Synthesis and thermoelectric properties of polycrystalline Bi-Sb alloys

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Resumen

Se estudia el comportamiento de las propiedades termoeléctricas de compuestos policristalinos de $Bi_{0.88}Sb_{0.12}$ preparados por el método de reacción de estado sólido. Las propiedades eléctricas y térmicas se estudiaron a partir de mediciones de coeficiente Seebeck $S(T)$, resistividad eléctrica $\rho(T)$ y conductividad térmica $\kappa(T)$ en función de la temperatura, en el rango de temperatura entre 77 y 300K. A partir del estudio de las propiedades de transporte se determinó el factor de potencia PF y la figura de mérito adimensional ZT, las cuales alcanzan máximos valores cercanos a $20\mu W/K^2 - cm$ y 0.35, respectivamente. Adicionalmente, las propiedades morfológicas y estructurales se estudiaron a partir del análisis de microscopía electrónica de barrido y difracción de rayos-x.

Palabras claves: Materiales termoeléctricos, propiedades de transporte, Compuestos Bi-Sb, Figura de mérito.

Abstract

We have studied the behavior of thermoelectric properties of $Bi_{0.88}Sb_{0.12}$ polycrystalline samples grown by solid state reaction method. The electrical and thermal properties of the samples were obtained by Seebeck coefficient $S(T)$, electrical resistivity $\rho(T)$ and thermal conductivity $\kappa(T)$ measurements as a function of temperature, in the temperature range between 77 and 300K. From $S(T)$, $\rho(T)$

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and $\kappa(T)$ data it was possible to determine the thermoelectric power factor PF and the dimensionless figure of merit ZT, which reach maximum values close to $20\mu W/K^2 - cm$ and 0.35, respectively. Additionally, the structural and morphological properties of the samples were studied by powder x-ray diffraction analysis (XRD) and scanning electron microscopy (SEM), respectively.

Keywords: Thermoelectric materials, Transport properties, Bi-Sb Compounds, Figure of merit.

1 INTRODUCTION

Bismuth is a semimetal, it is attractive as thermoelectric material due to the anisotropy of its energy bands, the low effective mass and high mobility of its charge carriers. When it forms alloys with antimony ($Bi_{1-x}Sb_x$), it is possible to control the structure of its energy bands and in this way handle its transport properties[1, 2].

These alloys form substitutional solid solutions, where the bismuth is the solvent and antimony the solute. The antimony atoms placed in the bismuth cites act as a neutralizer of positive charges. Therefore, the transport properties of the material are given mainly by the negative charge carriers, improving in this way its thermoelectric properties.

For low antimony concentrations ($x \leq 0.07$), this alloy is a semimetal, in the region $0.07 < x \leq 0.22$, it behaves as a semiconductor and for highest antimony content, the solid solution adopts a semimetal behavior [3, 4, 5].

The thermoelectric quality of a material is given by its thermoelectric figure of merit Z, which is a direct function of its transport properties. In dimensionless form this performance parameter is given by the expression [6, 7]:

$$ZT = \frac{S^2 T}{\rho\kappa} \tag{1}$$

where S is the Seebeck coefficient, ρ the electrical resistivity, κ the total thermal conductivity and T the absolute temperature.

The challenge of the research on thermoelectric materials is to find materials with high ZT values, which, according to the equation 1, can be getting by the reduction of thermal conductivity or by increasing the thermoelectric power factor. This is a perfomance parameter that determines the electrical properties of a thermoelectric material; which is defined by the expression[6, 7, 8]:

$$PF = \frac{S^2}{\rho} \tag{2}$$

Below room temperature the best thermoelectric material are single-crystal Bi-Sb alloys. However, in order to be used in real thermoelectric devices their poor mechanical properties need to be improved. In this sense, in this work we study the thermoelectric and transport properties of polycrystalline Bi-Sb samples grown by solid state reaction method. This is a simple method, which allows obtain polycrystalline samples of suitable size and additionally, their grain structure can improve the thermal properties because of the grain frontiers behave as effective phonon scattering centers.

2 EXPERIMENTAL

Samples with a nominal composition $Bi_{0.88}Sb_{0.12}$, were prepared by solid state reaction method, from a stoichiometric mixture of high purity Bi and Sb powders (Merck 99.999%). The annealing processes were carried out under a vacuum atmosphere at 250^0C, where the processing time took values from 5 to 50 hours.

The thermal conductivity data were obtained by using the stationary longitudinal heat flow method [9]. Assuming stationary conditions and a linear response, the thermal conductivity was calculated from the Fourier law, which is expressed as [9, 10]:

$$\kappa(T) = \frac{\dot{Q}l}{\rho A \Delta T} \tag{3}$$

where $\dot{Q}$ is the heat flow rate across the sample, l the length between differential thermocouple junctions, A the transversal section of the sample and ΔT the generated temperature difference. The accuracy of the thermal conductivity data was about $0.2W/K - m$.

TABLE 1. Lattice parameters of $Bi_{0.88}Sb_{0.12}$ alloys grown by solid state sintering method.

Sample	a=b (Å)	c (Å)
5Hrs	4.532(1)	11.840(2)
20Hrs	4.545(2)	11.850(2)
40Hrs	5.534(1)	11.831(1)
50Hrs	4.543(3)	11.842(1)

The Seebeck coefficient was measured by differential technique [11], with an accuracy about $0.5\mu V/K$ throughout the studied temperature range. The electrical resistivity data were obtained by using the standard DC four probe method.

Additionally, the structural and morphological properties of the samples were studied by powder x-ray diffraction analysis (XRD) and scanning electron microscopy (SEM), respectively.

3 RESULTS AND DISCUSSION

The x-ray diffraction analysis showed the samples are a semiconducting solid solution of $Bi_{0.88}Sb_{0.12}$, with a rhombohedral (hexagonal) crystalline structure, which coexist with residual Bi pure phases. The obtained lattice parameters do not change significantly with the annealing time (see Table 1).

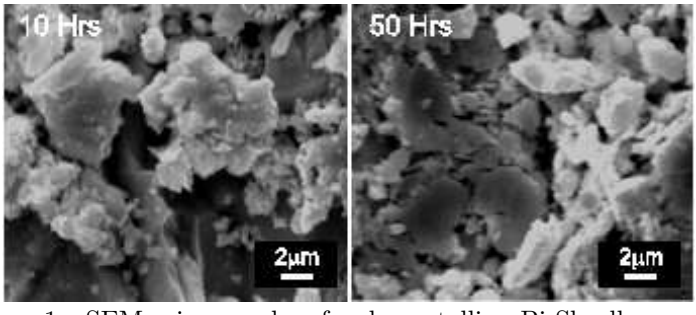

FIGURE 1. SEM micrographs of polycrystalline Bi-Sb alloys grown by solid state reaction method.

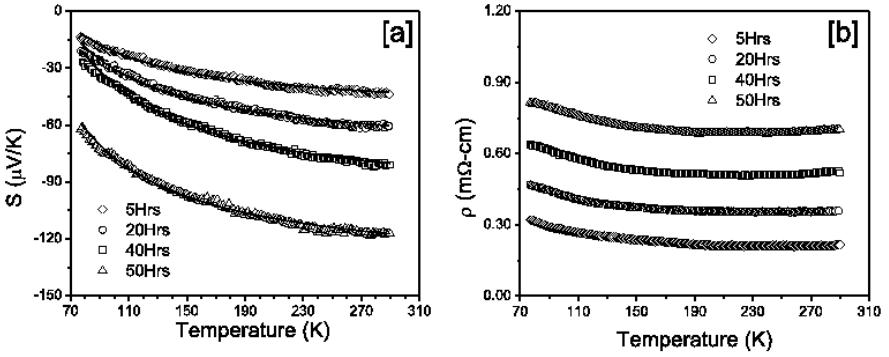

FIGURE 2. [a] Seebeck coefficient as a function of temperature, the solid lines are the best fit of experimental data to $S(T) = \frac{\kappa_B}{e}\left(\frac{E_C-\xi_F}{\kappa_B T} + B\right)$ model. [b] Temperature dependence of electrical resistivity as a function of temperature and the processing time.

SEM analysis show that both the grain structure and the homogeneity of the system increase with the processing time (see Figure 1).

The Seebeck coefficient is negative throughout the studied temperature range (see Figure 2a), indicating a n-type conduction. Its magnitude increases with the processing time, at room temperature, it takes values from $-45\,\mu V/K$ to $-120\,\mu V/K$, which are typical values of these narrow energy gap semiconductors[6].

For nondegenerate intrinsic semiconductor, assuming the contributing bands are parabolic with the same density of states and that the carriers are scattered primarily by acoustic phonons the Seebeck coefficient can be written as:

$$S(T) = \frac{\kappa_B}{e}\left(\frac{E_C - \xi_F}{\kappa_B T} + B\right) \tag{4}$$

where E_C, ξ_F, e, B, κ_B and T are conduction band edge, Fermi energy, electronic charge, scattering parameter, Boltzmann constant and the absolute temperature, respectively.
The term $E_C - \xi_F$ can be expressed as [3]:

$$E_C - \xi_F = \frac{1}{2}(E_{g0} - AT) \tag{5}$$

where E_{g0} is the band gap at 0K and A is a constant.

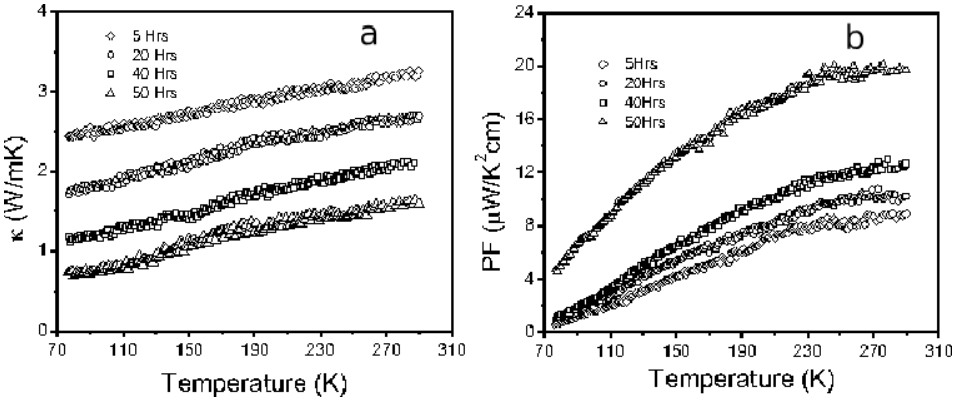

FIGURE 3. [a] Temperature behavior of total thermal conductivity for $Bi_{0.88}Sb_{0.12}$ alloys and [b]Thermoelectric power factor, PF ($PF = S^2/\rho$) as a function of temperature and the annealing time.

By fitting Seebeck coefficient experimental data to the equation 4 (see solid lines in Figure 2a), the least-squares fit yields the $E_C - \xi_F$ and B parameters. From equation 5 and the obtained $E_C - \xi_F$ parameter, the band gap was derived. Which increases with the processing time (see Table 2) from $6.5\,meV$ to $13.2\,meV$. The behavior of E_{g0} suggest that the samples are changing from semimetal to semiconductor as the thermal process increases.
On the other hand, the scattering parameter (B) increases with the annealing time, which have effects on the thermal properties of the samples.

The temperature dependence of electrical resistivity (see Figure 2b) shows a weak semiconducting behavior, its magnitude increases with the processing time, however in all cases $\rho(T)$ is less than $0.90\,m\Omega cm$.

The thermal conductivity shows a linear temperature behavior (see Figure 3a), its magnitude decreases with the processing time up to reach values close to $0.7\,W/K-m$. The behavior of $\kappa(T)$ suggest that the electronic and phononic structures are being changed as the alloying process take place in the samples. The reduction in $\kappa(T)$ with the processing time can be due to the increase in the grain

TABLE 2. Gap energy and scattering parameter obtained from fitting S(T) data to equations 4 and 5.

Sample	E_{g0}(meV)	B
5Hrs	6.5(1)	0.63(1)
20Hrs	9.1(2)	0.88(1)
40Hrs	12.5(2)	1.12(2)
50Hrs	13.2(3)	1.61(1)

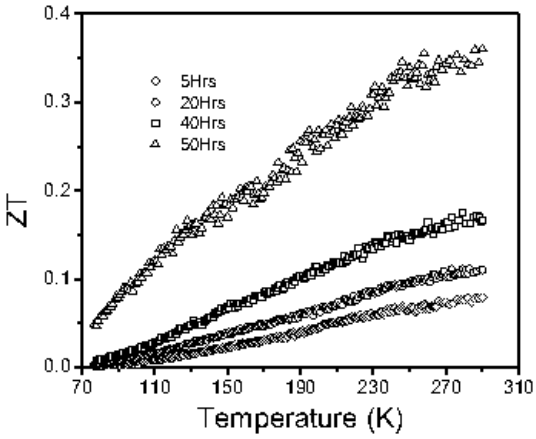

FIGURE 4. Temperature dependence of thermoelectric figure of merit ($ZT = S^2/\rho\kappa$) for different $Bi_{1-x}Sb_x$ alloys grown by solid state reaction method.

structure of the system (see Figure 1) which reduces the thermal flow transported by lattice vibrations.

The reduction observed in $\kappa(T)$ and the increase of $S(T)$ with the annealing time yield an important improvement of the thermoelectric properties (equation 1) of these polycrystalline compounds.

Furthermore, the temperature behavior observed in $S(T)$, $\rho(T)$ and $\kappa(T)$, make evident the effects of the replacement of bismuth by antimony atoms on the Fermi surface and the density of states of these alloys [12].

The Figure 3b shows the temperature behavior of thermoelec-

tric power factor (equation 2), which is given by both the electron (hole) effective mass and the carriers mobility, for the different studied samples. It increases with annealing time up to reach values close to $20\,\mu V/K^2 - cm$, in the temperature range between 230 and 290K. These values observed in PF are comparable to those of conventional thermoelectric materials.

On the other hand, from $S(T)$, $\rho(T)$ and $\kappa(T)$ data it was possible to calculate the dimensionless thermoelectric figure of merit, ZT (see Figure 4). Which shows a linear temperature behavior its magnitude increases with the processing time, reaching maximum values close to 0.35 at temperatures close to room temperature, in the case of the samples processed during 50 hours, these values are comparable with those exhibit by the same compounds prepared in single-crystal form and other conventional thermoelectric materials[6, 7].

4 CONCLUSIONS

By using the solid state reaction method it was possible to grow polycrystalline alloys with a nominal composition of $Bi_{0.88}Sb_{0.12}$. The x-ray diffraction analysis showed the presence of solid solution which coexist with pure Bi phases. From Seebeck coefficient, electrical resistivity and thermal conductivity measurements it was possible to calculate the thermoelectric power factor and the dimensionless figure of merit reaching maximum values near to $20\,\mu W/K^2 - cm$ and 0.35, respectively. These values are comparable with those exhibit for the same compounds grown in single-crystal form, suggesting that these kind of alloys can be prepared by this simple and inexpensive method. Furthermore, the phonon scattering generated by the grain structure increases the thermoelectric properties of these compounds.

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