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The effects of Ag nanoparticles on the thermoelectric properties of Ag_2Te-Ag composite fabricated using an energy-saving route

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ABSTRACT

We measure electricity consumption and thermoelectric property of Ag_2Te-Ag composites fabricated using green synthesis at room temperature followed by evacuated-and-encapsulated sintering at 500 °C for 10 h. As compared to Ag_2Te and Ag_2Te-Ag composites fabricated using other methods, we elucidate the effects of Ag nanoparticles on electronic transport of composites at temperatures between structural transition and 525 K based on the Matthiessen's rule and Kohler formula. We also present detailed methods of calculating the Lorenz number with single Kane band model and further deduce the lattice thermal conductivity. As a result, we find that electronic contribution dominates the temperature dependence of the total thermal conductivity of the composites. For energy consumption of heat treatment, the energy-saving approach in this study is only 15–18% of two typical procedures using melting process reported in the literature. If considering consolidation step reported in the literature, our procedure is more economic. We also demonstrate that the energy-saving route of fabricating the Ag_2Te-Ag composite leads to a zT value of 0.68 at 573 K, which is comparable to or even higher than that of Ag_2Te fabricated using high-energy consumption routes. It is more sensible for fabricating TE materials using less energy consumption.

1. Introduction

Clean energy supply continues to be the concerns in the 21st century for sustainable development of human well-being. Thermoelectric materials are green energy materials since they can be used to make thermoelectric modules for converting waste heat into electrical energy (Seebeck effect) or solid-state cooling applications (Peltier effect). However, thermoelectric sample is often fabricated at high temperatures, which consumes a lot of energy. Therefore, it would be desirable to develop methods of synthesizing thermoelectric materials with less energy consumption. The material synthesis pipeline includes the start materials, fabrication, heat treatment, and consolidation. In general, it is difficult to save energy on the start materials, because the information of producing consumption of start materials is not easy to get. However, using different method to reduce the consumption is available for fabrication, heat treatment, and consolidation. For example, replace the method of solid state reaction with wet chemical or hydrothermal for fabrication, sintering or annealing for shorter holding time or at lower temperature, using cold press or SPS (Spark Plasma Sintering) for consolidation. The difference of consumption may be negligible in laboratory, but it would be enlarge in a company. For mass production and commercialization of thermoelectric materials, energy-saving should be important and worth mentioned.

The efficiency of thermoelectric materials is determined by their dimensionless thermoelectric figure of merit, $zT = S^2\sigma T/\kappa$, where S, σ, T, and κ are the thermopower, the electrical conductivity, the absolute temperature, and the thermal conductivity respectively. The thermoelectric power factor is given as S^2/ρ, where S is the thermopower and ρ the electrical resistivity. The power factor indicates the ability of a thermoelectric material to produce useful electrical power under a given temperature difference. The size of power factor of thermoelectric materials is proportional to the weighted mobility, $U = \mu(m^*/m_e)^{3/2}$, where μ is the nondegenerate mobility of carriers and m^* the density-of-state effective mass. For a multi-valley band system, the m^* can be expressed as $N_v^{2/3}m_b^*$, where N_v is the number of valley and m_b^* the average band mass. Provided the carrier scattering is dominated by non-polar phonons, the nondegenerate mobility of carriers, would be proportional to

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$\left[\frac{1}{(m_b^*)^{\frac{3}{2}}}\right]\left(\frac{1}{m_c^*}\right)$, where m_c^* is the effective mass of the carriers along the conducting direction [1,2]. Therefore, the power factor is proportional to $N_v\left(\frac{1}{m_c^*}\right)$.

Ag_2Te exhibits polymorphism with its crystal structure stabilized in the different temperature regime [3]. Ag_2Te is a narrow-bandgap semiconductor exhibiting interesting properties such as topological surface states and ionic conduction [4,5]. The narrow bandgap is confirmed by our calculation in section 2.2 using full-potential linearized augmented plane wave in a framework of the density functional theory.

Based on the Hall and thermopower data, the estimated effective mass of Ag_2Te is very low [6]. Large thermoelectric power factors could be expected when using the relation between the power factor and the effective mass. However, it appears that various synthetic procedures results in distinct transport properties of Ag_2Te both in size and temperature dependence [7–17]. It is well known that the transport properties strongly depend on the fabrication details [18,19]. In this paper, we report the measurements and analyses of thermoelectric property of the Ag_2Te-Ag composite which is synthesized using one-pot aqueous synthesis at room temperature followed by evacuated-and-encapsulated sintering at 500 °C for 10 h. We adopt the single Kane band model to analyze the thermoelectric transport and give a detailed calculation of the Lorenz number, which is then used to derive the lattice thermal conductivity. As a result, we find that electronic contribution dominates the temperature dependence of the total thermal conductivity of the composite. With the energy-saving route of fabricating the Ag_2Te-Ag composite, a dimensionless figure of merit of $zT = 0.68$ is attained at 573 K. This value is comparable with the Ag_2Te fabricated using a complex high-energy consumption route, which consists of melting, sintering and hot pressing [13]. The energy consumption in this study is 15% of that used in the high-energy consumption routes without including the hot processing process.

2. Experimental procedure

The Ag_2Te-Ag composite was synthesized using a simple wet chemical method with reaction duration of 1 day at room temperature. The details of synthetic procedure and the formation mechanism have been discussed in the previous work [20].

Powder x-ray diffraction experiments were performed to check the phase purity of the samples. Microstructure characterization were performed using a JEOL JEM-2010 high-resolution transmission electron microscope (HRTEM) and a JEOL JSM-7800F Prime Schottky field emission scanning electron microscope (FE-SEM). For taking the HR-TEM micrograph, the samples were prepared by dispersing the powders of Ag_2Te-Ag composite in acetone with supersonic bath, and a drop of the composite solution is cast on carbon-coated copper grid. The electricity consumption was measured using a wattmeter which confirms to CNS 14607 (Chinese National Standards) with the uncertainty of ±0.3–0.4%.

For transport property measurements, the dried powders were cold pressed into a circular disk with diameter of 14 mm, followed by sintering at 500 °C for 10 h in an evacuated-and-encapsulated ampoule. Electronic and thermal transport properties were characterized on the same composite. Electrical resistivity and thermopower measurements were simultaneously carried out from 300 K to 573 K. Electrical resistivity measurements were carried out using standard four-probe techniques reversing the current sources to cancel extraneous voltages. Thermopower measurements were carried out using steady-state techniques. Thermal conductivity measurements were carried out using transient plane source techniques with very small temperature perturbations of the sample material by the Hot Disk thermal constants analyzer TPS 2500 S. Measurement details of the electrical resistivity, thermopower, and thermal conductivity were described elsewhere with the uncertainty of about ±3%, ±4%, and ±5% respectively [18,19].

3. Results and discussion

The powder x-ray diffraction patterns of as-synthesized and sintered Ag_2Te-Ag composite are shown in Fig. 1. The reflection peaks, which belong to monoclinic Ag_2Te, are labeled with their Miller indices, and those belonging to Ag are indicated by an asterisk. These results clearly indicate the formation of composite of monoclinic Ag_2Te and Ag [15]. The analytical results using Inductively Coupled Plasma-Mass spectrometry indicate that the weight percentage of Ag in the Ag_2Te matrix is 8.5%. The theoretical density of the Ag_2Te-Ag composite is estimated to be 8.780 gcm^{-3} by taking into account the weight percentage of Ag in the composite. The bulk density of 6.869 gcm^{-3} is determined using Archimedes' principle being 78.2% of the theoretical density (see Table 1). The FE-SEM image of Ag_2Te-Ag composite exhibits a morphology of chunks with porosity and silver particulates speckled on Ag_2Te grains (Fig. S1). The silver particulates arises from the reduction of $AgCl_2^-$ by the reductant $NaBH_4$. The HR-TEM micrographs shown in Fig. 2 indicate Ag nanograins grown beside Ag_2Te nanograins based on the estimation of the spacings of the HR-TEM fringes.

The electronic band structure calculation using full-potential linearized augmented plane wave (FP-LAPW) [21] in a framework of the density functional theory (DFT) is adopted to gain more insight about the distribution of the energy states especially in the vicinity of the Fermi level for the electronic structure of the monoclinic Ag_2Te system with space group $P2_1/c$ (No. 14). In this approach, the generalized gradient approximation (GGA) based on the parameterizations performed by Perdew-Burke-Ernzerhof (PBE) [22] has been used for the exchange correlation potential term implemented to the Kohn-Sham equation [21]. Furthermore, the energy value of −6.0 Ry is selected to separate valance states from the core states. To simplify the explanation of electronic

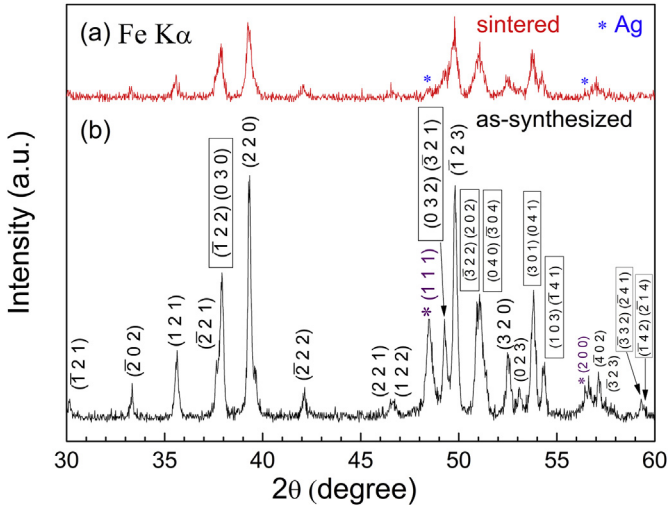

Fig. 1. Powder x-ray diffraction patterns of the Ag_2Te-Ag composite (a) sintered at 500 °C, and (b) as-synthesized. The symbol * indicates the (111) and (200) reflections of Ag.