Synthesis and structural characterization of dense polycrystalline Mg_9Sn_5 , a metastable Mg-Sn phase

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Key Words: Spark Plasma Sintering (SPS), Mechanical alloying, neutron diffraction, metastable phases, intermetallic phases

Abstract

We present a method for synthesizing bulk dense polycrystalline Mg_9Sn_5 , a phase that is related to the familiar Mg_2Sn phase but is metastable at ambient pressure and temperature. Our procedure requires significantly lower temperatures and pressures, which are in the 100 MPa range compared to the previously reported methods that required pressures in the GPa range. We used a combination of high energy ball milling and current activated pressure assisted densification (CAPAD) to synthesize and retain the high pressure phase in a bulk (low porosity) form. We show the effect of CAPAD processing temperature and pressure on the density and phase composition of the material. We also present the first neutron diffraction study to confirm phase identity and refine the structure of Mg_9Sn_5 .

1. Introduction

The controllable production of metastable materials is one of the most exciting challenges in processing science today [1]. The allure is that metastable phases can have radically different properties compared with their more stable brethren and thus potentially be used in new applications. Mg_2Sn is the only intermetallic phase found on the familiar Mg-Sn binary phase diagram, making it the only thermodynamically stable phase at ambient conditions [2]. Here we present the synthesis of Mg_9Sn_5 —a related phase that is not found on the Mg-Sn temperature–composition phase diagram and is therefore metastable at room temperature and pressure.

We used a combination of high energy planetary ball milling and Current Activated Pressure Assisted Densification (CAPAD) [3] to produce a bulk material that has previously only been synthesized in dense form at high pressures (in the Giga Pascal range). Moreover, to the best of our knowledge, this is the first time this metastable Mg-Sn phase has been made in a polycrystalline dense (low porosity) form. The stable phase, Mg_2Sn is a well-studied semiconducting material with applications in thermoelectric energy generation [4]. By contrast, the transport properties of Mg_9Sn_5 are relatively unknown, since reports of the preparation of

bulk, dense Mg_9Sn_5 are limited. Therefore our processing procedure presents an opportunity to further the understanding of Mg_9Sn_5 transport properties, which is currently an active area of research in our laboratories. While it is known that Mg_9Sn_5 is a semiconductor, a study of its transport properties, both thermal and electrical, will determine its utility as a thermoelectric material.

The crystal structure of this resulting phase has been refined via Rietveld analysis of powder neutron diffraction data. We expect the processing procedures presented here to be translatable to other alloy systems, opening the door for the production of other metastable alloys that are difficult to produce by other methods.

The semiconducting material, Mg_2Sn crystallizes in the cubic antiferroite structure under ambient pressures and temperatures. A metastable phase forms when subjected to high temperatures and pressures and persists upon returning to ambient conditions. This “dense” phase of Mg_2Sn was first synthesized at pressures and temperatures ranging from 2.5 – 5.5 GPa and 600 – 1200 °C, respectively, by Cannon and Conlin in 1964 and is described as having a hexagonal crystal structure [5]. Seifert also synthesized the high pressure metastable phase by applying 6 – 6.5 GPa and 600 – 1000 °C in 1967. Its crystal structure was described as being orthorhombic with a Ni_2Si -type structure [6]. In 1972 & 1995 [7], Dyuzheva grew single crystals from a melt and investigated the effect of high pressures and temperatures of 4 – 8 GPa and 50 – 1100 °C on phase relations of the Mg_2Sn system. This study also showed in depth x-ray diffraction investigations of the polymorphism of the system [8]. A crystal structure refinement was carried out in 1996 by Range *et al.* using single crystal samples synthesized at 5 GPa and 1400 °C. The resulting structural refinements concluded that the composition of this high pressure phase is in fact Mg_9Sn_5 which contains an excess of Sn compared to the thermodynamically stable Mg_2Sn [9].

The formation of the metastable phase has also been observed using ball milling methods. Schilz *et al.* used a planetary ball milling setup to produce the metastable and stable phases from a mixture of Mg, Si, and Sn and milling times up to 130 hours [10]. In 2002, Urretavizcaya *et al.* synthesized the metastable phase using mechanical alloying for 150 hours in different gases (H_2 and Ar) at gas pressures of 0.1 MPa and 0.5 MPa, respectively [11]. It is worth emphasizing that both of these ball milling treatments [8,9] produced a polycrystalline powder and not a bulk dense material.

2. Experimental procedure

2.1 Powder synthesis and consolidation

Planetary ball milling (PBM) is a useful mechanical alloying technique used to react multiple powders at room temperature conditions. The high frequency and repetition of ball-powder collisions fracture and cold weld the starting materials over the course of the entire

process. The method allows for grain size reduction and, in extreme cases, phase amorphization [12]. Elemental magnesium and tin powders (Alfa Aesar, 99+% metal purity) with stoichiometric ratio of 19:10 and 9:5 were planetary ball milled (Fritsch Pulverisette 7) at 450 RPM using stainless steel jars and balls for a total of 48 hours at room temperature. Due to its ductility, 200-300 mg of magnesium powder was added incrementally every 2 hours until reaching the targeted stoichiometric proportions to avoid agglomeration of the magnesium on the walls of the jars [13]. The final ball to powder weight ratio was 10:1. All powders and milling media were handled under an argon atmosphere.

CAPAD (also referred to as spark plasma sintering (SPS)) is a well-known method for powder consolidation. Graphite die and punch sets are loaded with the powder and a heating current is applied to the system under a mechanical load. This technique has been highly successful in producing bulk materials with unique microstructures. A custom built CAPAD device was used to consolidate the powder into bulk samples [14]. Graphite plunger and die sets similar to the high pressure setup described by Anselmi-Tamburini *et al.* [15] were used to produce 9.52 mm diameter disks. All samples were processed under vacuum with an applied mechanical pressure of 0 or 112 MPa and temperatures up to 600 °C with a heating rate of 200 °C/min. One plunger was removed in the 0 MPa case in order to ensure that no load (and therefore no pressure) was transferred to the powder. The maximum heating currents were varied between 400 and 1200 A. All samples were processed within 20 minutes. XRD phase characterization was performed with a PANalytical Empyrean diffractometer using a Cu K-alpha x-ray source ($\lambda_{K\alpha1} = 1.54056 \text{ \AA}$ and $\lambda_{K\alpha2} = 1.54440 \text{ \AA}$). Densities of the CAPAD processed samples were measured using the Archimedes method. Samples densified from the 9:5 ratio ball milled powder were analyzed using neutron diffraction.

2.2 Neutron diffraction

Time-of-flight neutron diffraction experiments were performed at the NPDF (Neutron Powder Diffractometer) beamline of the Manuel Lujan, Jr. Neutron Scattering Center, Los Alamos National Laboratory [16]. The CAPAD synthesized/densified bulk Mg_9Sn_5 sample (processed as described in section 2.1 from a 9:5 Mg:Sn PBM powder) was crushed into a fine powder in an argon-filled glove-box. The resulting powder was then sealed in a low background vanadium can measuring 0.63 cm in diameter. The sample was then mounted on the neutron diffractometer for room temperature data collection. High-resolution data were collected for about 14.5 hours simultaneously using four groups of detector banks with nominal diffraction angles of $\pm 46^\circ$, $\pm 90^\circ$, $\pm 119^\circ$ and $\pm 148^\circ$. The mass of powder used was 2.5g.

The obtained neutron data were analyzed using the Rietveld method with the General Structure Analysis System (GSAS) program of Larson and Von Dreele [17]. The starting structural parameters were taken from the single-crystal X-ray diffraction study of Range *et al.* (Space group: $R\bar{3}$ (No.146), $a = 13.222 \text{ \AA}$, $c = 13.150 \text{ \AA}$) [9]. Since the sample contains a small portion of MgO , we included periclase as a secondary phase in the analysis (Space group: $Fm\bar{3}m$).

3m (225), $a = 4.217 \text{ \AA}$). All four datasets from the detectors at $2\theta = \pm 46^\circ, \pm 90^\circ, \pm 119^\circ$ and $\pm 148^\circ$ were simultaneously analyzed. The refinements proceeded as follows: after the scale factor and four background terms (Shifted Chebyshev function) for each histogram had converged, lattice parameters and phase fractions were added and optimized. Eight or fourteen additional background terms were then added for each histogram, and the peak profiles were fitted to a TOF profile function [18]. On convergence of the preceding parameters), atomic coordinates and atomic displacement parameters (constrained to be equivalent on all six Mg sites and, separately, all Sn sites) were refined, yielding an R_{wp} value of 2.13%.

2.3 SEM/EDS

Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy images and measurements were made using a JEOL JSM 6360LV microscope at an accelerating voltage of 15-20 keV coupled to an Oxford Instruments EDS detector for elemental mapping experiments. A CAPAD processed Mg_9Sn_5 sample was mechanically cleaved and was immediately introduced into the vacuum chamber. The sample was mounted on copper tape with no need for further sputter treatment.

3. Results and Discussion

3.1 Synthesis and Densification

Figure 1 presents XRD phase analysis of the two starting elemental powders (Mg and Sn) and the planetary ball milled powders with 19:10 and 9:5 Mg:Sn stoichiometric ratios. The two ball milled powders both show the presence of two phases, Mg_2Sn and Mg_9Sn_5 , after 48 hours of milling. No crystalline Mg and Sn peaks can be detected. The integral peak intensities of the highest intensity Mg_2Sn peaks (111) are one third of the highest Mg_9Sn_5 peaks (300) in each of the two powders. The metastable phase is formed after the planetary ball milling due to the repeated impact, fracturing, and cold welding of the powder. These powders were dull blue/grey color in appearance. Similar results were reported by Urretavizcaya *et al.* [11] where they produced Mg_9Sn_5 after 150 hours using a magnetic field assisted high energy ball milling approach.

Figure 2 is the XRD analysis of two samples processed using CAPAD from the 9:5 ratio batch of powder. The samples were processed using 0 and 112 MPa of applied pressure at 600 °C. The sample processed at 112 MPa shows only the presence of the Mg_9Sn_5 phase while the sample processed at 0 MPa still shows both Mg_2Sn and Mg_9Sn_5 , indicating an effect of pressure on the formation of the metastable phase. It is not surprising that the pressure plays a significant role since as mentioned earlier, the phase is usually synthesized under high pressures. It is worth emphasizing however, that 112 MPa is significantly lower pressure than previously reported. It is also noteworthy that the peaks in the ball milled powder are considerably broader than those of

the CAPAD processed samples. This is likely due to residual stress and/or fine crystal size of the PBM powder.

In order to find the optimum processing conditions for producing bulk dense Mg_9Sn_5 , seven samples from the 19:10 ratio powder batch were processed using CAPAD at different temperatures with 112 MPa of applied mechanical pressure. Processing temperatures ranged from 100 °C to 600 °C. The effect of these processing temperatures on the composition of the samples is shown in **Figure 3**. Samples processed below 400 °C show relatively little change in composition from XRD analysis. Once the processing temperature exceeds 400 °C, the peak intensities for the Mg_2Sn phase begin to disappear. By 500 °C, the Mg_2Sn peaks are no longer detectable from the XRD data. The transformation occurring at temperatures higher than 400 °C is consistent with Dyuzheva *et al.* [8]. It should be noted that the pressure used in this previous preparation [6] is significantly higher than the one we have used.

The effect of CAPAD temperature on the transformation from the as-ball milled two phase ($\text{Mg}_2\text{Sn} + \text{Mg}_9\text{Sn}_5$) powder to a single phase Mg_9Sn_5 powder can be appreciated in **Figure 4**, where we plot the integral intensity ratios of the Mg_9Sn_5 (300) peak to the Mg_2Sn (111) peak, which are the highest intensity peaks for the respective phases. As mentioned previously, the intensity ratio of the as-ball milled powder (25 °C data point) was 0.33. The data in **Figure 4** reveal that the intensity ratio remains constant up to 450 °C of processing temperature. The intensity ratios of the samples produced at 500 °C and higher fall to zero indicating complete conversion to the Mg_9Sn_5 phase. For comparison, we also plot the intensity ratios of 9:5 stoichiometry PBM powder samples processed using 2 different pressures. As expected, the sample processed using 112 MPa falls directly on top of the 600 °C point from 19:10 stoichiometry. The sample processed without applied pressure demonstrates an incomplete conversion to Mg_9Sn_5 .

The conversion from two phases (Mg_2Sn and Mg_9Sn_5) to a single Mg_9Sn_5 phase with an applied pressure of 112 MPa and temperatures exceeding 500 °C indicate that Mg_9Sn_5 is more stable than Mg_2Sn under our processing conditions. It is interesting to note that *Mg_9Sn_5 is still metastable compared to the Mg_2Sn at ambient temperature and pressure* since as mentioned before, it is not found on the traditional temperature composition phase diagram. Previous reports of synthesis of bulk single crystals of this phase started with either elemental Mg and Sn or the Mg_2Sn phase [5–9,19] and required an order of magnitude higher pressure (GPa vs 100 MPa) to obtain Mg_9Sn_5 . It is likely that the Mg_9Sn_5 present in our PBM starting material acts as a seed or template for further conversion of Mg_9Sn_5 , but at this time it is not possible to confirm this. Further studies are on underway to establish a mechanism for the conversion as well as to analyze the kinetics of the process.

The effect of hold time at 400 °C was also investigated. Samples were held at 0, 5, 10, and 20 minutes upon reaching 400 °C as shown in **Figure 5**. There is very little change in the XRD patterns of the samples held for times shorter than 20 minutes. The sample held at 20

minutes shows a decrease in the Mg_2Sn (111) peak intensity. The intensity ratios plotted in **Figure 6** reinforces these findings.

One of the main goals of this work is to create bulk and dense materials using CAPAD. Since densification mechanisms are highly temperature dependent, we expect increasing densities up to the theoretical maximum with increasing temperature. From **Figure 7**, we can see increasing sample densities with increasing processing temperature. The densities of the samples reach a plateau of $\sim 3.8 \text{ g/cm}^3$ with temperatures exceeding 400°C . In addition to the densification mechanisms (decreasing porosity), the transformation of the crystal structure contributes to the density increase. Mg_9Sn_5 with a calculated density of 3.99 g/cm^3 is a denser phase compared to Mg_2Sn with a density of 3.6 g/cm^3 . Comparison of the 9:5 stoichiometry powder processed with 0 MPa and 112 MPa emphasize the drastic effect of pressure on the densification; with 0 MPa the sample density remains comparable to the green density, 2.25 g/cm^3 . In other words, the sample is still a powder, not a dense bulk solid with mechanical integrity.

Typically, hold time also plays a role in final densities. Samples processed at 400°C were held for 0, 5, 10, and 20 minutes. Hold times at this temperature and time range did not have a significant effect; all samples had a density of approximately 3.8 g/cm^3 (**Figure 8**).

3.2 Morphology and Chemical Composition Characterization

The morphology and chemical composition of the CAPAD processed Mg_9Sn_5 material was interrogated via SEM and EDS. A solid, densified sample of Mg_9Sn_5 that was CAPAD processed at 600°C and 112 MPa was mechanically cleaved and immediately introduced into the vacuum chamber of the electron microscope. **Figure 9** shows electron micrographs at both high (20,000 X) and low (5,500 X) magnification. In the low magnification image, the cleaving process shows both inter- and intra-granular fractures. Two domain sizes were observed, one large with smooth areas on the order of 1-2 μm . The second domain size, with smaller grains, is on the order of 100s of nanometers. The elemental map shows the material is composed solely of magnesium and tin and is homogeneously distributed throughout the sample, **Figure 10**. Also, the minor peaks observed between ~ 0.3 to 0.5 keV can be attributed to C, N, and O or to the weakly held outer shell electrons of tin (~ 0.4 to 0.5 keV). While every attempt was made to minimize environmental artifacts, the sample is mounted on copper tape, which has an organic-based adhesive. In addition to phase identification via powder XRD, quantification of the Mg/Sn signal ratio corresponds well to the 9:5 stoichiometry confirming not only the stoichiometry but also a lack of any amorphous phases that would not be detected by diffraction methods.

3.3 Crystal Structure Refinement

. Our Rietveld analysis of the obtained neutron diffraction data (**Figure 11**) indicates that the synthesized major phase adopts the same structure as the Mg_9Sn_5 phase prepared at high pressure [9]. Neutron patterns also reveal the existence of an MgO impurity in the sample, and its

content is determined to be ~4.4 wt.%. Existence of oxide phases in Mg-Sn alloys is not surprising since these alloys are known to be oxygen sensitive [3]. Although the sample preparation was done in Ar, the crushing of the synthesized bulk dense material into powders could have contributed to the oxide formation. The significantly higher surface area of the powder compared to that of the bulk material tends to result in oxide formation.

The final refinement agreement indices and obtained unit-cell parameters, atomic positions and atomic isotropic displacement parameters are listed in **Tables 1** and **2**, respectively, and the refined structure is shown in **Figure 12**. Similar to the structure of the high-pressure synthesized Mg_9Sn_5 phase, the structure of this phase is comprised of a three-dimensional framework of Mg atoms with Sn situated in the structural tunnels parallel to the c-axis. In each unit cell, there are six crystallographically distinct sites for Sn (**Table 2**). Sn1 and Sn2 occupy tunnels with a trigonal cross-section, whereas other Sn atoms (Sn3, Sn4, Sn5 and Sn6) occupy tunnels with a hexagonal cross-section (**Figure 12(a)**).

Range *et al.* [9] pointed out that their high-pressure synthesized Mg_9Sn_5 phase is similar to the so-called “dense form Mg_2Sn ” that had been reported earlier by Cannon and Conlin [5] and Dyuzheva *et al.* [7]. However, there are differences in c/a ratio between these phases. While the c/a ratios of “dense form Mg_2Sn ” are 1.027 and 1.007 (from Cannon and Conlin [3] and Dyuzheva *et al.*, [5] respectively), that of the high-pressure synthesized Mg_9Sn_5 phase is 0.9946 (Range *et al.*). Note that the c/a ratio of our Mg_9Sn_5 phase is 1.008, similar to one of the values for “dense form Mg_2Sn ”. These differences are probably due to subtle differences in Mg/Sn ratio among these samples.

4. Summary

We were able to synthesize bulk polycrystalline Mg_9Sn_5 , a metastable polymorph of Mg_2Sn , using a combination of mechanical alloying and CAPAD processing. This phase was synthesized at significantly lower pressures (112 MPa compared to 2-6 GPa) and temperatures (< 500 °C compared to 600-1200 °C) than previously reported. This is the first instance (that we know) of this phase produced in a dense polycrystalline form. It is also the first time that the Mg_9Sn_5 phase has been confirmed and detailed via neutron diffraction refinement.

Large polycrystalline samples like those presented here are excellent for property measurements and are easy to integrate into devices and applications. We expect the processing procedures developed here to be translatable to other alloy systems, opening the door for the production of other metastable alloys that are difficult to synthesize by other methods.

Acknowledgements

Support of this work from the UC Lab Fees Program (grant ID# 12-LR-239003) is most gratefully acknowledged. This work has benefitted from the use of the NPDF instrument at the

Lujan Center at Los Alamos Neutron Science Center (LANSCE), which was funded by the Department of Energy's Office of Basic Energy Sciences at the time of the measurements. Los Alamos National Laboratory is operated by Los Alamos National Security LLC under DOE Contract DE-AC52-06NA25396. The upgrade of NPDF has been funded by NSF through grant DMR 00-76488.

Figure Captions:

Figure 1. XRD powder patterns of the starting elemental powders and planetary ball milled powders with Mg:Sn stoichiometric ratios of 9:5 and 19:10. Dark squares represent the Mg_2Sn phase. Open squares represent the Mg_9Sn_5 phase.

Figure 2. XRD of 9:5 ratio powder processed at 600 °C with 112 and 0 MPa. Dark squares represent the Mg_2Sn phase. Open squares represent the Mg_9Sn_5 phase.

Figure 3. XRD powder patterns of the starting 19:10 ratio ball milled powder and CAPAD processed samples at various temperatures. Dark squares represent the Mg_2Sn phase. Open squares represent the Mg_9Sn_5 phase.

Figure 4. Integral intensity ratios of Mg_9Sn_5 (300) and Mg_2Sn (111) vs processing temperature (19:10 ratio starting powder).

Figure 5. XRD patterns of 19:10 ratio ball milled powder processed at 400 °C with varying hold times. Dark squares represent the Mg_2Sn phase. Open squares represent the Mg_9Sn_5 phase.

Figure 6. Integral intensity ratios of Mg_9Sn_5 (300) and Mg_2Sn (111) of samples processed at 400 °C with varying hold times.(19:10 ratio starting powder).

Figure 7. Green body density and densities of the CAPAD processed powder compacts. A photograph of a polished sample (9:5 ratio, 112 MPa, 600 °C, open triangle) is included for visual aid.

Figure 8. PBM ratio 19:10 (Mg:Sn) sample processed at 400 °C and held for different amounts of time.

Figure 9. SEM images of freshly cleaved densified Mg_9Sn_5 after CAPAD treatment at 600 °C and 112 MPa at low magnification (A, 5,500X) and high magnification (B, 20,000X).

Figure 10. The homogeneous nature of the sample is demonstrated by SEM. (Top) SEM/EDS mapping images of freshly cleaved densified Mg_9Sn_5 after CAPAD treatment at 600 °C and 112 MPa. (Bottom) Total EDS spectra from mapping experiment showing exclusively Mg and Sn. Si peak at 1.8 keV is a detector artifact.

Figure 11. Fitted neutron diffraction patterns collected at (a) $2\theta = 148^\circ$, (b) $2\theta = 119^\circ$, (c) $2\theta = 90^\circ$ and (d) $2\theta = 46^\circ$. Data are shown as red plus signs, and the solid green curve is the best fit to the data based on the structure model. Black and red tick marks below the pattern show the positions of allowed reflections for Mg_9Sn_5 and impurity phase MgO , respectively. The lower pink curve represents the difference between the observed and calculated profiles.

Figure 12. Crystal structure of Mg_9Sn_5 projected along (a) the c-axis and (b) the a-axis. Green balls represent Mg atoms, purple balls represent Sn atoms, and dashed blue lines outline a unit cell.

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Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.

Figure 11.

(a)

(b)

Figure 12.

Table 1. Unit-cell parameters and refinement agreement indices of Mg₉Sn₅ (space group *R*3).

a (Å)	c (Å)	c/a	V (Å ³)	R_{wp} (%)	R_p (%)	χ^2
13.2359(2)	13.3432(3)	1.008	2024.41(9)	2.13	1.31	4.28

Table 2. Atomic coordinates and atomic thermal parameters of Mg₉Sn₅

atom	x	y	z	U_{iso} (Å ² /100)
Mg1	0.245(1)	0.164(1)	0.0713(8)	1.03(4)
Mg2	-0.237(1)	-0.162(1)	-0.0976(10)	1.03(4)
Mg3	0.516(1)	0.414(1)	0.0671(9)	1.03(4)
Mg4	0.482(1)	-0.408(1)	-0.0872(9)	1.03(4)
Mg5	0.494(1)	0.593(1)	0.2474(8)	1.03(4)
Mg6	-0.495(1)	0.407(1)	-0.2576(8)	1.03(4)
Sn1	0.335(1)	0.336(1)	0.2396(6)	0.69(3)
Sn2	-0.336(1)	-0.338(1)	-0.2605(6)	0.69(3)
Sn3	0	0	0.3902(8)	0.69(3)
Sn4	0	0	-0.3991(8)	0.69(3)
Sn5	0	0	0.1425(8)	0.69(3)
Sn6	0	0	-0.2033(8)	0.69(3)