

THERMAL BEHAVIOR REGARDING THE THERMOELECTRIC Zn_4Sb_3 OBTAINED BY MELTING AND QUENCHING METHOD

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ABSTRACT: The present paper is focused on studying the thermal behaviour of the Zn_4Sb_3 material. The thermal behavior of Zn_4Sb_3 was investigated using differential thermal analysis which was taken on the temperature range 300 -1073K. The melting point and the solidification temperature of Zn_4Sb_3 were determined. Also, a characterization of the Zn_4Sb_3 material from an electrical point of view was done. It was shown the semiconducting behavior of the material as a function of temperature, and also as function of material electrical resistivity and electrical conductivity. Also, the optical and the electrical band gap were estimated.
KEYWORDS: zinc, antimony, melting, thermoelectric materials, differential thermal analysis, electrical

1. INTRODUCTION

A lot of attention has been focused on the thermoelectric materials in the last decades and lots of researches were dedicated to these for improving their properties and also the mechanical and thermal stability to be more attractive to be used in applications and to replace other types or materials (environmentally non-friendly or expensive). Thermoelectric materials have the property of converting wasted thermalenergy into electrical energy. The efficiency of a thermoelectric material for applications is given by the dimensionless figure of merit (ZT):

$$ZT=\alpha^2\sigma T/k \quad (1)$$

where α is the Seebeck coefficient, σ the electrical conductivity, ($\sigma = 1 / \rho$, ρ is the electrical resistivity) and k the total thermal conductivity [1], which means that a good thermoelectric material requires a high thermopower combined with a low electrical resistivity and a low thermal conductivity.

At first, semiconductors have been the materials of choice for the thermoelectric applications. Zn_4Sb_3, thermoelectric material, due to its excellent low thermal conductivity, represents a more environmental friendly material than the oldest categories of other thermoelectric materials which some were more toxic (e.g. PbTe, Bi_2Te_3), and also the obtaining cost for Zn_4Sb_3 are not so high. Using different approaches, experimentally and also theoretically, this material was intensively studied in the last decades for obtaining maximum performance in converting heat into energy [1-10].

For Zn_4Sb_3, three phases are known: α – stable below 263 K, β – stable between 263 and 765 K and γ which is stable above 765 K, respectively [1]. The studies revealed that β-Zn_4Sb_3 is expected to manifest metallic properties and thatthis phase is characterized by the deficiency of zinc atoms [11]. Mikhayluskin and Kim reportedalso that the disordered zinc atoms play the role of electron donors and their concentration determines the gap opening at the Fermi level to give rise to the p-type conduction[12, 13].

Also, the researchers present Zn_4Sb_3 as an excellent thermoelectric material, but with a low mechanical and thermal stability. It was concluded that the low thermal stability of Zn_4Sb_3 is due to the fact that often can appear a decomposition of the material below the expected range of temperature and that an appropriate method of synthesis (e.g. zone-melting technique) which may reduce the decomposition should be used [4, 8, 10, 14, 15]

In the present paper are presented results regarding the investigations of Zn_4Sb_3 using the differential thermal analysis and the temperature dependence for the measured and determined electrical parameters which characterize the material. Based on obtained experimental data we estimated the optical and also electrical band gap.

2. EXPERIMENTAL

2.1. Sample preparation

Zn_4Sb_3, thermoelectric material, was obtained by direct melting of high purity precursors. Zn and Sb, weighted in a stoichiometric ratio 4:3 which were sealed in an evacuated quartz ampoule and placed into an oven and kept at 1173K- isothermally for 24 hours as it was reported in a previous work [16].

2.2. Characterization techniques

Differential thermal analysis (DTA) was performed for obtained Zn_4Sb_3 material.A quantity about 67 mg Zn_4Sb_3 powder sample was placed in an Al_2O_3 crucible and Ar was used as the purge gas at a rate of 20 mL min^{-1}. The analysis was performed by a thermogravimetric analyzer:LABSYS Evo operating at temperatures range from room temperature to 1073K,both heating and cooling rates being $293Kmin^{-1}$, in order to evaluate the thermal stability.

The optical band gap (E_G) of the Zn_4Sb_3 material was estimated by recording the diffuse reflectance spectrum at room temperature, using a UV-VIS-NIR spectrometer Lambda 950 in the wavelength range of 240-400 nm.

For temperature dependence determination of the electrical parameters, the grounded powder mixture was used to form pellets at room temperature, with 12 mm diameter and 4 mm thickness, using a uniaxial press under about 300 MPa.On these pellets, using electrochemical methods, some deposition of copper were made to realize best contacts for measurements.

The electrical resistance (R) as a function of the temperature was measured by *the four-point probe method* in an oven in which the temperature was adjusted using an autotransformer. The range of the temperature in which the measurements were conducted is from the room temperature to 700K. The used intensity of the current was 100mA.

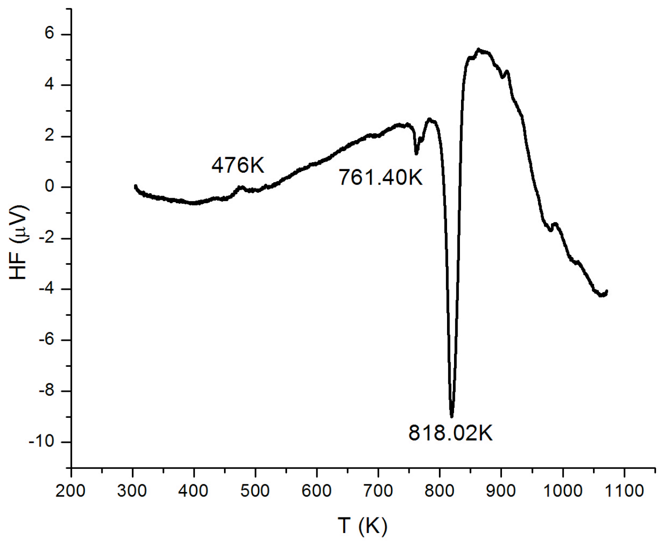
After the electrical measurements, X-ray diffraction (XRD) experiment was performed on the analyzed samples using a X'pert Pro MPD X-ray diffractometer, with monochromatic Cu Kα (λ = 1.5418 Å) incidentradiation.

3. RESULTS AND DISCUSSIONS

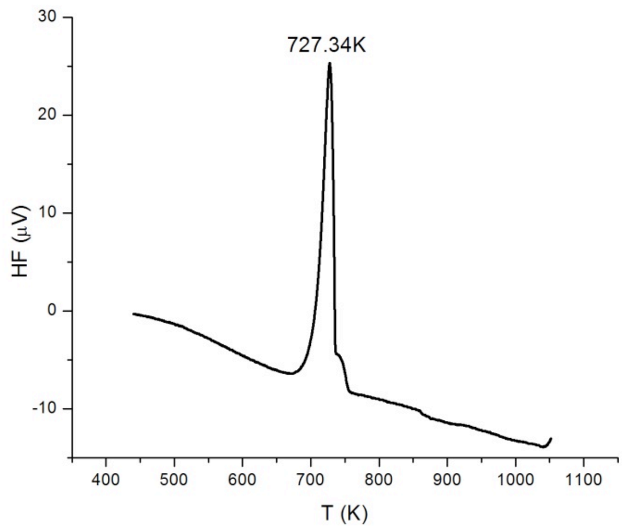
From the differential thermal analysis were associated the thermal reactions with the linear temperature between the room temperature and 1073K. The heat flows (HF) (on heating and cooling) were presented in figure 1(a) and (b). From figure 1(a) it can be seen that on heating, some endothermic peaks appear at 476K, 761.40K and at 818.02K. At 476K, the peak corresponds to the melting of the eutectic Zn-Sb compound. The peak from 761.40K can be associated to the transformation of β phase to γ phase and the peak from 818.02K represent the melting point of the Zn_4Sb_3 sample.

In figure 1(b), in the cooling process, an exothermic peak appears at about 727.34 K, indicating that the solidification process started.

The UV-VIS absorption spectrum recorded for prepared Zn_4Sb_3 is presented in figure 2. The maximum absorption is observed to be occurring at 283 nm for the spectrum recorded between 240 and 400 nm. $\{(k/s)h\upsilon\}^2$ vs. hν was plotted (inset), where *k* denotes the absorption coefficient, *s* is the scattering coefficient and *hυ*represents the photon energy. Using the Kubelka-Munk equations [17, 18], the optical band gap (E_G) for the analyzed material was estimated: E_G = 3.99 eV.



(a)



(b)

Figure 1. DTA curves for the (a) heating and (b) cooling cycle

Also, was studied the influence of temperature on the electrical parameters of elaborated Zn_4Sb_3sample. Using the data obtained from the electrical measurements regarding the electrical resistance and inserting these in the following equation, the electrical resistivity was determined:

$$\rho = RA/L \qquad (2)$$

where *L*represents the length and *A* represent the section of the sample.

In figure 3 is presented the electrical resistivity dependence of temperaturefor Zn_4Sb_3.It can be observed that the electrical resistivity of the sample is decreasing with temperature.

The decreasing is accentuated in the range 460-540K where is a high speed decreasing of ρ, reproduced decreasing being observed on the cooling process too. Anh *et al.* [19] obtained a similar behavior in the same range of temperature in several cases when it was applied hydrostatic pressure during measurements and a similar behavior was reported when the doped samples of Zn_4Sb_3were studied [1, 20-24].

According to Mott and Davies [25], in the case of powders which are polycrystalline materials, the values for the optical and electrical band gap are different because these have similar values only in the case of monocrystalline materials.

Using the data depicted in figure 3, was determined the electrical band gap (E_g) by linear fitting of dependence ln ρ - (1/T). From the linear fitting was obtained that E_g = 0.97 eV.

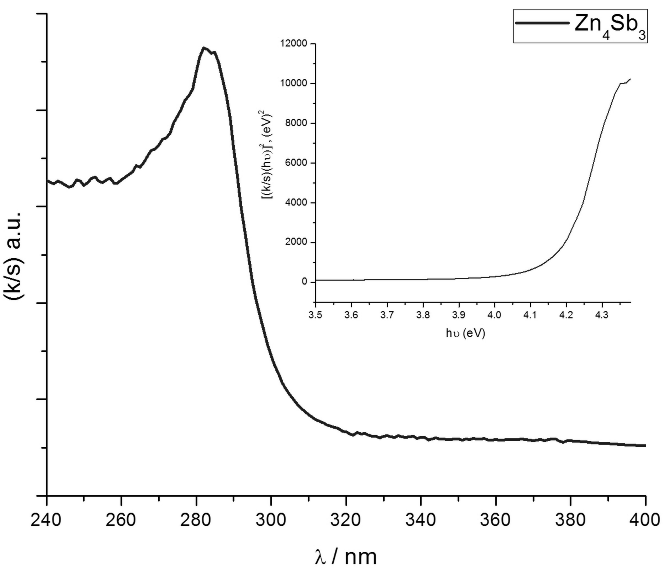


Figure 2. UV–Vis absorption spectrum and $\{(k/s)h\upsilon\}^2$ vs. hν (inset) of Zn_4Sb_3

The electrical conductivity (σ) of Zn_4Sb_3 sample increase with temperature increasing as can be observed from data plotted in figure 4; results depicted in figure 4 are in agreement with data presented in literature [26].

Regarding the temperature dependence of σ it is observed that the slope is changing before 460 K, this slope can be observed until 540 K, interval in which the σ value is increasing fast comparative with the range 300-460 K and 540-700 K.

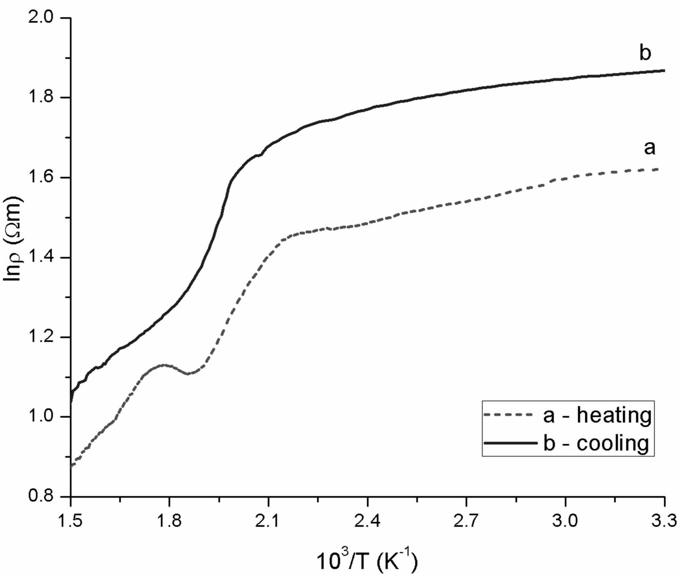


Figure 3. The electrical resistivity (ρ) dependence of temperature is presented for Zn_4Sb_3 obtained by the melting and quenching method: in the a) heating and b) cooling cycle

The thermal hysteresis which occurs suggests a phase transition. To check the recovery of the phase, after the electrical measurements were taken, an XRD analysis was performed.

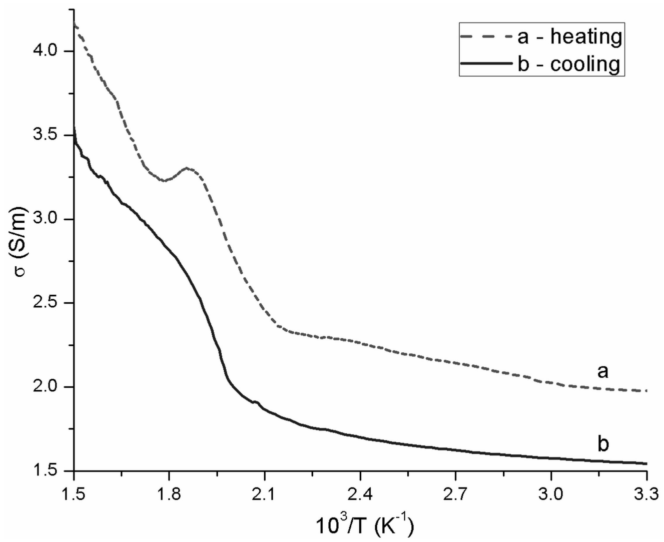


Figure 4. The electrical conductivity (σ) dependence of temperature on heating/cooling cycle for Zn_4Sb_3

As it can be seen in figure 5, the material composition changed as a consequence of the material's exposure at high temperatures during the electrical measurements that were taken in the surrounding environment (air). Beside studied Zn_4Sb_3, a new compoundwas formed:$Sb_{28}O_2Zn_{37.98}$.

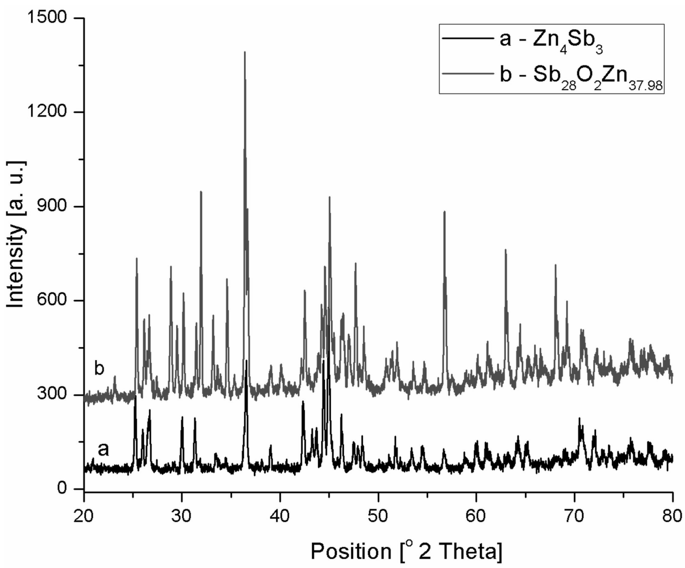


Figure 5. The XRD pattern of Zn_4Sb_3 sample after the electrical measurement were taken

4. CONCLUSIONS

Differential thermal analysis measurements were performed for Zn_4Sb_3 under argon ambient. As a result of the performed analysis, were obtained information about the melting and solidification point of the analyzed sample. The optical band gap for Zn_4Sb_3 was estimated from the UV-VIS measurements, E_G = 3.99 eV. The electrical parameters ρ and σ were measured as function of temperature on a heating - cooling cycle and from these it was observed the semiconducting behavior of Zn_4Sb_3. From linear fitting of ln ρ (1/T), the electrical band gap was also determined, E_g is 0.97 eV. The effects of the electrical measurements which were taken in air at high temperatures were shown.

5. ACKNOWLEDGEMENTS

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