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Correlation between the magnetic and thermoelectric properties in $Mg_{2-x}Mn_xSi$

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ABSTRACT

Single crystals of $Mg_{2-x}Mn_xSi$ (x = 0, 0.1, 0.2, 0.3, and 0.4) were prepared using a vertical Bridgman method. The formation of desired materials was confirmed using single-crystal and powder X-ray diffraction. The thermoelectric and magnetic properties were investigated for various Mn contents in the temperature range between 2 and 300 K and in magnetic fields up to 70 kOe. For various x values, $Mg_{2-x}Mn_xSi$ with $x = 0.2$ possesses the highest figure of merit. The experimental results revealed that the substitutional Mn atoms exhibit mixed valences of +3 (majority) and +2, giving rise to dramatic changes of carrier density and magnetic interaction. At the same time, the Seebeck coefficient and magnetic susceptibility show a sudden change at the same temperature. These results imply that the thermoelectric properties are correlated with the magnetic properties in the $Mg_{2-x}Mn_xSi$ crystals.

1. Introduction

The thermoelectric efficiency is estimated by the figure of merit, ZT, defined by $ZT = (S^2\sigma/\kappa)T$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature. For high performance of thermoelectric materials, it is important to have high Seebeck coefficient, high electrical conductivity, and low thermal conductivity at desired temperature range. However, it is difficult to achieve the above conditions simultaneously because these physical parameters are competing with each other. In commercial applications, the thermoelectric materials can be divided into three groups, depending on the temperature range of operation [1–5]: one is near-room-temperature region based on Bi–Te alloys, the other is intermediate-temperature region from 500 to 900 K based on Pb–Te alloys, and another is high-temperature region above 900 K based on silicide alloys.

Mg_2Si is well known as a semiconductor with an indirect band gap of 0.78 eV and a thermoelectric material with high energy conversion efficiency at high temperatures [6–12]. This material satisfies the requirement for commercial thermoelectric applications being environmental-friendly, and the elements are composed of light metals, abundant in the earth and cost effective. The Seebeck coefficient of pure Mg_2Si reaches up to $S = -500$ μV/K but only $ZT = 0.1$ [10,13], and thereby there have been many efforts to improve the thermoelectric properties with proper dopants into Mg_2Si. Appropriate doping enhances the thermoelectric performance because the impurity states strongly influences the electronic transport properties. Most of studies have been focused on polycrystalline Mg_2Si samples prepared by spark plasma sintering [6], hot pressing [7], and solid solution [8]. Doping elements used for improving thermoelectric performance in Mg_2Si are Al, Bi, Sb, Pb, and Ge [6–11]. In comparison with the polycrystalline samples, there have been a few reports on single crystals of Mg_2Si series. Recently, Akasaka et al. have reported that the ZT values are 0.65 at 840 K and 0.1 at 566 K for Bi- and Ag-doped Mg_2Si single crystals, respectively, synthesized by the vertical Bridgman growth method [12]. The Bridgman method is useful to prevent the evaporation of Mg near the melting point of Mg_2Si.

While the thermoelectric performance can be significantly improved with proper dopants, the thermoelectric properties at low temperatures even in pure Mg_2Si crystals have not been carefully reported so far. In this study, we focus on the correlation

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between the magnetic and thermoelectric properties by Mn substitution in Mg_2Si, which is more efficient at lower temperature, so that the low-temperature studies with single crystals are important. The Mn atoms in $Mg_{2-x}Mn_xSi$ have five 3d electrons, which are magnetic in nature. In the energy scheme, the half-filled 3d bands can not only affect the density of states at the Fermi level, which governs the electrical properties, but also change the spin states, which may be energetically more favorable. The main aim in this study is to find a correlation between the thermoelectric and magnetic properties by magnetic impurity doping at low temperatures. With increasing the Mn composition, both electrical conductivity and magnetization data are monotonically enhanced. It can be explained by an enhancement in the density of states, as the band overlap increases. Furthermore, we observe a sudden slope change in the Seebeck coefficient curve around 85 K, where the magnetic susceptibility shows a broad peak. This result proposes that the thermoelectric properties can be correlated with the magnetic properties via magnetic impurity doped bands.

2. Experimental procedure

Single crystals of $Mg_{2-x}Mn_xSi$ ($x = 0$, 0.1, 0.2, 0.3, 0.4) were grown by vertical Bridgman method. The starting elements of bulk Mg (99.9%), granular Si (99.999%), and bulk Mn (99.9%) were put into a Mo crucible with the stoichiometric amounts and the crucible was sealed by using arc melting under Ar atmosphere. Then, the crucible was heated up to 1100 °C for two days in a high-vacuum (2.0×10^{-6} Torr) Bridgman chamber with tungsten heater, and was cooled down to room temperature over one week as rotating at 5 rpm.

The crystal structure was analyzed by X-ray diffraction using a Rigaku DMAX 2500 diffractometer with CuKα radiation ($\lambda = 1.5406$ Å). The grown crystals were well cleaved and were cut into approximately $3 \times 3 \times 7$ mm^3 rectangular bar samples for the thermal and electronic transport measurements. Seebeck coefficient and thermal conductivity measurements were performed with a thermoelectric option in a Quantum Design physical property measurement system (PPMS). The Seebeck coefficient, thermal conductivity, and electrical conductivity were measured by conventional four-probe method, using silver paint or epoxy for the electrical contact. The error of each measurement was within 2%. The electronic transport properties were measured in a Gifford-McMahon (GM) refrigerator, and the magnetic properties were measured in a superconducting quantum measurement system-vibrating sample magnetometer (SQUID-VSM). The magnetic field was applied along the cleaved surface of the crystals.

3. Results and discussion

Fig. 1(a) and (b) show the single-crystal and powder X-ray diffraction (XRD) patterns of $Mg_{2-x}Mn_xSi$ ($x = 0$, 0.1, 0.2, 0.3, and 0.4) samples. The single-crystal XRD data were taken from a shiny and flat surface. The single-crystal diffraction peaks are well labeled with the (111) indices of the face-centered-cubic (fcc) CaF_2-type structure, where Si atoms occupy the corners and face-centered positions of the unit cell and Mg atoms occupy eight tetrahedral sites $\left(\pm\frac{1}{4}, \pm\frac{1}{4}, \pm\frac{1}{4}\right)a^3$. The high intensity of (111) peaks is known to stem from a cleavage characteristic of the anti-fluorite type structure of Mg_2Si [14]. In order to check the existence of secondary phases, we measured powder XRD patterns, which were obtained by grinding the single crystals. As shown in Fig. 1(b), the peak intensity of (111) is reduced and the (220) peak is enhanced. This result is consistent with the previous report that the area of the (111) plane decreases due to smaller grains [14]. The main diffraction peaks are indexed with the reported structure of Mg_2Si [12],

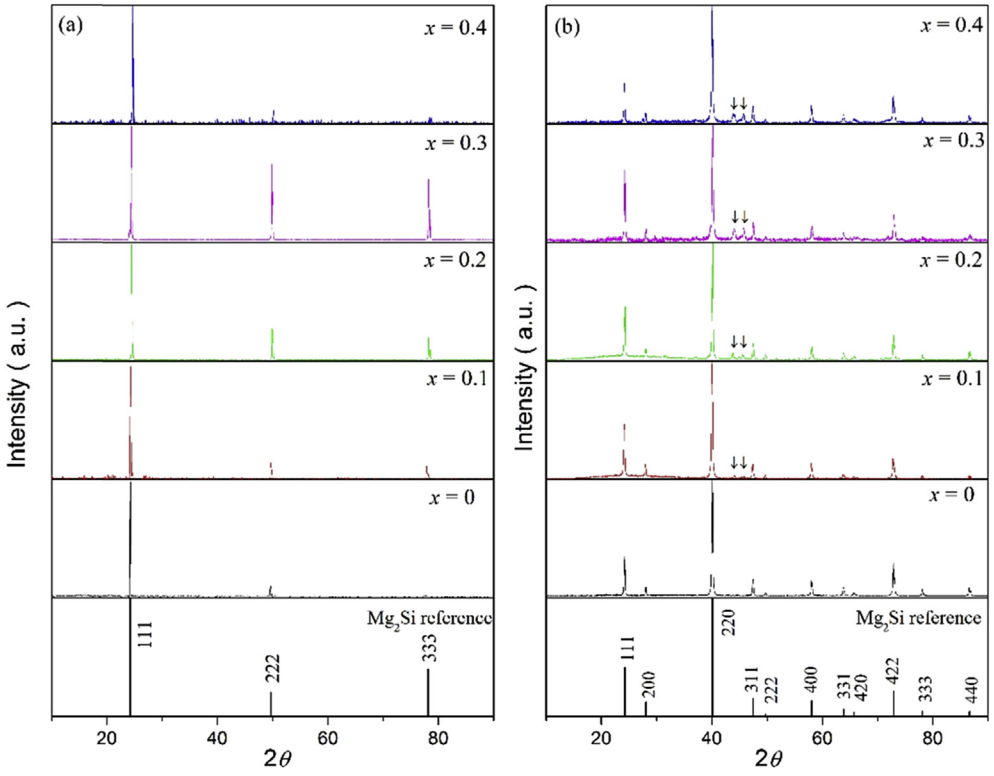

Fig. 1. (a) Single-crystal and (b) powder X-ray diffraction (XRD) patterns of $Mg_{2-x}Mn_xSi$ ($x = 0$, 0.1, 0.2, 0.3, 0.4). The reference data of Mg_2Si is plotted in the bottom panel.