Rapid synthesis of thermoelectric compounds by laser melting

Yoshiaki Kinemuchi,⁎, Masashi Mikami, Ichiro Terasaki, Woosuck Shin

⁎ Corresponding author.
E-mail address: y.kinemuchi@aist.go.jp (Y. Kinemuchi).

1. Introduction

Solid-state thermoelectric devices have gained attention for energy harvesting applications from wasted heat [1]. Currently, most research efforts are concentrated on discovering high performance materials [2–4]. Some studies have demonstrated the importance of heat recovery from low energy heat sources for practical applications [5], and unique devices for this purpose have been proposed [6,7].

No thermoelectric compound exists that is suitable for all applications; hence, materials need to be selected considering the temperature and atmosphere of the application [2]. For instance, (Bi,Sb)-Te alloys are widely applied below 200 °C, and oxides are potentially applicable above 700 °C in the atmospheric condition. For intermediate temperatures, there are plenty of materials can be utilized, and among them silicides and oxides are considered as cost-effective and environmentally benign compounds.

At present, devices are composed of a simple structure so-called n-type module that consists of square blocks of n- and p-type semiconductors. Thanks to the simplicity of the structure, the module is widely applied in industry. However, the rather rigid structure means it is only applicable on heat sources with flat surfaces, while the majority of the heat sources (such as human skin) are not flat. Flexible devices made from both organic [8] and organic/inorganic compounds [9] are being developed which have the potential to expand the range of applications for such devices, however, their properties are still limited.

Considering the fabrication methods for thermoelectric materials, rapid prototyping enables materials to be shaped into a variety of different structures [10]. Among the several rapid prototyping methods, laser sintering, laser melting, and laser metal deposition are potentially applicable for inorganic thermoelectric materials. These three processes have been reviewed by Gu et al. [11], where they showed that the main difference can be found in the melting state of the raw powders, in which partial melting occurs in laser sintering while complete melting is achieved in both laser melting and laser metal deposition. Hence, composite materials are obtained when using laser sintering [12], while the in-situ synthesis of chemical compounds is possible using the other methods [11]. Particularly, the in-situ synthesis can potentially expand the options for module design as exemplified by the functionally graded materials concept [13], which proved to be effective in enhancing the thermoelectric energy conversion efficiency. In this sense, the synthesis of thermoelectric compounds via laser melting is regarded as a key technology; however, reports of such studies are still limited [14,15].

In laser synthesis, simultaneously heating a mixture of precursor materials is a complicated process because the light absorptance of the materials greatly depends on the wavelength, and the heating temperature is determined by the input power density rather than the total input energy [10]. In addition, the differences in the melting temperatures and vapor pressures make it difficult to form the desired compounds.

In the present work, we investigate the heating characteristics of metal powders in terms of their light absorptance when illuminated by a diode laser with a wavelength of 940 nm. Based on these results, we demonstrate the synthesis of various thermoelectric compounds
including Bi-Sb alloys, and Mn-Al-Si alloys and oxides, using laser synthesis. These are all typical thermoelectric compounds utilized at low, middle, and high temperatures, respectively. Finally, we discuss and summarize the advantages and limitations of laser melting.

2. Materials and methods

2.1. Laser melting

Fig. 1 shows a setup of laser melting. A diode laser with a wavelength of 940 nm (Hamamatsu photonics, L10060, Japan) was used as the laser light source, which produced a continuous output beam after a programmed power was set. The minimum laser spot diameter was 1.2 mm and a maximum power of 70 W was available, resulting in a maximum power density around 60 W/mm². By varying the output power and working distance, the spot size and power density could be changed. The surface temperature during heating was monitored by a built-in infrared thermometer that could measure over a temperature range of 200–800 °C. The metal powders were placed in a chamber for laser synthesis experiments. To produce alloy materials the chamber was evacuated or filled with He gas prior to laser irradiation, while the oxides were synthesized in the ambient air. The position of chamber was controlled using an X-Y stage in a programmed pattern. Laser scanning was performed for the synthesis of oxides (a rate of 500 μm/s and a scan pitch of 500 μm), while the position of laser spot was fixed during the synthesis of alloys.

2.2. Sample preparation

Four kinds of samples, namely Bi-Sb alloys, Mn-Si alloys, and Mn-Al-Si alloys and oxides, were synthesized. All precursor powders were supplied by Kojundo Chemical Laboratory Co., Ltd., Japan. For the Bi-Sb alloys, powders of Bi (4 N, 75–150 μm) and Sb (5 N, diameter around 150 μm) were used as raw materials. For the Mn-Al-Si alloys, Mn (3Nup, ≤300 μm), Al (2Nup, ≤300 μm), and Si (3Nup, ≤45 μm) powders were used. The oxide thermoelectric compounds, Ca₃Co₄O₉ and rare-earth (R) doped SrTiO₃ were fabricated in this study. Ca₃Co₄O₉ (2 N) and Co₃O₄ (3Nup) powders were used for fabricating Ca₃Co₄O₉ samples. R₂O₃Sr₂O₅TiO₃ compounds were synthesized from SrCO₃ (3 N), Ti (3 N, ≤45 μm), and R₂O₃ (R = La, Pr, Sm, Dy, or Y; 3 N) powders. Before laser irradiation, the desired amounts of raw powders were homogeneously mixed using a planetary mixing (ARV-310, Thinky, Japan), pressed into pellets, and placed onto a quartz glass substrate. For the Bi-Sb alloys only, the mixed powders were poured in a ceramic crucible and laser irradiation was performed.

2.3. Characterization

The light absorptance values of the powders were measured using diffuse reflectance spectroscopy (V-670, Jasco, Japan). The crystalline phases of laser-synthesized samples were analyzed using X-ray diffraction (XRD, RINT2550, Rigaku, Japan). The observed XRD patterns are summarized in the Supporting Information. The lattice constant was evaluated from the peak positions of the XRD pattern measured using parallel beam optics. Here, the peak positions were defined by curve fitting with the Pearson VII. The composition of the alloys and oxides were analyzed by X-ray fluorescence analysis (EDX-8000, Shimadzu, Japan). The microstructures of the samples were observed by using scanning electron microscope (SEM, ERA-8900FE, ELIONIX, Japan). The theoretical thermopower was evaluated using the thermal probe method. [16] The theoretical thermopower was evaluated by density functional theory using the Wien2k package[17] and Boltztrap code[18] for Mn-Al-Si alloys based on the reported crystal structures.

3. Results and discussion

3.1. Laser heating characteristics

Thermoelectric materials normally contain more than two elements. Therefore, irradiating the mixture of precursor powders for synthesis fundamentally results in inhomogeneous heating because of the variation in light absorptance (which depends on the element and wavelength). Fig. 2 shows the laser heating characteristics of the various metal powders. As a result of the laser irradiation of the compacted powders, the sample temperatures initially increased with time and saturated after a certain period, typically 20–30 s in these experiments. The maximum attainable temperature under these conditions linearly increased with the applied power as shown in the inset of Fig. 2 (data for tungsten is shown, although similar curves were observed for all metals).

It was predicted from finite element analyses that the maximum temperature of the powders is affected by the power of the laser rather than the duration of laser irradiation [19]. Our experimental results agree with this prediction. In addition, the slope of the temperature vs. power plot is regarded as an index of the heating efficiency of the laser. As expected, the slope was higher for the materials with higher light absorptance. However, this was not a linear relationship, perhaps
arising from the differences in the thermal conductivities of the samples. Here, Cu and Al are good thermal conductors, having thermal conductivity values > 200 W/mK, while Ti and Mn have rather poor thermal conductivities of < 20 W/mK, at room temperature. The thermal conductivity values of Mg, Fe, and W are in between these extremes. Such a trend in the thermal conductivity as a function of light absorptance is connected with the thermal conductivity of the electrons in the metals; the free electrons reflect the light from the surface. Si is an exception due to its semiconducting properties. Light absorptance is caused by a band transition below wavelengths of 1200 nm and its thermal conductivity is rather high (c.a. 150 W/mK). Nevertheless, it is important to note that laser heating of materials is principally predictable based on the light absorptance, in spite of differences in either the thermal conductivity or absorptance mechanisms.

The parameters used during laser heating of the mixed materials greatly affect both the processing and final properties of the alloys. Via monitoring of the temperature during heating, it was clarified that the heating efficiency of the mixture was an average of the efficiency of individual materials. This suggests heterogeneous mixing in the sample, although this has not yet been experimentally proven. In addition, a large difference between the melting points of the materials critically influences the reaction. For instance, Mg₃Si (an n-type thermoelectric compound) can be prepared from the reaction between Mg and Si, with melting points differing significantly by 761 °C. When the temperature of the sample reached the melting point of Mg, the reaction between the two metals began, and the continued supply of laser power resulted in the synthesis of Mg₃Si in powder form. This clearly suggests that complete melting of both reactants is not a required condition for the synthesis of compounds by laser heating.

3.2. Synthesis of Bi-Sb alloys

Both Bi and Sb possess the arsenic rhombohedral structure and their light absorptance values are similar, and thus laser heating of the powder mixture is expected to be homogeneous. They have rather different melting points, 270 °C for Bi and 631 °C for Sb, and form complete solid solutions according to their phase diagram. Fig. 3 shows a photograph of a series of Bi-Sb samples after laser irradiation with powers of 5 W for x ≤ 0.7, 7 W for x = 0.8 and 8 W for x ≥ 0.9 and a spot size of 4 mm. The samples were irradiated for 100 s in a vacuum pressure of 3 Pa. Under these conditions, the powders fully melted below a Sb concentration of x = 0.7, while at x = 0.8 and 0.9, only partial melting was observed. For the pure Sb, solid state sintering was observed. Such differences in the melting properties are simply due to the different liquid formation temperatures of each composition.

The chemical compositions of the products agreed well with the nominal compositions, as shown in Fig. 4. We also observed the microstructure of a sample with a composition of x = 0.5 using SEM and mapped the Sb content using EDS, where it was found that phase separation occurred in the sample, as shown in the inset of Fig. 4. Since the liquidus and solidus lines are separated from each other in the Bi-Sb phase diagram, the compositional segregation arose during solidification. This phase separation was hard to eliminate, even by a long annealing process (300 °C for 80 h).

The XRD patterns (see the Supporting information) showed a gradual peak shift towards higher angles with increasing Sb concentration, indicating the occurrence of alloying. However, the peak shapes were irregular, implying incomplete alloying, as observed in the SEM image.

The thermopower values evaluated using the thermal probe method are shown in Fig. 5. It is known that Bi and Sb are n- and p-type semiconductors, respectively. We confirmed gradual variations in the thermopower as a function of Sb content, and the minimum thermopower was found at x = 0.1. This trend in the thermopower of Bi-Sb alloys produced by laser melting agreed well with a previous report [20].
3.3. Synthesis of Mn-Si alloys

As shown in Fig. 2, both Mn and Si absorb laser power effectively, although the vapor pressure of Mn is much higher than Si, i.e. four orders of magnitude higher at the melting temperature. In fact, a dark powder was observed on the chamber window during melting. In the worst case, the coated window started to absorb the laser beam, resulting in incomplete melting of the sample. Filling the chamber with He gas solved this problem. The high thermal conductivity of the He gas is thought to be the reason for this desirable effect, because the vapor instantly lost its thermal energy leading to a reduction of the mean free path. Thanks to this effect of the He gas, Mn-Si samples could be achieved over a wide range of compositions by simultaneous melting. Fig. 6 shows the composition of synthesized Mn$_{1-x}$Si$_x$ alloys determined by EDS as a function of the nominal composition. Within the accuracy of EDS, the composition of the products was found to be identical with the starting composition, indicating that any compositional differences arising from Mn loss due to vapor formation were negligible.

Table 1 shows the observed phases in the products. Comparing these data with the Mn-Si binary phase diagram, [21] shown in Fig. 7, it is noticed that the constituent phases correspond to the high temperature phases, indicating melting and quenching processes occurred. In addition, when the nominal composition was selected for the congruent melting composition, a single phase was observed (as seen for $x = 0.5$), while mixed phases were found for the other compositions. These results imply that the source materials were mixed homogeneously in the melting state and phase separation occurred during cooling. Considering the thermolectric performance of this system, the so-called higher manganese silicide (HMS) phase (known to be an effective p-type thermoelectric compound [22]) was formed as a single phase at $x = 0.63$.

3.4. Synthesis of Mn-Al-Si alloys

In the Mn-Al-Si ternary system, high performance n-type thermoelectric compounds have been reported [23,24], which are a potential counterpart of the p-type HMS phase. In the Mn-Al-Si system, Al melts at a relatively low temperature of 656 °C compared with Mn (1246 °C) and Si (1414 °C). We found systematic compositional deviations from the nominal composition when the mixture of Mn, Al, and Si powders were melted simultaneously, where the product composition was shifted towards a Mn-poor composition. Critically, the multi-phase product identified by XRD was incompatible with the phase diagram, indicating an inhomogeneous mixture of the precursor materials. To solve this problem, we used a mixture of Mn-Al alloy powders and Si powders, i.e. a pseudo-binary system for the precursor materials. We confirmed that the compositional deviation from the starting composition was not significant in binary systems such as Mn-Al, Al-Si, and Mn-Si alloys. Similarly, by using these pseudo-binary systems, stoichiometric amounts of Mn were observed and thus the synthesis of the desired compounds with various compositions was possible.

To date, the reported thermoelectric properties of this ternary system are limited to a few compositions. Hence, to further understand the properties of the Mn-Al-Si system we have surveyed the thermopower for a wide range of compositions. Laser melting proved to be a useful tool for such a purpose due to the possibilities for rapid syntheses. To obtain the thermopower map, MnAl$_4$, MnAl, and Mn$_2$Al$_3$ were mixed with Si to achieve the pseudo binary systems. The thermopower map evaluated by the thermal probe method is shown in Fig. 8a. The contour map of thermopower indicates that the lowest thermopower, a good n-type thermoelectric compound, exists near the composition of Mn$_5$Al$_7$Si$_4$. On the other hand, the highest thermopower, a good p-type thermoelectric compound, was found at Mn$_5$Al$_2$Si$_{15}$. To verify these experimental results, the data were compared with that from the literature, as well as the results of DFT calculations that can reasonably estimate the thermopower based on the known crystal structure (Fig. 8b). Here, the value of pure silicon was excluded because the thermopower is sensitive to the carrier concentration. Although the available data (the crosses in the figure) are limited, we can observe a trend in the behavior of the thermopower as a function of the composition, in which good n-type and p-type semiconductors exist. A suitable n-type compound can be found on the slightly Si poor side of the Mn$_5$Al$_7$Si$_4$ composition, while a p-type compound should be selected from the region near the HMS composition. The experimentally obtained map agreed reasonably well with this tendency. In addition, there exist large differences in the absolute value between the experimental and theoretical values, which originate from the thermal probe method tending to underestimate the thermopower for materials with high thermal conductivity. From the XRD analyses of these materials it was clarified that the product with the lowest thermopower consisted of the C$40$ phase with a minor amount of Mn$_5$(AlSi)$_{10}$. The sample with the highest thermopower had the HMS structure, which agrees with the ternary phase diagram at 700 °C. [25] These results indicate the feasibility of using laser melting to fabricate a

![Fig. 6](image-url) The compositional of Mn$_{1-x}$Si$_x$ after laser irradiation ($x_{\text{EDS}}$) compared to the nominal composition.
ternary system by selecting an adequate pseudo binary system as the starting materials.

3.5. Synthesis of oxide compounds

SrTiO$_3$ (n-type) \cite{26} and Ca$_3$Co$_4$O$_9$ (p-type) \cite{27} oxide thermoelectric compounds were synthesized. So far, the synthesis of oxide thermoelectric material of Bi$_2$Sr$_2$Co$_{1.8}$O$_x$ via laser floating zone has been reported, demonstrating the potential advantage of laser process.\cite{28} Conventionally, such materials are prepared from oxides or carbonates, however, carbonates and wide bandgap oxides such as TiO$_2$ are unsuitable for the laser melting (especially using diode lasers) because of their low light absorptance. Hence, we added metallic Ti as a light absorber for the synthesis of SrTiO$_3$, while Co$_3$O$_4$ acted as a heat source for the Ca$_3$Co$_4$O$_9$ synthesis. The morphologies of the oxide samples after laser scanning are shown in Fig. 9. For the SrTiO$_3$ sample illuminated with a power of 5 W it was found that cracks were formed near the vicinity of the laser spot in the non-melted region. These cracks healed during the scanning procedure when complete melting was achieved at a power of 10 W. It is worth mentioning that the melting temperature of SrTiO$_3$ is $2040 ^\circ C$, indicating excellent heating characteristics, even when using a conventional diode laser. The mixture of Ti and SrCO$_3$ resulted in single phase SrTiO$_3$, while the mixture of CaCO$_3$ and Co$_3$O$_4$ formed a multiphase of CaO and CoO. Ca$_3$Co$_4$O$_9$ is stable below $926 ^\circ C$ and decomposes above this temperature, while SrTiO$_3$ exists at a congruent melting composition. The formation of a multiphase in the synthesis of Ca$_3$Co$_4$O$_9$ again indicates the preferential formation of high temperature phases using the present process. The impurity doping required for the tuning of carrier concentration was demonstrated for SrTiO$_3$ by adding rare earth oxide dopants. The variation in lattice constant as a function of the size of the dopant is shown in Fig. 10. In this system, the solubility limit is rather narrow for the rare earth dopants with small radii, such as Dy and Y. Indeed, impurity phases other than SrTiO$_3$ existed for the samples doped with Dy and Y. On the other hand, the lattice constant linearly increased above the ion size of Sm, indicating the substitution of the rare earth elements on the Sr sites. There was no impurity phase found for these substitutions, and thus successful doping via laser melting was confirmed.

3.6. Evaluation of laser melting for thermoelectric compounds

Through the synthesis of various thermoelectric compounds, the advantages and limitations of laser melting for fabricating such materials became clear. Firstly, the laser melting is not equally suited to fabricating all kinds of materials, due simply to the different light absorptance characteristics of the materials. In particular, metals with good electrical conductivity, such as Ag, Cu, and Al, are difficult to melt because of their high optical reflectivity and high thermal conductivity. Wide band gap semiconductors are also unsuitable owing to their transparency to the light source. Fortunately, thermoelectric compounds can be prepared using several source materials that can absorb the light source effectively and allow laser melting to occur. In addition, (Bi,Sb)-Te alloys, currently the thermoelectric compounds used in applications, are composed of semimetals that can readily absorb the laser power.

Considering the process temperature, materials with high melting temperatures can be used by selecting suitable starting materials. It should be noted again that the formation of the high temperature phase precedes, because the process relies on melting and quenching phenomena. This sometimes causes a reduced solubility limit as seen
in SrTiO₃. Annealing may be required for certain compounds such as Ca₃Co₄O₉.

The rapid processing via laser melting is a distinct advantage, particularly for the potential application of surveying new compounds, as demonstrated for the Mn-Al-Si ternary system. In addition, local heating and the ability to scan the sample are basic advantages of the laser melting technique, which can expand the possibilities for device design, as demonstrated by the rapid prototyping experiments.

4. Conclusions

Laser melting using a diode laser with a light source of 940 nm was used to synthesize various thermoelectric compounds including Bi-Sb alloys, Mn-Si alloys, Mn-Al-Si alloys, Ca₃Co₄O₉, and SrTiO₃. Through the synthesis of these compounds and the evaluation of the heating characteristics of the source materials, we conclude the following.

1. The variation in the thermopower caused by compositional differences agreed reasonably well with reference data, indicating the potential for using laser melting for the synthesis of thermoelectric compounds and devices.
2. For the binary alloys, the compositions of the products were identical with the nominal ones. The resultant phases agreed well with the phase diagrams and high temperature phases were preferentially formed.
3. For the ternary compound Mn-Al-Si, a significant compositional difference was observed when the products were prepared from pure metals. By applying a pseudo binary system, namely laser melting of Mn-Al alloys and Si, the correspondence between the products and the phase diagram was confirmed.
4. Impurity doping was demonstrated in SrTiO₃, which is required for the tuning of the carrier concentration.
5. The heating characteristics are primarily determined by the light absorption of the material, in spite of the differences in either thermal conductivity or absorption mechanism.
6. The vapor from a melt sometimes caused contamination of the optical window, weakening the laser heating of the sample. Filling the chamber with He gas was able to keep the window clean.
7. Partial melting near the laser focal point caused cracks that were healed upon complete melting.

Acknowledgements

This article is based on results obtained from the Future Pioneering Program “Thermal management materials and technology” commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.matdes.2016.05.093.

References


