % Pt-doped sample showed an n-type transport with an electron concentration of 3 × 10$^{19}$ cm$^{-3}$. For the 50 at. % Pt-doped sample, the electron concentration was 9 × 10$^{20}$ cm$^{-3}$. The increased doping also led to enhanced electrical conductivity (Fig. 6-1(f)). The Seebeck coefficient of the undoped PbTe was positive, agreeing well with the carrier concentration measurement and the absolute values were large due to the small hole concentration (Fig. 6-1(h)). This Seebeck value is also higher than that of bulk p-type PbTe with a similar value of carrier concentration$^{23}$, owing to the quantum size effect. Meanwhile, the Pt-doped samples showed smaller values of Seebeck coefficients and the absolute Seebeck coefficients increased with ascending temperature (Fig. 6-1(h)), indicating a degenerate semiconductor behavior. Compared to bulk n-type PbTe with similar charge carrier concentrations$^{24}$, the Seebeck coefficient of 23 at. % and 50 at. % Pt-doped samples are 50%–100% higher than bulk PbTe, which benefit from the mixed-phase samples. At the same time, the electrical conductivity can be tuned by changing the ratio of PbTe to PtTe$_2$. Finally, the appropriately doped PbTe samples exhibited a higher power factor ($S^2\sigma$) than the undoped PbTe (Fig. 6-1(i)), by two orders of magnitude.
This work illustrated the importance of tuning the carrier concentration in an NHS-based thermoelectric material.

### 6.2.2 Tuning the Seebeck coefficient ($S$) through minority carrier blocking

Another way to optimize the power factor is the energy-filtering effect, which can increase the Seebeck coefficient while maintaining the same carrier concentration. Unwanted bipolar transport can also be inhibited by selectively blocking the minority carrier transport. Recently, our group had demonstrated this effect using a PbTe–Ag$_2$Te–PbTe NHS as an example$^5$. This NHS was synthesized based on a three-step strategy that had been previously developed by our group (Fig. 6-2(a)). A Te nanowire, PbTe–Te–PbTe NHS, and PbTe–Ag$_2$Te–PbTe NHS were

Figure 6-2. Synthesis and characterization of the Te nanowires, PbTe–Te nanowire heterostructures, and PbTe–Ag$_2$Te nanowire heterostructures. (a) Schematic for the three-step synthesis of PbTe–Ag$_2$Te nanowire heterostructures; (b) XRD patterns compared with the standards, (c–e) SEM images, (f–h) low-magnification TEM images with high-magnification TEM image insets of the Te nanowires (c and f), PbTe–Te nanowire heterostructures (d and g), and PbTe–Ag$_2$Te nanowire heterostructures (e and h). Scale bars in the main images represent 500nm and scale bars in the insets represent 50 nm. Experimental data and theoretical fitting of the thermoelectric properties. (i) Electrical conductivity, (j) Seebeck coefficient, (k) power factor, (l) thermal conductivity, and (m) ZT of the PbTe–Ag$_2$Te nanocomposite compared with those of the Ag$_2$Te nanocomposite. (n) The schematic band alignment between PbTe and Ag$_2$Te. Reprinted with permission from Ref. 90. Copyright American Chemical Society, 2015.
the products in each step respectively and they were unequivocally characterized by XRD, SEM, and TEM (Figs. 6-2 (b)–6-2(h)). The proposed band alignment (Fig. 6-2(n)) indicated that the electrons (minority carriers) were more strongly blocked than the holes (majority carrier), due to the different interfacial energy barrier of the valence band maximum and conduction band minimum.

The increasing trend of the Seebeck coefficient could be attributed to the diminished negative contribution from minority carriers, as S is expressed by

\[ S = \frac{S_h \sigma_h + S_e \sigma_e}{\sigma_h + \sigma_e} \]  

(6.1)

in which the minority carrier (electron) contributes negatively. Although the total electrical conductivity was impaired since both the electrical transports of electron and hole were scattered, the overall power factor could be enhanced because it was proportional to \( S^2 \) and \( \sigma^1 \). A more accurate understanding could be obtained through the Boltzmann transport equation (BTE). Comparing the BTE modeling with the experimental result, we found that the single Ag\(_2\)Te nanowire, without any interfacial energy barrier from PbTe, showed the highest electrical conductivity (Fig. 6-2(i), red line). With either the hole (majority charge carrier, cyan line in Fig.6-2(i)) or electron (minority carrier, pink line in Fig. 6-2(i)) barrier, the electrical conductivity would be slightly deteriorated. With both barriers, the lowest electrical conductivity could be simulated, agreeing well with the experiment (blue line, Fig. 6-2(i)). In contrast, when only the minority carrier was blocked (pink line, Fig. 6-2(j)), the Seebeck coefficient should have the largest value. If only the major carrier was blocked (cyan line, Fig. 6-2(j)), the Seebeck coefficient would be the lowest. In the case of pure Ag\(_2\)Te when no barrier was present (red line, Fig. 6-2(j)), a moderate Seebeck coefficient
could be obtained. In the PbTe–Ag$_2$Te–PbTe NHS (blue line, Fig. 6-2(j)), blocking of minority carriers was stronger than that of majority carriers; hence, the NHS possessed a second-best Seebeck coefficient. Then the power factor of the PbTe–Ag$_2$Te–PbTe NHS was larger than that of the pure Ag$_2$Te nanowire (Fig. 6-2(k)). Together with the lower thermal conductivity that arises from the enhanced phonon scattering through nanoinclusion of PbTe (Fig. 6-2(l)), the ZT value (0.66 at 390 K) obtained in the PbTe–Ag$_2$Te–PbTe NHS was largely improved, as compared to that of Ag$_2$Te (Fig. 6-2(m)). More importantly, we notice that the ZT value of this PbTe–Ag$_2$Te–PbTe NHS is higher than that of bulk PbTe–Ag$_2$Te–PbTe samples$^{25}$ with the same atomic ratio at low temperatures (from 300 to 400 K).

Similar effects were also found in the Bi$_2$Te$_3$–Bi$_2$Te$_{2.7}$Se$_{0.3}$NHS$^{26}$. The Bi$_2$Te$_3$ nanosheet was prepared by wet-chemical exfoliation using butyl lithium to disrupt the van der Waals interaction between the Te–Bi–Te–Bi–Te quintuple layer in the bulk Bi$_2$Te$_3$ precursor. Subsequently, a smaller nanosheet of Bi$_2$Te$_{2.7}$Se$_{0.3}$ was seeded and grown on the Bi$_2$Te$_3$ nanosheet to produce a Bi$_2$Te$_3$–Bi$_2$Te$_{2.7}$Se$_{0.3}$ NHS, using solution-phase synthesis. The Seebeck coefficient of the Bi$_2$Te$_3$–Bi$_2$Te$_{2.7}$Se$_{0.3}$ NHS was significantly enhanced as compared to the pristine Bi$_2$Te$_3$ nanosheet, at a similar carrier concentration. This could be ascribed to the band alignment between Bi$_2$Te$_{2.7}$Se$_{0.3}$ and Bi$_2$Te$_3$ and the ensuing energy filtering. When fitted with a single parabolic band model, the effective mass ($m^*$) of the electron in the Bi$_2$Te$_3$–Bi$_2$Te$_{2.7}$Se$_{0.3}$ NHS was approximately 1.2$m_0$ and it was apparently larger than that of Bi$_2$Te$_3$ (0.8$m_0$). This corresponded well with the enhanced Seebeck coefficient. Although the electrical conductivity was moderately reduced, due to the enhanced Seebeck coefficient and reduced thermal conductivity in the Bi$_2$Te$_3$–Bi$_2$Te$_{2.7}$Se$_{0.3}$
heterostructure, the overall power factor and the figure of merit were enhanced to approximately 1.17.

6.2.3 Enhancing the carrier mobility (μ) through modulation doping

Modulation doping had been first studied in semiconductor heterostructure devices. It was referred to as the enhancement of carrier mobility due to the spatially inhomogeneous doping. Modulation doping has been widely used in 2D semiconductor heterostructure devices. While in a nanocomposite, similar 3D modulation doping can also work. One example in traditional solid-state synthesis was BiAgSbSe doped with BiCl$_3$. The chlorine dopant was not uniformly distributed into the grains. There were both heavily doped and lightly doped regions. Between these grains, the modulation doping effect would work. One can imagine that by controlling the sintering condition, the limited diffusion and dissolution of the minor phase of an NHS into the major phase will create such a nanocomposite with multiple regions differently doped. Then a modulation doping mechanism can play a role to enhance the carrier mobility in this thermoelectric nanocomposite.

6.3 Reducing thermal conductivity (κ)

6.3.1 Alloying

Alloying will induce mass disorder and scatter the phonon at the length scale of several angstroms (atomic scale). It has been long studied since Callaway’s theoretical work in the 1960s. Taking Bi$_x$Sb$_{2-x}$Te$_3$ as an example, the lattice thermal conductivity can be expressed as$^{28}$
\[ \kappa_I = \frac{4\pi}{3} \frac{1}{(2\pi)^3} \sum_{\nu} \left[ \frac{2}{3} \int_{x} - \frac{1}{3} \int_{z} \right] \hbar^2 \omega^2(k, \nu) \frac{\frac{\hbar \omega(k, \nu)}{k_BT^2}}{e^{\frac{\hbar \omega(k, \nu)}{k_B T}} - 1} - v^2(k, \nu) \tau(k, \nu) k^2 \, dk \] (6.2)

in which \( \omega, v, \) and \( \tau \) stand for the vibration frequency, phonon group velocity, and scattering rate, respectively. \( k \) and \( v \) specify the phonon wave vector and the dispersion branch. The total scattering rate \( (\tau(k, \nu)) \) can be expressed as a sum of several typical scattering processes

\[ \tau_{ph}^{-1}(k, j) = \tau_{anh}^{-1}(k, j) + \tau_{mass}^{-1}(k, j) + \tau_{coup}^{-1}(k, j) + \tau_{DC}^{-1}(k, j) + \tau_{DS}^{-1}(k, j) + \tau_{b}^{-1}(k, j) \] (6.3)

where anh, mass, coupl, DC, DS, and b denote the phonon–phonon, mass disorder, coupling between phonon–phonon and mass-disorder, dislocation core, dislocation strain, and grain boundary process, respectively.

The scattering rate of mass disorder can be expressed as follows

\[ \frac{1}{\tau_{mass}(k, \nu)} = \frac{\pi}{2} g_{mass} \omega^2(k, \nu) DOS(\omega) \] (6.4)

\[ g_{mass} = \frac{\alpha_B}{\alpha_B + \alpha_S} (1 - \frac{M_B}{M_{B+S}})^2 + \frac{\alpha_S}{\alpha_B + \alpha_S} (1 - \frac{M_S}{M_{B+S}})^2 \] (6.5)

\[ \frac{M_{B+S}}{M_{B+S}} = \frac{\alpha_B M_B + \alpha_S M_S}{\alpha_B + \alpha_S} \] (6.6)

where \( \alpha \) is the atomic percentage, \( M \) is the atomic mass, and \( DOS \) is the phonon density of states. If \( \alpha_B = 1 \) (\( \alpha_S = 1 \), no alloying), then \( g_{mass} = 0 \). If \( \alpha_B = 50\% \) (\( \alpha_S = 50\% \), then \( g_{mass} = 0.0691 \). This enlarged \( g_{mass} \) will reduce the \( 1/\tau_{mass} \) and then \( 1/\tau_{total} \), reducing the lattice thermal conductivity.

Similar to doping, alloying can happen when high-temperature processing is performed in an NHS. Taking PbTe–PbS\(^{29}\) as an example, partial alloying was revealed from the high-resolution TEM (HRTEM) (Figs. 6-3(a)–6-3(c)) and XRD peaks (Fig. 6-3(d)). The thermal
conductivity of the PbTe–PbS NHS was prominently lower than that of pure PbTe or PbS (Figs. 6-3(e) and 6-3(f)). The author proposed that it was attributed to two possible factors: One was the partial alloying of PbTe and PbS, although the solubility limit of PbS in PbTe is only approximately 5 at. %; the other one was the enhanced phonon scattering at the grain boundary between PbTe and PbS.

Figure 6-3. (a) TEM micrograph of \((\text{PbTe})_{0.28}@(\text{PbS})_{0.72}\) core-shell nanoparticles with crystalline PbS shells. Insert displays the histogram of the particle size distribution. (b) HRTEM micrograph of a \((\text{PbTe})_{0.28} @(\text{PbS})_{0.72}\) core-shell nanoparticle. (c) Power spectrum analysis of the same \((\text{PbTe})_{0.28} @(\text{PbS})_{0.72}\) nanoparticle and PbTe and PbS crystallographic color maps. (d) XRD patterns of \((\text{PbTe})_{1-x}@(\text{PbS})_x\) core-shell nanoparticles with \(x = 0, 0.32, 0.40, 0.49, 0.72, \) and 1. Thermal conductivity (e) and porosity-corrected thermal conductivity and electronic contribution to the corrected thermal conductivity (f) of \((\text{PbTe})_{1-x}@(\text{PbS})_x\) nanomaterials. Reprinted with permission from Ref. 113. Copyright American Chemical Society, 2013.

6.3.2 Phonon scattering at nanograin boundaries

As the grains of each component are of nanosizes, phonons will be strongly scattered at the grain boundary in an NHS-based nanocomposite, lowering the thermal conductivity. The scattering rate of grain boundary scattering is expressed as
\[
\frac{1}{\tau_b (k, \nu)} = \frac{\nu(k,\nu)}{DF}
\]

(6.7)

where \(D\) is the grain size and \(F\) is the surface roughness factor and it is usually 1. As \(D\) decreases, \(1/\tau_b\) will increase and so will \(1/\tau_{tot}\), reducing \(\kappa_{lat}\).

Furthermore, when more than two phases exist, the minor phase may exist as an inclusion and this serves as an additional scattering center for phonon transport. The rationale of the nanoinclusion-induced scattering of phonons had been discussed in a series of theoretical work. The scattering rate of nanoinclusion scattering is expressed as

\[
\tau_{inclusion}^{-1} = \nu(\sigma_s^{-1} + \sigma_l^{-1})^{-1} \rho
\]

(6.8)

where \(\nu\) is the phonon group velocity and \(\rho\) is the density of nanoparticles. The cross-section limits of short-wavelength (s) and long-wavelength (l) scattering regimes are \(\sigma_s = 2\pi R^2\) and \(\sigma_l = (4/9) \pi R^2(\Delta D/D)^2 pat (\omega R/\nu)^4\). Here \(R\) is the radius of nano inclusion, \(\Delta D\) is the difference between the density of the inclusion and matrix material, and \(D\) is the matrix density. Based on this equation, we can speculate that by increasing the density of a nanoparticle, the difference between nanoinclusion and the matrix phase and the radius of the nanoparticle, the phonon scattering by nanoinclusion can be enhanced. Wu et al. had synthesized a PbTe–Bi\(_2\)Te\(_3\)–PbTe NHS using a three-step method similar to that used for synthesizing the PbTe–Ag\(_2\)Te–PbTe NHS. The intermediate products such as the Te nanowire and PbTe–Te–PbTe were unambiguously characterized using techniques of XRD, SEM, and TEM. The powder of the PbTe–Bi\(_2\)Te\(_3\)–PbTe NHS was hot-pressed into a pellet at 300 °C. The authors proposed that alloying (forming PbBi\(_2\)Te\(_4\), Pb\(_3\)Bi\(_4\)Te\(_9\)) should only happen at 850 K according to the phase diagram. Both of the nanograins of PbTe and Bi\(_2\)Te\(_3\) could be found in the thermoelectric nanocomposite when observed in TEM. The lattice thermal conductivity of 27 PbTe–1 Bi\(_2\)Te\(_3\) nanocomposite was 0.58 W·m\(^{-1}\)·K\(^{-1}\) at 320 K and 0.52 W·m\(^{-1}\)·K\(^{-1}\) at
620 K, while that of 2 PbTe–1 Bi$_2$Te$_3$ was merely 0.33 W·m$^{-1}$·K$^{-1}$ at 320 K and 0.61 W·m$^{-1}$·K$^{-1}$ at 620 K, all of which were much lower than either bulk PbTe (1.4 W·m$^{-1}$·K$^{-1}$ at 720 K) or Bi$_2$Te$_3$ (1.4 W·m$^{-1}$·K$^{-1}$ at 345 K). The significantly reduced $\kappa_{\text{lat}}$ was attributed to the nanosize of the crystal grain and the scattering of phonons by the Bi$_2$Te$_3$ nanoinclusion. Similar phenomena can also be found in the aforementioned PbTe–Ag$_2$Te–PbTe [5], Bi$_2$Te$_3$–Bi$_2$Te$_2.7$Se$_{0.3}$ [26], and PbTe–PbS$^{29}$ NHSs.

6.3.3 Porosity

One factor that can contribute to lowering thermal conductivity yet is commonly neglected in nanocomposites is porosity. Some theoretical work debated that although porosity can prominently reduce the lattice thermal conductivity (the surface of the pore can serve as an additional scattering site for phonons) and enhance the Seebeck coefficient (interfacial energy-filtering effect), electron mobility will be severely impaired (due to the charge carrier scattering at the boundary of pores), with the overall ZT often decreased. However, recently considerable experimental work revealed that porosity indeed might enhance the figure of merit. Taking the Bi$_2$Te$_3$ nanoplate as an example$^{32}$, the R. T. pressed nanopowder had a relative density of approximately 40%. Sintering at 200 °C would increase this value to 82% and it is 93% for 325 °C. The 200 °C -sintered sample showed only 40% of the electrical conductivity as compared with the 325 °C -sintered sample. The total power factor of the 82%-relative-density sample was only 40% that of the 93%-relative-density sample. Nonetheless, the lattice thermal conductivity of the 82%-relative-density sample was reduced to 40% of the 93%-relative-density sample and the electronic thermal conductivity was also much lower than that of the 93%-relative-density sample. Resultantly, the overall ZT of the
more porous (200 °C -sintered) Bi$_2$Te$_3$ nanocomposite was even higher than that of the denser one (325 °C). In the case of Wu et al.’s PbTe–Bi$_2$Te$_3$ nanocomposite$^{31}$, the authors found that $\kappa_{\text{lat}}$ is significantly diminished due to porosity and they had performed a detailed theoretical modeling on this effect. According to the effective-media theorem, $\kappa_l = \kappa_{l,0} \ast (1 - P)^{3/2}$, where $P$ is estimated from the relative density as $P = 1 - \rho/\rho_0$ and $\kappa_{l,0}$ is the lattice thermal conductivity of the imagined material with no porosity. This formula indicates that $\kappa_l$ can be reduced exponentially with relative density, explaining the extremely low thermal conductivity of the porous PbTe–Bi$_2$Te$_3$ nanocomposite.

![Graphical representation of thermal conductivity](image)

**Figure 6-4.** Thermal conductivity of the 2:1 (A) and 27:1 (B) PbTe/Bi$_2$Te$_3$ nanocomposites, including the total thermal conductivity (black squares), electron contribution (red circles), and lattice contribution (upward-pointing triangles). The down-triangles denote the remaining part after subtracting the electron contribution from the total thermal conductivity. The inlaid figure in (B) shows the lattice thermal conductivity of bulk PbTe and bulk Bi$_2$Te$_3$. Reprinted with permission from Ref. 115. Copyright American Chemical Society, 2013

6.4 Decoupling power factor and thermal conductivity by incorporating phase-transition material into nanowire heterostructure. To maximize the thermoelectric figure of merit of a material, a large power factor and a low thermal conductivity are desirable. However, many conflicting material parameters mentioned in the above discussion can affect power factor
and thermal conductivity at the same time. For example, increasing carrier mobility will enhance electrical conductivity while also increasing electrical thermal conductivity. One way to decouple power factor and thermal conductivity is to incorporate a phase-transition material into a nanowire heterostructure. In 2012, Liu et al. reported a ZT of 1.5 at 1,000 K in Cu$_{2-x}$Se$^7$. Cu$_{2-x}$Se undergoes a phase transition as the temperature is varied. The Se atoms piled into a face-centered cubic lattice while copper ions became superionic with liquid-like mobility. During the phase transition, the enhanced phonon interface scattering between layered Se atoms and liquid-like copper ions would decrease the lattice thermal conductivity. Furthermore, at high temperatures, Cu$_{2-x}$Se showed an ion liquid-like behavior and reduced specific heat close to 2NκB (theoretical value in liquid), where N is the number of particles and κB is the Boltzmann constant, which can further diminish thermal conductivity. At the same time, ionic conductivities keep the electrical conductivity as high as those of the other state-of-the-art thermoelectric materials. Yu et al. also achieved a ZT of 1.6 at 1,000 K in Cu$_2$Se in the same year$^{33}$. These two independent papers presented a new direction for thermoelectric materials discovery. Since then, phase-transition materials have attracted

Figure. 6-5 (a) Schematic illustration for the three-step synthesis of PbTe- Cu$_{1.75}$Te nanowire heterostructures; (b) XRD patterns compared with standard profiles.
increasing attention and have been extensively studied. Inspired by these discoveries, we explored the lead telluride–copper telluride thermoelectric nanowire heterostructure.

![Figure 6-6. Low-magnification TEM image of the Te nanowires (a), the PbTe-Te nanowire heterostructures (d), and the PbTe-Cu$_{1.75}$Te nanowire heterostructures (i). HRTEM of the Te nanowire (b) and its FFT image (c). HRTEM of the Te wire part (e) and the PbTe head part (f) of a typical PbTe-Te nanowire heterostructure and its FFT images (g: Te) (h: PbTe). HRTEM of the Cu$_{1.75}$Te wire part (j) and the PbTe head part (k) of the PbTe- Cu$_{1.75}$Te nanowire heterostructure and its FFT image (l: Cu$_{1.75}$Te) (m: PbTe)

As shown in Fig. 6-5(a), the PbTe– Cu$_{1.75}$Te nanowire heterostructures are synthesized through a three-step reaction. To obtain the nanowire heterostructures, tellurium nanowires
are synthesized first, followed by the growth of PbTe nanocubes at the two ends of the Te nanowires. Lastly, the remaining Te is converted into Cu$_{1.75}$Te. The PbTe–Cu$_{1.75}$Te nanowire heterostructures are first analyzed by XRD. Figure 6-5(b) presents the XRD patterns of the products from each step. After the first step, the XRD pattern of the product (Fig. 6-5(b) top) can be readily indexed to the pure hexagonal Te-phase (JCPDS #36-1452). After the second step, another set of peaks corresponding to the altaite PbTe (JCPDS #38-1435) appears in addition to the Te peaks, indicating the formation of PbTe. After the final step, all the Te peaks are replaced by the hexagonal Cu$_{1.75}$Te peaks (JCPDS #45-1287) in the XRD pattern (Fig. 6-5(b) bottom), which indicates the complete transformation of Te into Cu$_{1.75}$Te.

![Image](image.png)

Figure 6-7 Energy dispersive X-ray spectroscopy elemental mapping image of the PbTe-Cu$_{1.75}$Te heterostructure

The success of our synthesis strategy can be further confirmed by the TEM. As shown in Fig. 6-6(a), the Te nanowires synthesized in the first step have an average length of 1,436 ± 63 nm and an average diameter of 18.4 ± 1.1 nm. The HRTEM of the Te nanowires (Fig. 6-6(b)) and its fast Fourier transform (FFT, Fig. 6-6(c)) indicate that Te nanowires are single crystalline with the axial direction of (001). A low-resolution TEM picture of PbTe–Te is shown in Fig. 6-6(d) with an average diameter for Te nanowire of 19.5 ± 1.8 nm and the
average length reaches 1,495 ± 57 nm. The HRTEM of the wire part (Fig. 6-6(e)) and its FFT (Fig. 6-6(g)) indicate the wire is still single crystalline Te. The HRTEM of the head part (Fig. 6-6(f)) and its FFT (Fig. 6-6(h)) are indexed to single crystalline altaite PbTe with a growth direction along (220). After the final step, straight Te nanowires are converted into curved Cu$_{1.75}$Te nanowires and the average diameter of the wire part is increased to 22.2 ± 1.8 nm. Furthermore, the HRTEM of the wire part (Fig. 6-6(j)) and its FFT (Fig. 6-6(l)) can be indexed to single crystalline Cu$_{1.75}$Te while the HRTEM of the head part (Fig. 6-6(k)) and its FFT (Fig. 6-6(m)) shows that it is still PbTe. The energy dispersive X-ray spectroscopy (EDS, Fig. 6-7) elemental mapping image clearly confirms the dumbbell structure. The wire part only contains copper and tellurium elements while the lead element is concentrated in the head part that wraps and covers the tips of the Cu$_{1.75}$Te wire.

![Figure 6-8](image_url) (a) Specific heat capacity of Cu$_{1.75}$Te nanowire; Diffraction patterns of In-situ HRTEM observation of the phase transformation in a single Cu$_{1.75}$T nanowire, (b) Set temperature is 200°C and real temperature is 178°C; (c) Set temperature is 250°C and real temperature is 245°C, circles denote hexagonal phase and rectangles denote cubic phase; (d) Set temperature is 300oC and real temperature is 321°C
Figure 6-8 shows the specific heat capacity of Cu$_{1.75}$Te nanowire powder and the in situ TEM study of a single Cu$_{1.75}$Te nanowire. In Fig. 6-8(a), an endothermic peak occurs at 174 °C, which may denote a phase transition. The in situ HRTEM experiment further confirms the above hypothesis. The diffraction pattern in Fig. 6-8(b) can be indexed to hexagonal Cu$_{1.75}$Te at 178 °C (set temperature is 200 °C). When the temperature is increased to 245 °C (Fig. 6-8(c)), the hexagonal diffraction pattern coexists with the cubic diffraction pattern. With the temperature gradually increased to 321 °C (Fig. 6-8(d); set temperature is 300 °C), the hexagonal diffraction pattern vanishes and only the cubic diffraction pattern exists. Therefore, the Cu$_{1.75}$Te nanowire undergoes a phase transition at approximately 174 °C and during the heating process, the hexagonal-phase Cu$_{1.75}$Te turns into a cubic-phase Cu$_{1.75}$Te.

6.5 Conclusion and perspectives
The use of NHSs in thermoelectrics is an emerging and promising application. Recently, progress has been achieved in tuning the carrier concentration and using the energy-filtering effect to enhance the power factor. Meanwhile, alloying, nanostructuring, and porosity can reduce the lattice thermal conductivity. Synergistically, the figure of merit, ZT, can be improved in these NHS-based materials. By incorporating phase-transition materials, such as Cu$_{2-x}$Se and Cu$_{2-x}$Te, into NHSs, the power factor and the thermal conductivity can be decoupled, to achieve intrinsically lower thermal conductivity due to the liquid-like mobility of Cu, further optimizing the figure of merit. Presently, most of these NHS materials cannot be synthesized in a large scale. The present method adopted to sinter a nanocomposite disk is to produce multiple batches of same-quality materials and collect them together; this method is laborious and time consuming. One possible solution is to develop a large-scale synthesis
method for NHS materials. Another obstacle is that, during the consolidating step, sintering NHS materials together is difficult because of the different thermal stress coefficients of the multiple materials. Therefore, selecting materials with similar thermal stress coefficients for thermoelectric applications during the design step is helpful. However, the reported thermoelectric NHSs are usually based on canonical telluride compounds, especially for \( \text{Bi}_2\text{Te}_3 \) and \( \text{PbTe} \). Apart from the telluride-based NHSs, selenide- and sulfide-based ones may be considered, since Te is much more scarce and expensive than Se and S. Various solution-synthesized selenide and sulfide NHSs have been proposed\(^{18,19} \) since the seminal work of Murray et al\(^{34} \) on monodisperse metal chalcogenide nanocrystals. We anticipate that by using these selenide and sulfide NHSs as building blocks, thermoelectric materials with high efficiency, low material cost and low toxicity can be fabricated, facilitating the use of thermoelectrics in broader applications.

References


CHAPTER 7. GENERAL CONCLUSIONS

This research work to develop phase change materials for thermal switches and thermal sensors has achieved the following milestones:

(1) A solution-phase synthesis of iron telluride nanostructures with reversible and reproducible switching behavior between p- and n-type conduction is demonstrated by a simple change of temperature. A proof-of-concept thermally triggered p-n diode has been demonstrated. This device has a large electrical conductivity during normal operation which can minimize power consumption. While at high temperature, it will be triggered to a p-n diode with a fast response time to temperature rising.

(2) Development of a large-scale solution-phase synthesis method to synthesize silver telluride based on tellurium nanowire template. [1 1 0] axes is thermodynamic favorable growth direction for silver telluride nanowires and its structural phase transition can be realized by temperature- or electrically-driven method. In addition, the threshold DC voltage is less than 1 V and can result in sharp drop in conductance. These results indicate the potential application of using silver telluride as a low cost, self-recoverable, and low power consumption nanoscale short circuit protection devices.

(3) A new electromagnetic sensor prototype is presented by sintering electromagnetic absorption material and phase change material together. The electromagnetic absorption material will absorb electromagnetic wave in X band and increase temperature. This rising temperature will drive the phase change and have the potential application in electromagnetic sensor and switch.
REFERENCES


https://www.nature.com/articles/nnano.2009.266#supplementary-information (2009).

https://www.nature.com/articles/nature07970#supplementary-information (2009).