PHYSICS

TRANSPORT PROPERTIES OF HOT PRESSED $\beta - Zn_4Sb_3$ COMPOUNDS

PROPIEDADES DE TRANSPORTE DE COMPUESTOS $\beta - Zn_4Sb_3$ PREPARADOS POR EL MÉTODO DE PRENSADO EN CALIENTE

Mónica Morales*, Jorge I. Villa*, Julio E. Rodríguez*

Abstract

Morales, M., J. I. Villa, J. E. Rodríguez: Transport properties of hot pressed $\beta - Zn_4Sb_3$ compounds. Rev. Acad. Colomb. Cienc., 37 (1): 31-35, 2013. ISSN 0370-3908.

Single phase $\beta - Zn_4Sb_3$ samples were prepared by using hot pressing method. Their structural and morphological properties were studied by x-ray diffraction analysis (XRD) and Scanning Electron Microscopy (SEM), respectively. The transport properties were obtained from Seebeck coefficient $S(T)$ and electrical resistivity $\rho(T)$ measurements between 100 and 290K. $S(T)$ shows positive values suggesting a p-type material, its magnitude increases with the processing time, reaching maximum values close to $270\mu V/K$. The electrical resistivity measured by four D.C. probe method, increases with processing time, however its magnitude is less than $9m\Omega - cm$. We observe an order-disorder transition in the transport properties around 240K, which is a characteristic property of pure single crystals of $\beta - Zn_4Sb_3$. From $S(T)$ and $\rho(T)$ experimental data we calculate the thermoelectric power factor PF , this performance parameter reaches maximum values close to $10\mu W/K^2 - cm$, which makes this kind of compounds promising materials for thermoelectric applications.

Keywords: Zn_4Sb_3 compounds, Thermoelectric materials, Hot pressing method.

Resumen

Muestras monofásicas de $\beta - Zn_4Sb_3$ fueron preparadas por el método de prensado en caliente. Sus propiedades estructurales y morfológicas se estudiaron mediante análisis de difracción de rayos-X (DRX) y microscopía electónica de barrido (SEM), respectivamente. Las propiedades de transporte se estudiaron a partir de mediciones de coeficiente Seebeck S(T) y resistividad eléctrica $\rho(T)$, en el rango de temperatura entre 100K y 290K. S(T) muestra valores positivos sugiriendo un material tipo-p, su magnitud se incrementa con el tiempo de procesamiento alcanzando valores máximos cercanos a $270\mu V/K$. La resistividad eléctrica se incrementó con el tiempo de procesamiento. Sin embargo su magnitud fue en todos los casos menor que $9m\Omega - cm$. En las propiedades de transporte se observó una transición del tipo orden-desorden a temperaturas cercanas a 240 K, esto es una característica típica de materiales monocristalinos de $\beta - Zn_4Sb_3$. A partir de los datos experimentales de $S(T)$ y $\rho(T)$ se calculó el factor de potencia termoeléctrico PF, Este parámetro de rendimiento alcanzó valores máximos cercanos a

* Departamento de Física, Universidad Nacional de Colombia, Bogotá.

$10\mu W/K^2 - cm$, lo cual convierte esta clase de compuestos en materiales prometedores para aplicaciones termoeléctricas.

Palabras clave: Compuestos de Zn_4Sb_3, Materiales termoeléctricos, Método de prensado en caliente.

1 Introduction

Over the past years, much interest has been focused on the search for new thermoelectric materials driven by the need for more efficient materials for electronic refrigeration and power generation [1, 2].

Efficient thermoelectric devices require the development of new materials that combine high thermoelectric performance, low cost and high chemical stability. The thermoelectric performance is characterized by the figure of merit, ZT. This parameter is a direct function of the transport properties and is given by the expression [3, 4]: $ZT = S^2T/\rho\kappa$, where κ is the total thermal conductivity, S the Seebeck coefficient, ρ the electrical resistivity and T the absolute temperature.
The Zn_4Sb_3 compound is a promising thermoelectric material due to its high figure of merit values, which is a result of its particular low thermal conductivity and high Seebeck coefficient values [4, 5, 6].
For Zn_4Sb_3 compounds three structural modifications are known: $\alpha-$, $\beta-$ and $\gamma - Zn_4Sb_3$ which are stable below $263K$, between $263K$ and $765K$ and above $765K$, respectively. Due to it, the production of single phase Zn_4Sb_3 samples involves complicated processes[7, 8].

In this work we report on the study of transport and thermoelectric properties of $\beta - Zn_4Sb_3$ compounds prepared by hot pressing method.

2 Experimental

From high purity zinc and antimony powders (Merck 9.999%), the hot pressing method was used to prepare $\beta - Zn_4Sb_3$ samples. These components were thoroughly mixed in a ball mill during 40 hours, then the mixture was heated for 5 hours at 300^oC, 400^oC and 450^oC, under a pressure of $50MPa$.
Electrical resistivity and Seebeck coefficient data were obtained by using the standard D.C. four-probe method and the differential technique, respectively. Additionally, the structural and morphological properties of the samples where studied by XRD and SEM analysis, respectively.

3 Results

Morphological properties of the studied samples can be seen in the Fig. 1, it is possible to observe samples highly dense, with compact grains without a defined shape and size.

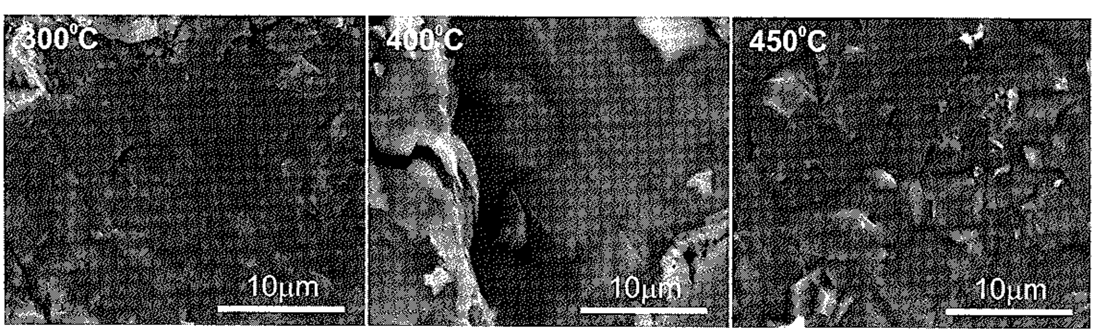

Figure 1: SEM micrographs of Zn_4Sb_3 polycrystalline samples grown by hot pressing method.

The x-ray diffraction analysis shows samples with $\beta-Zn_4Sb_3$ phase which has a rhombohedral (Hex.) crystal structure, of space group $R\bar{3}c$ and unit cell dimensions $a = b = 12.237(4)\AA$, $c = 12.446(5)\AA$ and $\gamma = 120.8^0$. Small quantities $ZnZb$ have been observed in the samples, which decreases with the processing temperature (see Fig. 2).

The behavior of electrical resistivity of Zn_4Sb_3 compounds corresponds to that of poor metals or heavily doped semiconductors [9]. The magnitude of $\rho(T)$ increases with the temperature and the annealing temperature (see Fig. 3a). $\rho(T)$ shows maximum values close to $9m\Omega - cm$ in the case of the sample annealed at 450^0C.

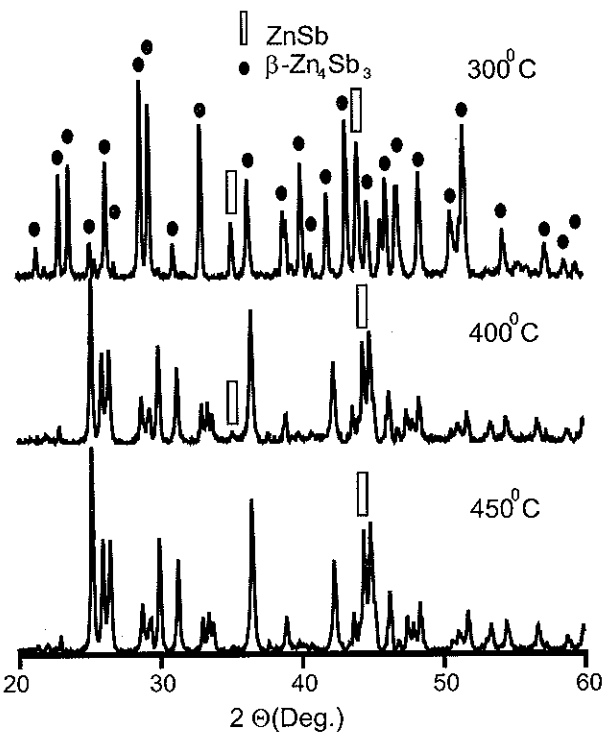

Figure 2: Room temperature powder x-ray diffraction patterns of Zn_4Sb_3 samples.

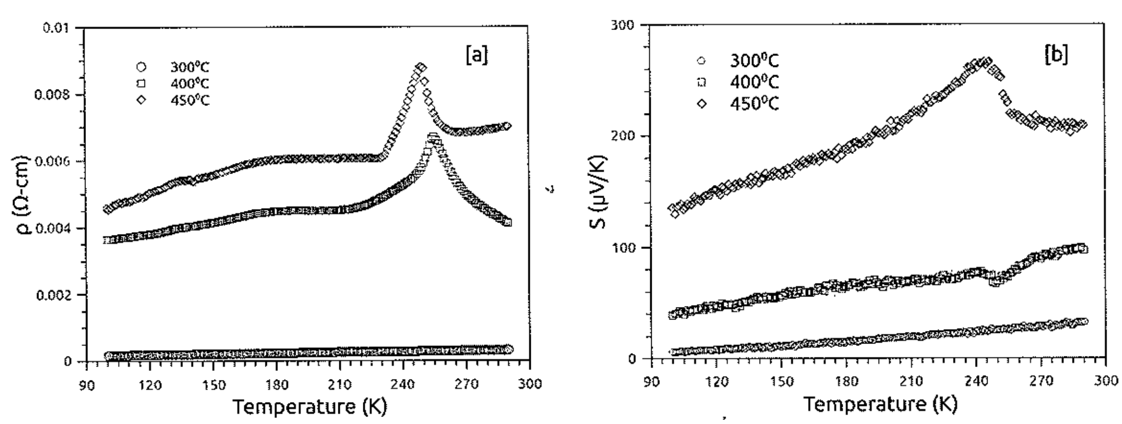

Figure 3: Temperature and annealing time dependence of electrical resistivity [a] and Seebeck coefficient[b] of polycrystalline Zn_4Sb_3 samples.

Figure 3b shows the temperature behavior of Seebeck coefficient. $S(T)$ is positive throughout the studied temperature range indicating a p-type conduction. The magnitude of $S(T)$ increases with the temperature reaching maximum values close to $270\mu V/K$.

Electrical resistivity and Seebeck coefficient show pronounced discontinuities between 235 and 255K, where the room temperature stable, disordered $\beta - Zn_4Sb_3$ goes to higher ordered $\alpha - Zn_4Sb_3$ phase. The β to α phase transition is given by the slight Zn deficiency of Zn_4Sb_3 with respect to its ideal crystallographic composition $Zn_{13}Sb_{10}$. It is important to note that the magnitude of this transition increases with the temperature of processing, that makes evident the increase of the quality of the samples [10, 11].

Good thermoelectric materials are those that exhibit high values of electrical conductivity and Seebeck coefficient and low thermal conductivity. The electrical properties of a thermoelectric material are evaluated through the thermoelectric Power Factor, PF. It is a function of the mobility and the effective mass of the electrical carriers. PF is expressed as [1] $PF = S^2/\rho$, where S is the Seebeck coefficient and ρ the electrical resistivity. From Seebeck coefficient and electrical resistivity experimental data the thermoelectric power factor was calculated. PF increases with the temperature, reaching maximum values close to $10\mu W/K^2 - cm$, for the sample annealed during five hours at 450^0C. The values of PF exhibited by these samples suggest that Zn_4Sb_3 compounds can be prepared by using the hot pressing method. This method avoids both the oxidation and the segregation of Zn and Sb, which are serious problems in the preparation of this kind of compounds.

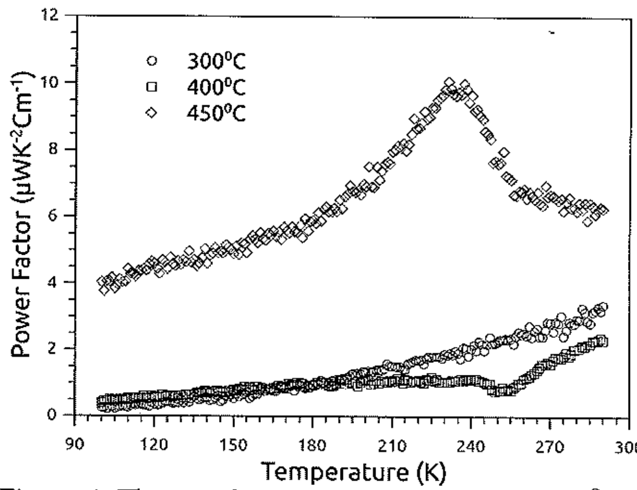

Figure 4. Thermoelectric power factor ($PF = S^2/\rho$) as a function of temperature of Zn_4Sb_3 samples.

4 Conclusions

By using the hot pressing method was possible to prepare single phase $\beta - Zn_4Sb_3$ samples. It, in all the studied samples, exhibit high Seebeck coefficient values and an electrical resistivity with maximum values less than $9m\Omega - cm$. From Seebeck coefficient and electrical resistivity was possible to calculate the thermoelectric Power Factor it in the case of the samples prepared at 450^0C, during 5 hours, reaches maximum values close to $10\mu W/K^2 - cm$.

An order-disorder transition was observed in the transport properties close to $240K$, which is associated with a reduction of symmetry between β- and α-Zn_4Sb_3 phases. This transition is a typical feature observed in pure single crystals $\beta - Zn_4Sb_3$ samples.

Acknowledgements

The authors would like to thank to "*La División de investigación de la Universidad Nacional de Colombia,* DIB" for the financial support.

References

[1] Rowe D. M. *CRC Handbook of thermoelectrics* (ed.D.M. Rowe), Boca Raton, CRC Press, 1995.

[2] Mahan G., Sales B. and Sharp J., *Physics Today* **50**, 42 (1997).

[3] Nolas G.S., Sharp J., Goldsmid H. J.,*Thermoelectrics, Basic principles and new materials developments*, Springer-Verlag, Berlin, 2001.

[4] Venkatasubramanian R., Siivola E., Colpitts T., O'Quinn B., *Nature*, **413**, 597 (2001).

[5] Chen G., Dresselhaus M.S., Dresselhaus G., Fleuriar J.P. and Caillat T., *Inter. Mater. Rev.*, **48**, 45-66(2003).

[6] Izard V., Record M.C., Tedenac J.C. and Fries S.G., *Calphad*, **25**, 567-581 (2001).

[7] Caillat T., Fleurial T. J., Borshchevsky A., *J. Phys. Chem. Solids*, **58**, 1119-1125 (1997).

[8] Ur S., Nash P. and Kim I., *J. Alloys Compd.*, **361**, 84-91 (2003).

[9] Wu Y., Nylen J., Naseyowma C., Garcia-Garcia F. and Haussermann U., *Chem. Mater.* **21** 151-155(2009).

[10] Bhattacharya S., Hermann R.P., Keppens V., Tritt T. M. and Snyder G. J., *Phys. Rev.B* **74**,134108 (2006).

[11] Souma T., Nakamoto G. and M. Kurisu, *J.Alloys Compd.*, **340**, 275-280 (2002).