RAPID COMMUNICATION

Study on thermoelectric performance by Na doping in nanostructured $Mg_{1-x}Na_xAg_{0.97}Sb_{0.99}$

Jing Shuai[a], Hee Seok Kim[a], Yucheng Lan[a], Shuo Chen[a], Yuan Liu[a], Huaizhou Zhao[a], Jiehe Sui[a,b,*], Zhifeng Ren[a,*]

[a]Department of Physics and TcSUH, University of Houston, Houston, TX 77204, USA
[b]National Key Laboratory for Precision Hot Processing of Metals and School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

Abstract

$MgAg_{0.97}Sb_{0.99}$ was found to be potentially a new class of thermoelectric materials with ZT values above 1 in the temperature from 100 to 300 °C. In this report, we systematically studied the effect of Na doping in Mg, $Mg_{1-x}Na_xAg_{0.97}Sb_{0.99}$, on the thermoelectric properties and found Na was effective to increase the carrier concentration and power factor, especially below 180 °C, which led to higher ZT values, a better self-compatibility factor, and ultimately a higher output power at the optimal Na concentration of $x=0.005$–0.0075.
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Introduction

Recent years have witnessed extensive studies on thermo-electric materials, which may play an important role in future energy conversion, production, management, and supply [1–5]. The efficiency of a thermoelectric material in a power generator or heat pump depends on the dimensionless thermoelectric figure of merit, ZT, defined as $ZT=(S^2\sigma/\kappa)T$, where S, σ, κ, and T are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively [6,7]. The numerator $S^2\sigma$ is called power factor (PF). Even though PF could be enhanced by engineering the electronic structure, and κ could be reduced by increasing the phonon scattering, it is very difficult to independently optimize them simultaneously since they are interrelated. The concept of "phonon-glass electron-crystal, PGEC" has been considered to be an effective way to decouple these interrelated quantities, but the experimental success is limited in only a few materials so far [8–10]. Recently, nanostructure approach was found to be the major technique for ZT enhancement by reducing the thermal conductivity and in some cases simultaneously improving the PF [11–14].

*Corresponding authors at: National Key Laboratory for Precision Hot Processing of Metals and School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China. Tel.: +1 713 743 8217; fax: +1 713 743 8201.
   E-mail addresses: suijiehe@hit.edu.cn (J. Sui),
zren@uh.edu (Z. Ren).

Several classes of materials currently under investigation including PbTe, PbSe, their doped compounds [15-18], skutterudites [19-21], metal oxides [22,23], and half Heuslers [24-29] are suitable for the intermediate temperature range (300-500 °C) and high temperature range (500-1000 °C). However, for applications below 300 °C, there is no other material than Bi_2Te_3 with ZT close to 1.4 [6,30,31] till recently when MgAgSb and its modified composition $MgAg_{0.97}Sb_{0.99}$ [32,33] were reported to have similar ZTs. $MgAg_{0.97}Sb_{0.99}$ exhibited ZT of $\sim$0.7 at room temperature and of 1.2 at 200 °C. A small amount of Ni has been used to alloy the Ag site and has resulted in enhancement of ZT to $\sim$1 at 50 °C and $\sim$1.4 at 180 °C. Herein, we report our effort on Na doping on Mg to make $Mg_{1-x}Na_xAg_{0.97}Sb_{0.99}$ with $x=0.005$, 0.0075, and 0.01. Na has been considered as an ideal hole dopant with little effect on the other physical properties in many materials [34,35]. It was found that the enhancement of thermoelectric properties mainly comes from the increased PF, leading to higher ZTs, better self-compatibility factors, and output power.

Experimental details

Synthesis process

Based on the undoped phase-pure composition $MgAg_{0.97}Sb_{0.99}$, we studied substitution of Mg by Na by the two-step process [33]. First, elemental magnesium metal pieces (Mg, Sigma Aldrich, 99.9% metal basis), silver metal pieces (Ag, Sigma Aldrich, 99.9% metal basis), and sodium (Na, Sigma Aldrich, 99.9% metal basis) were weighed according to the stoichiometry of $Mg_{1-x}Na_xAg_{0.97}Sb_{0.99}$ with $x=0$, 0.005, 0.0075, and 0.01 and loaded in a stainless steel jar with stainless steel balls for mechanical alloying by a high energy ball mill (SPEX 8000D) for 10 h. After this step, we added antimony chunks (Sb, Sigma Aldrich, 99.8% metal basis) into the jar to further milling for 8 h. The final nanopowders were then loaded into a graphite die with an inner diameter of 12.7 mm, and consolidated by direct current (DC) hot pressing at $\sim$300 °C for 5 min.

Characterizations

X-ray diffraction spectra were collected on a PANalytical multipurpose diffractometer with an X'celerator detector (PANalytical X'Pert Pro). The microstructures, examined on a freshly broken surface, were investigated by a scanning electron microscope (SEM, JEOL 6330 F). Transmission electron microscope (TEM, JEOL 2010 F) was used to explore the details of grain size. The electrical resistivity (ρ) and Seebeck coefficient (S) were measured using a four-point direct-current switching method and the static temperature difference method, respectively, both of which were conducted on a commercial system (ULVAC ZEM-3). The thermal conductivity was obtained by measuring the thermal diffusity (D) on a Nano flash apparatus (LFA 447, NETZSCH), specific heat (C_P) on a DSC (404 C, NETZSCH), and volumetric density (ρ_Δ) by Archimedes method. The Hall measurement at room temperature was measured using the Physical Properties Measurement System (PPMS D060, Quantum Design).
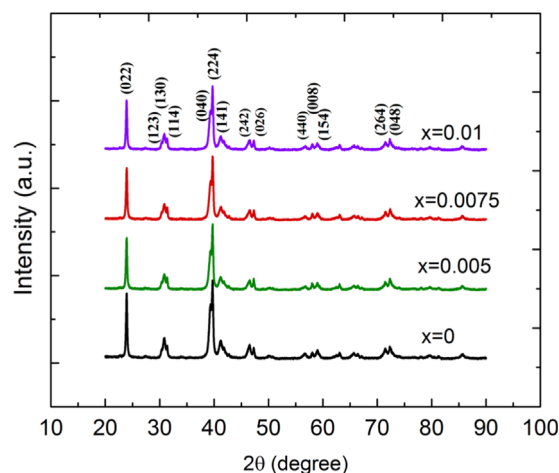

Fig. 1 XRD patterns of $Mg_{1-x}Na_xAg_{0.97}Sb_{0.99}$ ($x=0$, 0.005, 0.0075, and 0.01).

Results and discussion

Fig. 1 shows the XRD patterns of all samples. By comparing with the undoped pure phase $MgAg_{0.97}Sb_{0.99}$, no detectable impurity phases were found in $Mg_{1-x}Na_xAg_{0.97}Sb_{0.99}$ ($x=0.005$, 0.0075, and 0.01).

To study the influence of Na doping on the TE properties of the materials, samples with compositions $Mg_{1-x}Na_xAg_{0.97}Sb_{0.99}$ ($x=0$, 0.005, 0.0075, and 0.01) were prepared. As shown in Fig. 2(a), the electrical resistivity decreases with increasing Na content till $x=0.0075$, and the electrical resistivity of all the samples increases with temperature first to the maximum around 75-100 °C and then decreases. When the temperature is above 100 °C, the electrical resistivity decreases, which is consistent with the turning point in the Seebeck coefficient due to bipolar effect in Fig. 2 (b). Higher Na content leads to lower electrical resistivity due to the enhanced carrier concentration shown in Table 1. We compared the undoped sample with Na-doped samples of $x=0.005$, 0.0075, and 0.01, and found carrier concentration increases by 32.5%, 44.6%, and 43.2%, respectively. The carrier concentration (n_H) and Hall mobility (u_H), which are also shown in Table 1, affect the electrical resistivity (ρ) by the relationship $1/\rho = n_H e u_H$. Fig. 2(b) shows the temperature dependent Seebeck coefficient of all the Na doped samples. The Seebeck coefficient decreases with increasing Na content till $x=0.0075$, and increases with temperature from room temperature to 75-100 °C before decreases up to 275 °C. Combing the electrical resistivity and Seebeck coefficient, the PF of all Na doped samples are obtained as shown in Fig. 2(c). The increase in PF with temperature, especially below 100 °C, is pronounced as Na content increases. The highest PF among all the samples was found for $x=0.0075$. Na doping effectively optimizes carrier concentration and mobility, leading to lower electrical resistivity and the improvement of PF over the whole temperature range.

Fig. 3 shows the thermal transport properties of $Mg_{1-x}Na_xAg_{0.97}Sb_{0.99}$ with $x=0$, 0.005, 0.0075, and 0.01. Specific heat (C_P) of $MgAg_{0.97}Sb_{0.99}$, shown in Fig. 3(a), is used for all compositions since replacing a tiny amount of Mg by Na will not increase the C_p at all due to the fact that Na is next to Mg, and diffusivity (D) of all samples