



Mg₂Si nanocomposite converted from diatomaceous earth as a potential thermoelectric nanomaterial

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ABSTRACT

With recent literature demonstrating enhancement of the thermoelectric performance of nanoscale materials relative to their corresponding bulk materials, methods to synthesize low-dimensional nanomaterials in large scale at low cost are needed. We demonstrate a method for preparing nanostructured dimagnesium silicide (Mg₂Si) thermoelectric materials that are nanocomposites with MgO by the reduction of diatomaceous earth (diatoms) using a gas-displacement solid state reaction with magnesium vapor. The resulting semiconducting Mg₂Si preserves the general morphology of the original diatoms and their nanosized grains at least down to the size of 30 nm. This reaction represents a possible method for the production of large quantities of low-cost nanoscale thermoelectric materials with potential for enhanced thermoelectric performance.

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1. Introduction

There is intense interest in the development of thermoelectric power generation technologies that utilize renewable energy sources or increase energy efficiency by utilizing waste heat [1–5]. The efficiency of a thermoelectric material is described by its dimensionless figure of merit $ZT = \sigma S^2 T / \kappa$, where σ , S , T and κ are the electrical conductivity, Seebeck coefficient, absolute temperature, and thermal conductivity, respectively. Despite the significant efforts devoted to developing new bulk thermoelectric materials or optimizing the existing high-performance bulk thermoelectric materials [3,6] such as Bi₂Te₃ [7], very rarely has ZT of ~ 1 been exceeded [8]. Nanoscale materials with reduced dimensions have been studied for their potential ability to enhance the energy conversion performance of thermoelectric materials [1–3,6,9–11]. Theoretical calculations [1,2] and proof-of-principle [6,9–12] experiments of nanoscale systems such as two-dimensional superlattice nanostructures [1,6,12,13], one-dimensional superlattice nanowires [2], quantum dot superlattices [11], and composites of nanostructures dispersed in bulk thermoelectric materials have demonstrated both a decrease in thermal conductivity and an increase in the power factor σS^2 relative to the corresponding bulk systems. Indeed, impressive decreases of thermal conductivity have recently been reported for nanoscale systems, including a 100-fold enhancement of ZT for silicon nanowires [9,10]. This observed reduction of thermal

conductivity is believed to be the result of interface effects, which scatter phonons more effectively than electrons, thereby increasing the value of ZT [1,2,6,9,10]. However, the difficulty of scaling up and the high fabrication cost severely limit the potential of these nanomaterials in practical applications. Large-scale chemical synthesis of elaborate nanomaterials suitable for thermoelectric energy conversion is still needed.

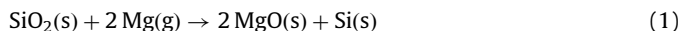
Transition metal silicides, such as dimagnesium silicide (Mg₂Si) and its related alloys (Mg₂X, X = Si, Ge, Sn) [14,15] and the higher manganese silicides [5,15], represent a class of intermetallic compounds that show promise as thermoelectric materials. Although they often have lower ZT s than the more common thermoelectric materials, metal silicides are attractive due to the high abundance and low toxicity of their constituent elements. Additionally, previous reports [14,16] have suggested that careful choice of dopants and alloy composition may yield high values of ZT : there has been a report of $ZT = 1.1$ near 800 K for the bulk Mg₂Si_{1-x}Sn_x alloy [14], and ZT as high as 1.68 has been claimed for bulk p-type Ag-doped Mg₂Si_{0.6}Ge_{0.4} at 629 K [17]. Although such promising bulk silicide figures of merit have been detailed, few studies of nanoscale thermoelectric silicides have been reported [18,19]. Synthesis of nanostructured silicides may provide a solution for achieving a low-cost enhanced ZT thermoelectric material.

We hereby propose and preliminarily demonstrate a synthetic method to prepare nanostructured thermoelectric silicide materials from diatomaceous earth, as an elegant method for the low-cost production of large quantities of nanomaterials with enhanced thermoelectric performance. The starting material and silicon source, diatomaceous earth, is nanostructured silica (SiO₂)

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microshells of unicellular algae [20]. This commercially available material, used in filtering applications in the food and pharmaceutical industries, is abundant, inexpensive, and non-toxic [21]. Our proposed synthesis converts diatomaceous earth to a composite of interdispersed Mg_2Si and MgO nanocrystallites, with nanoscale grain sizes suitable for enhanced ZT thermoelectric materials. The reduction of diatomaceous earth to silicon using magnesium vapor, as described in Eq. (1), has been reported [22]:



In previous efforts by these researchers, Mg_2Si was sometimes obtained as an undesired byproduct [23–25]. We have extended this reaction and optimized the conditions to instead obtain the promising thermoelectric Mg_2Si material as the main product by furthering the reaction with Mg:



In this paper, we describe the synthesis of the Mg_2Si nanocomposite from diatoms using the solid state gas-displacement reaction with Mg vapor. The morphology of the nanostructured material before and after conversion is examined using scanning electron microscopy (SEM). Structural characterization of the resulting nanostructured Mg_2Si -based composite was performed using transmission electron microscopy (TEM) with selected-area electron diffraction (SAED) and powdered X-ray diffraction (PXRD). Analysis of elemental composition was carried out using energy dispersive spectroscopy. The factors that influence these reactions and the morphology of the composite diatom replicas are also discussed.

2. Experimental details

Powdered magnesium (99.5%, 325 mesh) was purchased from Aldrich and bulk diatomaceous earth (Aqua Chem D.E. Filter Aid) was purchased from Biolabs Inc. (Lawrenceville, GA, USA). A home-built stainless steel autoclave, sealed with a stainless steel VCR gasket to prevent loss of gaseous species, was used.

In a typical reaction, 0.80 g of Mg powder and 0.10 g of diatom material, placed in separate stainless steel boats, were sealed in the autoclave in a glove box filled with dry nitrogen. The sealed autoclave was then removed from the glove box and placed in a preheated muffle furnace (SYBRON Thermolyne). Many reactions with various temperatures and durations were carried out, among which two are emphasized here: (1) to obtain the smallest average grain size in the products, the furnace was held at 615 °C for 8.5 h, after which the autoclave was removed to cool to room temperature before opening, (2) to obtain complete conversion to

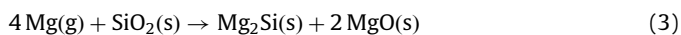
Mg_2Si and MgO , the reaction was run at 630 °C for 6 h, before removal for cooling. Additional reaction conditions are discussed later.

The morphology of the original diatoms and converted replicas were examined using a field emission scanning electron microscope (SEM, LEO SUPRA 1530) equipped with an electron dispersive spectroscopy (EDS) detector. SEM samples were prepared by dispersing diatoms in ethanol, then applying the suspension dropwise to silicon substrates or TEM grids (for EDS analysis) using a micropipette. Pristine diatoms were sputter coated with a thin layer of gold prior to imaging. Samples used for PXRD analysis were prepared by spreading sample powder onto glass slides coated with a thin layer of vacuum grease. PXRD was collected on a Siemens STOE diffractometer using $\text{CuK}\alpha$ radiation, using a step size of 0.04° (0.004° for selective peaks for Scherrer analysis). TEM samples were prepared by microtome of diatoms dispersed in epoxy, with the resulting thin microtome slices transferred to lacey carbon TEM grids. The TEM analysis was carried out on a Philips CM200 TEM with an accelerating voltage of 200 kV.

3. Results and discussion

We first examined the morphology of the diatoms as received before conversion using SEM, as seen in Fig. 1. SEM images reveal that the unconverted diatom material consists of multiple species, each having its own unique hierarchal structure, including nanoscale pores and interconnecting fingers. The crystalline phases of this nanostructured SiO_2 are mostly the cristobalite phase and some quartz phase as indicated in literature [20] and verified by X-ray diffraction (vide infra).

Our diatom conversion reactions utilized a much larger excess of Mg (the Mg:Si mole ratio was 22.4:1) and longer reaction times than previously reported [22–25], to ensure that the reduced Si completely reacted with Mg to form the silicide, as seen in the overall reaction equation below:



The optimal conditions for the conversion of SiO_2 diatoms to the nanocomposite of Mg_2Si and MgO with the smallest average grain size were found to be heating at 615 °C for 8.5 h. During the course of the reaction, the diatoms, which are white with a slight gray tint, were converted into a loose dark bluish-gray powder with a slight metallic luster. SEM images and one-to-one EDS analysis of several representative diatom replicas from the product (Fig. 2) reveal that the morphology is preserved in general after the reaction at this optimal conversion condition for obtaining minimum grain size, but there are variations in the degree of

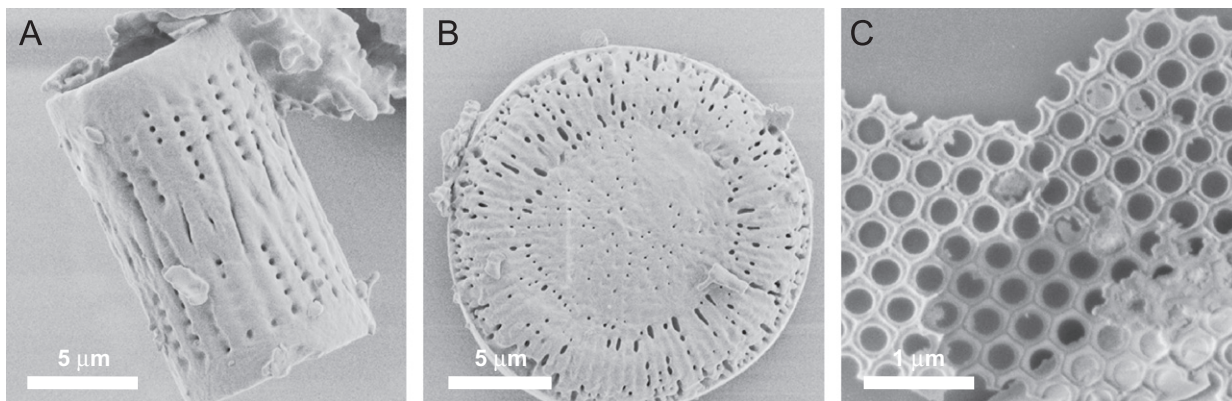


Fig. 1. SEM images of various species of diatoms prior to reduction with magnesium vapor. Their hierarchal structure includes interlocking fingers and nanoscale pores.

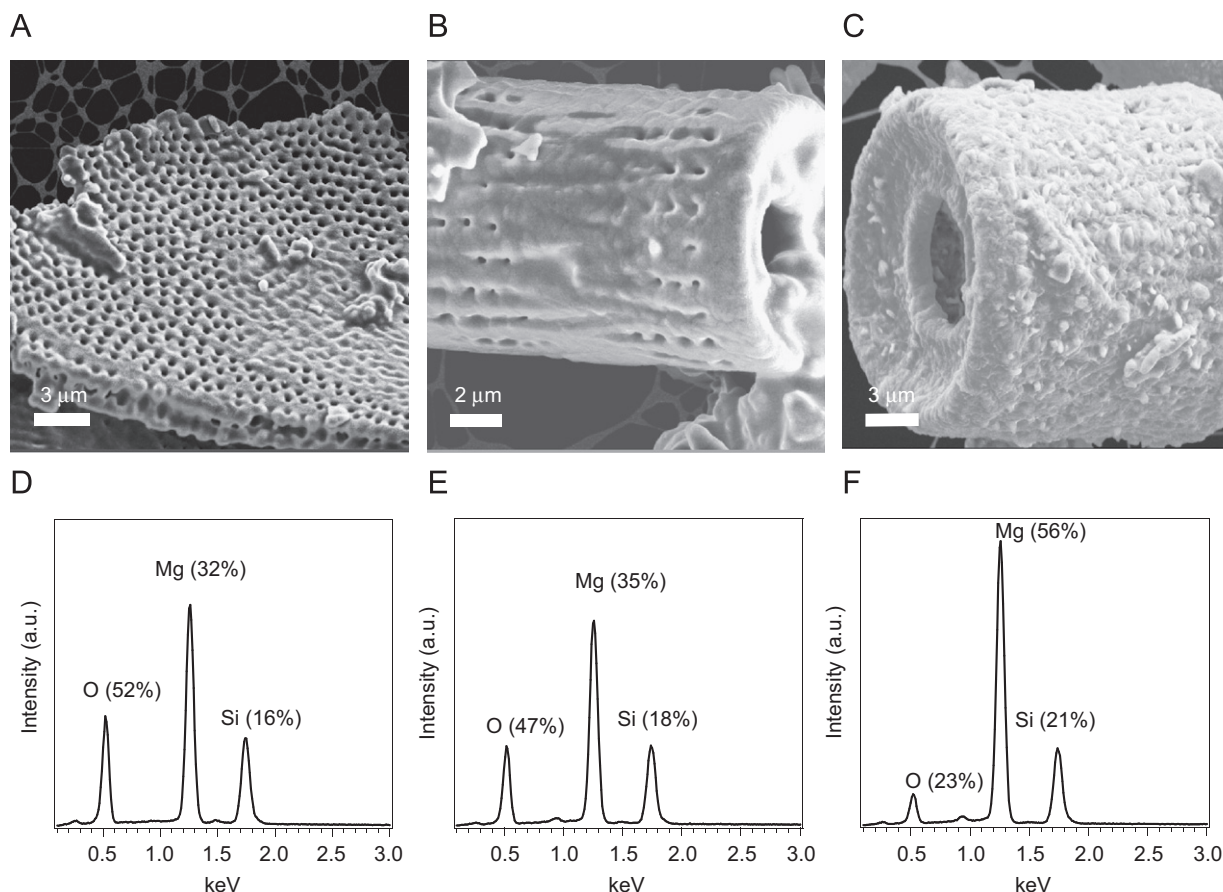


Fig. 2. SEM images of the converted diatom products taken from one synthetic batch performed at 615 °C, with the corresponding EDS spectra: (A) and (B) show little degradation of starting morphology; the respective EDS spectra (D) and (E) suggest that these diatoms have been converted to a mixture of Mg_2Si , Si and MgO. The replica shown in (C) and corresponding EDS spectrum (F) shows some filling of the nanoscale pores accompanies the complete conversion to the Mg_2Si and MgO composite.

conversions among individual diatoms within a single synthetic batch. On the basis of Eqs. (1) and (3), the expected Mg:O:Si atomic composition ratio of the products is 2:2:1 for conversion to a Si and MgO composite, and 4:2:1 for the full conversion to the Mg_2Si and MgO composite. Fig. 2A and B show images of the converted diatoms with the pore openings and certain fine features clearly preserved. The EDS analysis of the corresponding diatom replicas (Fig. 2D and E, respectively) suggest that the diatoms have not been fully converted to Mg_2Si and MgO. Some coarsening of the features can be seen in Fig. 2C, including filling of the nanoscale pores. EDS analysis of this diatom replica (Fig. 2F) indicates that this diatom has been fully converted to the desired Mg_2Si and MgO composite within the error of EDS analysis. The diatom replicas shown in Fig. 2 are the representative examples of the many individual replicas surveyed, both in morphology and in apparent degree of conversion as determined by EDS analysis. The filling in of the fine morphology seen in the fully converted diatoms may result from surface migration of material due to an increase in the diffusion constants of the materials as the phase transition temperature of Mg_2Si is approached. Although some degradation of morphology is observed in the fully converted products, the small grain size necessary for the realization of enhanced thermoelectric performance remains intact after heating, as discussed below.

Most of the major peaks in the PXRD pattern of products acquired at 615 °C (upper trace, Fig. 3A) can be indexed to diffraction of Mg_2Si and MgO, indicating that the diatom conversion reaction product is composed of a mixture of Mg_2Si and MgO. A small shoulder corresponding to the overlapping Si

(111) and possible SiO_2 (111) peaks (cristobalite phase) can be seen at $2\theta = 28.56^\circ$. From a Scherrer analysis of the Mg_2Si (220) peak, the average size of the crystalline Mg_2Si grains is estimated to be ~ 30 nm, compared to the ~ 20 nm grains of the original diatom material estimated from the Scherrer analysis of the SiO_2 (101) peak (Fig. 3C). This suggests that some grain coarsening occurred during reaction. The above calculations are likely overestimates of the grain sizes, as correction of instrumental peak broadening was not performed.

In order to achieve complete conversion to the Mg_2Si /MgO nanocomposite, it is more effective to heat at 630 °C for 6 h. PXRD of this higher temperature conversion (second trace, Fig. 3B) shows that none of the peaks due to SiO_2 or Si are left, and all peaks can be indexed to Mg_2Si and MgO. However, as would be expected for reaction at higher temperature, slightly more severe degradation of the morphology, such as the loss of the fine features and pores, was commonly observed in the SEM examination of most individual diatoms replicas (Fig. 4). Scherrer analysis of a high-resolution scan (step size = 0.004°) found that the average size of crystalline grains increases to 36 nm for these conditions.

The bright-field TEM image of the microtomed 615 °C conversion products embedded in epoxy (Fig. 5A) shows clear outlines of individual crystal grains. Measurement of a number of grains using Gatan Digital Micrograph imaging software yields typical grain sizes of 15–20 nm (measured as the longest dimension across a grain) as a conservative estimate. Comparison of the calculated grain size from PXRD to the size of grains observed in bright-field TEM micrograph suggests that the sizes of most grains

in the nanostructured Mg_2Si and MgO products are likely less than 30 nm, with a small fraction of large grains skewing the average estimated from the PXRD, which is a more global survey. Therefore, additional etching of the diatoms to reduce the grain size prior to conversion may be required to yield smaller grain sizes in the thermoelectric composite. The SAED pattern of the corresponding microtome sample (Fig. 5B) shows rings indicative of a polycrystalline material. Due to the complex composition of

the sample, diffraction rings overlap to form diffuse bands. These rings are indexed to Mg_2Si , MgO , and possibly Si phases, as well as a faint peak corresponding to the SiO_2 (200) reflection, in general agreement with PXRD pattern obtained from the same reaction (Fig. 3A). The SAED pattern obtained from the 630 °C conversion products (Fig. 5C) confirms the complete conversion to Mg_2Si and MgO . The sample was tilted to obtain the indexed Mg_2Si [103] zone axis pattern for one of the crystallites, with the polycrystalline ring pattern from the neighboring grains superimposed. No diffraction spots or rings due to Si or SiO_2 are visible in this pattern.

In this Mg gas-displacement solid state reduction of nanostructured SiO_2 to nanostructured Mg_2Si , there are several requirements to achieve the desired nanostructured product: (1) the reaction must be thermodynamically favorable at the conditions chosen; (2) sufficient time must be allowed for diffusion of reactants in the solid; and (3) the vapor pressure of the gaseous species must be sufficient for the reaction to occur. The Gibbs free energy of reaction (3), which is calculated to be -515.6 kJ/mol at 615 °C [26], reveals that the first requirement is easily satisfied. Due to the nanoscale dimensions of the grains in nanostructured SiO_2 diatoms, diffusion should be much less challenging compared with typical solid state reactions. Calculation of the partial pressure of Mg shows that $p_{\text{Mg}} = 1.4 \text{ Torr}$ at 615 °C [27], greatly exceeding the $2.4 \times 10^{-7} \text{ Torr}$ required for the reaction to be thermodynamically favorable and sufficient for the effective transfer of the Mg reductant [26]; hence, the third requirement is also met.

While temperature and reaction duration can be chosen to meet the requirements of solid state reactions, a fourth requirement is imposed if enhanced ZT due to interface effects of this nanostructured material is to be realized: *coarsening of the nanosized grains must be minimized or prevented*. It is therefore desirable to carry out the conversion at the lowest possible temperature and for the shortest duration that will allow the complete conversion of the SiO_2 starting material to the desired products, to prevent grain-size broadening and avoid production of the eutectic $\text{Mg-Mg}_2\text{Si}$ liquid which would result in severe loss of nanoscale morphology. For the Mg_2Si system, this requires processing temperatures below the lowest temperature eutectic at 638 °C between Mg_2Si and Mg [28], a requirement easily achieved due to the volatility of magnesium. Investigation of conditions different from the reported optimal conditions indeed showed the sensitivity to the reaction temperature and duration. As shown in Fig. 6, SEM images of diatoms converted at temperatures of 650 °C or higher reveal serious degradation of morphology and even faceting of some surfaces, which is not unexpected

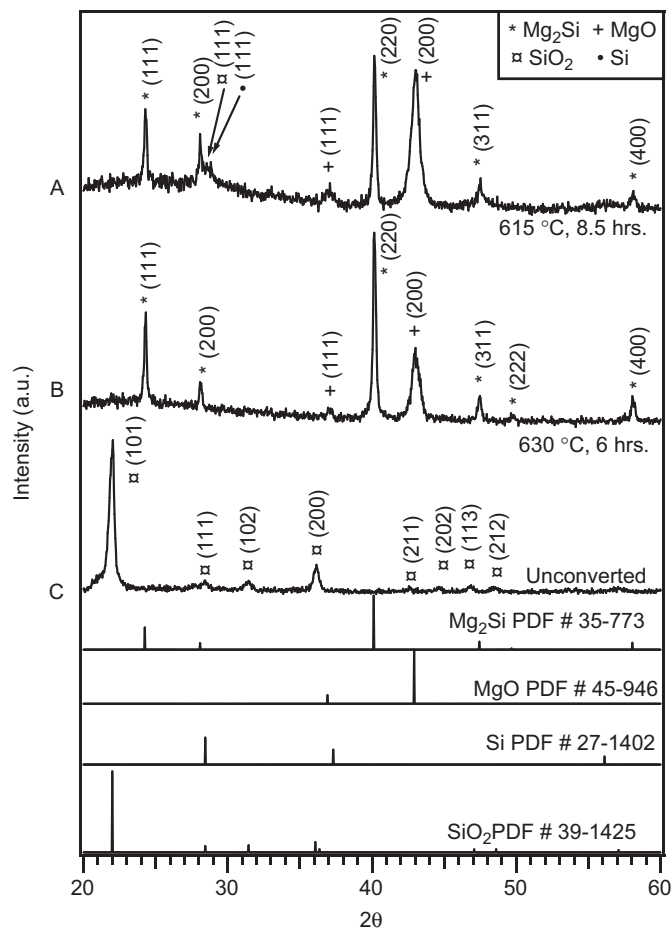


Fig. 3. PXRD of the converted products for various reaction conditions in comparison with that of the pristine diatoms and standard reference diffractograms: (A) products synthesized at 615 °C for 8.5 h, (B) products synthesized at 630 °C for 6 h and (C) unconverted diatoms.

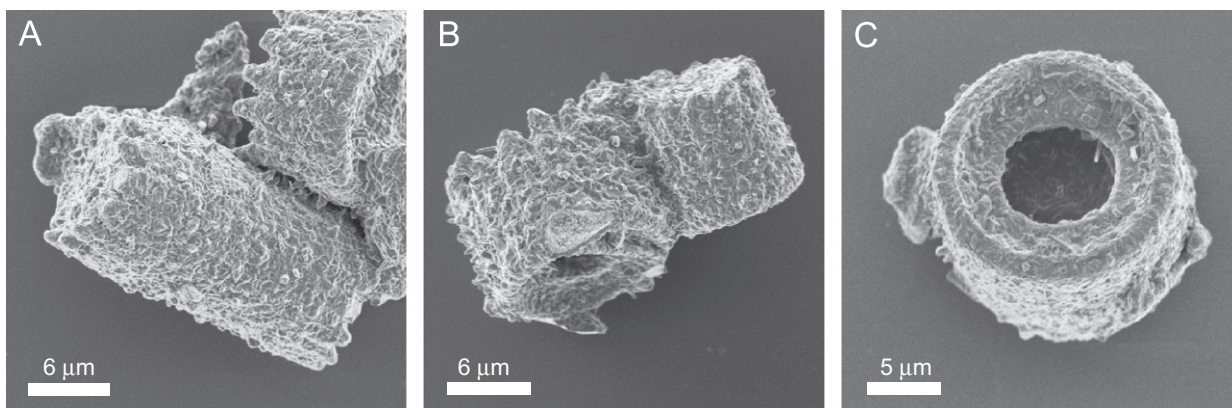


Fig. 4. SEM images of the products converted at 630 °C for 6 h, which resulted in increased loss of surface morphology.

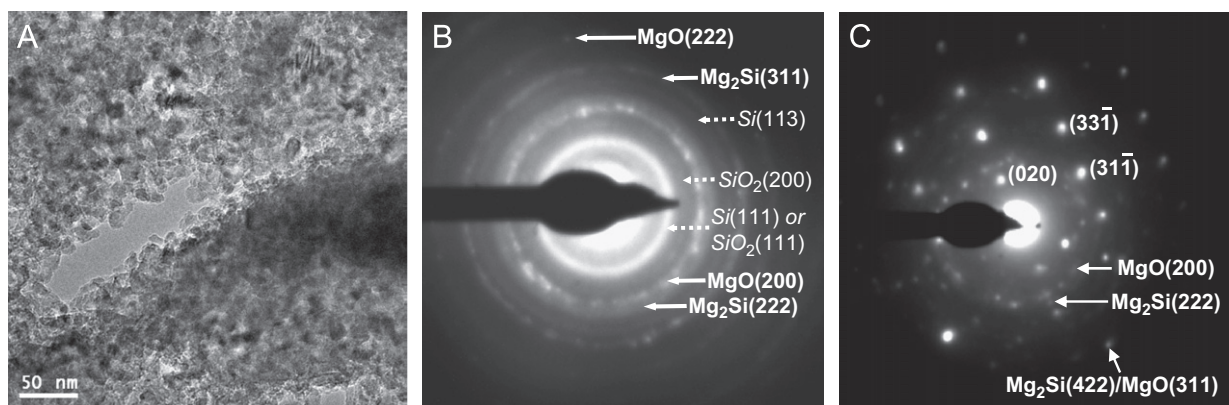


Fig. 5. BF-TEM and SAED patterns of the nanostructured Mg_2Si - MgO composites: (A) BF-TEM of microtomed reaction products from the 615 °C synthesis, (B) SAED pattern corresponding to sample shown in BF image and (C) SAED pattern of reaction products from the 630 °C synthesis.

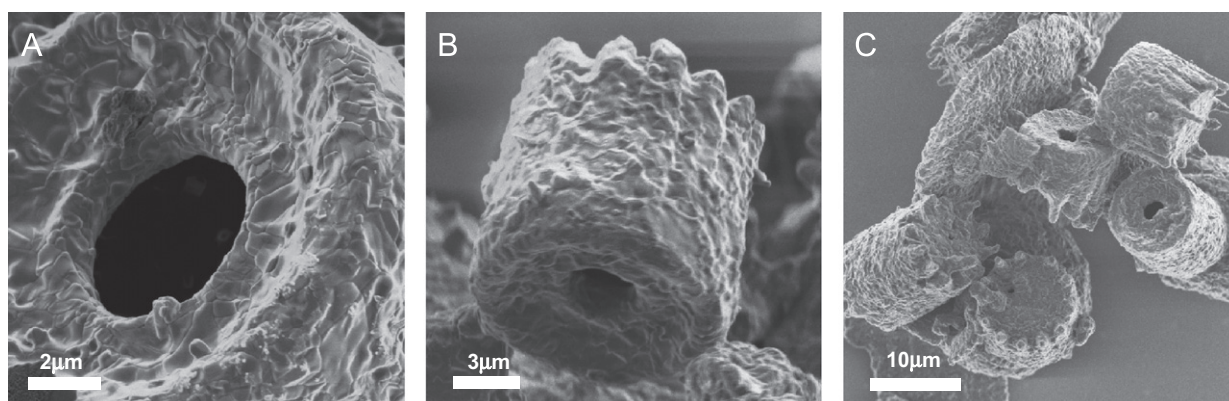


Fig. 6. SEM images of converted products from diatoms using non-optimal conditions at 650 °C, above the eutectic temperature of Mg_2Si , resulting in serious loss of morphology.

for temperatures exceeding the eutectic point (638 °C) between Mg and Mg_2Si . On the other hand, although reaction temperature could be reduced to facilitate the preservation of nanomorphology, the rate of conversion will also decrease as temperature decreases, requiring longer reactions to obtain the desired Mg_2Si product. PXRD patterns (not shown) of reactions at or below 600 °C for 8–10 h show few or no Mg_2Si peaks, indicating that lower temperatures are insufficient for conversion to Mg_2Si for the reaction durations studied. Therefore, the conditions reported above represent a reasonable compromise between these factors.

Calculations performed on nanocomposite materials, such as that of silicon nanowires dispersed in a $\text{Si}_x\text{Ge}_{1-x}$ bulk alloy, suggest that the optimum nanostructure dimension in order to achieve significant decreases in the thermal conductivity needs to be 10 nm or less, but somewhat larger dimensions (up to 150 nm) have also demonstrated an appreciable decrease of the thermal conductivity in some material systems [3]. The average grain sizes of acquired nanostructured Mg_2Si based on conservative estimates (20–36 nm) are within reasonable range to allow for some improvement in ZT of the thermoelectric materials, although even smaller grain sizes are more ideal. Even smaller grain size in the conversion products may be achieved by further optimization of reaction conditions, by using starting materials with smaller grain size, etching to reduce the grain size of the diatoms, or by choosing a more porous starting material to decrease diffusion distances in the SiO_2 starting material, thus allowing for shorter reaction durations.

Investigations are underway to explore these avenues for obtaining further reduced grain sizes.

4. Conclusions

We have demonstrated the conversion of diatomaceous earth into nanostructured Mg_2Si and MgO composites as a potential thermoelectric material with enhanced performance due to the nanoscale dimensions. This simple Mg gas-displacement reaction yields nanocomposites that maintain the basic morphology and original nanocrystallinity of the starting diatom material, with estimated Mg_2Si grain sizes of 20–36 nm after conversion. We are now working on doping the nanostructured silicides and the measurement of electrical and thermoelectric properties to investigate the potential enhancement of thermoelectric performance. This method could serve as a general strategy for the preparation of large quantities of nanostructured semiconducting silicide nanomaterials at low cost for potential thermoelectric applications.

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