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Thermoelectric performance of p-type $Nd_{1-x}In_xTe_3$ fabricated by high pressure sintering method

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ABSTRACT

Thermoelectric properties of $Nd_{1-x}In_xTe_3$ ($x = 0$, 0.01, 0.03, 0.05) fabricated by high pressure sintering method were investigated in the temperature range of 291 K–673 K. The results indicate that over 623 K –673 K, the thermal conductivity of moderately doped $Nd_{1-x}In_xTe_3$ ($x = 0.01$, 0.03 and 0.05) is 40%–50% lower than that of un-doped $NdTe_3$, which can be attributed to alloy scattering. Though the absolute values of the power factor are slightly reduced by the doping, the reduced thermal conductivity results in high values of *ZT* at 623 K. Specifically, the lightly In-doped compound $Nd_{0.99}In_{0.01}Te_3$ exhibits the best thermoelectric performance, with a figure of merit, *ZT*, of 0.18 at 623 K. This is almost a doubling of that of the un-doped $NdTe_3$ measured in this study, suggesting that the proper In-doping in $NdTe_3$ is a promising way to improve its thermoelectric performance.

1. Introduction

In the past two decades, the compelling need for more efficient and environmental friendly energy conversion technologies has driven an increasing interest in the field of thermoelectric (TE) materials. However, the low conversion efficiency of thermoelectric materials has limited their large-scale commercialization. The dimensionless figure of merit, *ZT*, ($=S^2\sigma TK^{-1}$, where *S*, σ, *T*, and *K*, are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively) represents the TE performance. Therefore, in order to improve the efficiency of TE devices, it is very important to search for materials with high *ZT* values [1–5]. Rare earth tellurides have great potential for high temperature TE energy conversion. It is theoretically expected that its $ZT_{max} = 13.5–14$ [6]. The mechanism of the electronic transport is that the 4f energy band can be located either in the valence band or in the conduction band. When the 4f energy band is resonant with the Fermi level, the density of states can be enhanced, which can in turn increase the Seebeck coefficient. Besides, the $R_{3-x}Te_4$ structure contains numerous cationic vacancies, which decreases the phonon thermal conductivity. Therefore, the thermoelectric properties of $R_{3-x}Te_4$ can be controlled by adjusting the composition, crystal structure and energy bands. Lanthanum telluride and other rare-earth chalcogenides of the Th_3P_4 structure type have been studied over the last several decades as potential high-temperature thermoelectric materials [7,8]. In the $La_{3-x}Te_4$ structure, where the distorted octahedron of lanthanum atoms create the six-fold lanthanum coordination around tellurium. Although the structure is shown with lanthanum at full occupancy, up to one-ninth of the lanthanum atoms can be vacant [9]. T. H. Ramsey found that p-type $LaTe_{1.8}$, which is a potential thermoelectric material, has a high Seebeck coefficient $|S| = 312$ μV/K at room temperature while it has a low electrical conductivity [10]. May et al. confirmed La_3Te_4 to be a good thermoelectric material and reported a $ZT = 1.1$ at 1275 K [9]. However, the TE properties of $NdTe_3$ (or the compounds with similar structure) have scarcely been investigated systematically. In order to study the TE performance of $NdTe_3$ as a p-type material, in addition to its electronic and phonon transport mechanisms, we introduced dopant In atoms as substitutes for Nd atoms in the matrix. Atom In ($5s^2p^1$) has less valence electron than atom Nd ($4f^46s^2$), therefore In doped in $Nd_{1-x}In_xTe_3$ as an acceptor, would contribute holes, and increases the electric conductivity of $NdTe_3$. Besides In doped in $Nd_{1-x}In_xTe_3$ will increase the alloy scattering on the carriers, which will decrease the thermal conductivity. We expected this approach could significantly increase the hole concentration and reduce thermal conductivity because atom In has less valence electrons than atom Nd and might decrease the thermal conductivity by introducing more alloy scattering to the carriers.

In this paper, we report the In-doped $NdTe_3$ series prepared by

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solid-state synthesis and high pressure sintering (HPS) method. Their thermoelectric properties were investigated in order to explore the effect of In atoms on the TE performance of $NdTe_3$.

2. Experiment details

Pure Nd (4 N), In and Te powders of 99.99% purity were used as starting materials. The Nd, In and Te were weighed out in appropriate atomic ratios, mixed in an agate mortar for 2 h, and reacted for 8 h in a vacuum atmosphere (10^{-3} torr)at 773 K. After being crushed, powdered and cold compacted, the alloy was sintered for 1 min under high pressure (6.0 GPa) in a cubic press at 773 K. The size of the sintered sample was $\Phi 16 \times 20$ mm. The electrical conductivity (σ) was measured by the standard four-probes method in the temperature range from 291 K to 673 K. The Seebeck coefficient (S) was measured concurrently when a temperature difference (5 K) was applied between two ends of the sample. The power factor (PF) was calculated by the formula: $PF = S^2\sigma$. The thermal diffusivity (λ) was measured in the temperatures ranging from 300 K to 673 K via the laser flash method (NETZSCH, LFA427, Germany); the specific heat (C_p) was measured using a thermal analyzing apparatus (DuPont 1090B, America); and the density (d) was measured via the Archimedes method. The thermal conductivity (K) was calculated from the density (d), specific heat (C_p) and thermal diffusivity (λ) using the relationship $K = \lambda C_p d$. The figure of merit, ZT, of the sample was calculated by substituting the measured data of S, σ and K at a given temperature into the formula: $ZT = S^2\sigma T/K$. The phase structure was determined by powder X-ray diffraction method (XRD, Rigaku D/MAX-2550P diffractometer, CuKα ($\lambda = 0.154056$ nm)). Accurate measurement of the lattice parameter was obtained through calibration with a silicon standard. The grain size and lattice distortion were estimated from the line broadening of the reflection peak with the instrumental broadening calibrated via the Hall method using a silicon standard. The morphology was analyzed by field-emission scanning electron microscopy (FEI Nova Nano SEM 450). Hall coefficient R_H measurements for $Nd_{1-x}In_xTe_3$ (x = 0, 0.01, 0.03, 0.05) at room temperature (PPMS-9T) were performed with applied magnetic field (H) up to 3 T. The Hall carrier concentration n and the Hall mobility μ_H were calculated from R_H based on the formulas $n = 1/(e{\cdot}R_H)$ and $\mu_H = R_H{\cdot}\sigma$, where e is the elementary electric charge. The dependences of the thermoelectric properties of the samples on the content of In were investigated.

3. Results and discussion

Fig. 1 shows the powder XRD patterns of the $Nd_{1-x}In_xTe_3$ ($x = 0$, 0.01, 0.03, 0.05) samples, in which almost all the main diffraction peaks correspond to the tetragonal $NdTe_3$ phase (PDF#19-0828) that belongs to the Th_3P_4 structure. There are also several peaks that correspond to the Te phase, which occurs in the In-doped compounds $Nd_{1-x}In_xTe_3$ (x = 0.01, 0.03, 0.05) as an impurity phase. It can be seen from Fig. 1 that the peak at $2\theta = 30°–33°$ splits into two when x = 0.01, 0.03, 0.05, which suggests that the $Nd_xIn_{1-x}Te_3$ decomposes into two phases. Of these two phases, one dissolves more In and has a larger cell size than the other. The values of the lattice parameters a and c for all samples have been calculated from XRD data through Rietveld refinement, as shown in Table 1. It can been seen that the lattice parameters a and c decrease with increasing content of In from $x = 0$ to $x = 0.05$ as the ionic radius of In^{3+} (0.81 Å) is less than that of Nd^{3+} (1.04 Å).. In addition, it can be observed from the XRD patterns that the ratio of the intensities of the (008) and (113) diffraction peaks for all samples is significantly larger than in the ICDD PDF#19-0829, indicating that all of the samples have a preferred orientation due to the high

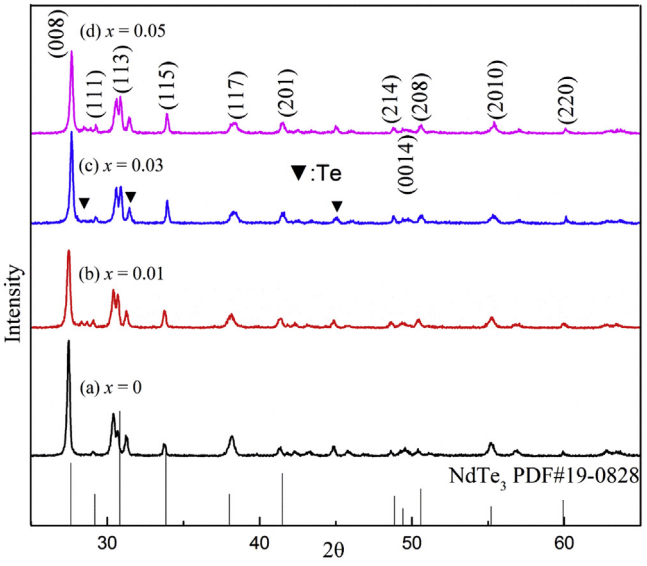

Fig. 1. Powder XRD patterns for the samples $Nd_{1-x}In_xTe_3$ (x = 0, 0.01, 0.03, 0.05).

Table 1
List of lattice parameters, preference factor and relative density for $Nd_{1-x}In_xTe_3$ (x = 0, 0.01, 0.03, 0.05) at room temperature.

	a(Å)	c(Å)	c/a	γ	Relative density
$NdTe_3$	4.342	25.732	5.926	0.26	97.3%
$Nd_{0.99}In_{0.01}Te_3$	4.327	25.723	5.944	0.24	98.1%
$Nd_{0.97}In_{0.03}Te_3$	4.318	25.715	5.955	0.21	97.6%
$Nd_{0.95}In_{0.05}Te_3$	4.301	25.702	5.975	0.23	98.7%

pressure sintering. Quantitatively, the preferred orientation can be described by an orientation factor, defined as $\gamma = (P–P_0)/(1–P_0)$, where P is the fractional intensity of the (00l) planes, P_0 is the value of P in the case of ideal isotropy and $P = \sum I(00l)/\sum I(hkl)$, where the sum is over all indices [10]. The calculated $\gamma = 0.21–0.26$ for the $Nd_{1-x}In_xTe_3$ samples of different In contents is shown in Table 1.

The typical SEM image for the sample $Nd_{0.99}In_{0.01}Te_3$ are shown in Fig. 2. The SEM images of other samples is similar to this sample. It demonstrates that the samples fabricated by HPS have a nanostructure whose grain sizes are about 80–100 nm, which is in agreement with the calculation results derived by the refinement, as shown in Table 1.

The temperature dependence of electrical conductivity σ,

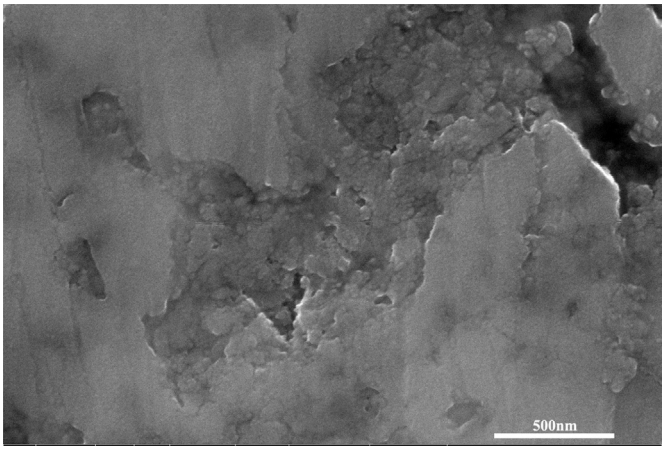

Fig. 2. FESEM images of being polished and eroded sample surface for the sample $Nd_{0.99}In_{0.01}Te_3$.