

Chapter 11

Silica-Based Materials for Thermoelectric-Legs Embedding

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Abstract Sol-gel chemistry was used to synthesize low-density SiO_2 aerogel for matrix embedding of silicide-based (Mg_2Si and $\text{MnSi}_{(2-x)}$) thermoelectric legs. In thermoelectric (TE) modules, the heat conduction in air and the convective and radiative contribution to the heat transfer play an important role in the reduction of the efficiency of the module. Silica aerogels are known for the lowest thermal conductivity of any non-evacuated solid. With this in mind, silica-based aerogel materials were employed to fill the void spaces between the thermoelectric legs of a module. In order to do this, different synthesis procedures were taken into account to produce suitable silica materials. It is important that the silica can be easily cast into place, avoiding mechanical cracks of the matrix. Silica aerogel typically requires a supercritical drying step to remove the pore fluid from the SiO_2 gel, avoiding the collapse of the pores. This procedure is not practical for TE-legs embedding and it is dangerous, expensive, and time-consuming. It is known that replacing the $-\text{OH}$ groups with organic hydrophobic substituents in the SiO_2 pores prevents the pore-shrinkage and the sintering of the matrix during solvent evaporation step. This allows synthesizing relatively light materials at low temperature and ambient pressure, with no need of supercritical drying of the gel. The obtained aerogels were characterized by thermogravimetric analysis and differential scanning calorimetry to evaluate the stability of the material and the chemical modification with increasing temperature. The thermal expansion of the silica was evaluated by means of dilatometry. Finally, the thermal diffusivity was measured with the laser flash method.

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Introduction

Thermoelectric devices are built up from thermoelectric legs made by conventional thermoelectric materials such as Bi_2Te_3 and PbTe , and less conventional Mg_2Si and $\text{MnSi}_{(2-x)}$ (higher manganese silicide, HMS) linked together by means of metal contacts. The thermoelectric legs are contacted electrically to obtain an electrical series configuration and a thermally parallel configuration, in order to keep all the legs on the same side at the same temperature. Embedding the legs in a chemically and electrical inert matrix could enhance the TE module performance by improving thermal insulation between the hot and the cold side. Furthermore, the matrix could act as a sublimation barrier, especially for materials where metallic elements tend to sublime into corrosive vapors [1]. Metal vapors can condense far from the material leg, creating problems such as thermal and/or electrical short circuits and consequently they can reduce the efficiency and the life of the module.

SiO_2 is an appealing candidate for TE module embedding because it is inert in the whole temperature range exploited for TE generation with several materials, such as skutterudites, TAGS, PbTe , and silicides. The most important feature is the versatility of SiO_2 towards the formation of different nano- and microstructures with a high degree of porosity. For this reason, the lightest solids ever obtained are silica aerogels.

Module encapsulation on silica aerogel has already been exploited by Salvador et al. [2] and Sakamoto et al. [1]. However, obtaining silica aerogel suitable for high temperature thermoelectric applications is not straightforward. Wet chemistry like sol-gel reactions of silane precursor is used to synthesize porous SiO_2 networks. The silica backbone created upon gelation of the silane precursor undergoes tensional stresses and it is sensitive to cracks. During the drying process necessary to obtain the SiO_2 matrix, the solvent evaporates from the pores and the latter tends to collapse because of the capillary forces, causing severe shrinkage of the structure. Two possible techniques are commonly exploited to reduce pore collapse: drying the aerogel in an autoclave under supercritical conditions, avoiding the formation of the liquid solid meniscus, and the functionalization of Si-OH groups of the pores with organic hydrophobic groups. Si-CH_3 groups are not reactive and they keep the pores “open.” Furthermore, the solvent inside the pores (usually alcohols) is replaced by nonpolar hexane (or other linear alkanes) which has a low surface tension, reducing the shrinkage during the drying step even at ambient pressure.

In this work, low-density silica was synthesized via ambient pressure drying with the aim to embed thermoelectric legs made of Mg_2Si and $\text{MnSi}_{(2-x)}$. Three samples named HMDZ_1 (from the Si precursor HMDZ-hexamethyldisilazane), MTMS_1 and MTMS_2 (from the Si precursor MTMS-methyltrimethoxysilane) are discussed here. Ambient pressure drying was preferred to autoclave drying because it is more versatile. In principle, all the synthetic steps could be carried out directly on the mold where the thermoelectric legs are placed.

The thermal behavior of the silica synthesized was investigated up to 600 °C, considering that the operating temperature of Mg_2Si and $\text{MnSi}_{(2-x)}$ is in the range 500–600 °C. The thermal diffusivity was evaluated for the sample showing adequate thermal behavior.

Experimental Procedure

HMDZ_1 was synthesized according to Wei et al. [3] modifying the synthesis procedure using hexamethyldisilazane (HMDZ) in place of trimethylchlorosilane (TMCS).

MTMS_1 was synthesized following the procedure reported by Xu et al. [4] with minor modifications.

MTMS_2 was obtained by reaction of methyltrimethoxysilane (MTMS) with an aqueous solution of oxalic acid (0.01 M) in methyl alcohol (MeOH) with $\text{MeOH:MTMS}=26$ and $\text{oxalic acid:MTMS}=0.004$ molar ratios. The system was stirred at room temperature for 1 h and then an aqueous solution of NH_3 (2.75 M) was added to the reaction mixture, keeping a molar ratio of $\text{NH}_3:\text{MTMS}=0.20$. After 1 h of stirring, the sol was poured into polyethylene molds and let to gel overnight. Residual MeOH was removed and the alcogels were aged in ethylic alcohol (EtOH) for 6 h at 60 °C. After aging, EtOH was removed washing the material several times with n-hexane and the materials were dried at 50 °C for 24 h. The samples were thermal treated at 100 °C for 1.5 h followed by 150 °C for 1.5 and finally they were kept at 200 °C for 1 h.

Thermogravimetric analysis were performed on a TA SDT Q600 TGA/DSC analyzer for the three samples under dry air (100 mL/min) using an alumina crucible.

Dilatometry measurements were recorded on a Netzsch DIL 402 PC dilatometer under an Ar atmosphere (90 mL/min) for sample HMDZ_1 cut as a 7.6-mm bar.

Thermal treatment on MTMS_1 and MTMS_2 was performed on a homemade apparatus with a flux of air of 200 mL/min in a Nabertherm P330 tubular furnace.

The thermal diffusivity was measured via laser flash method by means of a Netzsch Microflash LFA457, using a powder sample holder with an internal graphite coating.

Results and Discussion

Three types of SiO_2 matrices were synthesized with the idea of embedding the n- Mg_2Si and p-HMS (Higher Manganese Silicide) legs of a thermoelectric module. The matrix should be light and should act as thermal and electrical insulation barriers between the legs and between the hot and cold sides of the module. Among the large variety of organosilane precursors, tetraethoxysilane (TEOS) and methyltrimethoxysilane (MTMS) were chosen for their availability and fast hydrolysis and

condensation time [5]. It must be pointed out that sol-gel chemistry is very complex and the reactivity of the precursors does not depend only on their chemical nature but also on the applied reaction conditions [6, 7]. The solutions of the precursors are liquids of low viscosity before gelation time so it is possible to cast the SiO_2 matrix on modules of the desired shape.

In order to obtain silica materials with low densities, two main synthetic paths were followed. The first was the formation of hydrophilic alcogels via acidic hydrolysis (HCl) of TEOS and then condensation of the polysiloxane species with aqueous NH_3 , as previously reported by Wei et al. [3]. The as-obtained gels underwent silylation with hexamethylsilazane (HMDZ), less hazardous than trimethylchlorosilane (TMCS) usually employed. The silylation process changes the liquid-solid contact angle and reduces the capillary liquid tension avoiding cracking of the network during the drying process. Furthermore, it passivates the pore surface, limiting the condensation of $-\text{Si}-\text{OH}$ groups that leads to shrinkage of the gel [7]. After silylation, the gels were kept several days in hexane and then air dried to obtain a relative low-density hydrophobic silica (0.3 g/cm^3), indicated here as HMDZ_1.

In the second synthetic route, MTMS was used as the precursor because of the presence of the nonpolar CH_3-Si on the silane molecule. This avoids the silylation step reducing the processing time and costs. Two procedures were followed with MTMS. In the first, reported by Xu et al. [4], MTMS was hydrolyzed in MeOH with an aqueous solution of oxalic acid and then aqueous ammonia was added to obtain the alcogel. The gel was aged and dried replacing MeOH with EtOH, followed by thermal treatments at 50, 100, 150, and 200 °C. The aerogel so obtained (density 0.102 g/cm^3) was named MTMS_1.

It must be said that, for this reaction, toxic MeOH was replaced by EtOH first as the solvent. Unfortunately, any attempts to carry out the synthesis with MTMS in ethanol led to cracked transparent xerogel granules.

In the second synthesis procedure, a solution of aqueous ammonia was added after the hydrolysis of MTMS with oxalic acid in MeOH, working with a high content of water. It has been observed that adding F^- ions (within the NH_3 solution), which generally decreases the gelation time of the silica [8], did not considerably change the gelation time in this case. The excess of water should favor the acidic hydrolysis of MTMS, while the condensation process is enhanced by the high pH (9–10) of the solution after the addition of NH_3 .

The silica matrix was aged in ethanol, washed several times with ethanol and then n-hexane, and then dried. Thermal treatments at 50, 100, 150, and 200 °C were performed. Hydrophobic and light silica was obtained, indicated here as MTMS_2 (density 0.09 g/cm^3). As to the macroscopic scale, HMDZ_1 appeared as a semi-transparent solid while MTMS_1 and MTMS_2 were opaque. MTMS_1 retained its shape when small deformations were applied and it was quite easy to cut into slices without breaking the material. MTMS_2 appeared as a highly compressed powder, and after compression, it became powdery. However, it was possible to cut it into pieces of all shapes and thickness.

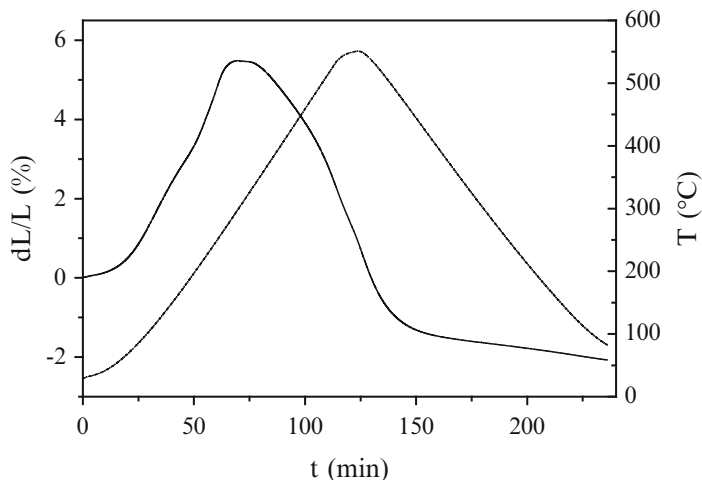


Fig. 11.1 Percentage of one-dimensional expansion dL/L versus time (*dash*) and temperature versus time (*solid*) for sample HMDZ_1

To understand the mechanical behavior of the SiO_2 materials synthesized, thermal expansion measurements from RT to 600 °C, the operative range for Mg_2Si and HMS thermoelectric materials, were performed on sample HMDZ_1 under an Ar atmosphere. The expansion (dL) curve versus time and temperature ramp is displayed in Fig. 11.1.

In the range 30–250 °C the relative expansion was not perfectly linear: the system expanded linearly up to 150 °C, a small decrease of the slope dL/L versus t was observed until 200 °C and then it increased up to 250 °C, from where the expansion became constant up to 330 °C. After 330 °C, HMDZ_1 underwent shrinking while heating up to 600 °C. After 600 °C, the cooling segments started and the shrinkage continued. This behavior could be explained by thermogravimetric (TGA) and differential scanning calorimetry (DSC) analyses (Fig. 11.2) performed in air: an important weight loss for HMDZ_1 occurred from 250 to 600 °C. This corresponds to the oxidation of the organic $-\text{CH}_3$ groups present on the surface of the pores. After oxidation, the pores $-\text{CH}_3$ groups, which could not react, were replaced by $-\text{OH}$ polar groups that could condense to give Si-O-Si new bonds, leading to pore collapse and consequently to material shrinkage.

Even if the dilatometry was performed under an argon flux of 100 mL/min, small amounts of oxygen impurities could cause the oxidation of methyl groups of the pores. It is important to consider that also under inert atmosphere chemical reaction, like pyrolysis of the methyl groups, could occur in the temperature range considered, leading to the rearrangement of the microstructure and possible shrinkage.

The HMDZ_1 dL/L curve reached the origin at 550 °C and the shrinkage continued linear until 475 °C. At this point, the slope of the curve decreased and remained constant up to 80 °C (below this temperature the dilatometer is no more able to control the cooling rate). From the DSC signal (Fig. 11.2) it can be observed that the

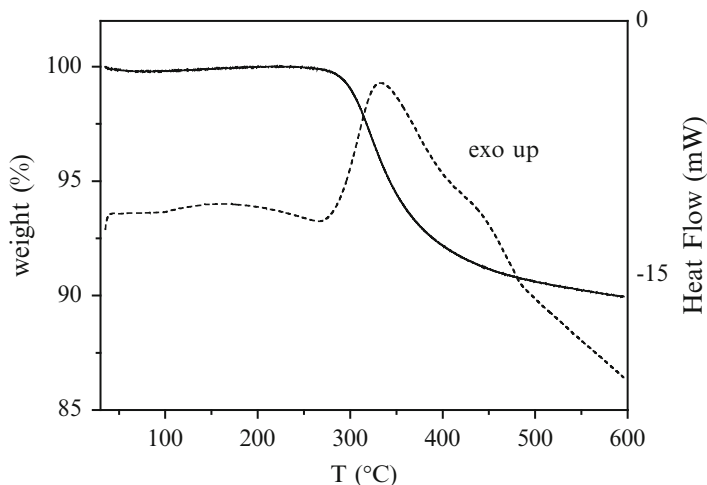


Fig. 11.2 TGA (solid) and DSC (dash) curves for HMDZ_1 (heating rate: 5 °C/min, air: 100 mL/min)

main peak at 350 °C had a shoulder at 450 °C that corresponds to the oxidation of secondary methyl groups, located on a different site of the silica network. This could affect the thermal expansion of the material.

After the thermal expansion measurement, HMDZ_1 showed several cracks that propagated during the measurement. This could be due to the collapse of pores during oxidation of $-\text{CH}_3$ groups and, probably, the silica network was not strong enough to resist the thermal stresses. On the basis of this consideration, and as observed by Sakamoto et al. [1], more “elastic” and deformable matrices are required in order to embed parallelepiped TE modules because the edges could act as stress intensifier causing the propagation of cracks. MTMS, with a methyl group bound directly to Si could lead to elastic and compressible aerogel materials, as reported by Xu et al. [4].

For MTMS_1 and MTMS_2, the thermal expansion curves were not recorded because it was not possible to determine the origin of the dilatometer measuring bar. Because the typical operating temperatures of the $\text{Mg}_2\text{Si}/\text{HMS}$ TE modules are between 500 and 600 °C, a thermal treatment was performed under air (200 mL/min) from RT to 600 °C (heating/cooling ramp 5 °C/min, 120 min at 600 °C) on both samples to check the presence of cracks and their integrity. MTMS_1 broke up into powdery pieces after the thermal treatment and it was not possible to measure its density. On the other hand, MTMS_2 retained its shape with a linear shrinkage of 10 %. The thermal treated MTMS_2 has a density of 0.11 g/cm³.

Thermogravimetric and differential scanning calorimetry analyses of MTMS_1 and MTMS_2 in air are shown in Fig. 11.3. In the case of MTMS_1, a sharp exothermic peak was present at 481 °C corresponding to the main weight loss in the TGA curve. These are related to the oxidation of CH_3 groups present in the Si-O-Si backbone. At 350 °C, a broad and less intense exothermic peak was present together

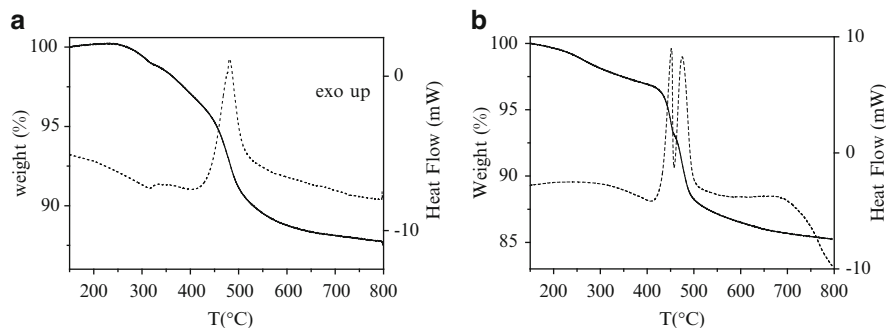


Fig. 11.3 DSC (*dash*) and TGA (*solid*) curves for MTMS_1 (a) and MTMS_2 (b) recorded with a heating rate of 3 °C/min in air (100 mL/min)

with a weight loss starting at 250 °C. This could be attributed to the oxidation of surface functional CH_3 groups but also to the evaporation and oxidation of residual organic solvent that could be trapped inside the silica matrix. It has to be noted that after the analysis, the residual sample appeared as powder after the thermal treatment at 600 °C.

For MTMS_2, a slight weight loss was present in the range 150–350 °C as observed for MTMS_1, but, in this region, the DSC signal is smooth. This could be an indication of the residual solvent evaporation, trapped into the silica matrix. The oxidation of organic CH_3 occurred from 400 °C. Two sharp and well-resolved exothermic peaks at 451 and 475 °C are an indication of two different sites for $\text{Si}-\text{CH}_3$ groups in the silica network, leading to site-affected oxidation enthalpy.

MTMS_1 and MTMS_2 showed similar thermal behaviors but the former one cracked upon heating at 600 °C. The density of MTMS after the thermal treatment was 0.21 g/cm³ and the matrix linearly shrunk by 18 % of the original length. The thermal behavior could be better understood considering the microstructure of the samples.

Secondary electron field emission (FE)—scanning electron microscope (SEM) micrographs for MTMS_2 before and after thermal treatment are displayed in Fig. 11.4. For comparison, also HMDZ_1 and MTMS_1 (before thermal treatment) are shown.

The microstructure of MTMS_2 seems to not be affected by the thermal treatment and it consists of micrometer-rounded silica particles attached to each other to form opened chain structures and leaving void opened spaces. This is consistent with the Ostwald ripening mechanism for silica formation, by which small particles re-dissolve and larger particles grow from the condensation of the dissolved ones. This mechanism is favored mainly in aqueous systems [5]. In this case, MTMS_2 was synthesized in the presence of a large excess of water. It has to be pointed out also that the sizes of the microspheres are highly homogeneous. By comparison, MTMS_1 showed compact agglomerates of grains of the order of 100 nm forming micrometer sized open spaces, as previously reported [4]. HMDZ_1 had similar globular structures as for MTMS_1 but smaller voids and pores (less than 200 nm)

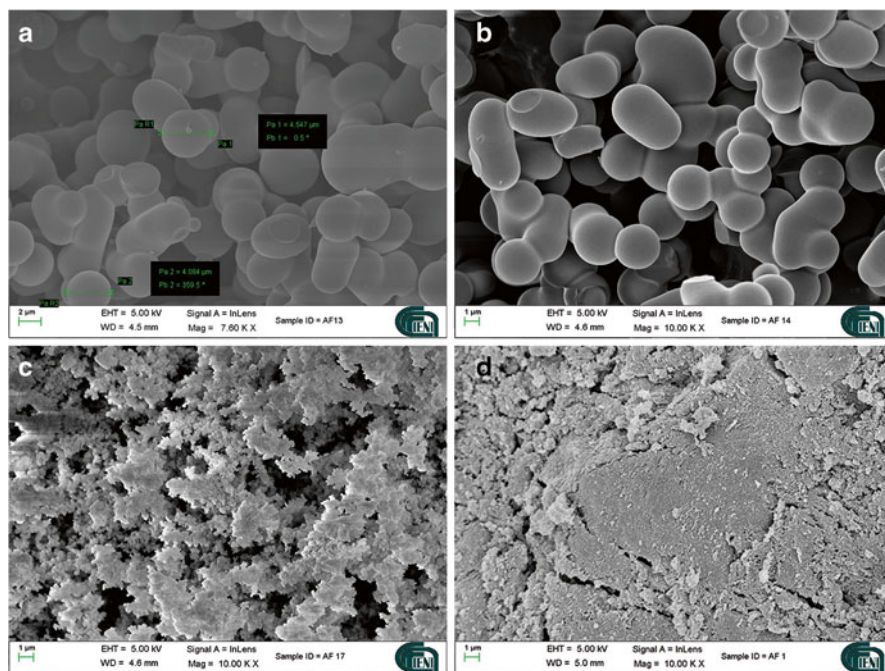


Fig. 11.4 Secondary electron SEM micrographs for MTMS_2 before (a) and after (b) thermal treatment at 600 °C; MTMS_1 (c) and HMDZ_1 (d)

around the agglomerates. The chained structures of MTMS_2 are probably held together via electrostatic forces and this could be the reason that, on macroscopic scale, this material appeared as pressed powder, retaining its shape. The chain agglomerations of silica microspheres and the presence of void spaces made MTMS_2 retain its shape upon thermal treatment. It is reasonable to consider that the chains can be rearranged during heating in the void spaces without breaking. Furthermore, the organic products of combustion have enough space to escape from the silica structure preserving the network. On the other hand, HMDZ_1 and MTMS_1 networks could be damaged because of the retention of organic products on the pores, which are less accessible to gases such oxygen or air.

The thermal diffusivity of MTMS_2 after thermal treatment at 600 °C was measured via the laser flash method. Thermal-treated MTMS_2 was chosen because the typical silicide TE module working temperature is in the range of 500–600 °C, and no organic groups are present in the SiO₂ matrix at these temperatures.

The measurement was carried out under an Ar atmosphere to avoid the oxidation of the graphite layer needed for the measurement. As it can be observed in Fig. 11.5, the thermal diffusivity decreased with temperature reaching a minimum value of 0.1047 mm²/s at 450 °C and then slightly increased at 600 °C (0.1099 mm²/s). It was not possible to evaluate the thermal conductivity because the value of the density (ρ), that should be used for this calculation, is not the measured one. In fact,

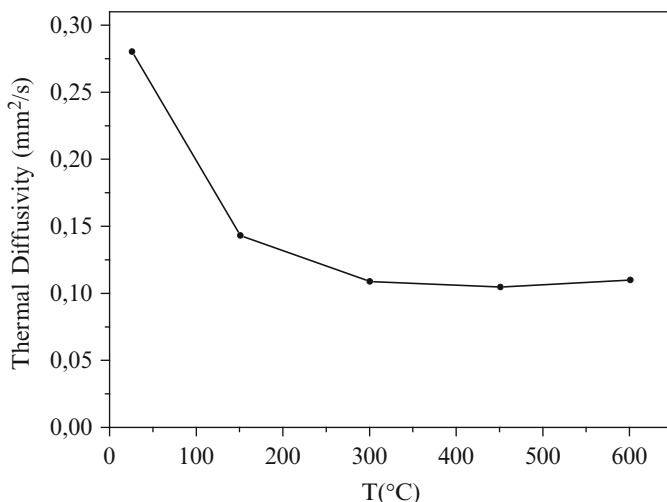


Fig. 11.5 Thermal diffusivity of MTMS_2 as function of the temperature

MTMS_2 was slightly pressed inside the sample holder here used and the density remained uncertain.

Furthermore, to the best of author knowledge, in the literature, thermal conductivity measurements on silica aerogel and light xerogel are usually performed via the hot-disc or the hot wire techniques [3], and the values are restricted to room temperature, so it is not possible to make a comparison in the temperature range here considered (25–600 °C). On this basis, only thermal diffusivity values are reported in Fig. 11.5. From a qualitative point of view, considering the low density of MTMS_2 together with an intrinsic low specific heat for silica, it is reasonable to expect values of thermal conductivity of the order of few mW/mK, as previously reported [3, 9].

Conclusions

Three types of SiO₂ matrices were considered with the aim of embedding Mg₂Si/HMS thermoelectric modules. HMDZ_1 and MTMS_1 were synthesized as already reported [3, 4] with minor variations of the synthesis procedure. MTMS_2 was synthesized according to the procedure here reported, adding more water to enhance the gelation step and to reduce gelation time and to obtain more elastic SiO₂ network. The SiO₂ was made hydrophobic to reduce shrinkage during the ambient pressure-drying of the gel, in order to obtain low-density and highly porous materials. These characteristics are required to avoid much weight increase after embedding TE modules, made of light Mg₂Si and MnSi_(2-x) and to control the thermal conductivity.

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