Results of studies on Cr, Fe, Ge and Re doping of higher manganese silicide single crystals prepared by Czochralski method are presented. Effective coefficients of said impurities distribution are determined and their influence on the microstructure and anisotropy of thermoelectric properties of these crystals is studied. Hot-pressing procedure for HMS-based thermoelectric material manufacture is elaborated. Possibility of material pressing temperature reduction via addition of deoxidizing impurity or effect of ultrasonic vibrations on material being pressed is shown. The average value of thermoelectric figure of merit of rhenium doped HMS samples produced by hot pressing was $\sim 0.7 \times 10^{-3} \text{K}^{-1}$ in the range 800–1300 K.

Introduction

The task currently urgent is to use in thermoelectric generators working at temperatures 600-100 K instead of conventional materials based on germanium, lead and tin chalcogenides, other easy-to-obtain, less expensive materials. From this standpoint, of big interest are silicides of transient metals that have rather high melting temperatures, are non-volatile in vacuum and much cheaper than monochalcogenides. Higher manganese silicide is one of the most promising materials to be used in thermal generators, the efficiency of which can be improved by doping with inactive and electroactive impurities. As electroactive impurities, chromium and iron were selected. Doping with rhenium as the element located in the same periodic system group as manganese and possessing large atomic weight enables considerable reduction of this material thermal conductivity. Besides, the effect of germanium dopants on thermoelectric properties of HMS was studied. To establish the influence of various dopants on the structure and electrophysical properties of HMS, studies were made on single-crystalline Czochralski-grown samples. Hot-pressing procedure for HMS-based materials manufacture was elaborated as well.

The diagram of state of part of Mn-Si system according to data from [1] is shown in Fig. 1.

According to this diagram, between manganese monosilicide and silicon there exists a compound formed according to peritectic reaction iron + MnSi $\leftrightarrow$ Mn$_3$Si$_5$ at 1159 °C.
As long as chilling temperature and temperature of peritectic reaction of HMS formation differ as little as by 5 degrees, with crystallization of alloys the peritectic reaction has the time to proceed completely, which enables single crystals of this compounds to be pulled from the melt by Czochralski method.

Crystalline structure of HMS was investigated in a series of papers [2-4]. From the analysis of these papers it can be concluded that HMS has homogeneity region extending from \( MnSi_{1.67} \) to \( MnSi_{1.77} \), and this region has a variety of structures that can be described by formula \( Mn_{2n}Si_{2n+m} \). The lattice is trigonal with increased “c” axis. The following structures are described: \( Mn_3Si_5 \), \( Mn_4Si_7 \), \( Mn_{11}Si_{19} \), \( Mn_{12}Si_{26} \), \( Mn_{26}Si_{35} \), \( Mn_{27}Si_{37} \). Fig. 2 shows \( 1/4 \) of \( Mn_{11}Si_{19} \) unit cell (a). Mn subcell (b) according to data from [2] and schematic illustration of \( Mn_4Si_7 \) projection to (100) plane (c) according to data from [3].

![Fig. 2. (a)-1/4 of Mn_{11}Si_{19} unit cell. (b)-Mn subcell. (c) - projection of Mn_{4}Si_{7} structure to (100) plane](image)

In the homogeneity region HMS structures are distinguished for different number of manganese subcells in the elementary cell. The distances between \( Mn \) layers in them are constant, and the distances between \( Si \) layers are related to chemical phase composition and are greater than those between \( Mn \) layers. Mismatch between Mn and Si layers results in formation of lattice with “c” period multiple of different periods in Mn subcell. Analysis of interatomic distances of these structures indicates to the presence of areas oriented perpendicular to “c” axis, that differ in the character of interaction between atoms, which explains the anisotropy of properties in different crystallographic directions.

**Investigation results**

**Doping of HMS single crystals**

A series of HMS crystals and HMS solid solutions with iron, chromium and germanium was prepared by Czochralski method (Fig. 3) [5-7].

The charge for pulling was prepared by melting components in a high-frequency furnace in evacuated quartz ampoules. Pulling was made with different rates from 0.5 to 0.03 mm/min. the rates of crucible and inoculation rotation were 10-20 rpm. inoculations were oriented in [100] and [001] directions. To prevent crystal from cracking, it was slowly cooled at the rate of 30 K/h. Crystals had diameter 15-20 mm, length 50-70 mm. The most homogeneous HMS crystals were grown from the
melt with 47.5 weight % Si. Their composition can be described by formula $MnSi_{1.72\pm0.02}$. Etching of microsections with aqueous solution HF (1:1) revealed a striped microstructure of these crystals, the stripes in this case being located perpendicular to “c” axis irrespective of growth direction (Fig. 4a).

![Fig. 3. HMS crystals (a). doped with Cr (b) and Ge(c) grown in [100] (a). [100] (b) and [001] (c) directions.](image)

![Fig. 4. Microstructures of (001) and (100) planes of MnSi$_{1.72}$ crystals undoped (a) and doped with Fe(b), Cr(c), Ge(d) unannealed (1) and annealed for 200 h at 1000 °C(2).](image)

Composition of striped inclusion determined by means of X-ray microanalysis corresponds to manganese silicide which is precipitated when temperature of melt due to temperature fluctuations at crystallization front becomes higher than the temperature of peritectic reaction. As shown by annealing of HMS crystals, $MnSi$ solubility increased at temperatures 800-1000 °C. Doped HMS crystals also contained inclusions of $MnSi$ phase (Fig. 3 b, c, d). The character of precipitations in Ge-doped crystals differed from the rest of crystals studied (Fig. 3 d), however, after annealing at 1000 °C for 200 h the amount of inclusions decreased (Fig. 3 (2)), and at annealing for 400 h at 1000 °C these crystals became single-phase.
Effective coefficients of iron, germanium and chromium distribution in HMS were determined, which under the above growth conditions made: 0.8 ± 0.08 for iron 1.5 ± 0.15 for chromium 0.2 ± 0.02 for germanium [8].

Investigations of thermal and electrical properties performed on single-crystal HMS samples in crystallographic directions [100] and [001] made it possible to determine certain electrophysical parameters of this material – scattering mechanism, carriers mobility, effective mass of holes density of states, as well as to study the effect of dopants on its thermoelectric properties. The values of electrophysical parameters at room temperature in two crystallographic directions [100] (1) and [001] (2) and anisotropy factors for some crystals are given in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Composition</th>
<th>p×10^20 cm^-3</th>
<th>Direction</th>
<th>α. μV/K</th>
<th>α1/α2</th>
<th>σ. Ohm/cm</th>
<th>σ1/σ2</th>
<th>σ_p×10^15 W/cm·K</th>
<th>κ_p1/κ_p2</th>
<th>Z×10^3 K^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>undoped</td>
<td>7.3</td>
<td>1</td>
<td>80</td>
<td>0.60</td>
<td>930</td>
<td>4.65</td>
<td>31</td>
<td>4.43</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>134</td>
<td></td>
<td>200</td>
<td></td>
<td>7</td>
<td>4.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Fe. 2.5%</td>
<td>6.7</td>
<td>1</td>
<td>94</td>
<td>0.65</td>
<td>625</td>
<td>2.84</td>
<td>25</td>
<td>1.32</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>145</td>
<td></td>
<td>220</td>
<td></td>
<td>19</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>Cr. 2.6%</td>
<td>21</td>
<td>1</td>
<td>86</td>
<td>0.83</td>
<td>950</td>
<td>1.79</td>
<td>22</td>
<td>1.22</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>104</td>
<td></td>
<td>530</td>
<td></td>
<td>18</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>Ge. 1.7%</td>
<td>31</td>
<td>1</td>
<td>87</td>
<td>0.93</td>
<td>1470</td>
<td>1.34</td>
<td>20</td>
<td>1.18</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>94</td>
<td></td>
<td>1100</td>
<td></td>
<td>17</td>
<td>1.39</td>
<td>0.39</td>
</tr>
</tbody>
</table>

In the undoped HMS crystals there was discovered strong anisotropy of electric conductivity (σ), thermoelectric coefficient (α) and total (κ) and lattice (κ_p) thermal conductivity. Such anisotropy of these parameters is related to peculiarities of crystal-chemical structure of HMS. MnSi phase precipitated along (001) planes also reduces electric conductivity in the direction of “c” axis, as long as macro- and microcracks often occur in these planes. Doped crystals possess considerably lower anisotropy of thermoelectric properties in these crystallographic directions. Anisotropy reduction is most pronounced in germanium-doped crystals. HMS are characterized by large concentration of holes (7×10^2 °Сm^-3). chromium and germanium doping was attended by a considerable increase in charge carrier concentration and their mobility reduction.

Investigation of temperature dependences of thermoelectric coefficient and electric conductivity of crystals was made in the temperature range of 20–1100 °C in two crystallographic directions. For all investigated crystals anisotropy of properties was manifested in the temperature range of 20–500 °C. At higher than 700 °C temperature in the intrinsic conductivity region the
anisotropy disappeared. The thermal energy gap for HMS-based crystals made 0.8±0.1 eV. The energy gap value obtained from optical absorption measurements proved to be equal to ~1.2 eV at room temperature.

**Preparation of HMS-based materials by hot pressing**

Studies made on rhenium-doped HMS samples melted in quartz ampoules showed that thermoelectric figure of merit of such material can reach 0.8×10⁻³ K⁻¹ in the temperature range of 700–900 °C. However, due to material anisotropy, the reproducibility of properties on these samples was insufficient. The most technological method for preparation of high-temperature thermoelectric materials under industrial conditions is hot pressing method. Therefore, hot-pressing procedure for manufacture of rhenium-doped HMS-based materials was elaborated. The process of material preparation comprised the steps as follows:

- components melting in quartz ampoules evacuated to pressure 10⁻³ mm Hg on a high-frequency installation.
- ingot grinding in jasper container.
- powder pressing in graphite press molds.

It was established that the finer is the powder, the higher is the efficiency of resulting pressed samples. Powder was used with the amount and size of particles as shown in Fig. 5.

![Fig. 5. Quantity and size of particles on mechanical grinding.](image-url)

In this powder 82 % of particles had the size less than 2 μm 18 % of particles – from 2 to 40 μm. Pressing was made in graphite press molds under different processing modes. To eliminate interaction of sample material with graphite, the internal contacting surfaces of press mold were coated with a thin layer of silicon nitride. Current was passed through the press mold and it was heated to the required temperature measured by chromel-alumel thermocouple or optical pyrometer. No material oxidation took place in pressing, since heated press mold served as a protective shield. 2-3 samples of size 10×6×16 mm were prepared for each processing. It was established that the larger is material density, the higher is its thermoelectric figure of merit, since in case of material underpressing the reduction in electric conductivity exceeds considerably thermal conductivity reduction. With pressure temperature increase from 800 °C to 1100 °C the density of samples increases from 2.3 to 5.3 g/cm³, achieving maximum value at temperature 1140 °C (melting temperature 1185 °C). Double increase in pressing pressure (from 100 to 200 kg/cm²) produces no marked effect on powder sintering process (see Fig. 6).
To produce briquettes of required density, pressing temperature should be kept close to material melting temperature. To reduce pressing temperature, titanium was added as deoxidizer. In this case pressing temperature was reduced by ~200° with introduction of 2 weight % Ti. However, material efficiency thereby was reduced due to second-phase titanium precipitation. Good results were obtained with the use of ultrasonic vibrations of frequency 19 kHz in the course of pressing. Well-pressed samples were obtained at temperature 1000 °C and pressure 50 kg/cm².

Fig. 7 shows temperature dependences of thermoelectric coefficient, electric conductivity and thermal conductivity in the range of 20 – 800 °C for rhenium-doped HMS produced by hot pressing.
The average value of thermoelectric figure of merit Z of this material in the range of 200–600 °C is $0.7 \times 10^{-3} \text{K}^{-1}$.

**Conclusions**

Czochralski method was used to prepare doped HMS single crystals in different crystallographic directions. Anisotropy of thermoelectric properties as a function of doping addition ($\text{Fe}$, $\text{Cr}$, $\text{Ge}$) was studied.

Conditions for manufacture of rhenium-doped HMS-based material by hot pressing were elaborated.

**References**


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