1992

High temperature rare earth and Si-Ge thermoelectric materials

Sang Hyun Han
Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/rtd

Part of the Metallurgy Commons

Recommended Citation
Han, Sang Hyun, "High temperature rare earth and Si-Ge thermoelectric materials " (1992). Retrospective Theses and Dissertations. 10114.
https://lib.dr.iastate.edu/rtd/10114

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.
High temperature rare earth and Si-Ge thermoelectric materials

Han, Sang Hyun, Ph.D.
Iowa State University, 1992
High temperature rare earth and Si-Ge thermoelectric materials

by

Sang Hyun Han

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Materials Science and Engineering
Major: Metallurgy

Approved:

Signature was redacted for privacy.

In Charge of Major Work
Signature was redacted for privacy.

For the Major Department
Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1992
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>GENERAL INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td><strong>PAPER I.</strong> PREPARATION OF THE METAstable HIGH TEMPERATURE PHASE (γ-Dy₂S₃) AND THE METAstable HIGH PRESSURE γ-R₂S₃ (R = Y, Er, Tm, Yb AND Lu) BY MECHANICAL MILLING</td>
<td>3</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>4</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>5</td>
</tr>
<tr>
<td>EXPERIMENTAL PROCEDURES</td>
<td>7</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>9</td>
</tr>
<tr>
<td>CONCLUSIONS AND SUMMARY</td>
<td>48</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>49</td>
</tr>
<tr>
<td>APPENDIX</td>
<td>52</td>
</tr>
<tr>
<td><strong>PAPER II.</strong> THERMOELECTRIC PROPERTIES OF Cu DOPED DYSPROSIUM SESQUISULFIDE</td>
<td>55</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>56</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>57</td>
</tr>
<tr>
<td>EXPERIMENTAL PROCEDURES</td>
<td>64</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>68</td>
</tr>
<tr>
<td>CONCLUSIONS AND SUMMARY</td>
<td>117</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>119</td>
</tr>
<tr>
<td><strong>PAPER III.</strong> EFFECT OF THE DOPING PROCESS ON THE ELECTRICAL ACTIVITY OF PHOSPHORUS IN Si₈₀Ge₂₀</td>
<td>122</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>123</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>124</td>
</tr>
</tbody>
</table>
GENERAL INTRODUCTION

The Seebeck effect\(^1\) which underlies the conversion of heat energy into the electrical energy has been known for more than 170 years, but it is only the last 30 years that the development of new and improved thermoelectric materials has made possible the fabrication of practical thermoelectric devices.\(^2\) The use of thermoelectric devices has to date been restricted to specialized applications where combinations of their desirable properties outweigh their relative efficiency and high cost. One of the specialized applications is the radioisotope thermoelectric generators (RTGs).\(^2\) Over the past decades the development and application of RTGs have been continued for deep space missions.\(^3\) So far, many materials have been investigated for high temperature thermoelectric materials, i.e. Si-Ge alloys\(^4,5\), bismuth tellurides\(^6\), lead tellurides\(^7\), boron-rich borides\(^8\) and rare earth chalcogenides\(^9\)-\(^11\). Among these, the rare earth chalcogenides have received increasing attention in recent years with particular interest centered on the high temperature thermoelectric materials because of their high melting points\(^12\), low thermal conductivities\(^9,10\) and the self doping ability to change continuously from a metallic conductor to an insulator\(^10,13\).

The thermoelectric properties of silicon-germanium alloys have been studied since 1960.\(^5\) Si-Ge alloys are still in use today as the main materials in RTGs, providing reliable electrical power for the Voyager, Galileo and Ulysses space crafts. Various efforts to improve the thermoelectric performance of Si-Ge alloys have also been reported.\(^14,15\)

This thesis is an effort to develop potential high temperature thermoelectric materials. In this study, mechanical alloying (MA) was utilized as a doping and alloying process. MA is a dry, high energy ball milling process which was developed by
scientists and engineers to prepare commercial oxide dispersion-strengthened (ODS) alloys. Currently MA is widely used to produce amorphization, nanocrystalline structures, intermetallic compounds.

**Thesis Organization**

This thesis consists of three papers. Paper I is concerned with the preparation of metastable crystalline high temperature polymorph of Dy$_2$S$_3$ or metastable crystalline high pressure polymorphs of R$_2$S$_3$ (R = Y, Er, Tm, Yb and Lu) by mechanical milling (MM). In Paper II, copper doped dysprosium sesquisulfide compounds, which have the $\eta$-orthorhombic structure, were examined as potential high temperature thermoelectric materials. Paper III deals with the use of mechanical alloying and gaseous state diffusion to extend the electrical activity of phosphorus above the maximum reported equilibrium limit in Si$_{60}$Ge$_{20}$ alloys. The papers are followed by a General Summary. References cited in the General Introduction follow the General Summary.
PAPER I. PREPARATION OF THE METASTABLE HIGH TEMPERATURE PHASE ($\gamma$-Dy$_2$S$_3$) AND THE METASTABLE HIGH PRESSURE $\gamma$-R$_2$S$_3$ 
(R = Y, Er, Tm, Yb AND Lu) BY MECHANICAL MILLING
ABSTRACT

The preparation of the metastable crystalline high temperature and high pressure polymorphs of $R_2S_3$, where $R = Y$, Dy, Er, Tm, Yb and Lu was investigated at room temperature by mechanical milling (MM). For $\eta$-Dy$_2$S$_3$, the metastable high temperature $\gamma$-phase was obtained by MM. For $\delta$-Y$_2$S$_3$, $\delta$-Er$_2$S$_3$ and $\varepsilon$-Yb$_2$S$_3$ the metastable high pressure $\gamma$-phase was obtained, whereas for the $\delta$-Tm$_2$S$_3$ and $\varepsilon$-Lu$_2$S$_3$ samples the metastable high pressure $\gamma$-phases coexisted with the corresponding equilibrium ambient polymorphic phase. In case of Dy$_2$S$_3$ and Y$_2$S$_3$ the $\gamma$-cubic phase was present even after 160 hour MM.
INTRODUCTION

Mechanical alloying (MA) is a dry, high energy ball milling, non-equilibrium process which was developed by scientists and engineers in the late 1960s to produce commercial oxide dispersion-strengthened (ODS) alloys.\textsuperscript{1, 2} MA also allows two materials with widely different melting points to be alloyed. It is believed that the balance between cold welding and fracturing causes two materials to be alloyed during ball milling.\textsuperscript{2} However, over the past ten years, MA has been widely used to produce amorphization\textsuperscript{3, 4}, nanocrystalline structures\textsuperscript{5}, intermetallic compounds\textsuperscript{6}, and solid solutions.\textsuperscript{7} Mechanical milling (MM) is a similar process, except a single phase material is subjected to the high energy ball milling, usually to produce fine crystalline or amorphous powders.\textsuperscript{8} The formation of the metastable crystalline phases has been reported by Fecht et al.\textsuperscript{9} who found the existence of a bcc phase in Al\textsubscript{0.5}Zr\textsubscript{0.5} which had formed during MA of a mixture of Al and Zr powders; and by Loeff et al.\textsuperscript{10} who found a fcc pure phase when a 50:50 Zr-Cr arc-melted alloy was milled. Normally rapid quenching processes (melt spinning, atomizing etc.) have been used extensively to obtain high temperature metastable phases at room temperature.\textsuperscript{11, 12} Since these techniques use high cooling rates, the lattice atoms at the high temperature do not have sufficient time to redistribute to the room temperature configuration. Therefore the high temperature structure is obtained as a metastable phase at room temperature. During MM or MA the local temperature is raised, the sample is subjected to momentary high pressures, and a high density of defects is introduced into the material. All of these factors can affect the crystal structure.

Among the rare earth sesquisulfides, the heavy rare earth sulfides (R\textsubscript{2}S\textsubscript{3}, where R = Y, Gd to Lu) have a large number of polymorphs.\textsuperscript{13} As part of this thesis research
we found and reported that the metastable crystalline high temperature polymorph of
$\text{Dy}_2\text{S}_3$ or metastable crystalline high pressure polymorphs of $\text{R}_2\text{S}_3$ (R = Y, Er, Tm, Yb
and Lu) can be prepared by MM.\textsuperscript{14, 15} This discovery opened a new door for the
synthesis of metastable crystalline polymorphs.
EXPERIMENTAL PROCEDURES

Sample (R₂S₃) Preparation

High purity dysprosium (Dy) and yttrium (Y), erbium (Er) and lutetium (Lu) metals (prepared at the Materials Preparation Center of the Ames Laboratory) were electropolished to remove the thin oxide coatings from the surfaces. For thulium (Tm), distilled Tm was used without electropolishing, whereas in case of ytterbium (Yb) the surface was filed to remove the oxide impurity layers. Rare earth sesquisulfides (Dy₂S₃, Y₂S₃, Er₂S₃, Tm₂S₃, Yb₂S₃ and Lu₂S₃) were prepared by the direct combination of stoichiometric amounts of each Dy, Y, Er, Tm, Yb, Lu metal and sulfur (purchased from ASARCO, 99.999 at.% pure) with iodine (~ 10 mg each) in a quartz ampoule at 850 – 950°C. After sealing the rare earth metal and sulfur in a quartz capsule the mixture was heated to 500°C. The quartz ampoule was held at 500°C for one day and then temperature was increased to 650°C to vaporize sulfur. After all sulfur was vaporized, the temperature was increased by 100°C increments daily until the target temperature of 950°C was reached. Finally, each quartz ampoule was held at 950°C for three days to homogenize the sample and then air-cooled to ambient temperature. These materials are the starting materials for mechanical milling. Impurity levels of Dy₂S₃ are summarized in Appendix (Table A.1).

Mechanical Milling (MM)

The sesquisulfide powder was placed in a tungsten carbide vial and sealed in a helium atmosphere using a helium-filled glove box. The vial employed an O-ring seal to contain the internal atmosphere of helium. The powders were mechanically milled as a function of time (the times varied from as low as 10 min. to as high as 160 h) in a Spex
8000 mixer/mill using three 10 mm diameter tungsten carbide balls. The weight ratio of balls to powders was 5:1.

**X-ray diffraction**

X-ray diffraction was carried out on a SCINTAG diffractometer using Cu $K_\alpha$ radiation. Single crystal x-ray diffraction analysis of dysprosium sesquisulfide (Dy$_2$S$_3$) was carried out at room temperature with Rigaku-AFC6R and monochromatized Mo $K_\alpha$ radiation. The data refinement was done with the TEXAN program.
RESULTS AND DISCUSSION

Crystal structure characterization

Rare earth sesquisulfides ($R_2S_3$) have a large number of polymorphic structures which have various near neighbor arrangements of the rare earth and the sulfur atoms. Among them, the crystal structure of the cubic $\gamma$- $R_2S_3$ phases ($R = $ La to Tb) has been well studied. However, heavy $R_2S_3$ ($R = $ Dy to Lu) compounds have complicated polymorphic structures, see Table 1.

Yttrium sesquisulfide ($Y_2S_3$)

Three polymorphic phases for yttrium sesquisulfide have been reported. The $d$-monoclinic structure is a stable form at room temperature, but both the $\gamma$-cubic and $\eta$-orthorhombic phases are high pressure and high temperature forms, respectively. The $d$-monoclinic ($Ho_2S_3$ type) $Y_2S_3$ has 12 yttrium atoms and 18 sulfur atoms per cell. The yttrium sesquisulfide prepared in this study is the $d$-monoclinic phase. X-ray diffraction pattern of this $d$-monoclinic $Y_2S_3$ is shown in Figure 1. The unit cell lengths for $Y_2S_3$ are consistent with the reported values, whereas its $\beta'$ angle (80.80°) is quite different from the reported value (98.67°) (Table 1). However, a $\beta'$ value of 81.10° has been reported for $\delta$-$Y_2S_3$, $\delta$-$Dy_2S_3$ and $\delta$-$Er_2S_3$.

Dysprosium sesquisulfide ($Dy_2S_3$)

Dysprosium sesquisulfide is known to occur in three polymorphic forms. Sleight et al. reported $\alpha$-orthorhombic ($Gd_2S_3$ type) and $d$-monoclinic ($Ho_2S_3$ type) $Dy_2S_3$. White et al. found the $d$-monoclinic ($Ho_2S_3$ type) $Dy_2S_3$. In addition, $\gamma$-cubic (defect $Th_3P_4$ type) polymorph was reported. The $\gamma$-$Dy_2S_3$ is a high temperature form. In
Table 1. Crystallographic data for $R_2S_3$ ($R =$ Y, Dy, Er, Tm, Yb and Lu)

<table>
<thead>
<tr>
<th>Formula</th>
<th>Color</th>
<th>Phase</th>
<th>Space group</th>
<th>Structure type</th>
<th>Lattice parameter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_2S_3$</td>
<td>yellow</td>
<td>$\delta$-monoclinic</td>
<td>P2$_1$/m</td>
<td>Ho$_2$S$_3$</td>
<td>17.52 4.02 10.17 98.67</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\eta$-orthorhombic</td>
<td>Pnma</td>
<td>U$_2$S$_3$</td>
<td>10.60 3.86 10.44</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>yellow</td>
<td>$\gamma$-cubic</td>
<td>I43d</td>
<td>Th$_3$P$_4$</td>
<td>8.31</td>
<td>21</td>
</tr>
<tr>
<td>Dy$_2S_3$</td>
<td>brown</td>
<td>$\alpha$-orthorhombic</td>
<td>Pnma</td>
<td>Gd$_2$S$_3$</td>
<td>7.28 3.88 15.10</td>
<td>19</td>
</tr>
<tr>
<td>green</td>
<td></td>
<td>$\delta$-monoclinic</td>
<td>P2$_1$/m</td>
<td>Ho$_2$S$_3$</td>
<td>17.50 4.02 10.18 98.67</td>
<td>22</td>
</tr>
<tr>
<td>black</td>
<td></td>
<td>$\gamma$-cubic</td>
<td>I43d</td>
<td>Th$_3$P$_4$</td>
<td>8.29</td>
<td>21, 23</td>
</tr>
<tr>
<td></td>
<td>brown</td>
<td>$\eta$-orthorhombic</td>
<td>Pnma</td>
<td>U$_2$S$_3$</td>
<td>10.61 3.80 10.43</td>
<td>24</td>
</tr>
<tr>
<td>Er$_2S_3$</td>
<td>yellow</td>
<td>$\delta$-monoclinic</td>
<td>P2$_1$/m</td>
<td>Ho$_2$S$_3$</td>
<td>17.40 3.98 10.09 98.67</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\eta$-orthorhombic</td>
<td>Pnma</td>
<td>U$_2$S$_3$</td>
<td>10.53 3.82 10.37</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\gamma$-cubic</td>
<td>I43d</td>
<td>Th$_3$P$_4$</td>
<td>8.24</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\delta$-orthorhombic</td>
<td>P2$_1$/m</td>
<td>Ho$_2$S$_3$</td>
<td>17.39 3.99 10.10 80.60</td>
<td>This study</td>
</tr>
<tr>
<td>Tm$_2S_3$</td>
<td>yellow</td>
<td>$\delta$-monoclinic</td>
<td>P2$_1$/m</td>
<td>Ho$_2$S$_3$</td>
<td>17.36 3.96 10.04 98.78</td>
<td>19, 25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\delta$-monoclinic</td>
<td>P2$_1$/m</td>
<td>Er$_3$Sc$_6$</td>
<td>11.11 3.87 10.87 108.88</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\theta$-cubic</td>
<td>Ia$\bar{3}$</td>
<td>Ti$_2$O$_3$</td>
<td>10.51</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\eta$-orthorhombic</td>
<td>Pnma</td>
<td>U$_2$S$_3$</td>
<td>10.48 3.81 10.35</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\gamma$-cubic</td>
<td>I43d</td>
<td>Th$_3$P$_4$</td>
<td>8.23</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>yellow</td>
<td>$\varepsilon$-rhombohedral</td>
<td>R$\text{5}c$</td>
<td>Al$_2$O$_3$</td>
<td>6.77 18.24 27</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\delta$-monoclinic</td>
<td>P2$_1$/m</td>
<td>Ho$_2$S$_3$</td>
<td>17.30 3.98 10.30 80.50</td>
<td>This study</td>
</tr>
<tr>
<td>Compound</td>
<td>Crystal System</td>
<td>Space Group</td>
<td>Pearson Symbol</td>
<td>Parameters (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>----------------</td>
<td>-------------</td>
<td>----------------</td>
<td>----------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yb$_2$S$_3$</td>
<td>$\delta$-monoclinic</td>
<td>P2$_1$/m</td>
<td>Yb$_2$S$_3$</td>
<td>18.15 4.06 10.37 100</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\eta$-orthorhombic</td>
<td>Pnma</td>
<td>U$_2$S$_3$</td>
<td>10.44 3.79 10.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0-cubic</td>
<td>Ia3</td>
<td>Mn$_2$O$_3$</td>
<td>12.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\varepsilon'$-rhombohedral</td>
<td>P6$_3$cm</td>
<td>Yb$_2$S$_3$</td>
<td>6.77 18.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>? orthorhombic</td>
<td>a</td>
<td>Unknown</td>
<td>6.79 9.98 3.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>? cubic</td>
<td>b</td>
<td>Unknown</td>
<td>10.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\gamma$-cubic</td>
<td>I43d</td>
<td>Th$_3$P$_4$</td>
<td>8.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\varepsilon$-rhombohedral</td>
<td>R3c</td>
<td>Al$_2$O$_3$</td>
<td>6.77 18.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>yellow</td>
<td>$\varepsilon$-rhombohedral</td>
<td>R3c</td>
<td>Al$_2$O$_3$</td>
<td>6.75 18.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>yellow</td>
<td>$\varepsilon$-rhombohedral</td>
<td>R3c</td>
<td>Al$_2$O$_3$</td>
<td>6.75 18.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>black</td>
<td>$\varepsilon$-rhombohedral</td>
<td>R3c</td>
<td>Al$_2$O$_3$</td>
<td>6.72 18.16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>white</td>
<td>$\varepsilon$-rhombohedral</td>
<td>R3c</td>
<td>Al$_2$O$_3$</td>
<td>6.73 18.17</td>
<td></td>
</tr>
</tbody>
</table>

This study

---

*a Pearson symbol o??

*b Pearson symbol cF?
Figure 1. X-ray diffraction pattern of δ-monoclinic (Ho$_2$S$_3$ type) Y$_2$S$_3$. 
this study brown-colored Dy$_2$S$_3$ was prepared, but the x-ray powder pattern of this Dy$_2$S$_3$ did not match those of the above. Recently, a fourth polymorph (η-orthorhombic, U$_2$S$_3$ type) for Dy$_2$S$_3$ was found$^{24}$, but they did not report the x-ray powder pattern of this new η-Dy$_2$S$_3$. Therefore, a single crystal x-ray diffraction experiment was carried out in order to characterize the crystal structure of the prepared Dy$_2$S$_3$. The results are summarized in Appendix (Table A.2 and A.3). The Dy$_2$S$_3$ investigated has the η-U$_2$S$_3$ type, which has 8 Dy atoms and 12 S atoms per cell (Figure 2). The lattice parameters are $a = 10.566\AA$, $b = 3.853\AA$, and $c = 10.424\AA$. There are two types of Dy and three types of S. The number of sulfur atoms around Dy (1) is eight at average distance of 2.88Å, while Dy (2) has seven sulfur atoms at average distance of 2.76Å (Figure 3 (a) and (b)). The sulfur atoms in η-orthorhombic Dy$_2$S$_3$ are coordinated by five dysprosium atoms. The resultant data is consistent with that of Meetsma et al.$^{24}$ However, the preparation methods are quite different from each other. According to Meetsma et al.$^{24}$, the starting material for vapor transport was (DyS)$_2$TaS$_2$ prepared by high temperature (800°C) reaction of the elements. In this study, η-Dy$_2$S$_3$ was prepared by direct combination of stoichiometric amounts of Dy metal and sulfur with iodine (10 mg) in a quartz ampoule at 950°C. X-ray diffraction patterns of this Dy$_2$S$_3$ is shown in Figure 4. So far, it is known that at ambient pressure this structure occurs with rare earth selenides (Gd to Dy) and tellurides (Pr to Gd)$^{13}$. At high pressure and high temperature it also forms with rare earth sulfides (Y to Lu)$^{20}$.

From the resultant data (Appendix), the electron density distribution maps were drawn at $y = 0.25$ and $0.75$ (Figures 5 and 6). Since dysprosium atom has larger number of electrons (66) compared to sulfur (16), the electron density of Dy is much higher than that of S. As shown in Figures 5 and 6, the dark spots indicate high electron density of Dy, i.e. the position of Dy atom, and the gray areas indicate
Figure 2. The structure of \( \eta \)-orthorhombic (\( U_2S_3 \) type) \( \text{Dy}_2S_3 \). The shaded atoms are dysprosium and the open atoms are sulfur.
Figure 3. Coordination of Dy1 (a) and Dy2 (b) in $\eta\text{Dy}_2S_3$. 
Figure 4. X-ray diffraction pattern of \( \eta \)-orthorhombic (\( U_2S_3 \) type) \( Dy_2S_3 \).
Figure 5. 3-dimensional electron density distribution of $\eta$-Dy$_2$S$_3$ at $y = 0.25$ (250 in Figure). The dark spots are the electron densities of Dy atoms and the gray areas are the electron densities of S atoms.
Figure 6. 3-dimensional electron density distribution of $\gamma$-Dy$_2$S$_3$ at $y = 0.75$ (750 in Figure). The dark spots are the electron densities of Dy atoms and the gray areas are the electron densities of S atoms.
relatively low electron density of S, i.e. the position of S atom.

**Erbium sesquisulfide (Er$_2$S$_3$)**

Erbium sesquisulfide also has three polymorphic structures. Like Y$_2$S$_3$, $\delta$-monoclinic Er$_2$S$_3$ is the stable form at room temperature$^{19}$ and the $\eta$- and $\gamma$-phases are high pressure and high temperature forms, respectively.$^{20, 21}$ In this study, $\delta$-monoclinic Er$_2$S$_3$ modification was prepared. The x-ray diffraction patterns are shown in Figure 7, and the lattice parameters are listed in Table 1.

**Thulium sesquisulfide (Tm$_2$S$_3$)**

It has been known that thulium sesquisulfide has six different polymorphic structures depending on temperature and pressure.$^{35}$ If Tm$_2$S$_3$ is prepared at 1000°C, it occurs in the $\delta$-monoclinic phase (Ho$_2$S$_3$ type)$^{19}$, whereas at a preparation temperature of about 800°C, $\theta$-cubic phase is obtained.$^{26}$ The $\delta$-monoclinic (Er$_3$ScS$_6$ type)$^{25}$, $\gamma$-cubic (defect Th$_3$P$_4$ type)$^{21}$ and $\eta$-orthorhombic (U$_2$S$_3$)$^{20}$ structures are high temperature and high pressure phases. $\epsilon$-rhombohedral Tm$_2$S$_3$ was reported by Range et al.$^{27}$ In this study the $\delta$-monoclinic (Ho$_2$S$_3$) Tm$_2$S$_3$ was obtained. The lattice parameters and x-ray diffraction patterns of this Tm$_2$S$_3$ are summarized in Table 1 and Figure 8, respectively.

**Ytterbium sesquisulfide (Yb$_2$S$_3$)**

Among rare earth sesquisulfides ytterbium sesquisulfide has the largest number (8) of the polymorphs. They are listed in Table 1. The $\delta$-monoclinic Yb$_2$S$_3$ is obtained at 1000°C$^{28}$, while the $\epsilon$-rhombohedral Yb$_2$S$_3$ (Al$_2$O$_3$ type) forms from Yb$_2$O$_3$ and H$_2$S at 1000 to 1300°C.$^{29}$ The $\epsilon'$-rhombohedral Yb$_2$S$_3$ (Yb$_2$S$_3$ type) is also obtained from
Figure 7. X-ray diffraction pattern of \(\delta\)-monoclinic (Ho\(_2\)S\(_3\) type) Er\(_2\)S\(_3\).
Figure 8. X-ray diffraction pattern of δ-monoclinic (Ho₂S₃ type) Tm₂S₃.
the elements in evacuated quartz ampoule at 980°C, whereas θ-cubic Yb₂S₃ (Mn₂O₃ type) forms between 650 and 950°C. The η-orthorhombic (U₂S₃ type) and γ-cubic (Th₃P₄ type) Yb₂S₃ exist only at high temperature and high pressure. Other two polymorphic phases are α?α and cF (Pearson symbols), but their structures are unknown. In this study, the yellow colored ε-rhombohedral Yb₂S₃ was obtained. This ε-Yb₂S₃ has 12 Yb atoms and 18 S atoms per cell. X-ray diffraction patterns and lattice parameters are given in Figure 9 and Table 1.

**Lutetium sesquisulfide (Lu₂S₃)**

For lutetium sesquisulfide, 4 different polymorphic structures have been reported. Range et al. and Sleight et al. found the ε-rhombohedral Lu₂S₃ (Al₂O₃ type), while ε'-rhombohedral phase (Yb₂S₃ type) was reported by Eliseev et al. The η-orthorhombic (U₂S₃ type) and γ-cubic polymorphic structures exist at high temperature and high pressure. Three different colors of ε-Lu₂S₃ have been known, i.e. black, gray, pale yellow. However, white-colored ε-Lu₂S₃ (Al₂O₃ type) was prepared in this study, see Table 1 and Figure 10.
Figure 9. X-ray diffraction pattern of ε-rhombohedral (Al₂O₃ type) Yb₂S₃.
Figure 10. X-ray diffraction pattern of $\varepsilon$-rhombohedral (Al$_2$O$_3$ type) Lu$_2$S$_3$. 
Dysprosium sesquisulfide (Dy₂S₃) and yttrium sesquisulfide (Y₂S₃)

According to the Dy-S phase diagram α-Dy₂S₃ phase exists from room temperature to 1190°C. Above this temperature the α-phase transforms to the cubic γ-Dy₂S₃ form (the defect Th₃P₄ type structure). For the η-Dy₂S₃ the η ↔ γ phase transformation at 1190°C is expected because there are only slight differences between α-(Gd₂S₃ type) and η-structures (U₂S₃ type).

η-Dy₂S₃ transforms gradually into the γ-Dy₂S₃ with the milling time (Figure 11). Between 20 and 40 min. nearly 50% of η-phase has been converted. After 200 min. MM, all of the η-phase transformed into γ-phase. The γ-phase is a defect Th₃P₄ structure (R₈/3V₁/3S₄, where v = vacancy) and has 26.67 atoms in unit cell, i.e. 10.67 Dy atoms and 16 S atoms. As shown in Figure 12, (111), (130) and (310) orthorhombic peaks begin to disappear at 10 min. and simultaneously (211) cubic peak starts to form. After 200 min. MM, all three orthorhombic peaks have completely disappeared and only (211) cubic peak exists. In the 2θ range of 33 - 37°, the (412), (221), (301), (410) and (311) orthorhombic peaks diminish with the milling time and the (310) cubic peak grows (Figure 13). Figure 14 also shows the diminution of (041), (141), (411) and (311) orthorhombic peaks and the growth of cubic (321) peak. As is seen from Figures 12 - 14 the η-Dy₂S₃ transformed to γ-Dy₂S₃ some where between 60 and 200 min.

For yttrium sesquisulfide (Y₂S₃) only the δ-Y₂S₃ exists from 20°C to the melting point (1900°C) at one atmosphere pressure, and γ-Y₂S₃ is found to exist only at high pressure. Figure 15 shows x-ray diffraction patterns of Y₂S₃ with MM time. The δ-monoclinic phase begins to transform at 10 min. and after 200 min. MM the δ-phase has completely transformed into the γ-phase. In the 2θ range of 33 - 37°, the (412),
Figure 11. X-ray diffraction patterns of $\eta$-Dy$_2$S$_3$ as a function of milling time: (a) 0 min.; (b) 10 min.; (c) 20 min.; (d) 40 min.; (e) 60 min.; and (f) 200 min.
Figure 12. X-ray diffraction patterns of \( \eta \)-\( \text{Dy}_2\text{S}_3 \) as a function of milling time between \( 25^\circ \) and \( 28^\circ \): (a) 0 min.; (b) 10 min.; (c) 20 min.; (d) 40 min.; (e) 60 min.; and (f) 200 min.
Figure 13. X-ray diffraction patterns of $\text{I}_1\text{Dy}_2\text{S}_3$ as a function of milling time between 33° and 37°: (a) 0 min.; (b) 10 min.; (c) 20 min.; (d) 40 min.; (e) 60 min.; and (f) 200 min.
Figure 14. X-ray diffraction patterns of $\text{Y}_2\text{S}_3$ as a function of milling time between 40° and 44°: (a) 0 min.; (b) 10 min.; (c) 20 min.; (d) 40 min.; (e) 60 min.; and (f) 200 min.
Figure 15. X-ray diffraction patterns of $\delta$-Y$_2$S$_3$ as a function of milling time: (a) 0 min.; (b) 10 min.; (c) 20 min.; (d) 40 min.; (e) 60 min.; and (f) 200 min.
(113), (204) and (700) monoclinic peaks gradually disappear with the milling time and
simultaneously (310) cubic peak grows between (412) and (113) monoclinic peaks
(Figure 16).

The stabilization of the high temperature \( \gamma \)-phase of \( \text{Dy}_2\text{S}_3 \) and the high pressure
\( \gamma \)-phase of \( \text{Y}_2\text{S}_3 \) obtained at room temperature as metastable phase by MM is quite
surprising, especially in view of the high transformation temperature for \( \text{Dy}_2\text{S}_3 \) and the
non-existence of \( \gamma \)-\( \text{Y}_2\text{S}_3 \) at one atmosphere pressure. In the MM (or MA) process the
material is subjected to highly energetic compressive impact forces.\(^{38}\) These impact
forces cause a repeated cold welding and fracturing of materials.\(^2\) This cold welding
results when two flattened particles overlap so that their clean surface regions contact
and the high strain rate deformation and cumulative straining accompanying these
collisions lead to particle fracture.\(^{39}\) In addition, the impact of the ball on the material
being alloyed (milled) generates simultaneously a dynamic transient high pressure and
temperature spike.\(^8\) The continuous ball impacts cause a high density of the defects
(point defects and dislocations) in the materials.\(^3,9\) Davis et al.\(^{40}\) claimed that
temperature rises in typical powder alloys during MA in the Spex mill are \( \leq 350\text{K} \), but
Maurice et al.\(^{39}\) estimated that for the niobium (Nb) temperature rise is \( 634\text{K} \).
Recently, Bhattacharya et al.\(^{41}\) reported the actual temperature profile in the powder
compact after a collision event \( (T_c = 668^\circ\text{C}) \). However, even assuming that the highest
estimated temperature rise is value, we see that it is much too low for the \( \eta \)- (or \( \alpha \)-)
\( \text{Dy}_2\text{S}_3 \) to \( \gamma \)-\( \text{Dy}_2\text{S}_3 \) transition, which occurs at \( 1190^\circ\text{C} \).

The maximum pressure reached in MM or MA is estimated to be \( 10\text{ kbars} \).\(^{39}\)
Based on the results of Eatough et al.\(^{21}\), it appears that pressure has little effect on the
transition temperature of \( \text{Dy}_2\text{S}_3 \) ( a pressure of 70 kbars at \( 1200^\circ\text{C} \) was required to
convert \( \alpha \) to \( \gamma \) phase). On the contrary, it has been reported by Range et al.\(^{42}\) that the
Figure 16. X-ray diffraction patterns of $\delta$-Y$_2$S$_3$ as a function of milling time between 33° and 37°:
(a) 0 min.; (b) 10 min.; (c) 20 min.; (d) 40 min.; (e) 60 min.; and (f) 200 min.
\( \alpha \leftrightarrow \gamma \) phase transition temperature in \( \text{Dy}_2\text{S}_3 \) increases with increasing pressure. For example, 2 kbars is needed to convert \( \alpha \) to \( \gamma \) phase at 1200°C, while 11 kbars is needed at 1600°C. Thus, it is unlikely that during this dynamic process the pressure-temperature conditions reached were sufficient for the transformation to the cubic \( \gamma \)-form to take place under conditions approaching equilibrium conditions.

The cubic form of \( \text{Y}_2\text{S}_3 \) was obtained by Eatough et al.\textsuperscript{21} by heating to 2000°C under a pressure of 77 kbars, which are far from the maximum temperature (\( \leq 668\,^\circ\text{C} \))\textsuperscript{41} and pressure (10 kbars)\textsuperscript{39} reached in MM or MA. In addition, it has been reported by Range et al.\textsuperscript{20} that \( \eta \)-orthorhombic \( \text{Y}_2\text{S}_3 \) (\( \text{U}_2\text{S}_3 \) type) forms at 850°C and a pressure of 20 kbars. Therefore, it is likely that the sequence of the phase transition of \( \text{Y}_2\text{S}_3 \) is as follows:

\[
\begin{align*}
850^\circ\text{C}, 20 \text{ kbars} & \quad \downarrow \quad 2000^\circ\text{C}, 77 \text{ kbars} \\
\delta \text{-monoclinic (H}_2\text{S}_3 \text{ type)} & \quad \Rightarrow \quad \eta \text{-orthorhombic (U}_2\text{S}_3 \text{)} & \quad \Rightarrow \quad \gamma \text{-cubic (Th}_3\text{P}_4 \text{) phase}
\end{align*}
\]

In this study, however, the \( \eta \)-orthorhombic \( \text{Y}_2\text{S}_3 \) was not observed during MM. As shown in Figure 16, \( \gamma \)-cubic phase begins to form even at 10 min. MM without forming any other intermediate phase. Thus it is clear that \( \gamma \)-\( \text{Y}_2\text{S}_3 \), and most likely \( \gamma \)-\( \text{Dy}_2\text{S}_3 \), were not formed by a momentary surge through the equilibrium regimes where the cubic phase could have formed and then been retained during the rapid decrease of pressure and temperature.

**Erbium, thulium, ytterbium and lutetium sesquisulfides**

Erbium sesquisulfide (\( \delta \)-\( \text{Er}_2\text{S}_3 \)) and thulium sesquisulfide (\( \delta \)-\( \text{Tm}_2\text{S}_3 \)) are isostructural with \( \delta \)-\( \text{Y}_2\text{S}_3 \) and have the monoclinic \( \delta \)-phase type structure.\textsuperscript{19} For \( \text{Er}_2\text{S}_3 \),
the metastable crystalline high pressure polymorph, $\gamma$-Er$_2$S$_3$ was obtained by MM for 2 h (Figure 17), whereas for Tm$_2$S$_3$, even after 40 h of MM, the equilibrium monoclinic $\delta$-phase still was present along with the metastable high pressure cubic $\gamma$-phase (Figure 18). In this pattern impurity peaks from tungsten carbide vial and balls are observed.

The room temperature equilibrium ytterbium$^{26}$ and lutetium$^{19}$ sesquisulfides ($\varepsilon$-Yb$_2$S$_3$ and $\varepsilon$-Lu$_2$S$_3$) have the rhombohedral $\varepsilon$-phase type structure. Figure 19 shows the phase transformation of $\varepsilon$-Yb$_2$S$_3$ as a function of milling time. As can be seen, the intensity of the main peaks from $\varepsilon$-phase drops rapidly and metastable high pressure cubic $\gamma$-phase lines appear simultaneously within an h, but it takes 2 to 4 h for the $\varepsilon$-phase to be completely converted to the $\gamma$-phase.

In the case of Lu$_2$S$_3$, even though MM for 40 h, only a small fraction of $\varepsilon$-phase was transformed into the metastable high pressure $\gamma$-polymorph (Figure 20). Although only partially successful in the cases of Tm$_2$S$_3$ and Lu$_2$S$_3$, it is shown for these two ionic compounds that MM or MA can cause the equilibrium crystalline phase to transform at least partially into a metastable crystalline polymorph.

Figure 21 shows the lattice parameters of the $\gamma$-R$_2$S$_3$ prepared by MM as a function of the atomic number of the rare earth element. It is seen that increasing atomic number, which is consistent with those for the $\gamma$-R$_2$S$_3$ prepared by a high temperature/high pressure-decompression technique$^{21}$, exhibiting the normal lanthanide contraction. Table 2. lists the volumes before and after MM for all of the R$_2$S$_3$ phases studied. Maximum volume change (~12.45%) was observed for $\varepsilon$/$\gamma$-phase transformation of Yb$_2$S$_3$.

According to Eatough et al.$^{21}$, the complete transition to $\gamma$-cubic phase occurred for R$_2$S$_3$ (R = Ho to Yb) at 2000°C and 77 kbars in 3 min., but Lu$_2$S$_3$ was about 50% converted to the $\gamma$-form under these conditions. This is consistent with the mixed
Figure 17. X-ray diffraction patterns of $\delta$-Er$_2$S$_3$ as a function of milling time: (a) 0 min.; (b) 10 min.; (c) 20 min.; (d) 40 min.; (e) 1 h; and (f) 2 h. The (hkl) values for the $\gamma$-Er$_2$S$_3$ phase are shown on the x-ray pattern for the 2 h MM sample (f).
Figure 18. X-ray diffraction patterns of $\delta$-Tm$_2$S$_3$ after 40 h MM. The lines marked "$\delta$" correspond to the $\delta$-Tm$_2$S$_3$ phase, while the "$\gamma$ (hkl)" ones indicate the $\gamma$-Tm$_2$S$_3$ phase lines.
Figure 19. X-ray diffraction patterns of \( \epsilon \)-Yb\(_2\)S\(_3\) as a function of milling time: (a) 0 min.; (b) 10 min.; (c) 20 min.; (d) 40 min.; (e) 1 h; (f) 2 h; (g) 4 h; and (h) 10 h. The (hkl) values of the \( \gamma \)-Yb\(_2\)S\(_3\) phase are shown on the x-ray pattern for the 10 h MM sample (h).
Figure 20. X-ray diffraction patterns of $\varepsilon$-$\text{Lu}_2\text{S}_3$ as a function of milling time: (a) 0 h; (b) 1 h; (c) 10 h; (d) 20 h; and (e) 40 h. The (hkl) values for the $\gamma$-$\text{Lu}_2\text{S}_3$ phase are shown on the 40 h x-ray pattern (e).
Figure 21. Lattice parameters of \(\gamma\)-phase rare earth sesquisulfides.
Table 2. Lattice parameters of "as milled" samples and volume changes between before and after MM

<table>
<thead>
<tr>
<th>$R_2S_3$</th>
<th>$a$ (Å)</th>
<th>Volume of $\gamma-R_2S_3$ (Å³/atom)</th>
<th>Volume of m. temp. phase (Å³/atom)</th>
<th>Volume change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-Y$_2$S$_3$</td>
<td>8.283</td>
<td>21.31</td>
<td>23.61 (δ)</td>
<td>-9.74</td>
</tr>
<tr>
<td>$\gamma$-Dy$_2$S$_3$</td>
<td>8.271</td>
<td>21.22</td>
<td>21.20 (η)</td>
<td>+0.09</td>
</tr>
<tr>
<td>$\gamma$-Er$_2$S$_3$</td>
<td>8.258</td>
<td>21.12</td>
<td>23.05 (δ)</td>
<td>-8.37</td>
</tr>
<tr>
<td>$\gamma$-Tm$_2$S$_3$</td>
<td>8.243</td>
<td>21.00</td>
<td>23.32 (δ)</td>
<td>-9.95</td>
</tr>
<tr>
<td>$\gamma$-Yb$_2$S$_3$</td>
<td>8.238</td>
<td>20.96</td>
<td>23.94 (κ)</td>
<td>-12.45</td>
</tr>
<tr>
<td>$\gamma$-Lu$_2$S$_3$</td>
<td>8.225</td>
<td>20.86</td>
<td>23.76 (ε)</td>
<td>-12.21</td>
</tr>
</tbody>
</table>
structures ($\varepsilon$- and $\gamma$-phases) after 40 h MM Lu$_2$S$_3$. According to the pressure-temperature diagrams of the R$_2$S$_3$\textsuperscript{42}, higher and higher pressures are necessary to achieve conversion to the $\eta$-orthorhombic (U$_2$S$_3$ type) phase in going from Ho to Lu: Ho$_2$S$_3$, 4.3 kbars; Er$_2$S$_3$, 7.1 kbar; Tm$_2$S$_3$, 11.4 kbars; Yb$_2$S$_3$, 22.6 kbars; and Lu$_2$S$_3$, 29.0 kbars at 1200°C each. Therefore, it is likely that with decreasing size of the rare earth elements the limiting radius ratio for the $\eta$-phase can be only attained by an increased compression of the sulfur atoms. In addition, the formation temperature of the $\gamma$-polymorphs decreases with increasing the pressure and reaches the minimum value and then increases with the pressure.\textsuperscript{42} The minimum temperature for the $\gamma$-phase formation increases with increasing the atomic number. Below the minimum temperature, other metastable phases ($\delta$-Er$_3$ScS$_6$ type or $\eta$-U$_2$S$_3$ type) form with increasing the pressure.\textsuperscript{42} However, the MM conditions used in this study caused the $\delta$-phase (or $\varepsilon$-phase) to be transformed into the $\gamma$-phase directly.

Among the R$_2$S$_3$, where R = Y, Dy, Er, Tm, Yb, and Lu, only $\delta$-Tm$_2$S$_3$ and $\varepsilon$-Lu$_2$S$_3$ could not be transformed entirely into the high pressure $\gamma$-phase. Consideration of the enthalpies of formation of the ambient equilibrium rare earth sesquisulfide phases\textsuperscript{43} may be helpful in understanding the observed behaviors. The enthalpies of formation of Tm$_2$S$_3$ and Lu$_2$S$_3$ appear to be the most negative (-297 ± 30 kcal/mol) of the rare earth sulfide phases, but because of the large error limits associated with these and the heats of formation values of the other R$_2$S$_3$ phases it is difficult to know if this is an important factor. What would be more important and significant is to know the free energy of formation values of both the equilibrium and the corresponding metastable $\gamma$-R$_2$S$_3$ phase.

As mentioned above, the local maximum temperature or pressure rises cannot explain the preparation of metastable high temperature or high pressure polymorphs by
MM. MM (or MA) process generates severe deformation and this deformation introduces a high density of defects (point defects and dislocations). The energy induced by MM can be stored in the crystalline compound in the form of grain boundaries, defects and chemical disorder. With increasing milling time, the defects are accumulated in the lattice and then they begin to distort the lattice, which causes the free energy of the crystalline lattice to increase. When this lattice destabilization induced by the free energy increase reaches a certain critical point, the η (or δ or ε)-phase of the $R_2S_3$ starts to be transformed to the metastable $\gamma$-polymorph which is more stable, i.e. has a lower free energy, than its original phase at that point. This change in the relative free energies is illustrated in Figure 22.

**Long term milling of Dy$_2$S$_3$ and Y$_2$S$_3$**

Dysprosium sulfide and yttrium sulfide were mechanically milled between 4 h and 160 h to observe the possibility of the amorphization of the $R_2S_3$ compound. As shown in Figures 23 and 24, cubic peaks were still present even after 160 h milling. Therefore it is concluded that MM (or MA) does not produce the amorphization of Dy$_2$S$_3$ and Y$_2$S$_3$ ionic compounds. In Dy$_2$S$_3$ the impurity peaks begin to appear at 40 h, whereas for Y$_2$S$_3$ the impurity peaks appear at 80 h milling. It is noticed that these impurities are tungsten carbides (WC) by comparing with JCPDS (Joint Committee of Powder Diffraction Standards) data (Figure 25). The amount of tungsten was determined chemically (Table 3). Between 40 and 80 h MM Dy$_2$S$_3$ and Y$_2$S$_3$ are seriously contaminated by tungsten carbide (2.03 to 17.82 ± 0.05 at.% W). This impurity comes from a tungsten carbide vial and balls.
Figure 22. Schematic of free energy change: (a) before MM (or MA); (b) during MM (or MA).
Figure 23. X-ray diffraction patterns of Dy$_2$S$_3$ as a function of milling time: (a) 4 h; (b) 10 h; (c) 20 h; (d) 40 h; (e) 80 h; (f) 120 h; and (g) 160 h.
Figure 24. X-ray diffraction patterns of Y$_2$S$_3$ as a function of milling time: (a) 4 h; (b) 10 h; (c) 20 h; (d) 40 h; (e) 80 h; (f) 120 h; and (g) 160 h.
Figure 25. X-ray diffraction patterns of 160 h MM Dy$_2$S$_3$. The middle strip is $\gamma$-Dy$_2$S$_3$ x-ray pattern and the bottom strip is tungsten carbide (WC) x-ray pattern from JCPDS data.
Table 3. Chemical analysis of tungsten (W) in MM $Y_2S_3$

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Milling Time (hr.)</th>
<th>Tungsten (± 0.03 at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_2S_3$</td>
<td>4</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>2.03</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>17.82</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>23.13</td>
</tr>
</tbody>
</table>
CONCLUSIONS AND SUMMARY

Equilibrium η-orthorhombic Dy$_2$S$_3$ and equilibrium δ-monoclinic Y$_2$S$_3$ completely transformed into the metastable high temperature γ-cubic Dy$_2$S$_3$ and the metastable high pressure γ-cubic Y$_2$S$_3$ in the milling time between 60 min. and 200 min., respectively. For Er$_2$S$_3$, the δ-phase completely transformed into the high pressure γ-phase in somewhere between 1 and 2 h MM. In the case of Tm$_2$S$_3$ the equilibrium δ-monoclinic phase was still present along with the metastable high pressure γ-cubic phase even after 40 h of MM, whereas for Yb$_2$S$_3$, it took 2 to 4 h MM for the equilibrium ε-phase to be completely converted to the γ-phase. For Lu$_2$S$_3$, even through MM for 40 h, only a small fraction of equilibrium ε-phase was transformed into the metastable high pressure γ-polymorph.

It is likely that the formation of the metastable high temperature or high pressure γ-phase of R$_2$S$_3$ is associated with the free energy increase of the equilibrium phase induced by the defect accumulation during MM. MM did not produce amorphization of Dy$_2$S$_3$ and Y$_2$S$_3$ even after 160 h milling.

As a consequence, it is believed that MM (or MA) can be a new route to synthesize the metastable high temperature crystalline or high pressure crystalline polymorph.
REFERENCES


APPENDIX

Table A.1. Impurity level data of Dy$_2$S$_3$ by Laser Source Mass Spectrometric Analysis (values are in ppm weight)

<table>
<thead>
<tr>
<th>Element</th>
<th>Impurity Level (ppm weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.003</td>
</tr>
<tr>
<td>Be</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>B</td>
<td>0.014</td>
</tr>
<tr>
<td>C</td>
<td>26</td>
</tr>
<tr>
<td>N</td>
<td>0.2</td>
</tr>
<tr>
<td>O</td>
<td>0.089</td>
</tr>
<tr>
<td>F</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Ne</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Na</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt;0.08</td>
</tr>
<tr>
<td>Al</td>
<td>&lt;0.06</td>
</tr>
<tr>
<td>Si</td>
<td>&lt;0.6</td>
</tr>
<tr>
<td>P</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Cl</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Ar</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>K</td>
<td>&lt;0.66</td>
</tr>
<tr>
<td>Ca</td>
<td>&lt;0.07</td>
</tr>
<tr>
<td>Sc</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>Ti</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>V</td>
<td>&lt;0.04</td>
</tr>
<tr>
<td>Li</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt;0.06</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;0.8</td>
</tr>
<tr>
<td>Co</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>Ga</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Ge</td>
<td>&lt;0.09</td>
</tr>
<tr>
<td>As</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>Se</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Br</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Rb</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Sr</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Y</td>
<td>&lt;0.08</td>
</tr>
<tr>
<td>Sr</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Zr</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Nb</td>
<td>&lt;0.08</td>
</tr>
<tr>
<td>Mo</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Ru</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Ce</td>
<td>2.0</td>
</tr>
<tr>
<td>Pr</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Nd</td>
<td>&lt;0.08</td>
</tr>
<tr>
<td>Sm</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Eu</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Gd</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Tb</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>Tl</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;0.6</td>
</tr>
<tr>
<td>Bi</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Ra</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Th</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>U</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Ho</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Er</td>
<td>&lt;0.6</td>
</tr>
<tr>
<td>Tm</td>
<td>&lt;0.09</td>
</tr>
<tr>
<td>Yb</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>Lu</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Hf</td>
<td>&lt;0.8</td>
</tr>
<tr>
<td>Ta</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>W</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>Re</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Os</td>
<td>&lt;0.7</td>
</tr>
<tr>
<td>Ir</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>Pt</td>
<td>&lt;0.7</td>
</tr>
<tr>
<td>Au</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>Tl</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;0.6</td>
</tr>
<tr>
<td>Bi</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Th</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>U</td>
<td>&lt;0.2</td>
</tr>
</tbody>
</table>
Table A.2. Data collection and refinement parameters for Dy$_2$S$_3$

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>Dy$_2$S$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>421.2 g/cm$^3$</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.01 x 0.01 x 0.1 mm</td>
</tr>
</tbody>
</table>
| Lattice parameters| a = 10.586 (6) Å  
                      | b = 3.853 (5) Å 
                      | c = 10.424 (7) Å, V = 424 (1) Å$^3$ |
| Space group       | Pnma (# 62) |
| No. formula units (Z) | 4 |
| Calc. density (D)  | 6.59 g/cm$^3$ |
| Structure factor (F(000)) | 720 |
| Absorption constant (μ) (Mo K-alpha) | 364.89 /cm |
| Transmission range | 0.4277 - 1.0000 |
| Diffractometer    | Rigaku - AFC6R |
| Radiation         | Mo K-alpha (λ = 0.71069) |
|                   | Graphite-monochromated |
| Temperature       | 23°C |
| Octants measured  | ± h, ± k, l |
| Scan method       | omega - 2 theta |
| 2-theta (max.)    | 49.95° |
| No. reflections   | 1617 |
| No. observations (I > 3.00) | 876 |
| No. variables     | 32 |
| Residuals: R; Rw  | 3.7; 5.7 % |
| R (avg.)          | 8.3 % (all data) |
Table A.3. Positional parameters for Dy$_2$S$_3$

<table>
<thead>
<tr>
<th>atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy (1)</td>
<td>0.01014 (8)</td>
<td>0.25</td>
<td>0.31293 (8)</td>
</tr>
<tr>
<td>Dy (2)</td>
<td>0.1921 (1)</td>
<td>0.25</td>
<td>-0.00415 (8)</td>
</tr>
<tr>
<td>S (1)</td>
<td>0.9529 (4)</td>
<td>0.25</td>
<td>0.8729 (4)</td>
</tr>
<tr>
<td>S (2)</td>
<td>-0.2274 (4)</td>
<td>0.25</td>
<td>0.1969 (4)</td>
</tr>
<tr>
<td>S (3)</td>
<td>0.1193 (4)</td>
<td>0.25</td>
<td>0.5547 (4)</td>
</tr>
</tbody>
</table>
PAPER II. THERMOELECTRIC PROPERTIES OF Cu DOPED DYSPROSIUM SESQUISULFIDE
ABSTRACT

The Hall effect, electrical resistivity, and Seebeck coefficient have been studied in Cu$_x$(Dy$_2$S$_3$)$_{1-x}$ compounds with the $\eta$-orthorhombic structure in the composition range $0.006 \leq x \leq 0.15$ in order to determine their potential as high temperature (25 - 1000°C) thermoelectric materials. In this temperature and composition range Cu-doped Dy$_2$S$_3$ behaves as a degenerate semiconductor and shows itinerant conduction. The electrical resistivity and the Seebeck coefficient increased with increasing temperature and then reached the maximum values of 4.55 to 7.13 m$\Omega$-cm and -164 to -177 $\mu$V/°C around 850°C for MA and then hot pressed Cu$_x$(Dy$_2$S$_3$)$_{1-x}$, respectively, and 4.35 to 5.30 m$\Omega$-cm and -163 to -168 $\mu$V/°C at 950 - 1000°C for melted and then hot pressed Cu$_x$(Dy$_2$S$_3$)$_{1-x}$, respectively. The maximum power factor of 7.9 $\mu$W/cm•°C$^2$ at Cu$_{0.039}$(Dy$_2$S$_3$)$_{0.961}$ was obtained at 690°C.
INTRODUCTION

Over the past decade various chemical batteries and solar cells have been used as power sources. However, there are some applications in which neither of these types of power source is adequate. This is especially true of applications in which sunlight is not readily available and which require extremely long operating times (seven years or more). In these situations only the radioisotope thermoelectric generators (RTGs) have proven to be reliable. These RTGs have been successfully utilized in the NASA Pioneer, Voyager, Galileo and Ulysses space missions and are expected to be used in the Cassini, 1996. It has been known that radioactive plutonium-238 and strontium-90 have been used as heat sources which supply a constant temperature difference across the thermoelements.¹

Theoretical background

The Seebeck effect can be used to convert heat energy directly into the electrical energy.² For a thermoelectric power generator, the efficiency of the energy conversion process is the most important factor in order to save the energy and the cost. The maximum conversion efficiency ($\eta_{\text{max}}$) of the heat to the electrical energy using a thermoelectric couple (Figure 1) is given by

$$\eta_{\text{max}} = \frac{T_h - T_c}{Th} \frac{\sqrt{1 + Z \bar{T}} + 1}{\sqrt{1 + Z \bar{T}} + (T_c + T_h)}$$ (1)

where $T_h = \text{temperature of the hot junction}$, $T_c = \text{temperature of the cold junction}$, $ar{T} = (T_h + T_c) / 2$, and $Z = \text{the combined figure of merit}$ and is given by
Figure 1. Thermoelectric couple as power generator.
\[ Z = \frac{(S_n - S_p)^2}{[(\rho_n \kappa_n)^{\frac{1}{2}} + (\rho_p \kappa_p)^{\frac{1}{2}}]^2} \]  

where \( S_n \) = Seebeck coefficient of n-type semiconductor, \( S_p \) = Seebeck coefficient of p-type semiconductor, \( \rho_n \) = electrical resistivity of n-type semiconductor, \( \rho_p \) = electrical resistivity of p-type semiconductor, \( \kappa_n \) = thermal conductivity of n-type semiconductor, and \( \kappa_p \) = thermal conductivity of p-type semiconductor. The first term in the equation (1) is simply the thermodynamic efficiency of a reversible Carnot cycle and the second term is the decrease in this efficiency resulting from the irreversible heat conduction along the branches of the couple and the power dissipation in the form of Joulean heat.\(^3\) From equation (1), it is seen that for the maximum power generating efficiency the factor \( ZT \) needs to be maximized, i.e., to obtain as high a value of \( Z \) over as wide a temperature range as possible.

\( Z \), which is called the figure of merit, is a material parameter and for a single material is given by\(^2\)

\[ Z = \frac{S^2}{\rho \kappa} \]  

Initially a conductor possesses a uniform distribution of charge carriers, but under a temperature gradient the free carriers at the hot end have a greater kinetic energy and tend to diffuse to the cold end. The build up of charge results in a back emf which opposes a further flow of charge. This back emf per unit temperature difference is the Seebeck coefficient \((S)\).\(^1\) The Seebeck coefficient is negative for n-type semiconductors and positive for p-type semiconductors.\(^1\) The Seebeck coefficient is a complicated function of the carrier concentration. It decreases with an increase in the
carrier concentration and tends to zero for metal.\textsuperscript{4} The electrical conductivity ($\sigma = 1/p$) is the ratio of the current density in the material and the applied electric field. It is proportional to both the carrier concentration and the carrier mobility. The thermal conductivity ($k$) is the heat current in the material divided by the temperature gradient. For unipolar conductor, in which a single sign of charge carrier predominates, the total thermal conductivity is expressed as\textsuperscript{5}

$$k = k_{ei} + k_{ph}$$  \hspace{1cm} (4)

Here, $k_{ei}$ is the electronic contribution to the thermal conductivity and carried by the charge carriers. Thus, it has a close relation to the electrical conductivity. $k_{ph}$ is the phonon (lattice) contribution to the thermal conductivity and related to the thermal motion of the phonon (lattice).

The schematic representation\textsuperscript{2} of the dependence of the Seebeck coefficient, the electrical conductivity and the thermal conductivity as a function of the carrier concentration ($n$) is plotted in Figure 2. It is seen that for insulators the electrical conductivity is quite low, while at the same time the Seebeck coefficient is large. For metals, the electrical conductivity is large, but the Seebeck coefficient is too small. As a consequence, semiconductors are seen to have the optimum combination of $S$ and $\sigma$ values, and maximum power factor ($S^2\sigma$) occurs for heavily-doped or near-degenerate semiconductors corresponding to a carrier concentration range of $10^{19} - 10^{20}/\text{cm}^3$. The factors $S$, $\sigma$ and $k$ in the expression for the figure of merit are all functions of the Fermi energy in the semiconductor which is itself dependent on the carrier concentrations and energy band configuration.\textsuperscript{4}

Therefore, it is clear that the following general properties\textsuperscript{4} are desirable in a good thermoelectric material:

(a) high Seebeck coefficient ($S$) to produce maximum voltage in the circuit
Figure 2. Schematic representation of the dependence of Seebeck coefficient (S), electrical conductivity (\(\sigma\)), thermal conductivity (\(\kappa\)) and the power factor (\(S^2\sigma\)) on the carrier concentration (\(n\)).
(b) small electrical resistivity ($\rho$) to minimize losses due to Joule heating
(c) small thermal conductivity ($\kappa$) to retain maximum heat for conversion at the hot junction and avoid heat losses down to the cold junction.

**Rare earth chalcogenides**

Over the past 30 years, many materials have been investigated for high temperature thermoelectric materials, i.e. Si-Ge alloys, bismuth tellurides, lead tellurides, rare earth chalcogenides and boron-rich borides. Among these, the rare earth chalcogenides, which have the defect Th$_3$P$_4$ structure, have received considerable attention as potential high temperature thermoelectric materials in the past decade because of their high melting points, low thermal conductivity and the self-doping ability to change continuously from a metallic conductor to an insulator. The high temperature $\gamma$-phases of the rare earth chalcogenides form a cubic defect Th$_3$P$_4$ structure over a composition range $R_2X_3$ to $R_3X_4$ (where $R = $ La to Sm and $X = $ S, Se and Te). It is common to write the formula for the unit cell as $4(R_{3-x}V_xX_4)$, where $v$ is a rare earth metal vacancy and $0 \leq x \leq 1/3$.

For $x = 1/3$, i.e., $R_2S_3$, there are 1 and 1/3 vacancies per unit cell and two $R^{3+}$ ions contribute six electrons and three $X^{2-}$ ions accept six electrons so that $R_2X_3$ is an insulator, whereas for $x = 0$, i.e., $R_3X_4$, there are no vacancies and three $R^{3+}$ ions contribute nine electrons and four $X^{2-}$ ions accept eight electrons. Hence, $R_3X_4$ is metallic. Thus, the electrical properties are changed between these two extremes by altering the ratio of rare earth to chalcogen ions.

Although the high temperature thermoelectric properties of rare earth sulfide compounds have been widely investigated, only the cubic $\gamma$-phase sulfides have been studied to date. In this study, copper (Cu) doped dysprosium sesquisulfide
(Dy$_2$S$_3$) compounds, which have the \(\eta\)-orthorhombic structure, were examined as potential thermoelectric materials. These materials are of interest for use in high temperature thermoelectric applications because of their high melting point$^{19}$, low thermal conductivity and large energy band gap$^{20}$. 
EXPERIMENTAL PROCEDURES

Preparation of dysprosium sesquisulphide (Dy$_2$S$_3$)

The preparation of Dy$_2$S$_3$ was discussed in Han et al.\textsuperscript{21}

Doping process (mechanical alloying and melting)

Copper (Cu) and dysprosium sesquisulfide (Dy$_2$S$_3$) powders were placed in a tungsten carbide (WC) vial and sealed in a helium filled glove box. The powders were mechanically alloyed usually for 6 h in a Spex 8000 mixer/mill using three 10 mm diameter tungsten carbide balls. The weight ratio of balls to powders was 4.7:1.

For melting technique, Cu and Dy$_2$S$_3$ powders were placed in a tungsten crucible in the vacuum induction furnace. The vacuum chamber was evacuated to $10^{-6}$ torr and the temperature then increased to 1600°C and was held for 10 min. and then furnace-cooled to ambient temperature.

Hot pressing

The mechanically alloyed or melted and then ground powders were loaded into a half inch graphite die inside of a helium-filled glove box. The loaded die was carried in a helium-filled plastic bag to a hot press apparatus. The vacuum chamber was evacuated to $10^{-7}$ torr. The powders were heated to 1100°C and then hot pressed with a force of 138 MPa (20ksi) for 1 h at 1100°C and then slowly furnace-cooled to ambient temperature (Figure 3).
Figure 3. Temperature and pressure changes during hot pressing.
X-ray diffraction

The crystal structures of MA and hot pressed Cu_x(Dy_2S_3)_1-x (x = 0.025 to 0.15) were characterized by SCINTAG x-ray diffractometer using Cu Kα radiation.

Heat treatment

Hot pressed samples were heat treated at 1100°C for 2 weeks or 4 weeks. Heating and cooling rates were 2°C/min. to avoid the crack initiation due to the thermal shock. Each sample was protected by the double sealing (with the sample inside a tantalum crucible, which was inside a quartz ampoule).

Metallography

Metallographs of the as-pressed and as-heat treated samples were taken using a Zeiss-Axiomat optical microscope. Samples were etched with a solution of 2% nitric acid and 98% methanol.

Hall effect measurement

Hall effects of Cu_x(Dy_2S_3)_1-x compounds were measured at room temperature by van der Pauw technique. The electrical resistivity was measured at 45, 50 and 55 mA and then averaged. The carrier concentration was measured at 90 mA under a magnetic field of 1 tesla. Hall mobility was calculated from the relationship between Hall coefficient, carrier concentration and electrical resistivity ($R_H = -1/ne$ and $\rho = 1/ne\mu$).
High temperature electrical resistivity and Seebeck coefficient measurement

The electrical resistivity and the Seebeck coefficient measurements were made by the standard dc four-point probe technique\textsuperscript{25} and the method of the slope of the thermal emf versus temperature plot\textsuperscript{26}, respectively. Both properties were measured simultaneously on the same sample in a vacuum chamber (\(\sim 10^{-6}\) torr) in the temperature range of 25 -1000\(^\circ\)C by a computer-controlled data acquisition system.
RESULTS AND DISCUSSION

According to the Cu-Dy$_2$S$_3$ phase diagram 8 mol% Cu is soluble in the $\alpha$-Dy$_2$S$_3$ phase from room temperature to 1190°C. Above this temperature the $\alpha$-phase transforms to the cubic $\gamma$-Dy$_2$S$_3$ form (the defect Th$_3$P$_4$ type structure) which dissolves 10 mol% Cu at the monotectic temperature 1350°C. A similar behavior is expected in the Cu-(η-Dy$_2$S$_3$) system because there are only slight differences between $\alpha$-(Gd$_2$S$_3$ type) and η-structures (U$_2$S$_3$ type).

After 6 h of MA the two phase mixture of Cu and orthorhombic η-Dy$_2$S$_3$ (Figure 4 (a)) the alloy powders (x = 0.025 to 0.15) were found to have formed the cubic $\gamma$-phase (Figure 4 (b)). After hot pressing (HP) at 1100°C, the cubic Cu$_x$($\gamma$-Dy$_2$S$_3$)$_{1-x}$ transformed to the equilibrium η-orthorhombic phase (Figure 4 (c)) except for the alloy with x = 0.025 which transformed to the $\alpha$-orthorhombic structure (Figure 5). Therefore, the sequence of the phase transformation for Cu$_x$(Dy$_2$S$_3$)$_{1-x}$ is as follows:

For x = 0.05 to 0.15

For x = 0.025

Undoped Dy$_2$S$_3$ has the η-orthorhombic phase under the same processing. It is not known why the small amount of Cu causes $\alpha$-phase (Gd$_2$S$_3$ type) to form. The Cu$_x$(Dy$_2$S$_3$)$_{1-x}$ alloys were analyzed chemically for Cu (Table 1). As shown in Table 1, during the processing some losses of Cu occurred, but most of the MA samples are close to the nominal compositions, while the melted alloys showed significant losses.
Figure 4. X-ray diffraction patterns of Cu$_{0.050}$(Dy$_2$S$_3$)$_{0.950}$: (a) initial $\eta$-phase (b) $\gamma$-phase after 6h MA (c) $\eta$-phase after hot pressing at 1100°C for 1h.
Figure 5. X-ray diffraction patterns of Cu$_{0.025}$(Dy$_2$S$_3$)$_{0.975}$: (a) initial $\eta$-phase (b) $\gamma$-phase after 6h MA (c) $\alpha$-phase after hot pressing at 1100°C for 1h.
Table 1. Chemical analysis of Cu-doped Dy$_2$S$_3$ compounds

<table>
<thead>
<tr>
<th>Doping Technique</th>
<th>Cu (at.%)</th>
<th>Nominal composition</th>
<th>Chemically determined composition (± 0.05 at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical</td>
<td>2.5</td>
<td>$\text{Cu}_0.025$($\text{Dy}_2\text{S}<em>3$)$</em>{0.975}$</td>
<td>$\text{Cu}_0.023$($\text{Dy}_2\text{S}<em>3$)$</em>{0.977}$</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>$\text{Cu}_0.050$($\text{Dy}_2\text{S}<em>3$)$</em>{0.950}$</td>
<td>$\text{Cu}_0.045$($\text{Dy}_2\text{S}<em>3$)$</em>{0.955}$</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>$\text{Cu}_0.075$($\text{Dy}_2\text{S}<em>3$)$</em>{0.925}$</td>
<td>$\text{Cu}_0.068$($\text{Dy}_2\text{S}<em>3$)$</em>{0.932}$</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>$\text{Cu}_0.100$($\text{Dy}_2\text{S}<em>3$)$</em>{0.900}$</td>
<td>$\text{Cu}_0.095$($\text{Dy}_2\text{S}<em>3$)$</em>{0.905}$</td>
</tr>
<tr>
<td></td>
<td>12.5</td>
<td>$\text{Cu}_0.125$($\text{Dy}_2\text{S}<em>3$)$</em>{0.875}$</td>
<td>$\text{Cu}_0.112$($\text{Dy}_2\text{S}<em>3$)$</em>{0.888}$</td>
</tr>
<tr>
<td></td>
<td>15.0</td>
<td>$\text{Cu}_0.150$($\text{Dy}_2\text{S}<em>3$)$</em>{0.850}$</td>
<td>$\text{Cu}_0.137$($\text{Dy}_2\text{S}<em>3$)$</em>{0.863}$</td>
</tr>
<tr>
<td>Alloying</td>
<td>5.0</td>
<td>$\text{Cu}_0.050$($\text{Dy}_2\text{S}<em>3$)$</em>{0.950}$</td>
<td>$\text{Cu}_0.066$($\text{Dy}_2\text{S}<em>3$)$</em>{0.994}$</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>$\text{Cu}_0.075$($\text{Dy}_2\text{S}<em>3$)$</em>{0.925}$</td>
<td>$\text{Cu}_0.020$($\text{Dy}_2\text{S}<em>3$)$</em>{0.980}$</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>$\text{Cu}_0.100$($\text{Dy}_2\text{S}<em>3$)$</em>{0.900}$</td>
<td>$\text{Cu}_0.034$($\text{Dy}_2\text{S}<em>3$)$</em>{0.966}$</td>
</tr>
<tr>
<td></td>
<td>12.5</td>
<td>$\text{Cu}_0.125$($\text{Dy}_2\text{S}<em>3$)$</em>{0.875}$</td>
<td>$\text{Cu}_0.039$($\text{Dy}_2\text{S}<em>3$)$</em>{0.961}$</td>
</tr>
</tbody>
</table>
Room temperature Hall effect

Hall effect measurement of as-pressed and as-heat treated samples was performed at room temperature. According to the sign of the Hall coefficient, all Cu$_x$(Dy$_2$S$_3$)$_{1-x}$ alloys were n-type semiconductors, i.e. the carrier type is the electron, which was expected.

For MA and then hot pressed Cu$_x$(Dy$_2$S$_3$)$_{1-x}$, the electron concentration increases with increasing Cu doping level to 10 at.% and then decreases slightly, but as the samples were heat treated at 1100°C for 2 weeks and 4 weeks, the electrically active electron concentrations were increased (Figure 6). In the case of 10 at.% Cu doped Dy$_2$S$_3$, as-pressed electron concentration was $1.32 \times 10^{20}$/cm$^3$, while as-2 and 4 week heat treated samples had the carrier concentrations of $1.48 \times 10^{20}$/cm$^3$ and $1.77 \times 10^{20}$/cm$^3$, respectively.

For melted and then hot pressed Cu$_x$(Dy$_2$S$_3$)$_{1-x}$, the number of the electrically active electrons also increased due to the heat treatment (Figure 7). The maximum electron concentration was $2.34 \times 10^{20}$/cm$^3$. It is believed that the heat treatment causes Cu atoms to have sufficient thermal energy and time to diffuse into the Dy$_2$S$_3$ matrix. It is shown that the melting technique for Cu doping is more effective than MA, because the higher electron concentration was obtained even at the lower Cu doping level.

Since the electrical resistivity ($\rho$) is a measure of a material's inherent resistance to the current flow, it is dependent on both the carrier concentration and the carrier mobility. Figure 8 shows the electrical resistivity as a function of the electron concentration. As the electron concentration increases, the electrical resistivity decreases. At the maximum electron concentration ($2.34 \times 10^{20}$/cm$^3$) attained in these alloys the electrical resistivity reached a value of 0.68 m$\Omega$-cm. The electrical resistivity data as a function of the electron mobility are shown in Figure 9. As expected, the
Figure 6. Electron concentration of Cu$_x$(Dy$_2$S$_3$)$_{1-x}$ prepared by MA and then hot pressing as a function of Cu doping level (x).
Figure 7. Electron concentration of Cu$_4$(Dy$_2$S$_3$)$_{1-x}$ prepared by melting and then hot pressing as a function of Cu doping level (x).
Electrical resistivity of Cu-doped Dy$_2$S$_3$ as a function of electron concentration.

Figure 8. Electrical resistivity of Cu-doped Dy$_2$S$_3$ as a function of electron concentration.
samples with a high mobility have the lowest electrical resistivities. Both data are well consistent with the typical relationship\textsuperscript{24} between mobility ($\mu$), resistivity ($\rho$) and carrier concentration ($n$), i.e. $\rho = (n\mu)^1$.

Zhuze et al.\textsuperscript{12} reported that the Hall mobility decreases with increasing carrier concentration at a constant temperature in $R_2X_4$ (where $R$ = La to Nd and $X$ = S, Se and Te), but Wood et al.\textsuperscript{9} claimed that the trend of decreasing mobility with increasing carrier concentration for rare earth chalcogenides was not observed in the lanthanum sulfide system. Takeshita et al.\textsuperscript{15} also reported that the Hall mobility is invariant with the carrier concentration in the $LaS_x$ (where $x$ = 1.33 to 1.49) in the range of 2.65 - 3.71 cm$^2$/V-s. In the $Cu_x(Dy_2S_3)_{1-x}$ system, however, it is shown that the Hall mobility increases with the carrier concentration (Figure 10). This trend is quite unusual. Generally, as the carrier concentration increases, Hall mobility decreases at a constant temperature. For heavily doped Si-Ge alloy, Solmi et al.\textsuperscript{30} observed a rapid drop in mobility with increasing carrier concentration. According to Slack et al.\textsuperscript{31}, the mobility decrease in heavily doped Si-Ge alloy is believed to be caused by the electron populations entering the L conduction band at higher energy and a drop-off in the mobility appears in the electron concentration range above $10^{20}$/cm$^3$. Slack et al.\textsuperscript{31} insisted that in the Si-Ge mixed crystal at a given carrier concentration the carrier mobility is lower than in either doped Si or Ge. The reason for this reduction in the mobility is the disorder scattering produced by the fluctuations in the lattice potentials at the lattice sites. Therefore, in addition to the ionized impurity and lattice vibration scattering, the disorder scattering by alloying also affects the carrier mobility. The carrier mobility is also dependent on the type of bonding, being highest in covalent and lowest in ionic semiconductors.\textsuperscript{1} Temperature also affects the carrier mobility. Cutler et al.\textsuperscript{32} observed that in the $Ce_{3-x}S_4$ ($0 < x < 0.3$) Hall mobility increases with increasing
Figure 9. Electrical resistivity of Cu-doped Dy$_2$S$_3$ as a function of electron mobility.
Figure 10. Hall mobility of Cu-doped Dy$_2$S$_3$ as a function of electron concentration.
temperature because of the Hall coefficient decrease, but Wood et al.\textsuperscript{9} expected that the carrier mobility decreases approximately as $1/T$, as for metallic behavior in the lanthanum sulfides. According to Slack's modeling\textsuperscript{31}, the carrier mobility is independent of temperature at low temperature and varies as $T^{-a}$ at high temperature, where $a$ is a constant.

In this study, Cu-doped Dy$_2$S$_3$ alloys behave significantly different from the lanthanum sulfides. The differences are as follows: First, in the case of La$_{3-y}$S$_4$ carrier electrons originate from an excess of La metal above the La$_2$S$_3$ stoichiometry (self-doping), while for Cu$_x$(Dy$_2$S$_3$)$_{1-x}$, it is the Cu dopants that release carrier electrons in Dy$_2$S$_3$ matrix. Secondly, La$_{3-y}$S$_4$ systems have $\gamma$-cubic structures (the defect Th$_3$P$_4$ type), but Cu-doped Dy$_2$S$_3$ has an $\eta$-ortorhombic structure (U$_2$S$_3$ type). Thirdly, La$_{3-y}$S$_4$ has a high electron concentration ($n = 3.6 - 60 \times 10^{20}/\text{cm}^3$) and low mobility ($\mu = 2 - 4 \text{ cm}^2/\text{V-s}$), whereas as-heat treated Cu$_x$(Dy$_2$S$_3$)$_{1-x}$ has a lower electron concentration ($n < 2.5 \times 10^{20}/\text{cm}^3$) and higher mobility ($\mu = 25 - 47 \text{ cm}^2/\text{V-s}$).

For a good thermoelectric material, the low carrier concentration and the high carrier mobility are desirable because the low carrier concentration causes the high Seebeck coefficient and the high mobility results in the low electrical resistivity. It is likely that the high temperature heat treatment causes the Dy$_2$S$_3$ matrix to be more chemically homogeneous than as-pressed matrix and also enables Cu dopant to be more electrically active in Dy$_2$S$_3$ matrix. As a result, the electron concentration and the Hall mobility increase simultaneously.

The conduction mechanism of Cu-doped Dy$_2$S$_3$ alloys can be expected from the scattering distance. The scattering distance is given by\textsuperscript{2}

$$\lambda_s = 0.735 \mu_H (T/100)^{1/2}$$

(5)
where $\lambda_s = \text{scattering distance} (\text{Å}), \mu_H = \text{Hall mobility (cm}^2/\text{V-s}), \text{and } T = \text{absolute temperature (K)}. \text{ The scattering distance values (}\lambda_s\text{) of Cu-doped Dy}_2\text{S}_3 \text{ alloys were calculated from the Hall mobility data at room temperature (Table 2). In the case of as-pressed samples, the scattering distances are 2.7 - 10.6 Å, while for as-heat treated samples, they are 34.1 - 58.5 Å. The fact that $\lambda_s$ is below 1 Å suggests that the conduction mechanism is a hopping process for localized electrons.}^{32} \text{ Thus, it is believed that the conduction mechanism of Cu-doped Dy}_2\text{S}_3 \text{ is itinerant conduction because these alloys have scattering distances greater than 1 Å.}

**Room temperature Seebeck coefficient**

According to simple theory for nearly free electrons, the Seebeck coefficient ($S$) is given by

$$S = \left( \frac{8\pi^2 k^2 T m^*}{3e h^2} \right) \left( \frac{\pi}{3n} \right)^2 (1 + R)$$

where $k = \text{Boltzmann's constant}, m^* = \text{effective mass}, e = \text{electron charge}, n = \text{carrier concentration}, T = \text{absolute temperature}$,

$R = (d \ln \lambda_s / d \ln E)_F$, $\lambda_s$ is the scattering distance, $E = \text{kinetic energy}$, and $E_F = \text{Fermi energy}$. Therefore, if this relation holds, the room temperature values of S are expected to vary as $n^{-2/3}$. Room temperature Seebeck coefficients of Cu doped-Dy$_2$S$_3$ are plotted as a function of $n^{-2/3}$ in Figure 11. It is seen that Cu-doped Dy$_2$S$_3$ alloys are n-type semiconductors and the Seebeck coefficients depend linearly on the negative two-thirds power of the electron concentration indicating that the behavior of Cu-doped Dy$_2$S$_3$ alloy is metallic.

The density of states effective mass $(m^*)$ values were calculated from the carrier concentration and the Seebeck coefficient data by the equation (6), assuming the
Table 2. Scattering distance of as-pressed and as-heat treated Cu-doped Dy$_2$S$_3$

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Scattering distance (Å) as pressed</th>
<th>Scattering distance (Å) as heat treated (1100°C, 2 weeks)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_{0.006}$Dy$_2$S$<em>3$$</em>{0.994}$</td>
<td>3.2</td>
<td>38.8</td>
</tr>
<tr>
<td>Cu$_{0.034}$Dy$_2$S$<em>3$$</em>{0.966}$</td>
<td>7.5</td>
<td>58.5</td>
</tr>
<tr>
<td>Cu$_{0.036}$Dy$_2$S$<em>3$$</em>{0.961}$</td>
<td>7.9</td>
<td>58.2</td>
</tr>
<tr>
<td>Cu$_{0.075}$Dy$_2$S$<em>3$$</em>{0.925}$</td>
<td>6.9</td>
<td>40.4</td>
</tr>
<tr>
<td>Cu$_{0.106}$Dy$_2$S$<em>3$$</em>{0.900}$</td>
<td>10.6</td>
<td>37.7</td>
</tr>
<tr>
<td>Cu$_{0.125}$Dy$_2$S$<em>3$$</em>{0.875}$</td>
<td>8.7</td>
<td>34.1</td>
</tr>
<tr>
<td>Cu$_{0.150}$Dy$_2$S$<em>3$$</em>{0.850}$</td>
<td>2.7</td>
<td>43.8</td>
</tr>
</tbody>
</table>
Figure 11. Seebeck coefficient of Cu-doped Dy$_2$S$_3$ as a function of a negative two-third power of the electron concentration ($n$).
lattice vibration scattering gives \( \lambda \) independent of \( E \), i.e. \( R = 0 \). The density of states effective mass (\( m^* \)) values of Cu-doped Dy\(_2\)S\(_3\) are invariant in the range of 0.8 - 1 with the carrier concentrations (Table 3). Spitzer et al.\(^{34}\) found that for p-type Si \( m^* \) does not change from 0.37\( m_0 \) at a 0.96\( \times 10^{19} \)/cm\(^3\) doping level, while for p-type Ge it increases a factor of 2 from 0.27\( m_0 \) at 1.1\( \times 10^{19} \)/cm\(^3\). For the lanthanum chalcogenides, it was reported\(^{12}\) that \( m^*/m_0 \) falls in the range of 2.0 \( \pm \) 0.5.

High temperature electrical resistivity

The electrical resistivity (\( \rho \)) and the Seebeck coefficient (\( S \)) of the as-heat treated \( \text{Cu}_x(\text{Dy}_2\text{S}_3)_{1-x} \) alloys were measured in the temperature range of 25 - 1000°C, see Figure 12. The electrical resistivity increases with increasing temperature, indicating that Cu doped Dy\(_2\)S\(_3\) alloys are metallic. The electrical resistivity consists of a temperature-dependent contribution and two temperature-independent contributions\(^{35}\), which can be expressed as:

\[
\rho_T = \rho_0 + \rho_{IT} + \rho_{mT}
\]

where \( \rho_T \) = total electrical resistivity, \( \rho_0 \) = the residual electrical resistivity due to impurities, defects and strains, \( \rho_{IT} \) = the electrical resistivity due to the interaction of the conduction carriers with the lattice vibrations, and \( \rho_{mT} \) = the electrical resistivity due to the magnetic disorder. For this study, the third term of the right side of the equation is constant because the temperature of measurement (25 - 1000°C) is well above the magnetic ordering temperature of Cu-doped Dy\(_2\)S\(_3\). As a result, temperature-dependent electrical resistivity is caused by only the interaction between the carriers and the lattice vibrations. As temperature increases, the carrier electrons are significantly scattered by the enhancement of the lattice vibrations, resulting in an.
Table 3. The density of states effective mass of Cu-doped Dy$_2$S$_3$ for various carrier concentrations

<table>
<thead>
<tr>
<th>$n$ (x10$^{19}$/cm$^3$)</th>
<th>$S$ ($\mu$V/K)</th>
<th>$m^a/m_0^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.2</td>
<td>-65.50</td>
<td>0.84</td>
</tr>
<tr>
<td>14.8</td>
<td>-65.39</td>
<td>0.91</td>
</tr>
<tr>
<td>14.3</td>
<td>-65.52</td>
<td>0.89</td>
</tr>
<tr>
<td>12.5</td>
<td>-72.41</td>
<td>0.90</td>
</tr>
<tr>
<td>12.1</td>
<td>-71.29</td>
<td>0.87</td>
</tr>
<tr>
<td>11.8</td>
<td>-75.42</td>
<td>0.90</td>
</tr>
<tr>
<td>14.6</td>
<td>-59.33</td>
<td>0.81</td>
</tr>
<tr>
<td>15.3</td>
<td>-65.28</td>
<td>0.93</td>
</tr>
<tr>
<td>17.6</td>
<td>-61.82</td>
<td>0.97</td>
</tr>
<tr>
<td>14.0</td>
<td>-63.39</td>
<td>0.89</td>
</tr>
<tr>
<td>17.7</td>
<td>-59.77</td>
<td>0.94</td>
</tr>
<tr>
<td>15.6</td>
<td>-63.90</td>
<td>0.92</td>
</tr>
<tr>
<td>18.7</td>
<td>-59.16</td>
<td>0.96</td>
</tr>
<tr>
<td>20.3</td>
<td>-50.27</td>
<td>0.86</td>
</tr>
<tr>
<td>20.8</td>
<td>-52.78</td>
<td>0.92</td>
</tr>
</tbody>
</table>

$^a$effective mass  
$^b$electron rest mass
Temperature dependence of the electrical resistivity of Cu-doped Dy$_2$S$_3$ prepared and then hot pressing.

Figure 12. Temperature dependence of the electrical resistivity of Cu-doped Dy$_2$S$_3$ prepared by MA and then hot pressing.
increase in the electrical resistivity.

Around 850 - 900°C the electrical resistivities reach maximum values (x = 0.075, 4.55mΩ-cm; x = 0.100, 6.99 mΩ-cm; x = 0.125, 7.13mΩ-cm; and x = 0.15, 4.96 mΩ-cm) and then begin to decrease above 900°C (Figure 12). This trend might be explained by the effect of the intrinsic conduction above 900°C. The intrinsic conduction results from the thermal excitation of an electron, which leaves behind a hole in the valence band. Therefore the number of electrons is equal to the number of holes in the intrinsic conduction. However, according to Henderson et al., the energy band gap of Dy₂S₃ is 3.0 eV and remains unchanged even when the electrical conductivity of the sample varies considerably. This large energy band gap of Dy₂S₃ shifts the onset of the intrinsic conduction arising from the thermal generation of electron-hole pairs (excitons) to higher temperature. The electron-hole pair generation must be avoided, because it results not only in a significant decrease in the Seebeck coefficient, but also an increase in the thermal conductivity by the ambipolar contribution resulting from the diffusion of electron-hole pairs from high temperature end to the low temperature end. Thus, in addition to a high melting point, chemical stability and mechanical strength, a large energy band gap is also one of the requirements in the design of the high temperature thermoelectric materials. Thus, it should be considered unlikely that the electrical resistivity decrease above 900°C is due to the effect of the intrinsic conduction. In the case of lanthanum sulfides, the carrier concentrations are almost invariant with temperature. Zhuze et al. also reported that the carrier concentrations of Nd₃S₄, Nd₃Te₄ and La₃Te₄ compounds are constant over the temperature range of 300 - 1100 K. This behavior is likely due to a self-doping mechanism. Thus, the carrier concentration of the rare earth chalcogenides only depend on the composition, i.e. the chalcogen to rare earth metal ratio. In addition,
according to their data, the electrical resistivities of rare earth chalcogenides increase monotonically with increasing temperature. This is because the additional carrier sources do not exist, i.e. no dopants.

In the case of Cu-doped Dy$_2$S$_3$, however, the carrier concentration depends on the electrical activity of Cu dopant in Dy$_2$S$_3$ matrix. Hence, as Cu dopants become electrically active at the high temperature, the carrier concentration increases. As a result, the electrical resistivity begins to decrease at the high temperature.

In addition to the carrier concentration, the microstructure also affects the electrical resistivity. Cu$_{0.100}$(Dy$_2$S$_3$)$_{0.900}$ and Cu$_{0.125}$(Dy$_2$S$_3$)$_{0.875}$ samples show higher resistivities than those of Cu$_{0.075}$(Dy$_2$S$_3$)$_{0.925}$ and Cu$_{0.150}$(Dy$_2$S$_3$)$_{0.850}$ (Figure 12). The resistivity gap between these two groups is enlarged with increasing temperature. Metallographic data are shown in Figures 13 and 14. As seen in Figure 13, Cu$_{0.100}$(Dy$_2$S$_3$)$_{0.900}$ and Cu$_{0.125}$(Dy$_2$S$_3$)$_{0.875}$ samples have microcracks which contribute to the electrical resistivity increase by crack boundary scattering, whereas microcracks are not observed in Cu$_{0.075}$(Dy$_2$S$_3$)$_{0.927}$ and Cu$_{0.150}$(Dy$_2$S$_3$)$_{0.850}$ samples (Figure 14). Therefore, it is likely that microcracks degrade the electrical conductivity more significantly at the high temperature than at room temperature. Figure 15 shows the electrical resistivity of Cu-doped Dy$_2$S$_3$ by melting and then hot pressing as a function of temperature. The room temperature values of these samples are lower (0.66 - 1.18 m $\Omega$-cm) than those of MA and then hot pressed samples (1.25 - 1.67 m$\Omega$-cm) because Cu-doped Dy$_2$S$_3$ prepared by melting technique have larger carrier concentrations than those of samples prepared by MA (see Figures 6 and 7). The maximum electrical resistivities appear at higher temperature (950°C) than those of samples by MA.

Figures 16 and 17 show the metallographic data of the as-pressed and the as-2 week heat treated Cu-doped Dy$_2$S$_3$ prepared by melting technique. Unexpectedly, the
Figure 13. Metallography of Cu$_x$(Dy$_2$S$_3$)$_{1-x}$: (a) $x = 0.100$ (b) $x = 0.125$. (250X)
Figure 14. Metallography of $\text{Cu}_x(\text{Dy}_2\text{S}_3)_{1-x}$: (a) $x = 0.075$ (b) $x = 0.150$. (250X)
Figure 15. Temperature dependence of the electrical resistivity of Cu-doped Dy$_2$S$_3$ prepared by melting and then hot pressing.
Figure 16. Metallography of Cu$_{0.034}$(Dy$_2$S$_3$)$_{0.966}$: (a) as-pressed (b) as-heat treated at 1100°C for 2 weeks. (250X)
Figure 17. Metallography of Cu_{0.036}(Dy_2S_3)_{0.961}: (a) as-pressed (b) as-heat treated at 1100°C for 2 weeks. (250X)
significant grain growth is not observed in the as-2 week heat treated 
$\text{Cu}_{0.034}(\text{Dy}_2\text{S}_3)_{0.966}$ (Figure 16), but some pores are observed. $\text{Cu}_{0.039}(\text{Dy}_2\text{S}_3)_{0.961}$ sample also does not show the significant grain growth between before and after 2 
week heat treatment (Figure 17 (a) and (b)). A comparison of the electrical resistivities 
between 2 week and 4 week heat treated $\text{Cu}_{0.075}(\text{Dy}_2\text{S}_3)_{0.925}$ samples was made 
(Figure 18). From room temperature to 500°C, there is no difference between two 
samples, but above 500°C, the 4 week heat treated sample shows a higher resistivity 
than that of the 2 week heat treated sample. The average degradation of the electrical 
resistivity in the temperature range of 500 - 1000°C is 5.5%. It is likely that this 
degradation is due to the degraded microstructure, because 4 week heat treated 
sample shows higher density of pores than that of 2 week heat treated sample (Figure 
19).

**High temperature Seebeck coefficient**

The Seebeck coefficient data of the as-2 week heat treated Cu-doped Dy$_2$S$_3$ 
alloys are shown in Figure 20. The Seebeck coefficients of $\text{Cu}_x(\text{Dy}_2\text{S}_3)_{1-x}$ increase 
monotonically with increasing temperature, indicating that all samples are n-type 
semiconductors and metallic, but at 800°C they begin to deviate from linearity. As 
mentioned in the electrical resistivity data, this behavior of the Seebeck coefficient at 
the high temperature is not due to the intrinsic conduction, but due to the carrier 
concentration enhancement by an increase in the electrical activity of the Cu dopants. 
Cu-doped Dy$_2$S$_3$ samples show Seebeck coefficients of -59 to -66 μV/°C were 
measured at room temperature and -164 to -177 μV/°C around 850°C as maximum 
values. The melted and then hot pressed samples also show the same behavior as 
those of the MA and then hot pressed samples (Figure 21). They are all 2 week heat
Figure 18. Temperature dependence of the electrical resistivity of the as-2 and 4 week heat treated Cu$_{0.075}$ (Dy$_2$S$_3$)$_{0.925}$ samples.
Figure 19. Metallography of Cu$_{0.075}$(Dy$_2$S$_3$)$_{0.925}$ after heat treatment at 1100°C for 4 weeks. (250X)
Figure 20. Temperature dependence of the Seebeck coefficient of Cu-doped Dy$_2$S$_3$ prepared by MA and then hot pressing.
Figure 21. Temperature dependence of the Seebeck coefficient of Cu-doped Dy$_2$S$_3$ prepared by melting and then hot pressing.
treated samples. They have Seebeck coefficients of -50 to -53 μV/°C at room
temperature and -163 to -168 μV/°C at 950 - 1000°C as maximum values. These
values are slightly lower than those of the MA and then hot pressed samples. It is
believed that the higher carrier concentration causes the lower Seebeck coefficient.

The Seebeck coefficient data between the 2 and 4 week heat treated
Cu$_{0.075}$(Dy$_2$S$_3$)$_{0.925}$ samples are compared in Figure 22. From room temperature up to
400°C, the 4 week heat treated sample has slightly high values, but above 400°C, the 2
week heat treated sample has a higher Seebeck coefficient than those of the 4 week
heat treated sample. The average degradation of the Seebeck coefficient from 500 up
to 1000°C is 3.8%.

**High temperature power factor**

Power factor ($S^2/ρ$) is an important parameter in measuring the overall electrical
effectiveness of a thermoelectric material. Power factors of Cu-doped Dy$_2$S$_3$ were
calculated from the electrical resistivity and the Seebeck coefficient data. Figure 23
shows the power factor data of the MA and then hot pressed Cu$_x$(Dy$_2$S$_3$)$_{1-x}$ as a
function of temperature. The power factors increase with increasing temperature and
reach the maximum values between 500 and 700°C. Cu$_{0.075}$(Dy$_2$S$_3$)$_{0.925}$ shows the
maximum power factor of 7.7 μW/cm·°C$^2$ at 700°C among the Cu$_x$(Dy$_2$S$_3$)$_{1-x}$ alloys.
The power factor data of melted and then hot pressed Cu$_x$(Dy$_2$S$_3$)$_{1-x}$ alloys are shown in
Figure 24. Cu$_{0.039}$(Dy$_2$S$_3$)$_{0.961}$ has the maximum power factor of 7.9 μW/cm·°C$^2$ at
690°C. Comparing the power factor data in Figures 23 and 24, it appears that Cu
doping by melting is more effective in the temperature range of 25 - 600°C than that by
MA.

Comparing the maximum power factor (36 μW/cm·°C$^2$ at 600°C) of n-type
Figure 22. Temperature dependence of the Seebeck coefficient of the as-2 and 4 week heat treated Cu$_{0.075}$(Dy$_2$S$_3$)$_{0.925}$ samples.
Figure 23. Temperature dependence of the power factor of Cu-doped Dy$_2$S$_3$ prepared by MA and then hot pressing.
Figure 24. Temperature dependence of the power factor of Cu-doped Dy$_2$S$_3$ prepared by melting and then hot pressing.
Si$_{80}$Ge$_{20}$ alloy, it appears that the maximum power factor of Cu-doped Dy$_2$S$_3$ is four and half times less than that of n-type Si$_{80}$Ge$_{20}$ alloy. However, if we assume that the thermal conductivity ratio of Cu-doped Dy$_2$S$_3$ (20 mW/cm·°C) to n-type Si$_{80}$Ge$_{20}$ alloy (40 mW/cm·°C) at room temperature can be extended to the elevated temperature, the maximum figure of merit of Cu-doped Dy$_2$S$_3$ is two and quarter times less than that of n-type Si$_{80}$Ge$_{20}$ alloy, indicating 0.44x10$^{-3}$/°C around 700°C.

Figure 25 shows the power factor data of both of the as-2 and 4 week heat treated Cu$_{0.075}$(Dy$_2$S$_3$)$_{0.925}$ alloys. The 4 week heat treated sample reached lower maximum value (7.2 µW/cm·°C$^2$) at lower temperature (600°C) as compared to those of the 2 week heat treated sample (7.7 µW/cm·°C$^2$ at 700°C). It is not clear what parameters are responsible for the degradation of the electrical properties of Cu-doped Dy$_2$S$_3$ after the 4 week heat treatment. For γ-lanthanum sulfides, Nakahara et al.16 reported that long term heat treatment severely degrades the electrical properties of γ-lanthanum sulfides because of the formation of β-La$_2$S$_3$, which is actually a lanthanum oxysulfide (La$_{10}$S$_{14}$O).38 However, in the lanthanide β-phase only exists for light rare earth sulfides (La to Nd).39 Hence, this β-phase does not exist in the dysprosium sulfide system. The 500 to 1000°C average degradation of the power factor due to longer heat treating times is 11.6 %.

The hysteresis of the electrical properties due to the thermal cycle

The 4 week heat treated Cu$_{0.100}$(Dy$_2$S$_3$)$_{0.900}$ was run twice under identical conditions to observe the effect of thermal cycling on the electrical properties. The electrical resistivity data are shown in Figure 26. Below 550°C two curves are almost identical, but above 550°C the average hysteresis of 3.9 % is observed in the temperature range of 550 - 1000°C. The average values of the hysteresis of the
Figure 25. Temperature dependence of the power factor of the as-2 and 4 week heat treated \( \text{Cu}_{0.075}\text{(Dy}_2\text{S}_3)_{0.925} \) samples.
Figure 26. Hysteresis of the electrical resistivity of the as-4 week heat treated Cu$_{0.10}$(Dy$_2$S$_3$)$_{0.90}$ as a function of temperature.
Seebeck coefficient (Figure 27) and the power factor (Figure 28) are 5.3 % and 8.4 % in the temperature range of 100 - 1000°C, respectively. It is unlikely that this hysteresis is associated with the precipitation of Cu dopants after the first run, because the second run sample shows lower electrical resistivity over the temperature range of 550 - 900°C. Furthermore, it is interesting to note that at ~ 900°C the values of the first and second runs are nearly the same.

Reduced Fermi energy

The most general expression for the Seebeck coefficient (S) for a given carrier concentration (n) of one sign is given by

\[ S = \pm \frac{k}{e} \left[ \frac{r + 2}{r + 1} \frac{F_{r+1}}{F_r} \left( \frac{\eta}{kT} \right) - \frac{\eta}{kT} \right] \]

where \( k \) = Boltzmann's constant, \( e \) = electron charge, \( T \) = absolute temperature, \( r \) = exponent of the energy dependence of the charge carrier, and \( \eta \) = Fermi energy.

\[ F_r \left( \frac{\eta}{kT} \right) = \int_0^\infty \frac{x' \, dx'}{e^{x'/(kT)} + 1} \]

where \( x' = \text{reduced energy of the electron (}\epsilon/kT\)).

The + sign is for the valence band, while the - sign is for the conduction band. The reduced Fermi energy (\( \eta^* \)) is expressed as follows:

\[ \eta^* = \frac{\eta}{kT} \]

Figure 29 shows the dependence of the Seebeck coefficient (S) on the reduced Fermi energy (\( \eta^* \)) for various \( r \) values. In this study, it is assumed that the charge carriers
Figure 27. Hysteresis of the Seebeck coefficient of the as-4 week heat treated Cu$_{0.10}$(Dy$_2$S$_3$)$_{0.90}$ as a function of temperature.
Cu_{0.10}(Dy_{3}S_{3})_{0.90} at 1100°C for 4 weeks

- 1st run
- 2nd run

Figure 28. Hysteresis of the power factor of the as-4 week heat treated Cu_{0.10}(Dy_{3}S_{3})_{0.90} as a function of temperature.
Reduced Fermi energy

Figure 29. Dependence of the Seebeck coefficient on reduced Fermi energy for various $r$ values.
are scattered only by the lattice vibrations \( (r = 0) \). The reduced Fermi energy \( (\eta^*) \) determined from the Seebeck coefficient is shown as a function of Cu doping level and temperature in Figures 30 and 31. It is seen from the curves that all Cu-doped \( \text{Dy}_2\text{S}_3 \) alloys have degenerate charge carrier (electron) concentrations with the degree of degeneracy falling rapidly with increasing temperature. According to Ioffe\(^2\) and Chasmar et al.\(^4\), the semiconductor is at least partly degenerate when \( \eta^* > -2 \) and when \( \eta^* > 2 \), it must be regarded as strongly degenerate. Thus, for Cu-doped \( \text{Dy}_2\text{S}_3 \) prepared by MA and then hot pressing, it is seen that samples are strongly degenerate in the temperature range of 25 - 350°C, while for samples prepared by melting and then hot pressing, the temperature range for the strong degeneracy is extended to 500°C. For the lanthanum sulfides, the optimum figure of merit (\( Z \)) is obtained at a reduced Fermi energy \( (\eta^*) \) of 0.9. It appears that the optimum figure of merit for the \( \text{Cu}_{0.034}(\text{Dy}_2\text{S}_3)_{0.966} \) alloy can only be reached at temperatures greater than 1000°C.

**Search for new dopants**

Eight different elemental dopants (Ag, Au, Ca, Mg, Al, Mo, Nb and Ni) and two compound dopants (FeS and Cu\(_2\)S) were examined to see if the thermoelectric properties of \( M_x(\text{Dy}_2\text{S}_3)_{1-x} \) could be improved relative to Cu. These ten samples were prepared by the same process as Cu-doped \( \text{Dy}_2\text{S}_3 \), and then Hall effect values were measured at room temperature. The results are listed in Table 4. All samples are n-type semiconductors. Ag and Au belong to the same group as Cu. However, the solubility of Au in \( \text{Dy}_2\text{S}_3 \) is too limited (2.84x10\(^{17}\)/cm\(^3\)) and the carrier mobility of Ag is too small (0.14 cm\(^2\)/V-s) compared to Cu. Thus, they have high electrical resistivities. Mo also has a too limited solubility (2x10\(^{18}\)/cm\(^3\)). Andreev et al.\(^{40}\) reported the phase diagram of FeS-\( \text{Dy}_2\text{S}_3 \) system, which indicated that the maximum solubility of FeS in
Figure 30. Temperature dependence of the Reduced Fermi energy of Cu-doped Dy₂S₃ prepared MA and then hot pressing.
Figure 31. Temperature dependence of the reduced Fermi energy of Cu-doped Dy$_2$S$_3$ prepared by melting and then hot pressing.
Table 4. Phase transition and Hall effect data of new elements-doped Dy$_2$S$_3$

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Dopant atomic size(Å)</th>
<th>at.%</th>
<th>Structure</th>
<th>$\rho$ (mΩ·cm)</th>
<th>$\mu$ (cm²/v-s)</th>
<th>$n$ (/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-Dy$_2$S$_3$</td>
<td>1.44</td>
<td>10</td>
<td>11 β γ α</td>
<td>3320</td>
<td>0.14</td>
<td>1.37x10¹⁹</td>
</tr>
<tr>
<td>Au-Dy$_2$S$_3$</td>
<td>1.44</td>
<td>2.44</td>
<td>11 β γ α</td>
<td>8000</td>
<td>2.75</td>
<td>2.84x10¹⁷</td>
</tr>
<tr>
<td>Mo-Dy$_2$S$_3$</td>
<td>1.36</td>
<td>10</td>
<td>11 β γ α</td>
<td>136.51</td>
<td>22.84</td>
<td>2.00x10¹⁸</td>
</tr>
<tr>
<td>FeS-Dy$_2$S$_3$</td>
<td>1.20</td>
<td>10</td>
<td>11 β γ α</td>
<td>21252</td>
<td>6.17</td>
<td>2.00x10¹⁷</td>
</tr>
<tr>
<td>Mg-Dy$_2$S$_3$</td>
<td>1.60</td>
<td>5</td>
<td>11 β γ α</td>
<td>12.99</td>
<td>4.26</td>
<td>3.56x10¹⁹</td>
</tr>
<tr>
<td>Ca-Dy$_2$S$_3$</td>
<td>1.97</td>
<td>5</td>
<td>11 β γ α</td>
<td>4500</td>
<td>4.14</td>
<td>3.56x10¹⁷</td>
</tr>
<tr>
<td>Ni-Dy$_2$S$_3$</td>
<td>1.25</td>
<td>10</td>
<td>11 β γ α</td>
<td>4500</td>
<td>4.14</td>
<td>3.56x10¹⁷</td>
</tr>
<tr>
<td>Cu$_2$S-Dy$_2$S$_3$</td>
<td>5</td>
<td>5</td>
<td>11 β γ α</td>
<td>58.32</td>
<td>6.91</td>
<td>1.55x10¹⁹</td>
</tr>
<tr>
<td>Al-Dy$_2$S$_3$</td>
<td>1.43</td>
<td>10</td>
<td>11 β γ α</td>
<td>3.33 (1100°C-2h.)</td>
<td>4.07 (1100°C-2h.)</td>
<td>2.71x10¹⁹</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.52 (1100°C-2h.)</td>
<td>51.09 (1100°C-2h.)</td>
<td>1.28x10¹⁹</td>
</tr>
<tr>
<td>Nb-Dy$_2$S$_3$</td>
<td>1.43</td>
<td>5</td>
<td>11 β γ α</td>
<td>7.38 (1100°C-2h.)</td>
<td>29.18 (1100°C-2h.)</td>
<td>2.90x10¹⁹</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.38 (1100°C-2h.)</td>
<td>49.29 (1100°C-2h.)</td>
<td>1.51x10¹⁹</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.96 (1100°C-2h.)</td>
<td>30.90 (1100°C-2h.)</td>
<td>4.08x10¹⁹</td>
</tr>
<tr>
<td>Cu-Dy$_2$S$_3$</td>
<td>1.28</td>
<td>3.9</td>
<td>11 β γ α</td>
<td>0.66 (1100°C-2h.)</td>
<td>45.97 (1100°C-2h.)</td>
<td>2.08x10²⁰</td>
</tr>
</tbody>
</table>
Dy$_2$S$_3$ matrix is 9 mol% at 1217°C. It is believed from Hall effect data that FeS is not electrically active in Dy$_2$S$_3$ matrix. Mg-doped Dy$_2$S$_3$ has high carrier mobility (40.65 cm$^2$/V-s) and slightly limited carrier concentration (3.05x10$^{19}$/cm$^3$), whereas Ca-doped Dy$_2$S$_3$ has lower mobility (2.46 cm$^2$/V-s) and high carrier concentration (1.96x10$^{20}$/cm$^3$). It is unlikely that the atomic size of the dopant affects the electrical activity in Dy$_2$S$_3$, because nickel (Ni) doped Dy$_2$S$_3$ has too limited electron concentration and low mobility, even though the atomic size of Ni (1.25 Å) is smaller than that of Cu (1.28 Å). Cu$_2$S is also not an electrically active dopant in Dy$_2$S$_3$. Al- and Nb-doped Dy$_2$S$_3$ alloys have slightly limited carrier concentrations, but have high mobilities. Thus, their electrical resistivities can compete with Cu-doped Dy$_2$S$_3$. However, the heat treatment degraded the electron concentrations of both of alloys, increasing the electrical resistivity. As a consequence, it is likely that potential dopants for Dy$_2$S$_3$ are Mg, Al and Nb.

Some dopants were found to transform η-Dy$_2$S$_3$ structure into α- or γ-phase. In Table 4, the first five dopants (Ag, Au, Mo, FeS and Mg) transformed η-phase (U$_2$S$_3$ type) into α-phase (Gd$_2$S$_3$) (Figure 32), while Ca caused the high temperature γ-form to be stable at room temperature (Figure 33). The last four dopants (Ni, Cu$_2$S, Al and Nb) did not affect the Dy$_2$S$_3$ structure (Figure 34).
Figure 32. X-ray diffraction patterns of Ag$_{0.1}$(Dy$_2$S$_3$)$_{0.9}$: (a) initial $\eta$-phase (b) $\gamma$-phase after 6 h MA (c) $\alpha$-phase after hot pressing at 1100°C for 1 h.
Figure 33. X-ray diffraction patterns of Ca$_{0.05}$(Dy$_2$S$_3$)$_{0.95}$: (a) initial $\eta$-phase (b) $\gamma$-phase after 6 h MA (c) $\gamma$-phase after hot pressing at 1100°C for 1 h.
Figure 34. X-ray diffraction patterns of Ni_{0.1}(Dy_2S_3)_{0.9}: (a) initial η-phase (b) γ-phase after 6 h MA (c) η-phase after hot pressing at 1100°C for 1 h.
CONCLUSIONS AND SUMMARY

Cu-doped Dy₂S₃ alloys, which are n-type semiconductors, were prepared by two different methods. The first involved MA of the two components (Cu and Dy₂S₃) and then hot pressed Cu-doped Dy₂S₃. The second consisted of melting the two components and then hot pressed Cu-doped Dy₂S₃. Further heat treatment enhanced the electron concentration up to 1.77x10²⁰/cm³ and 2.34x10²⁰/cm³, respectively. It is believed that the conduction mechanism of Cu-doped Dy₂S₃ is itinerant conduction because of its scattering distance greater than 1 Å.

Around 850 - 900°C the electrical resistivities of Cu-doped Dy₂S₃ prepared by MA and then hot pressing reach the maximum values of 4.55 to 7.13 mΩ-cm, depending upon the alloy compositions, whereas for melted and then hot pressed Cu-doped Dy₂S₃, the maximum values are 4.35 to 5.30 mΩ-cm around 950 - 1000°C. MA and then hot pressed Cu-doped Dy₂S₃ alloys show the maximum Seebeck coefficients of -164 to -177 μV/°C around 850°C, while melted and then hot pressed samples have the maximum Seebeck coefficients of -163 to -168 μV/°C at 950 - 1000°C. For the MA and then hot pressed samples, Cu₀.₀₇₅(Dy₂S₃)₀.₉₂₅ shows the maximum power factor of 7.7 μW/cm⁻°C² at 700°C, whereas in the melted and then hot pressed samples Cu₀.₀₉₃(Dy₂S₃)₀.₉₀₁ has the maximum power factor of 7.9 μW/cm⁻°C² at 690°C.

Comparing the maximum power factor (36 μW/cm⁻°C² at 600°C) of n-type Si₈₀Ge₂₀ alloy, it appears that the maximum power factor of Cu-doped Dy₂S₃ is four and half times less than that of n-type Si₈₀Ge₂₀ alloy. However, if we assume that the thermal conductivity ratio of Cu-doped Dy₂S₃ (20 mW/cm⁻°C) to n-type Si₈₀Ge₂₀ alloy (40 mW/cm⁻°C) at room temperature can be extended to elevated temperatures, the maximum figure of merit of Cu-doped Dy₂S₃ is two and quarter times less than that of
n-type Si_{60}Ge_{20} alloy, about 0.44×10^{-3}/°C around 700°C. However, if we consider how long Si-Ge alloys have been under development to optimize their properties (~30 years), compare to our initial studies the Cu-doped Dy_2S_3 alloys show some promise as thermoelectric materials.
REFERENCES


25. Meaden, G. T. In Electrical resistance of Metals; Plenum, New York, 1965; p 143.


PAPER III. EFFECT OF THE DOPING PROCESS ON THE ELECTRICAL ACTIVITY OF PHOSPHORUS IN Si$_{80}$Ge$_{20}$
ABSTRACT

The electrical activity of phosphorus in Si$_{80}$Ge$_{20}$ by two non-conventional doping processes has been measured over the temperature range 25 - 1250 °C. Both solid state (mechanical alloying) and gaseous phase doping processes were found to extend the electrical activity of phosphorus in Si$_{80}$Ge$_{20}$ alloys beyond the maximum equilibrium activity ($2.1 \times 10^{20}$/cm$^3$) to 2.50 to $2.97 \times 10^{20}$/cm$^3$ within the temperature range 900 - 1200°C. It is likely that this extended electrical activity of phosphorus is associated with a high density of defects.
INTRODUCTION

Silicon-germanium (Si-Ge) alloys have been developed for high temperature thermoelectric materials over the past 30 years. Early research work had focused on P-doped Si-Ge alloys for the n-leg and B-doped Si-Ge for the p-leg. However, for n-type Si-Ge, phosphorus solubility is too low to produce the high carrier concentrations needed for optimum figure of merit (Z).\(^1\) Several years ago, it was reported that gallium phosphide (GaP) enhances phosphorus solubility beyond the maximum equilibrium limit in Si-Ge alloys.\(^2,3\) Many researchers have used GaP-doped Si-Ge alloys to obtain high carrier concentrations by zone leveling, liquid phase epitaxy (LPE)\(^4,5\) and mechanical alloying (MA)\(^6\). MA is a high energy ball milling process, which was originally developed to produce complex oxide dispersion-strengthened (ODS) alloys.\(^7,8\) Over the past ten years, MA has been used widely to produce amorphization\(^9\), nanophase structures\(^10\) and metastable alloys.\(^11\) Last year, it was reported that MA can be used to produce high temperature or high pressure phases of the rare earth sulfides as metastable phases at room temperature.\(^12,13\)

Recently, we found that mechanical alloying and gaseous state diffusion can extend the electrical activity of phosphorus above the maximum reported equilibrium limit in Si\(_{90}\)Ge\(_{20}\) alloys. The results of this study are reported below.
EXPERIMENTAL PROCEDURES

Phosphorus doping by mechanical alloying (MA)

Phosphorus, silicon, and germanium powders were placed in a hardened steel vial and sealed in a helium-filled glove box. These powders were mechanically alloyed for 6 h in a Spex 8000 mixer/mill using three 12.70 mm diameter hardened steel balls and three 6.35 mm diameter hardened steel balls. The weight ratio of balls to powders was 5.6.

Phosphorus doping process by gaseous diffusion (GD)

First, undoped Si_{80}Ge_{20} powders were prepared by MA and then P-doped Si_{80}Ge_{20} alloys were prepared by the direct combination of the weighed amounts of phosphorus and Si_{80}Ge_{20} in a quartz ampoule at 800°C. The sample was initially heated to 500°C in a few hours. Thereafter the temperature was increased by 100°C increments each half day until the target temperature of 800°C was reached. The quartz ampoule was then held at this temperature for 3 days and air quenched. The temperature difference between the hot zone and the cold zone of the quartz ampoule was 200 ± 5°C at 800°C.

Hot pressing

Powder from each process was loaded into a graphite die inside a helium-filled glove box. The die was transported in a helium-filled plastic bag to a hot press apparatus for consolidation. The vacuum chamber was evacuated to 10^{-7} torr. Each sample was hot pressed with an applied pressure of 138 MPa for 45 min. at 1130°C and furnace-cooled to room temperature. Hot pressed compacts were cut and then
heat treated at 100°C temperature intervals for either 20 min., or 1 day at temperatures of 200°C to 1250°C. The resultant room temperature carrier concentrations and Hall mobilities were measured using the van der Pauw Hall method. The results of the chemical analysis of phosphorus in Si$_{60}$Ge$_{20}$ alloys are listed in Table 1.

High temperature electrical resistivity and Seebeck coefficient measurement

The electrical resistivity and the Seebeck coefficient measurements were made by the standard dc four-point probe technique\textsuperscript{14} and the method of the slope of the thermal emf versus temperature plot\textsuperscript{15}, respectively. Both properties were measured simultaneously on the same sample in a vacuum chamber (~ 10\textsuperscript{-6} torr) in the temperature range of 25 - 1000°C by a computer-controlled data acquisition system.
Table 1. Chemical analysis of phosphorus in Si$_{50}$Ge$_{20}$ alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Nominal P (at.%)</th>
<th>Chemically determined P (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG-P1</td>
<td>1</td>
<td>0.67</td>
</tr>
<tr>
<td>SG-P2</td>
<td>2</td>
<td>1.18</td>
</tr>
<tr>
<td>SG-P3</td>
<td>3</td>
<td>1.52</td>
</tr>
<tr>
<td>SG-X1</td>
<td>2</td>
<td>1.38</td>
</tr>
<tr>
<td>SG-X2</td>
<td>3</td>
<td>1.55</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

As shown in Figure 1, the electrical activity of phosphorus in two as-hot pressed Si_{60}Ge_{20} alloys decreases slightly with increasing temperature to 500°C and then increases rapidly up to 900°C. Above 1100°C retrograde P solubility occurs which causes a decrease in the electrical activity. Each point in Figure 1 represents the measured carrier concentration after a 20-min. heat treatment at the indicated temperature followed by air cooling to ambient. The initial room temperature value of 1.5x10^{20}/cm^{3} represents the "as-pressed" condition with no prior heat treatment. Since precipitation of dopants out of solution occurred during the furnace-cool phase, these carrier concentrations are lower than would be observed following a short thermal "reset" at 1050°C. Maximum observed phosphorus activity in one Si_{60}Ge_{20} alloy, designated SG-P2 (1.2 at.% P), was 2.97x10^{20}/cm^{3} and the corresponding mobility and electrical resistivity were 40.5 cm^{2}/V-s and 0.52 mΩ-cm, respectively. A second alloy, designated SG-P1 (0.7 at.% P), had a carrier concentration of 2.60x10^{20}/cm^{3} and a Hall mobility and electrical resistivity of 42.8 cm^{2}/V-s and 0.56 mΩ-cm, respectively, after 1000°C, 20 min. reset. To date, the maximum phosphorus solubility in Si_{60}Ge_{20} by conventional melting techniques has been reported to be about 2.1X10^{20}/cm^{3}.

Since these samples were held at temperature for 20 min., it is unlikely that the solubility line represents "true" equilibrium. Therefore a second slice (SG-P2-1) was held at each temperature for 24 hours to obtain equilibrium electrical activity at least at temperatures greater than 500°C (Figure 2). The solubility in this sample decreased to 0.9x10^{20}/cm^{3} at 500°C because significant dopant precipitation of the P atoms out of the Si-Ge matrix. However, at 1100°C, P doped Si_{60}Ge_{20} still had a carrier concentration of 2.86x10^{20}/cm^{3}. Therefore, it is likely that the extension of phosphorus
Figure 1. Electron concentration of two P doped Si$_{80}$Ge$_{20}$ alloys prepared by MA as a function of temperature. (Each point represents the room temperature carrier concentration measured following a 20-min. heat treatment at the indicated temperature combined with air cooling to ambient.)
Figure 2. Electron concentration of 1.18 at.% P doped Si$_{90}$Ge$_{20}$ by MA as a function of temperature and heat treatment time.
solubility in Si_{50}Ge_{20} induced by MA is not a temporary phenomenon or metastable situation.

During MA, the powder is subjected to highly energetic compressive impact forces in a ball mill. These impact forces enable material to be repeatedly cold welded and fractured. In this process, ball milling introduces a high density of defects (point defects and dislocations) into the material. In this study, phosphorus doping occurs simultaneously with the Si and Ge alloying process. Therefore doping by MA is more complicated than that of conventional melting techniques. It was noted in brittle-brittle systems (especially Si-Ge alloys) that thermal activation (diffusion) is required for MA. Additional effects induced by MA are a local temperature increase and high localized pressure. The temperature rise induced by the impact of the ball on the powder is estimated at 350°C in metallic solids and for ionic compounds it may reach 500°C. The maximum pressure reached in MA is estimated to be 1 GPa. Therefore, two possible models may be assumed for phosphorus doping during MA. First, phosphorus can be trapped alone between two balls (or ball and vial wall). In this case phosphorus might be locally vaporized because its melting and boiling points are 44.1°C and 280°C, respectively. This phosphorus vapor would increase the ambient pressure inside the vial and hence this positive pressure might contribute to P diffusion. Secondly, phosphorus can be trapped along with Si or Ge (or SiGe alloy) between balls (or ball and vial wall). At this point ball impacts enable phosphorus atoms to directly diffuse into the clean surface of Si (or Ge) and simultaneously produce defects, which trap excess phosphorus atoms. Most of the trapped P atoms are electrically inactive at room temperature.

Figure 3 shows the electrical activity of phosphorus after an initial 1050°C, 20 min.
Figure 3. Electron concentration of P doped Si₉₀Ge₂₀ after 1050°C, 20 min. reset as a function of temperature.
reset as a function of temperature. As shown, after 1050°C, 20 min reset phosphorus solubility of the 1.18 at.% sample in Si₈₀Ge₂₀ was 2.85x10²⁰/cm³. The elevated electrical activity of phosphorus did not change significantly when annealed for 20 min. at 200 and 300°C, decreased to 1.5x10²⁰/cm³ (this value is the same as equilibrium solubility of the as-hot pressed sample) when annealed for 20 min. at 550°C and increased again with increasing temperature up to 1050°C at 20 min. resets. Therefore, when the electrical properties of the 1050°C reset sample are measured from room temperature to 1000°C, the behavior of carrier concentration with temperature should follow the trend shown in Figure 3. Figure 4 shows the electron concentration in Si₈₀Ge₂₀ prepared by a gaseous diffusion process. Since the boiling point of phosphorus is 280°C, P is readily vaporized in the quartz above 500°C and then diffuses into the fine mechanically alloyed Si₈₀Ge₂₀ powders in the hot zone (800°C) under a temperature difference (200 ± 5°C). The amount of phosphorus vapor diminishes with time. Since the particle size of MA Si₈₀Ge₂₀ was about 1µm, this short diffusion distance might contribute to an increased P diffusion rate. As P atoms diffuse into powdered Si-Ge, it is likely that some of the excess P becomes trapped at defects or dislocations and that others interact with either vacancies or Si to form P-v or SiP complexes. This process also increased the electrical activity of phosphorus to 2.88x10²⁰/cm³ at elevated temperature for the same reason as the case of MA. The behavior of electron concentration with temperature is almost the same as that of MA sample.

Generally, when dopants are added in silicon, two diffusion mechanisms control the doping process. Most of the group V elements preferentially diffuse via vacancies, whereas for the group III elements diffusion via self-interstitial is responsible for the doping process. However, phosphorus atoms diffuse via self-interstitial in silicon,
Figure 4. Electron concentration of P doped Si₈₀Ge₂₀ by gaseous doping process as a function of temperature.
even though they belong to group V. The high energy ball milling produces high
density of defects (point defects and dislocations) in very fine powders of SiGe.
Therefore the extension of the electrical activity of phosphorus is probably associated
with a diffusion enhancement by the high density of these defects. It has been
reported that high angle boundaries in pure Si are diffusion-active whereas coherent
twin boundaries (low angle boundaries) are not. For example, the symmetric
coherent twin interface was found to have very weak electrical activity because this
defect requires only a few dislocations to account for the misorientation between the
grains. The asymmetric interface structures were found to have a larger electrical
activity due to the misfit dislocations in the interface. At the core of dislocation,
dangling bonds exist and these dangling bonds tend to form stable $sp^3$ covalent bonds
by capturing charge carriers. In addition, the elastic strain around dislocations
creates a Cottrell atmosphere. Therefore, it is likely that an undersized impurity such
as P might occupy an atomic site in the compression region around the dislocation in
order to thermodynamically reduce the total energy of the SiGe matrix.

When vacancies are in the nearest neighbor sites of the phosphorus atoms,
phosphorus-vacancy complexes can form. So far, it is known that there exist
phosphorus-vacancy ($P-v$) and phosphorus-vacancy-phosphorus ($P-v-P$ or $P_2-v$)
configurations. $P-v$ has two different states, a neutral charge state and a negative
charge state. Recent work points out the possibility of $P_3-v$ and $P_4-v$ in heavily doped
Si. Therefore high energy ball impacts might behave in a similar fashion to high
energy particle irradiation, in that it can introduce a high density of defects in silicon and
germanium. It is likely in Si-Ge alloys prepared by MA that after the electrical activity of
phosphorus reaches a maximum limit, some of the excess phosphorus atoms interact
with vacancies and others are trapped at the dislocations or grain boundaries during
ball milling. However, for Si-Ge alloys prepared by conventional melting techniques, it is unlikely that there is a high enough defect density to accommodate a comparable number of P-v interactions or P trapping at dislocations.

In order to address the question of how this defect structure affects the transport properties of these alloys at high temperature, one must consider the effect of temperature on the phosphorus-vacancy complexes. At room temperature most phosphorus-vacancy complexes (P-v) exist in a neutral state and hence they are electrically inactive. However, as the temperature increases, thermal energy enables P-v complexes to be activated and excess phosphorus begins to diffuse onto substitutional sites in SiGe lattice at the expense of vacancies. During a thermal reset a large number of excess phosphorus atoms trapped at the dislocations and grain boundaries are activated to overcome the diffusion barrier and become electrically active, and most of these are retained to room temperature upon cooling from the reset temperature. At elevated temperature, additional contributions would be expected from the dislocations which would compete with dopant precipitation (within the temperature range 400°C to 700°C) effects. No estimate of dislocation and defect densities in MA alloys has yet been proposed. As a consequence, these two effects may account for the extension of the electrical activity of phosphorus in Si$_{90}$Ge$_{20}$ prepared by MA beyond maximum limit. Further research is needed to understand the mechanisms operating in this system at both room and elevated temperatures.

The dependence of the temperature on the electron concentration for various ratio of Si to Ge is shown in Figure 5. According to Rosi$^{25}$, the solid solubility of n-type impurities increases with silicon content. Si$_{90}$Ge$_{20}$ prepared by MA also shows the same trend. As the ratio of Si to Ge increases, phosphorus solubility increases. This increased P solubility leads to higher carrier concentration.
Figure 5. Electron concentration of P-doped Si-Ge alloys as a function of temperature.
Hall mobility versus electron concentration is shown in Figure 6 for Si$_{80}$Ge$_{20}$ alloys prepared by both MA and gaseous diffusion process. The electron concentration at room temperature should be $2.5 \times 10^{20}$/cm$^3$ and the Hall mobility should be greater than 40 cm$^2$/V-s to obtain an optimized high figure of merit. These optimum conditions appear to be obtainable in P doped Si$_{80}$Ge$_{20}$ alloys by MA or gaseous diffusion process.

High temperature electrical properties

All P-doped Si$_{80}$Ge$_{20}$ alloys were thermally reset at 1050°C for 20 min. to obtain the maximum carrier concentration. The dependence of the electrical resistivity of P-doped Si$_{80}$Ge$_{20}$ alloys on temperature is shown in Figure 7. All samples are metallic and n-type semiconductors. The electrical resistivity at room temperature is 0.50 - 0.56 mΩ-cm and increases with increasing temperature. At 600 - 650°C the electrical resistivity reaches the maximum value of 1.63 - 1.74 mΩ-cm and then decreases above 650°C. This decrease above 650°C is not due to the intrinsic conduction, but due to an increase in carrier concentration caused by the dissolution of P precipitates and then the enhancement of the electrical activity of P solute atoms.

Figure 8. shows the Seebeck coefficient of P-doped Si$_{80}$Ge$_{20}$ alloys as a function of temperature. The room temperature Seebeck coefficient is -77 to -78 μV/°C. The Seebeck coefficient also increases with increasing temperature and reaches the maximum value of -232 to -240 μV/°C at 650 to 700°C. As the carrier concentration increases significantly above 650°C (Figure 3), the Seebeck coefficient decreases (equation (6) in Paper II).

The power factor for P-doped Si$_{80}$Ge$_{20}$ alloys is shown in Figure 9. The power factor of SG-P1 sample remains lower than the other alloys throughout the temperature
Figure 6. Hall mobility versus electron concentration at room temperature for P-doped Si_{60}Ge_{20} alloys by MA (SG-P) and gaseous doping process (SG-X)
Figure 7. Electrical resistivity of P-doped Si$_{80}$Ge$_{20}$ alloys as a function of temperature.
Figure 8. Seebeck coefficient of P-doped Si<sub>60</sub>Ge<sub>20</sub> alloys as a function of temperature.
Figure 9. Power factor of P-doped Si$_{60}$Ge$_{20}$ alloys as a function of temperature.
range of 200 to 1000°C. This lower power factor is likely due to the lower phosphorus solubility of SG-P1 than those of the other alloys. The power factor data is slightly scattered above 500°C, but SG-X1, SG-X2 and SG-P2 have high power factors (34 to 35 μW/cm°C²) even above 800°C. SG-P2 alloy has the highest average power factor of 33 μW/cm°C² between 300 and 1000°C.
MA enhanced the electrical activity of phosphorus in Si\textsubscript{80}Ge\textsubscript{20} alloys up to 2.97\times10^{20}/\text{cm}^3 above the maximum reported equilibrium limit (2.1\times10^{20}/\text{cm}^3) in the temperature range 900 - 1200°C. A gaseous phase diffusion process also increased the electrical activity of phosphorus to 2.88\times10^{20}/\text{cm}^3 in Si\textsubscript{80}Ge\textsubscript{20} alloys. It is likely that this extended electrical activity of phosphorus is associated with a high density of defects.

The designated SG-X1, SG-X2 and SG-P2 alloys have high power factors (34 to 35 $\mu$W/cm.$^\circ$C$^2$) even above 800°C and SG-P2 alloy has the highest average power factor of 33 $\mu$W/cm.$^\circ$C$^2$ between 300 and 1000°C. This maximum power factor value can compete with that of GaP-doped Si\textsubscript{80}Ge\textsubscript{20} alloy (\sim 36 $\mu$W/cm.$^\circ$C$^2$). Therefore, it is likely that the MA and gaseous phase diffusion processes can be used to optimize the electrical properties of n-type Si\textsubscript{80}Ge\textsubscript{20} alloy without a GaP dopant.
REFERENCES


14. Meaden, G. T. In Electrical resistance of Metal; Plenum, New York, 1965; p 143.


GENERAL SUMMARY

The preparation of the metastable crystalline high temperature and high pressure polymorphs of $R_2S_3$, where $R = Y, Dy, Er, Tm, Yb$ and $Lu$, was investigated at room temperature by mechanical milling (MM). For $Dy_2S_3$ the pure metastable high temperature $\gamma$-phase was obtained by MM. For $Y_2S_3, Er_2S_3$ and $Yb_2S_3$ the pure metastable high pressure $\gamma$-phase was obtained, whereas for the $Tm_2S_3$ and $Lu_2S_3$ samples the metastable high pressure $\gamma$-phases coexisted with the corresponding equilibrium ambient polymorphic phase. In case of $Dy_2S_3$ and $Y_2S_3$ the $\gamma$-cubic phase was present even after 160 hour MM. Therefore, it is concluded that MM (or MA) does not cause amorphization of $Dy_2S_3$ and $Y_2S_3$.

The Seebeck coefficient, electrical resistivity, and Hall effect have been studied in $Cu_x(Dy_2S_3)_{1-x}$ compounds with the $\eta_1$-orthorhombic structure in the composition range $0.006 \leq x \leq 0.15$ in order to determine their potential as high temperature (25 to 1000°C) thermoelectric materials. In this temperature and composition range Cu-doped $Dy_2S_3$ behaves as a degenerate semiconductor and shows itinerant conduction. The electrical resistivity and the Seebeck coefficient increased with increasing temperature and then reached the maximum values of 4.35 to 7.13 m$\Omega$-cm and -163 to -177 $\mu$V/$^\circ$C, respectively. The maximum power factor of 7.9 $\mu$W/cm$^2$$^\circ$C at $Cu_{0.039}(Dy_2S_3)_{0.961}$ was obtained at 690°C. As a result of search for new dopants, it appears that Mg, Al and Nb are potential dopants for $Dy_2S_3$.

The electrical activity of phosphorus in $Si_{80}Ge_{20}$ by two non-conventional doping processes has been measured over the temperature range 25 - 1250°C. Both solid state (mechanical alloying) and gaseous phase doping processes were found to extend the electrical activity of phosphorus in $Si_{80}Ge_{20}$ alloys beyond the maximum equilibrium.
activity ($2.1 \times 10^{20}/\text{cm}^3$) to 2.5 to $2.9 \times 10^{20}/\text{cm}^3$ within the temperature range 900 - 1200°C. It is likely that this extended electrical activity of phosphorus is associated with a high density of defects.
REFERENCES


ACKNOWLEDGEMENTS

The author wishes to thank Dr. Karl A. Gschneidner, Jr. for his guidance and encouragement. The author also wishes to thank Bernard Beaudry for his technical suggestions and helpful discussions. The author sincerely thanks Bruce Cook and Joel Harringa for their helpful discussions and technical training. The author would like to acknowledge Nile Beymer for his technical help. The author also thanks Joel Calhoun for his help in search for literatures in RIC's library. Dr. Robert Jacobson and his group members are thanked for a single crystal x-ray diffractometer and helpful comments. The author also thanks Slavi Sevov for his single crystal x-ray data analysis. The author is indebted to Hal Sailsbury for his help in metallography. The author wishes to thank Hiroyuki Takeya for his helpful discussion.

Special thanks are to the author's parents who have raised, supported and encouraged him and the author prays his mother to get well soon.

Finally, the author's wife Moon-Sun Huh and his daughter Hey-Jung Han are deeply thanked for their love and encouragement.

This work was performed at Ames Laboratory under contract no. W-7405-eng-82 with the U. S. Department of Energy. The United States government has assigned the DOE Report number IS-T 1636 to this thesis.