Fast synthesis of nanocrystalline Mg_2Si by microwave heating: a new route to nano-structured thermoelectric materials

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The ultra fast synthesis of nanocrystalline Mg_2Si was carried out using microwave radiation. The elemental precursors were first milled together under dry conditions to get fine particles. The resulting mixture of powders of Mg and Si was cold pressed before being heated by microwave irradiation. Precursors and products were analyzed by X-ray diffraction and scanning electron microscopy. The high energy ball milling parameters utilized to prepare the reactive powders have quite an influence on the behavior of the mixture under irradiation. Moreover, SEM imaging demonstrates that the power and time of irradiation are crucial for the grain growth of the Mg_2Si and must be adequately controlled in order to avoid the decomposition of the phase. Our results show that we successfully managed to easily and quickly synthesize homogeneous nanocrystalline Mg_2Si with particle size smaller than 100 nm using a microwave power of only 175 W for two minutes on powders ball milled for two hours.

Introduction

Thermal to electric energy conversion is nowadays clearly identified as a source of alternative "clean" energy. The reduction of fuel consumption is a way to reduce CO_2 emissions in the automotive industry by scavenging the heat loss on exhaust systems for instance. Evidently, the relatively high cost combined with the limited efficiency of these thermoelectric generators is a real drawback to their large scale development. The efficiency of such a converter is directly proportional to the thermoelectric figure of merit of materials constituting the device. In turn, this figure of merit, labeled ZT, defines the thermoelectric quality of a given material. This dimensionless value is equal to $\alpha^2 T/\rho\kappa$, where T represents the absolute temperature, α the seebeck coefficient, ρ the electrical resistivity and κ the total thermal conductivity.[1] Usually, the quantities α, ρ, and κ for conventional 3D crystalline materials are interrelated in such a way that increasing ZT by manipulating these variables independently is unfeasible. Whereas α and ρ vary inversely with the carrier concentration, ρ and κ are related by the Weidemann Franz law $\kappa_{el} = LT/\rho$, where L is the Lorenz constant and $\kappa_{el} = \kappa - \kappa_{lat}$ with κ_{lat} representing the heat transported by the phonon. However, nanostructuring of bulk materials has shown that major reduction in thermal conductivities can be achieved by the multiplication of grain boundaries and therefore by the creation of extensive interfacing between the particles enhancing the phonon scattering at the grain boundaries, evidently decreasing κ_{lat}.[2]

Magnesium silicide is now accepted to be an extremely promising material for thermoelectric application.[3] Indeed, it is made of widely abundant, cheap, light and moreover non-toxic elements, all critical criteria that must be addressed in order to envisage a large scale production of thermoelectric generators for heat scavenging applications. Furthermore, the n-type doped version of Mg_2Si is already a state of the art material,[3] with a thermoelectric figure of merit higher than unity whereas many efforts have been devoted to increasing the performance of p-type Mg_2Si.[3,4]

Mg_2Si can be synthesized by mechanical alloying, by conventional high temperature reaction or by directly processing powders of the elements by spark plasma sintering.[3,4] However, these techniques never provide nanocrystalline materials because they use metallic precursors whose sizes are micrometric or because they use long periods of time of heating that are favorable to grain growth. In contrast, microwave heating can be extremely fast and if applied on small enough particles, this method can limit the grain growth to a minimum. To the best of our knowledge, microwave synthesis has never been employed to produce magnesium silicide whereas it has been shown in many reports that it is indeed possible to heat metals using microwave irradiation whether for synthetic purposes or sintering applications.[5,6] Therefore, using a microwave synthetic method for the fabrication of thermoelectric material, not only can reduce the price of the synthesis by reducing its time but also could lead to nanostructured materials with potentially reduced thermal conductivity and therefore improved thermoelectric performance. Here we report on the fast synthesis of nanocrystalline Mg_2Si by fast microwave heating of high energy ball milled powders of the elements and we discuss the possibility offered by such a combination of techniques on material science.

Experimental

Powders processing

The powders containing elemental magnesium and silicon in a 2 : 1 ratio are prepared by the high energy ball milling of magnesium turnings (Alfa Aesar Puratronic 99.98%) and silicon lumps (Alfa Aesar 99.9999%) both used as received. Due to the reactivity of magnesium towards air and moisture, all manipulations were performed under nitrogen in a glove box or sealed tubes. Six grams of a stoichiometric amount of the pure elements were placed in a 20 ml tungsten carbide bowl containing six 10 mm diameter tungsten carbide balls. The grinding bowls were equipped with a fitting lid and a silicone o-ring that insured that the assembly was

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airproof so that the milling occured under a nitrogen atmosphere (always done in order to avoid the oxidation of the reactants). These assemblies were then placed in a high energy ball mill (Fritsch pulverisette 7 Premium line). The powders were processed for 2, 4, or 6 times 30 min at a speed of 450 rounds per minute with a pause of 1 min in between periods of 30 min and this led to batches B1, B2, and B3, respectively.

After completion of the milling program, the grinding bowls were opened in a glove box and the resulting powder was cold pressed under 3 tons in order to obtain 500 mg "pucks". Each puck was subsequently inserted into a 12 mm outside diameter fused silica tube equipped with a valve so that the microwave heating of the puck could be conducted under nitrogen. Evidently, the cold pressing was performed in order to facilitate the solid-state reaction between the magnesium and the silicon particles.

Microwave heating apparatus

The microwave device consisted of a microwave generator working at 2.45 GHz (SAIREM, 20 KSM) that delivers microwave radiation with a tunable power of up to 2 kW. The radiation was guided along a commercial TE10 waveguide equipped with two circulators that absorb the reflected power and therefore protect the generator. Immediately placed after the circulators, a three-stub tuner was used to adapt the impedance of the wave guide with respect to the cavity and to concentrate the radiation into the applicator. Finally, the line was ended by a TE10m rectangular single mode microwave cavity.[7]

Two modes were excited, namely TE102 and TE103, the first enabled the study of the effect of the magnetic field on the sample's absorption while the latter was used to probe the effect of the electric field on the sample's absorption (Fig. 1). In order to assess the microwave absorption of pure silicon, a lump and ball milled powders were tested. For elemental magnesium, due to its malleable nature, it is impossible to ball mill it without the addition of another element. Accordingly, pucks of a mixture of magnesium and fused silica (SiO_2) were prepared exactly like the pucks made of elemental silicon and magnesium. Fused silica was chosen because it is microwave transparent and it has about the same density as elemental silicon so that the pucks resulting from the mixture Mg/SiO_2 and Mg/Si were very similar in terms of mass and volume. Furthermore, since the hardness of Si and fused SiO_2 is very comparable, it seems reasonable to assume that the size of the magnesium particles is about the same in both types of puck.

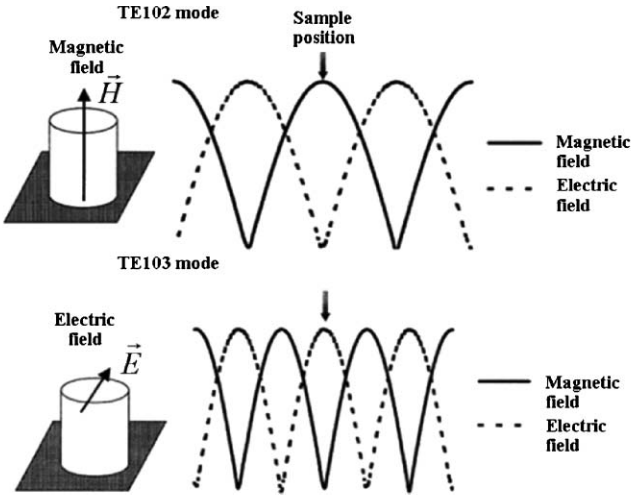

Fig. 1 Electric and magnetic field amplitude profiles in the cavity depending on the excited mode (TE102 or TE103). Arrows indicate the ideal positioning of the sample for each mode.

Differential thermal analysis and thermogravimetry measurements (DTA/TG)

A Netzsch thermal analysis system STA 449F3 cell equipped with a TASC414/4 controller was used to evaluate the thermal properties of Mg_2Si powder under different atmospheres (air, regular nitrogen, and purified argon) from room temperature to up to 1250 K. Typically, between 12 and 20 mg of polycrystalline sample were placed in an alumina crucible and heated under flowing gas at a rate of 20 K min^{-1}. After a baseline was established, data were acquired using the software provided with the instrument.

Characterization

The crystalline phases were identified by X-ray diffraction (XRD) using Cu Kα radiation (Philips X'Pert diffractometer). In order to evaluate the size of the particles in the precursor ball milled mixture, scanning electron microscopy (Zeiss Supra 55 operated at 5 kV) for the cold pressed pucks and of the raw powders extracted from the ball mill was performed. Unfortunately, the malleable nature of the Mg makes both type of sample look alike as the Si grains seems to be embedded in a magnesium "mush" and no grain size analysis can be conducted on such pucks. However, the magnesium could be dissolved in diluted nitric acid solution and the remaining Si particles rinsed and filtered for analysis by SEM. The microwaved powders were observed by SEM and energy dispersive spectroscopy (EDAX-EDS) was used to check the chemical composition.

Results and discussion

Microwave heating mode

As stated above, in our microwave apparatus, two modes were excited, namely TE102 and TE103. Whether in the TE102 or TE103 mode, no sign of heating could be observed on the puck prepared with elemental magnesium and fused silica (see Experimental) using a power of 200 W. In contrast, an elemental silicon lump or ball milled powders could be heated to a red hot color by using low power in the TE102 mode while no heating could be observed using the TE103 mode. This shows that silicon highly absorbs microwaves in an H field whereas it is rather transparent in E mode. This behavior can be related to the semiconducting property of silicon which favors the H coupling.[7,8] Furthermore, the fact that the puck prepared with elemental magnesium and fused silica does not significantly absorb microwaves (in both modes) leads us to conclude that silicon will act as a microwave coupler in the pucks of mixed Mg and Si powders. Consequently, in the following, it was chosen to use only the TE102 mode for the processing of the pucks of mixed Mg and Si powders.

Powder preparation

The use of a high energy ball mill to grind a mixture of Mg and Si (in a ratio of 2 : 1) can be really problematic. In fact, the same method is usually utilized to synthesize Mg_2Si directly from the milling of the corresponding elements, but because of the difference of brittleness between the hard and easy to crush silicon and the soft and very malleable magnesium, this synthetic method is usually performed under wet conditions (addition of hexane in the bowls) to prevent agglomeration of magnesium on the walls of the bowls and on the balls and therefore to assure the good completion of the reaction. However, a major drawback of using wet conditions is the removal of the liquid medium in order to recover the powdery products. Furthermore, the "wet" synthesis complicates the preparation method, hence an increased cost and time of production. Thus our primary target was to be able to produce fine powders of a mixture of magnesium and silicon in dry conditions without having the problem of agglomeration of the powder. We find that depending on the classical parameters associated with ball milling, namely, milling time and speed, ball to powder ratio and diameter of the balls, different products can be obtained. However, we repeatedly obtained fine powders and upon opening of the grinding bowls, no sign of agglomeration could be found using the cycling program described above (see Experimental). The three batches B1, B2 and B3 were analyzed by X-ray diffraction and only pure magnesium and pure silicon could be detected for B1 (Fig. 2) and B2 while B3 also contained traces of Mg_2Si. More importantly no sign of oxidation could be observed, although an amorphous oxide layer could be present and not detectable by way of X-ray diffraction. After removing the magnesium from the ball milled mixture (see Experimental), the silicon particles could be inspected by SEM. As already reported, the Si particles are readily fragmented to smaller particle upon increasing the milling time.[4] Due to the high reactivity of fine powders of magnesium, no other analysis could be conducted. The cold pressed pucks of B1, B2 and B3 were then heated using microwave irradiation in the TE102 mode. The three batches could indeed be heated, however several differences could be observed depending on the batch.

Influence of the grinding time on the necessary power to initiate the reaction

The minimum power necessary to successfully heat up B1 is 125 W, while it is 150 W and 300 W for B2 and B3, respectively. Furthermore, the heating of B3 is clearly inhomogeneous as it starts on the periphery of the sample and slowly propagates to the heart of the sample. As stated above, B3 is the only mixture that contains not only pure Mg and Si but also the alloy Mg_2Si so that the phenomena associated with the microwave heating of such a mixture could be very complex as the behaviors of Mg, Si and Mg_2Si towards microwave radiation are certainly different. Therefore, only the different results and observations between B1 and B2 will be discussed hereafter. At the beginning

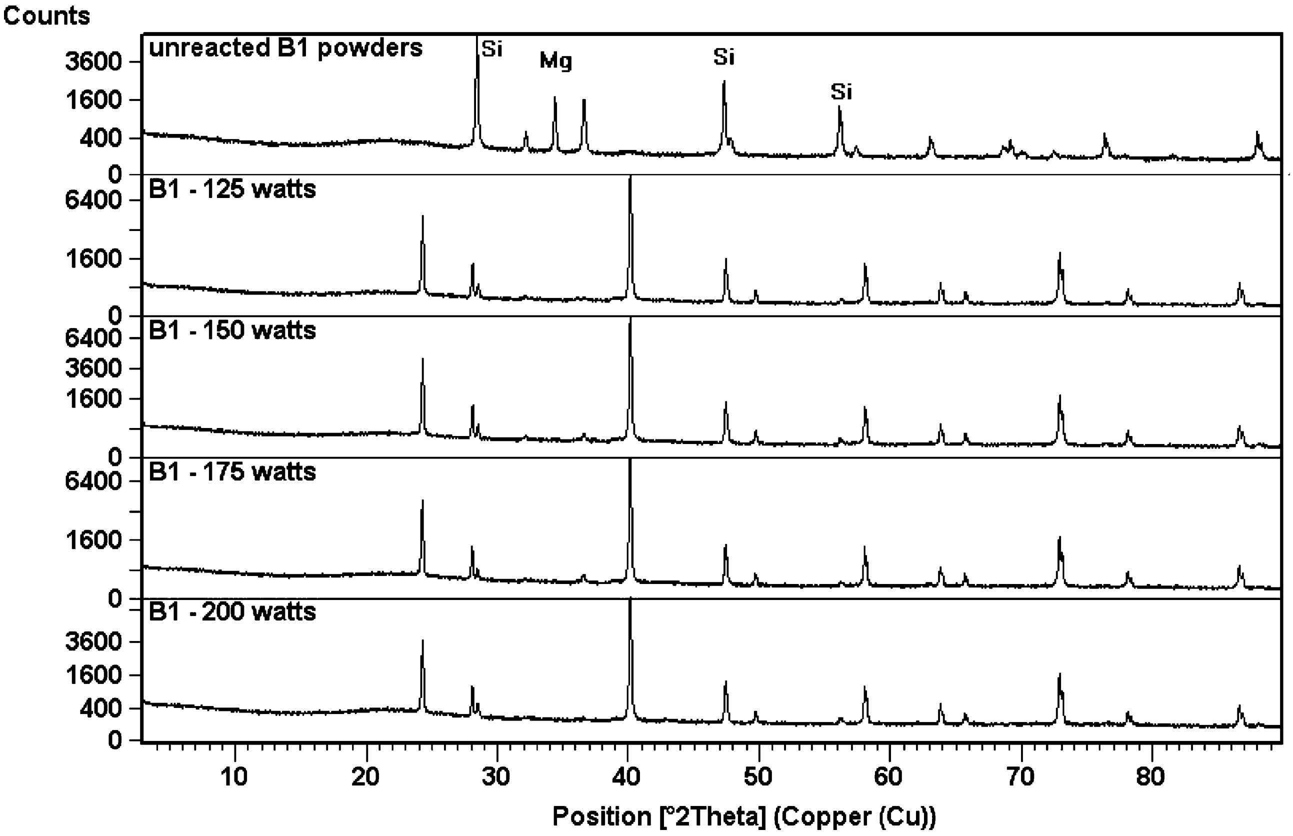

Fig. 2 Powder diffraction patterns of unreacted ground powders obtained by high energy ball milling (top) and of microwaved B1 pucks at t_0 for powers of 125 W, 150 W, 175 W and 200 W, respectively (from the second from the top to the bottom). Note that the diffractograms all show the characteristic peaks of Mg_2Si and traces of elemental silicon.

of the process, the compact is a mixture of silicon and magnesium grains that are randomly distributed. At such low power and according to our experiment (see above) only silicon seems to absorb the microwaves, it is thus assumed that eddy currents are individually distributed within the silicon grains. This occurs at the very beginning of the heating process (Fig. 3) and as the heating progresses, the absorbing Mg_2Si phase is synthesized and percolation paths are created between grains. The consequence is that eddy currents can flow all around the cylindrical puck (Fig. 3). Evidently, it is the outer surface of the sample that will first be inductively heated due to the screening effect of the eddy currents.[8] The heat is then transported from grain to grain towards the center of the sample. However, the velocity of the reaction is such that it is merely impossible to visualize any temperature difference between the periphery and the center of the pucks. Since the only distinction between B1 and B2 is the grinding time, the major difference observed upon heating should be reasonably associated with the difference in size between the powders of the two batches. Fig. 4 shows micrographs of silicon particles extracted from the pucks of B1 (top) and B2 (bottom). They demonstrate the difference in size of the Si particles present in the pucks B1 and B2. As in smaller particles less heat can be carried or stored, it seems reasonable that for B2 (containing the smaller Si particles) a higher microwave power is needed than for B1 to initiate the reaction between elemental silicon and magnesium.

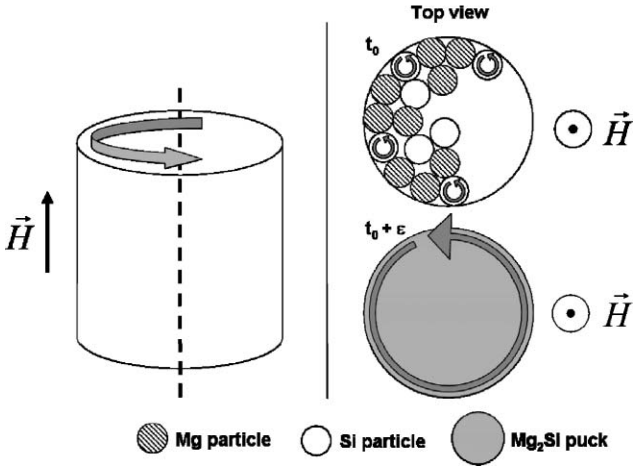

Fig. 3 Scheme depicting the assumed eddy currents distribution within the puck at the initial stage of the heating (t_0) and once the Mg_2Si phase has been synthesized ($t_0 + \varepsilon$).

Influence of the power on the reaction

As state above, a power of 125 W is necessary to initiate the reaction for B1. In fact it has been observed that the reaction starts after about three minutes of irradiation, including the time to correctly adjust the resonance. When increasing the power, this initiation time t_0 (defined as the necessary time to visualize the incandescence of the sample) is reduced by a factor of two for every increase of 25 W in power, thus for a power of 200 W (the highest we used for B1) t_0 is about 30 s. The total reaction time can therefore be reduced to less than a minute. It is noteworthy that the time necessary for the reaction between elemental silicon and magnesium to form Mg_2Si is extremely small, not to say that the reaction is nearly instantaneous. Moreover, according to the X-ray diffraction patterns there is no noticeable difference between the resulting Mg_2Si powders (Fig. 2) as they all show the antifluorite Mg_2Si and traces of elemental silicon. These traces can be attributed either to the loss of magnesium by evaporation during the heat treatment before the reaction synthesis takes place, or to the beginning of decomposition of Mg_2Si into Si and Mg followed by the evaporation of the magnesium. This second hypothesis is supported by the appearance of a morphological change as the grains appear to have coalesced together under the action of the elevated temperature as indicated by SEM imaging (Fig. 5) of the surface of the B1 sample obtained after a longer heat treatment (t_0 + 10 min) using a power of 200 W. The same micrograph also shows islands of silicon-rich regions detected by EDS. This result is also directly correlated to the thermogravimetric analysis (Fig. 6) performed under dry inert gas that does not show any sign of decomposition up to 850 °C, the temperature at which a slight loss of mass can be observed that corresponds to the evaporation of the magnesium. This phenomenon is more visible on the corresponding DSC curve and evidences the decomposition of Mg_2Si around 850 °C under an inert atmosphere. For comparison, the same experiment was conducted under air and a mass increase characteristic of an oxidation starts at a temperature of only 400 °C.

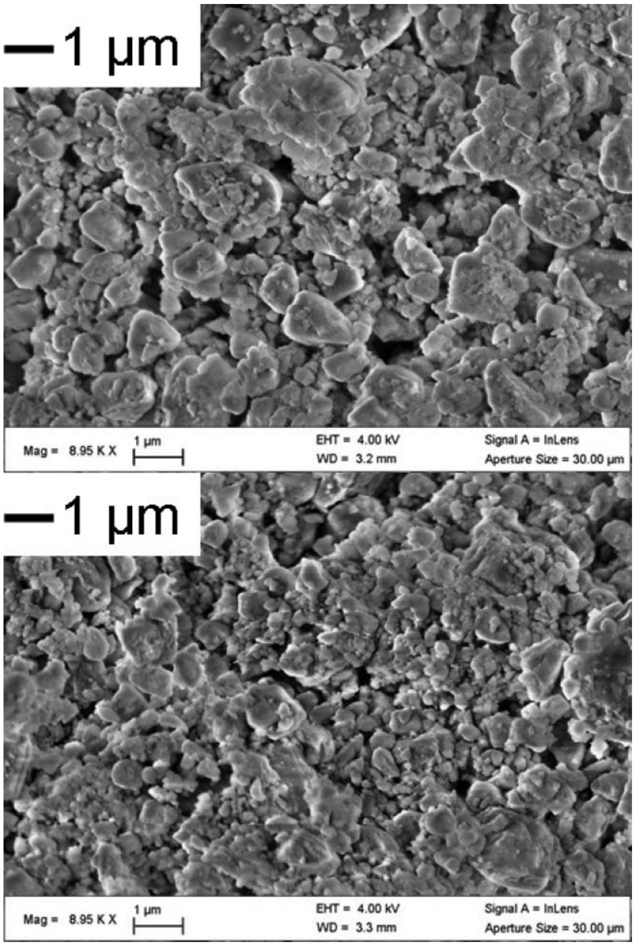

Fig. 4 Representative electron microprobe images of elemental Si particles extracted from ball milled B1 (top) and B2 (bottom) pucks.

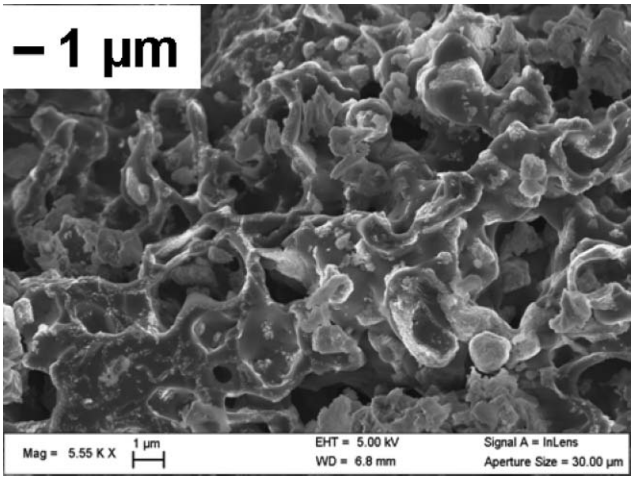

Fig. 5 Representative electron microprobe image of B1 powder irradiated with a power of 200 W for 10 min. Note the silicon islands formed on the surface of the grains and the "fused" aspect of the Mg_2Si matrix.

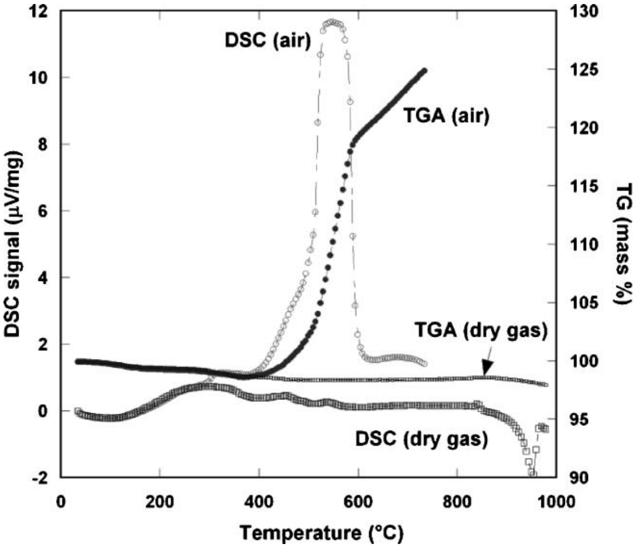

Fig. 6 DSC signal (µV/mg) and TG (mass%) traces as a function of temperature for Mg_2Si powder under air and dry inert gas.

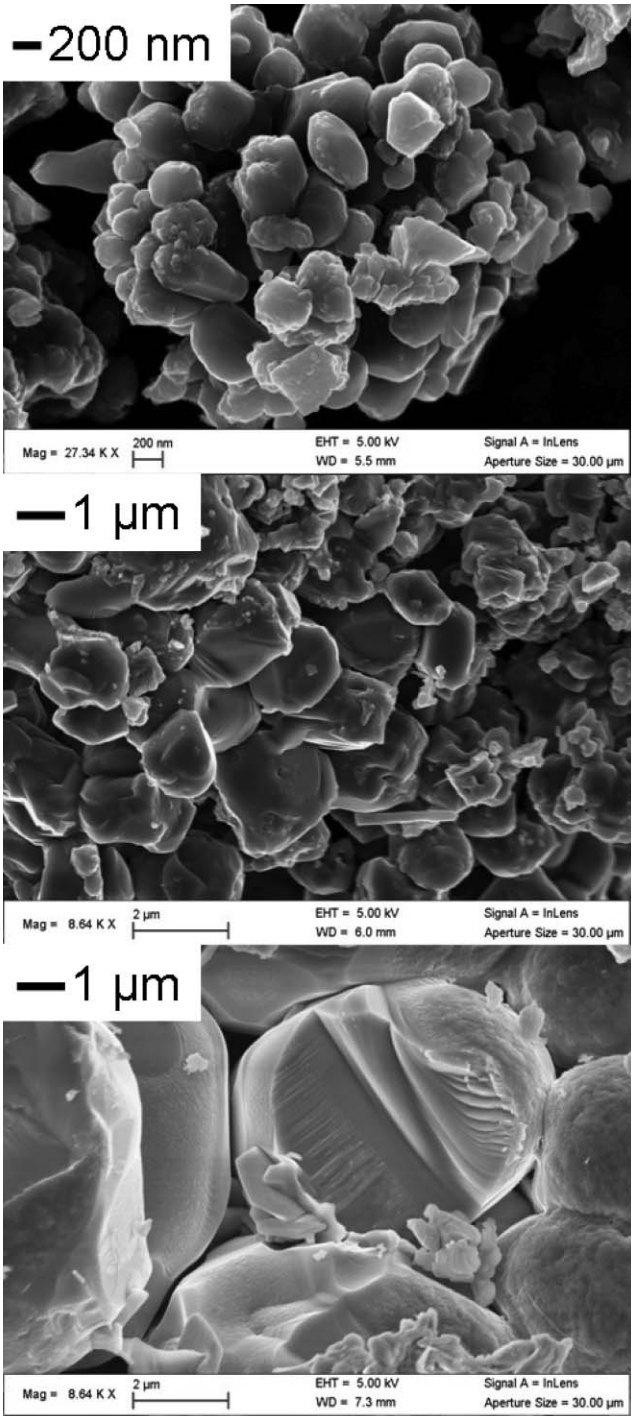

Fig. 7 Micrographs showing the evolution of the grain size of a B1 puck irradiated with a power of 150 W at t_0 (top), t_0 + 5 min (center) and t_0 + 10 min (bottom).

Influence of the time of synthesis on the grain size

As the use of a fast synthetic technique like the microwave heating can provide a facile route to micro and/or nanostructured materials, the time of synthesis has a real influence on the grain size. Fig. 7 shows the evolution of the grain size of a B1 puck irradiated with a power of 150 W at t_0 (top), t_0 + 5 min (center) and t_0+10 min (bottom). All photographs show that the samples are relatively homogeneous and composed of rather spherical grains that build up aggregates. In all cases, EDS analysis confirms the stoichiometry of the phase (Mg_2Si) and no traces of elemental silicon or magnesium can be detected neither by X-ray diffraction analysis nor by SEM/EDS mapping analysis. For a t_0 treatment, the grains are about 200 nm in diameter while after only five minutes of heating they have grown to a size of between 1 and 2 microns. After 10 min under 150 W, they are even larger as their size reaches 4 microns. Interestingly, even after 10 min of exposure at 150 W there is no evidence of decomposition of Mg_2Si in Mg and Si, as indicated by the absence of morphological change, Si-rich regions and coalesced grains, as is the case for the t_0 + 10 min at a power of 200 W as shown above (Fig. 5).

Towards nanostructured Mg_2Si

The ultimate aim of using a fast synthesis technique is to easily produce nanosized materials. This is especially crucial for

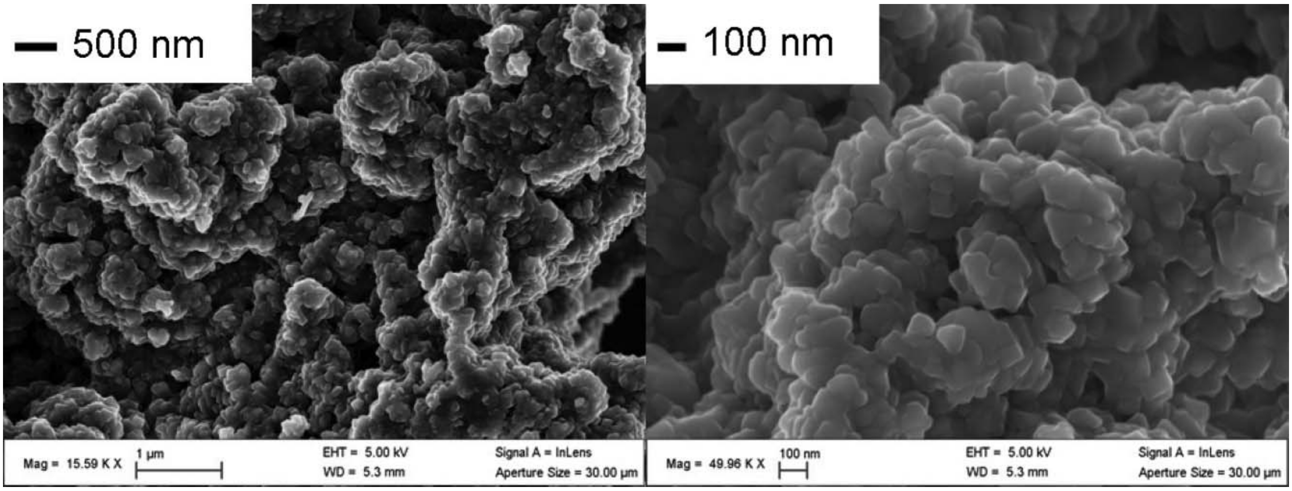

Fig. 8 B2 sample after t_0 + 2 min of microwave irradiation at a power of 175 W.

the possible development and improvement of thermoelectric properties through the lowering of the thermal conductivity due to the increased number of grain boundaries in nanostructured materials. Fig. 8 shows the nano character of a B2 sample at t_0 + 2 min irradiated with a power of 175 W. As evidenced by the left micrograph, the sample's composition is homogeneous and it is composed of cauliflower-like aggregates of smaller particles. The size of these particles is smaller than 100 nm as shown on the right picture and it seems that the grain size is very homogeneous. It is absolutely outstanding that without optimization of neither the grinding parameters of the elements nor the microwave irradiation parameters we are able to obtain nanosize grains of Mg_2Si in a very short time (4 periods of 30 min of grinding and merely 2 min of microwave heating). Forthcoming work will focus on using the same synthetic technique on optimized composition in order to assess the effect of the particle size on the transport properties.

Conclusion

For the first time, Mg_2Si has been synthesized through the microwave irradiation of mixtures of elemental powders of Mg and Si prepared by high energy ball milling under dry conditions. Elemental silicon easily absorbs the microwave radiation and a fairly low power is enough to warm it up while it is not possible to heat magnesium powder pressed in puck at such low power, thus, the reaction between magnesium and silicon can be initiated by a microwave irradiation through the heating of the silicon particles. However, the high energy ball milling parameters utilized to prepare the reactive powders have quite an influence on the behavior of the mixture under irradiation. With increasing the ball milling time, the size of the silicon particles is decreased and influences the microwave heating parameters. In fact, for smaller particles, a higher power is necessary to initiate the reaction between silicon and magnesium. Nonetheless, the power must be finely controlled in order to avoid the sublimation of magnesium that triggers the decomposition of Mg_2Si at around 850 °C. The microwave synthesis is indeed a fast technique and the grain growth can actually also be very fast, the time of irradiation is therefore another crucial parameter that needs to be correctly adjusted.

We successfully synthesized aggregates of Mg_2Si nanoparticles of less than 100 nanometres. Evidently, further optimization of the synthesis parameters is underway and might lead to even smaller particles of Mg_2Si. More important is the validation of this synthetic process that couples high energy ball milling with microwave irradiation for producing nanostructured materials. This new process could be very valuable for the improvement of the thermoelectric materials by nanostructuration, a very "hot" topic in the thermoelectric community,[9] especially when coupled with fast densification by spark plasma sintering. Perhaps more pragmatically, the short time and the little power needed for the microwave preparation of Mg_2Si reduces the costs of production of a very promising and environmentally benign thermoelectric material.

Acknowledgements

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References

1 H. J. Goldsmid, *Thermoelectric Refrigeration*, Plenum Press, New York, 1964.

2 M. S. Dresselhaus, G. Chen, M. Y. Tang, R. Yang, H. Lee, D. Wang, Z. Ren, J.-P. Fleurial and P. Gogna, *Adv. Mater.*, 2007, **19**, 1043–1053.

3 K. Mars, H. Ihou-Mouko, G. Pont, J. Tobola and H. Scherrer, *J. Electron. Mater.*, 2009, **38**, 1360–1364; R. B. Song, Y. Z. Liu and T. Aizawa, *Phys. Status Solidi RRL*, 2007, **1**, 226–228; V. K. Zaitsev, M. I. Fedorov, E. A. Gurieva, I. S. Eremin, P. P. Konstantinov, A. Yu. Samunin and M. V. Vedernikov, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **74**, 045207; G. S. Nolas, D. Wang and M. Beekman, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **76**, 235204; J. Tani and H. Kido, *Intermetallics*, 2007, **15**, 1202–1207; M. I. Fedorov, V. K. Zaitsev, I. S. Eremin, E. A. Gurieva, A. T. Burkov, P. P. Konstantinov, M. V. Vedernikov, A. Yu. Samunin, G. N. Isachenko and A. A. Shabaldin, *Phys. Solid State*, 2006, **48**, 1486–1490; R. Song, Y. Liu and T. Aizawa, *Mater. Sci. Technol.*, 2005, **21**, 618; L. M. Zhang, Y. G. Leng, H. Y.

Jiang, L. D. Chen and T. Hirai, *Mater. Sci. Eng., B*, 2001, **86**, 195–199; J. M. Munoz Palos, M. D. Cristina and P. Adeva, *Mater. Trans.*, 1996, **37**, 1602.

4 R. B. Song, T. Aizawa and J. Q. Sun, *Mater. Sci. Eng., B*, 2007, **136**, 111–117; T. Aizawa and R. Song, *Intermetallics*, 2006, **14**, 382–391.

5 Reviews: M. P. Mingos, *Adv. Mater.*, 2004, **5**, 857; C. Gabriel, S. Gabriel, E. H. Grant, B. S. J. Halstead and D. P. Mingos, *Chem. Soc. Rev.*, 1998, **27**, 213; K. J. Rao, B. Valdhyanathan, M. Ganguli and P. A. Ramakrishnan, *Chem. Mater.*, 1999, **11**, 882.

6 C. Mastrovito, J. W. Lekse and J. A. Aitken, *J. Solid State Chem.*, 2007, **180**, 3262–3270; J. W. Lekse, T. J. Stagger and J. A. Aitken, *Chem. Mater.*, 2007, **19**, 3601–3603; J. W. Lekse, A. M. Pischera and J. A. Aitken, *Mater. Res. Bull.*, 2007, **42**, 395; G.-T. Zhou, V. G. Pol, O. Palchik, R. Kerner, E. Sominski, Y. Koltypin and A. Gedanken, *J. Solid State Chem.*, 2004, **177**, 361–365; O. Palchik, A. Gedanken, V. Palchik, M. A. Slifkin and A. M. Weiss, *J. Solid State Chem.*, 2002, **165**, 125–130; Q. Xia, J. Yi, Y. Peng, S. Luo and L. Li, *Mater. Lett.*, 2008, **62**, 4006–4008.

7 In a TE10m single mode microwave cavity, it is possible to preferentially select the H field or the E field to irradiate the sample, depending especially on the material absorption mechanisms. Otherwise, in such a cavity, the required amount of power to heat the sample is very low owing to the amplification of the electromagnetic fields provided by the resonance. In a multimode cavity, the electromagnetic fields distribution is averaged in the space and it is difficult to distinguish the contribution on the heating of the H or the E fields. See for example: R. Peelamedu, R. Roy, L. Hurtt, D. Agrawal, A. W. Fliflet, D. Lewis III and R. W. Bruce, *Mater. Chem. Phys.*, 2004, **88**, 119–129.

8 S. Marinel and G. Desgardin, *Adv. Mater.*, 1998, **10**, 1448–1452.

9 M. G. Kanadzidis, *Chem. Mater.*, 2010, **2**, 648–659.