

# Synthesis and thermoelectric properties of higher manganese silicide

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Received April 19, 2024

Revised October 16, 2024

Accepted October 16, 2024

The paper considers the features of synthesis (directly during the sintering process) of higher manganese silicide from nanosized powders in an spark plasma sintering. Thermoelectric characteristics of the obtained material are studied. It is established that higher manganese silicide has a high value of thermoelectric efficiency  $ZT = 0.66$  at  $T = 635^\circ\text{C}$ . It is also shown that the value of thermoelectric efficiency is affected by high-temperature holding.

**Keywords:** Higher manganese silicide, thermoelectric, Seebeck coefficient, thermoelectric figure of merit, spark plasma sintering.

DOI: 10.61011/SC.2024.07.59543.6350H

## 1. Introduction

Higher manganese silicide  $\text{MnSi}_{1.73-1.75}$  is considered as one of the candidates for use as a high-temperature thermoelectric branch of  $p$ -type of conductivity in  $n$ -GeSi pair. Major reason for search of a substitute for  $p$ -GeSi material is its relatively low thermoelectric efficiency ( $ZT$ ):  $ZT = \alpha^2 T / \rho \lambda$ , where  $\alpha$  — Seebeck coefficient,  $\rho$  — resistivity,  $T$  — average temperature between hot and cold faces of material,  $\lambda$  — thermal conductivity coefficient.

The higher manganese silicide, in addition to the operating temperature range close to germanium-silicon, is also distinguished by the possibility of using equivalent fabrication processes, in particular,  $\text{MnSi}_{1.73-1.75}$  may be formed similar to a solid solution  $\text{Ge}_x\text{Si}_{1-x}$  by methods of powders sintering, including nano-powders [1–8].

Sintering of powders is currently one of the most advanced methods of thermoelectric materials synthesis, featuring low thermal conductivity relative to its crystalline counterpart due to additional scattering of phonons at grain boundaries [9,10]. The most common is the sintering of pre-synthesized compounds of higher manganese silicide [11,12]. At that, physical and chemical processes occurring during sintering of the non-fixed Mn-Si powders, are described scarcely.

This paper describes the synthesis of higher manganese silicide powders in an electro-pulse plasma sintering unit, as well as impact of processes occurring during synthesis on the powders thermoelectric characteristics.

## 2. Powders grinding

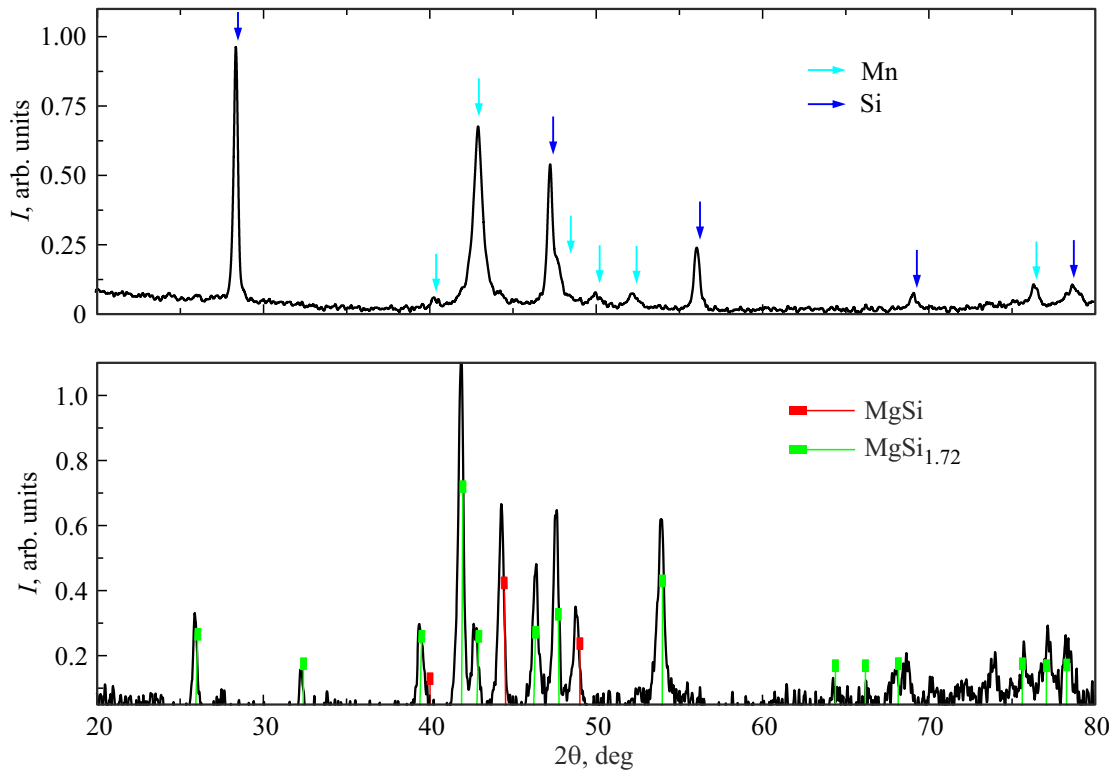
For the synthesis of higher manganese silicide in the electro-pulse plasma sintering unit, powders obtained by grinding of bulk crystalline ingots of ultra-high pure (UHP)

manganese and silicon doped with boron atoms to a concentration of  $\sim 10^{15} \text{ cm}^{-3}$  were used as the initial powder mixture. The content of the elements was determined by weighing the starting materials and then converting from weight percentages to atomic ones.

Manganese–silicon compound has a complex phase diagram, in particular, manganese and silicon cannot form a continuous row of solid solutions. When mixing the components in the material, as a rule, a multiphase material with an interface between the phases is formed. The concentration of these phases will be determined by thermodynamic conditions, and the phase itself is formed due to a chemical reaction, the rate of which significantly exceeds the rate of thermal diffusion, which allows us considering the compound formation as an instantaneous process [13]. Such high-speed motion of particles is called a reactive diffusion.

In most of the well-known papers devoted to the synthesis of higher manganese silicide, this compound is being fabricated precisely during the grinding process. When grinding Mn-Si powder, the formation of the MnSi compound is based on a rapid process of reactive diffusion: because of heating caused by particles collision, a chemical reaction may occur, leading to the formation of phases of manganese silicide (the process of mechanical synthesis). This method has several disadvantages, the main one of which is significant mechanical wear of the mill cup. In addition, difficulties can be noted in control of higher manganese silicide formation process, since „adjustment“ parameters are the grinding speed and time, which do not directly impact the phase composition.

Worth mentioning is selection of the process modes where synthesis of higher manganese silicide occurs directly during the sintering process. This is achieved by selecting special grinding modes (low rotation speed of the mill drum



**Figure 1.** X-ray diffraction spectra of Mn-Si powder (top) and sintered MnSi sample (bottom).

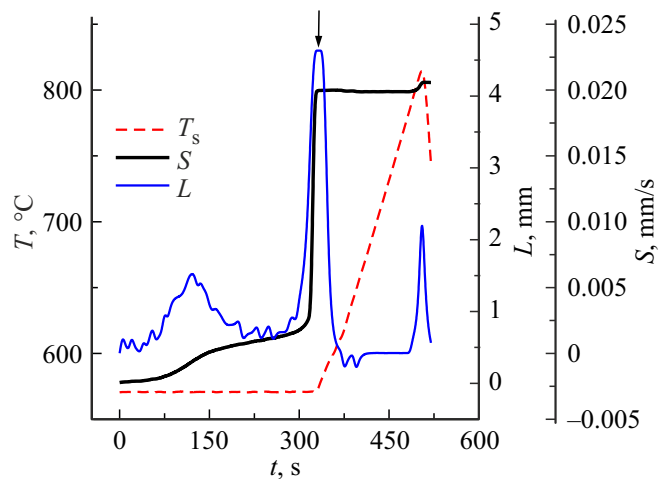
and short grinding time allow the formation of a powder of unbound particles of Mn and Si). In this case, the synthesis of the powder is carried out during sintering process and can be managed and controlled by the choice of sintering modes.

Mn-Si powder was obtained by grinding the ingots in alcohol medium for 6 h with a speed of 250 rpm. The ingots were ground using planetary mill Fritsch Pulverisette. The phase composition was controlled by measurements using X-ray diffraction method. For Mn-Si mixture the composition of initial components corresponded to the higher manganese silicide ( $\text{MnSi}_{1.75 \pm d}$ ). Here  $d$  — modulation of material composition ( $\sim 0.02$ ), when higher manganese silicide structural ordering is preserved [14,15]. Figure 1 (top) illustrates X-ray diffraction spectrum of Mn-Si powder. It follows from the X-ray diffraction spectra that only silicon and manganese phases are present in the initial powder, which indicates that no mechanical synthesis was observed during the powder grinding process.

### 3. Experimental results and discussion

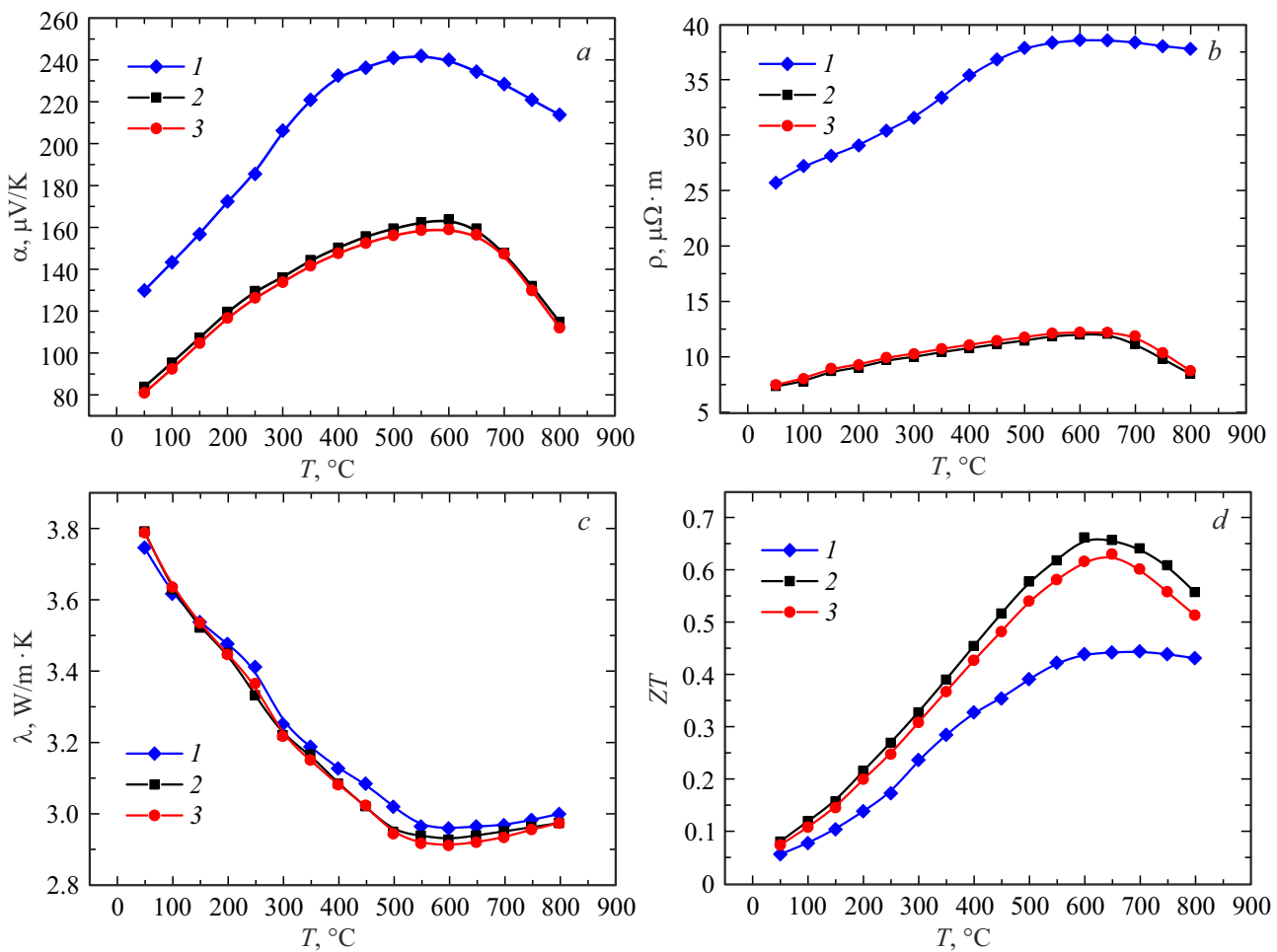
#### 3.1. Powders sintering analysis

Powders were sintered in the electro-pulse plasma sintering unit DR SINTER model SPS-625 (Japan). The fundamentals of analysis of physical processes occurring in the electro-pulse plasma sintering unit incorporate the so-called



**Figure 2.** Characteristic sintering diagram for Mn-Si powders ground in the mode of sintering time dependence on: 1 — temperature  $T_s$  (dashed line), 2 — shrinkage  $L$  (black curve) and 3 — shrinkage speed  $S$  (blue curve).

„sintering curves“ — a family of time dependencies ( $t$ ) of physical values, characterizing the process, which are set and (or) measured *in situ*. Among such values controlled in the unit are the following: sintering temperature ( $T_s$ ) — temperature of the mold exterior wall, powder shrinkage ( $L$ ) — variation of material thickness under the action



**Figure 3.** Temperature dependencies of Seebeck coefficient (a), resistivity (b), thermal conductivity coefficient (c) and ZT coefficient (d) for samples 2 and 3. For comparison, the diagrams illustrate the temperature dependencies of thermoelectric characteristics of sample 1 — without annealing. The numbers of curves coincide with the numbers of samples.

of pressing force and heating of the mold and the shrinkage rate ( $S$ ) — first shrinkage derivative with respect to time. Figure 2 shows characteristic sintering curves for the studied Mn-Si powder. On the shrinkage versus time curve we may see a singularity associated with an abrupt decrease in the thickness of the mold at the sintering temperatures of 540–570 °C (red arrow). This feature was observed for all experiments on the sintering of manganese and silicon powders. The time during which shrinkage occurs is in most cases less than the time interval measured by the test unit (5 s), which does not allow making a reliable calculation of the shrinkage rate.

As a result of shrinkage, the X-ray diffraction spectrum undergoes significant changes with respect to the spectrum of the initial powder (Figure 1, below). The basic phase registered on the spectrum of the sintered sample is the higher manganese silicide. Hence, the behavior of the shrinkage curve shown in Figure 2, a should be associated with a solid-phase chemical reaction and formation of manganese silicides phases. Possibility of such reaction has been discussed earlier in some papers [15–18]. Note that the

chemical reaction is accompanied by a drastic shrinkage of the powder, which may be caused by material compaction because of reactive diffusion between Mn and Si grains. The obtained results indicate that the main mechanism of Mn-Si powders shrinkage at a stage of low-temperature sintering is the reactive diffusion with formation of manganese silicides.

### 3.2. Analysis of thermoelectric properties

It is known from the literature that in order to achieve high thermoelectric characteristics, it is necessary to achieve a high phase content of higher manganese silicide at a very low concentration of manganese monosilicide [19–22]. We've selected optimal parameters such as powder composition, sintering rate, and press pressure, leading to fabrication of a material with a high concentration of the higher manganese silicide phase. At the same time, the samples were characterized by high porosity, resulting from insufficient shrinkage of powder during sintering. High material porosity resulted in relatively high values of

Parameters of a series of samples with variation of sintering rate and annealing duration

№ of sample	Rate sintering, °C/min	Duration and annealing, min
1	25	0
2	50	0
3	25	20

resistivity  $\rho$ , which was the reason for reduction of  $ZT$  compared to the equivalents known from the literature.

Additional shrinkage of Mn-Si powder may be implemented due to high pressing pressure, the value of which determines the degree of shrinkage of powders and, accordingly, the degree of material porosity. However, there are other ways to provide additional powder shrinkage. The use of alternative approaches may be desirable when the equipment does not allow setting the required high pressure of the press. Such approaches include an increase in the heating duration, as well as additional high-temperature annealing, which can be implemented immediately after the sintering process.

To analyze the effect of high-temperature exposure on thermoelectric characteristics, a series of samples was prepared, the parameters of which are shown in the table below. Maximal sintering temperature for all samples was 1000°C, pressure — 70 MPa. Sample 1 was formed at a heating rate of 25°C/min, without additional high-temperature exposure. In sample 3, additional exposure was introduced at a maximal sintering temperature for 20 min. In sample 2, apart from a 20-minute exposure the heating rate was increased to 50°C/min.

Figure 3 shows experimentally obtained temperature dependencies of thermoelectric characteristics of samples 1, 2 and 3 (see Table). First of all, we note that the obtained values of thermoelectric efficiency  $ZT$  for samples 2 and 3 are comparable with known international equivalents. The behavior of temperature dependences of thermoelectric characteristics is well consistent with the literature data, in particular [19–22].

From Figure 3, *b* we see that samples 2 and 3 have low resistivity compared to the sample 1. Decline in resistivity is reached due to the high-temperature exposure. A solid-phase chemical reaction probably occurs at the first stage of synthesis between Mn and Si grains, accompanied by the formation of manganese silicides (this can be seen from a comparison of X-ray diffraction spectra before and after sintering — Figure 1). However, this process is not enough to effectively sinter the grains to each other. As a result, in a sample synthesized without additional annealing, the grains are not well connected to each other, which provides an increase in resistivity (this is also evidenced by the low mechanical strength of the samples). High-temperature exposure provides additional sintering of the grains, which reduces porosity and, accordingly, leads to the resistivity

decline. As a result, despite low value of Seebeck coefficient for samples 2 and 3, the increase of  $ZT$  for them is observed (Figure 3).

The best thermoelectric properties were obtained for sample 2. Maximal thermoelectric efficiency  $ZT = 0.66$  was reached at a temperature of  $T = 635^\circ\text{C}$ . Thus, the synthesis of manganese silicide from the initial Mn-Si powders makes it possible to form a thermoelectric material with extremely achievable efficiency characteristics for this type of compound.

## 4. Conclusion

The grinding of Mn-Si powders was analyzed. The parameters have been selected at which mechanical synthesis does not occur during grinding of the powder mixture. The processes of manganese silicides synthesis by method of powders sintering in an electro-pulse plasma sintering unit have been studied. It has been established that the formation of manganese silicides phases by powder sintering method is based on a solid-phase chemical reaction. It was demonstrated that high thermoelectric characteristics of materials based on higher manganese silicide arise from additional shrinkage, which shall be provided upon termination of the solid-phase reaction leading to the formation of this compound. High values of thermoelectric efficiency of higher manganese silicide have been reached.

## Funding

The study was financially supported by the Ministry of Education and Science of the Russian Federation within the scope of the State Assignment (project FSWR-2023-0037).

## Conflict of interest

The authors declare that they have no conflict of interest.

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*Translated by T.Zorina*