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Rapid synthesis of thermoelectric compounds by laser melting

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The synthesis of thermoelectric compounds, including Bi-Sb and Mn-Si binary systems, Mn-Al-Si ternary system, and rare-earth doped $SrTiO_3$, has been successfully demonstrated using a continuous laser diode with a 940 nm light source. Owing to the high power density of the laser (60 W/mm^2 at the maximum), the precursor powders immediately melted and reacted when irradiated by the laser. Subsequent quenching led to the stabilization of high temperature phases in the resultant compounds. Any compositional differences between the laser treated compounds and the starting materials were negligible. The thermoelectric properties varied according to the composition, as expected, demonstrating the feasibility of laser melting as a rapid synthesis tool for thermoelectric compounds. Several advantages and limitations of the synthesis conditions are also discussed.

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 are considered as cost-effective and environmentally benign compounds.

At present, devices are composed of a simple structure so-called π-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

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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/mm^2. 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, ≤300um), and Si (3Nup, ≤45 μm) powders were used. The oxide thermoelectric compounds, $Ca_3Co_4O_9$ and rare-earth (R) doped $SrTiO_3$ were fabricated in this study. $CaCO_3$ (2 N) and Co_3O_4 (3Nup) powders were used for fabricating $Ca_3Co_4O_9$ samples. $R_{0.5}Sr_{0.95}TiO_3$ compounds were synthesized from $SrCO_3$ (3 N), Ti (3 N, ≤45 μm), and R_2O_3 (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.

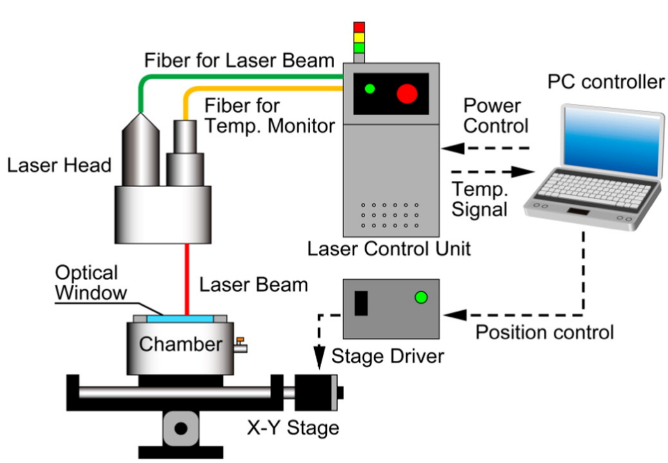

Fig. 1. Laser melting setup.

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 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

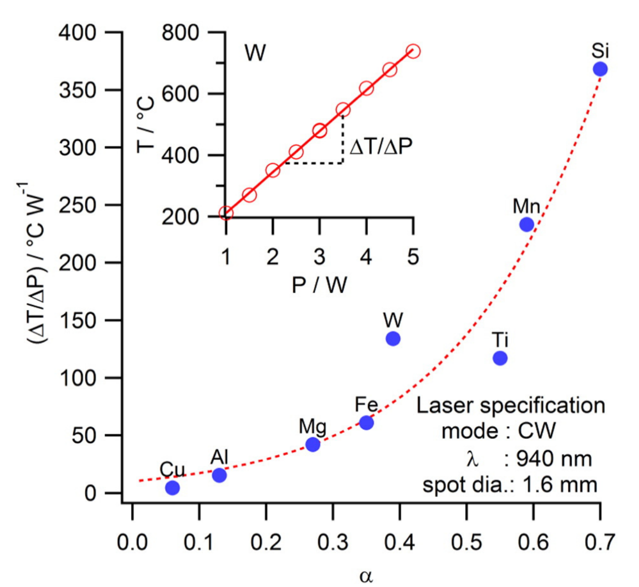

Fig. 2. Heating characteristics of various metals illuminated by a laser diode. The inset shows the saturated maximum temperature (T) under continuous laser irradiation with a certain power (P). The slope (ΔT/ΔP) is plotted as a function of light absorptance (α).