

## Computational and experimental analysis on Te-Doped ZnSb thermoelectric material

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### Abstract

In this study we report a combined theoretical and experimental work on the tellurium doping of thermoelectric ZnSb. We investigated the influence of tellurium on the phase's stabilities by density functional theory (DFT) calculations. During experimental validation by means of SEM and EPMA characterization “needlelike” areas of Te-doped ZnSb were identified. The experimental results also highlight that for the compositions  $\text{Zn}_{0.5}\text{Sb}_{0.5-x}\text{Te}_x$  ( $x=0.001, 0.05, 0.1$ ) the system reaches a non-equilibrium state where ZnSb, ZnTe and Te-doped ZnSb are simultaneously present. The determination of the doping mechanism has demonstrated the formation of Te-doped  $\text{Zn}_4\text{Sb}_3$  after quenching, leading to the formation of Te-doped ZnSb due to the zinc diffusion during annealing. Presumed from experimental observation oxygen prevents the tellurium diffusion, which was confirmed by DFT calculations. These results lead to the conclusion of an inert processing chain as a necessary prerequisite for production of n-type ZnSb, which puts hurdles on a cheap and easily scalable tellurium doping for homogeneous and competitive products.

### Graphical Abstract

## Keywords

DFT calculations, oxygen impurity, tellurium doping, thermoelectricity, microstructural characterization, transient Potential-Seebeck Microprobe, scanning.

## 1. Introduction

According to NASA's observation, the first six months of 2016 have set new temperature records [1]. Global warming has now to be considered as a part of everyone's everyday life. Seeking for alternatives to fossil sources of energy is becoming a matter of urgency. Able to generate electricity from waste heat, thermoelectric materials have to be integrated in the list of renewable energies used instead of fossil sources. The efficiency of thermoelectric materials is usually related to their figure of merit  $ZT = S^2\sigma/\kappa T$ , with  $S$  the Seebeck coefficient,  $\sigma$  the electrical conductivity,  $\kappa$  the thermal conductivity,  $T$  the temperature and  $S^2\sigma$  the power factor. For energy harvesting application with variable temperatures for the heat sources and sinks, the highest  $ZT$  values are sought [2].

In the range of temperatures 400-700 K, ZnSb is a well-known compound [3-10] and has a relatively large power factor ( $4-12 \cdot 10^{-4} \text{Wm}^{-1}\text{K}^{-2}$ ). It is based on abundant and non-toxic compound compared to other interesting thermoelectric materials and with thermoelectric properties yet to be improved. Apart from one exception [11], polycrystalline ZnSb, doped or not, has always been reported as a p-type semiconductor [10, 12-18]. However, in order to obtain a thermoelectric device, one needs to associate two semiconductors of p and n type. To avoid cracks due to the different coefficients of thermal expansion between these two materials, comparable thermo-mechanical properties are needed. Thus, it is interesting to develop p and n type semiconductors from the same compound, ensuring moreover high packing and power density in devices by functional compatibility in terms of optimal current

density, which is determined under given temperature conditions by the similarity of electrical conductivities of materials being used.

Variations can be found in the literature concerning the experimental results on n-type poly- or single crystalline ZnSb. Indeed, Ueda et al. [11] reported a n-type conductivity for 2.03 at. % and 1.06 at. % Te-doped ZnSb, while 3.02 at. % Te-doped ZnSb showed a p-type behavior. On the contrary Kostur et al. [12] previously reported that doping polycrystalline ZnSb with tellurium leads to an increased hole concentration and thus a reinforced p-type behavior. Kostur et al. [19] reported a p-type behavior for Te-doped single crystals in the range 100 to 400 K, whereas Abou-Zeid et al. [20] reported a negative Seebeck coefficient (n-type behavior) for Te-doped single crystals at low temperature and a positive Seebeck coefficient (p-type behavior) above 200 K. These variations are also present in the density functional theory (DFT) calculations. On the one hand the calculations made by Faghaninia et al.[21] showed an induced p-type conductivity with tellurium doping. On the other hand the calculation results obtained by Zhao et al. [22] and Niedziolka et al. [23] were in agreement with the experimental results obtained by Ueda et al.. In the latter the author predicted a favorable formation energy for the antisite defect  $\text{Te}_{\text{Sb}}$  (-0.031 eV/defect) and predicted a n-type behavior for the so doped material.

In this study we will first briefly present our DFT results on tellurium defects in ZnSb, suggesting difficulties to integrate tellurium atoms in the ZnSb structure. In a next step the syntheses are introduced. The doping is studied via scanning electron microscopy, microprobe (EPMA), and X-ray diffraction analyses. The bulk Seebeck coefficient and local distribution is studied by the transient Potential-Seebeck Microprobe (T-PSM) and will be presented for evaluation of the doping effectiveness.

## **2. Procedures**

## a. Calculation details

The DFT calculations are performed using the Vienna ab initio simulation package (VASP) [24, 25] and the projector augmented waves (PAW) technique [26, 27] within the generalized gradient approximation (GGA). The Perdew-Burke-Ernzerhof parameterization (PBE) is applied [28].

Standard versions of the PAW potentials for the elements are used. For Sb five electronic states are included in the valence shell ( $5s^25p^3$ ), twelve are considered for Zn ( $3d^{10}4p^2$ ) and 6 for Te ( $5s^25p^4$ ) and O ( $2s^22p^4$ ). For oxygen, the “soft” pseudopotential is selected.

For ZnSb (*Pbca*, oP16, prototype CdSb), a 2\*2\*2 supercell containing 128 atoms is generated. For multiple defects, the distribution of atoms is generated by Special Quasi-random Structures (SQS [29]) using the ATAT software suite [30] to avoid artificial order effects in the distribution of the defects. For interstitials, the coordinates of the interstitial position are taken from [23]. For the other binary phases such as  $Sb_2Te_3$ , ZnTe,  $Sb_2O_3$ ,  $TeO_2$  and ZnO conventional cells are used, table 1.

The total energy of each structure is minimized by relaxing the volume of the cell and the ionic positions starting from the experimental cell parameters and crystallographic positions, table 1 [31].

The calculations are performed using the “accurate” precision setting in the VASP input file to avoid wrap-around errors. The first Brillouin zone is integrated using Monkhorst-Pack k-point meshes (5x5x5 for the supercells and 11x11x11 to 19x19x19 for the binary phases). The plane-wave energy cutoff and the reciprocal space meshes (k-points) are increased to achieve total energies with a precision less than 0.5 meV/atom. The cutoff energy is set at 500eV and the number of k-points ranges from 27 to 400 depending on the structure.

The calculated enthalpy of formation of a binary phase is given by equation (1), those of a phase containing two point defects by equation (2) for example. In this equation we suppose a ZnSb (2\*2\*2 supercell) with one vacancy on a Zn site and one tellurium atom in substitution of an Sb atom generated by SQS.

$$\Delta_f H^0(A_x B_y) = E(A_x B_y) - xE(A) - yE(B) \quad (1)$$

$$\Delta_f H^0(\text{Zn}_{63}\text{Sb}_{63}\text{Te}_1) = [E(\text{Zn}_{63}\text{Sb}_{63}\text{Te}_1) - 63E(\text{Zn}) - 63E(\text{Sb}) - E(\text{Te})]/127 \quad (2)$$

In these 2 equations, E(phase) corresponds to the DFT-calculated energy of the different phases.

## **b. Experimental procedure**

The elements (5N Sb Alfa Aesar 4N Zn Sigma Aldrich) were introduced in stoichiometric amounts in a silica tube of 13 mm external diameter and 60 mm length. The tube was previously heated under dynamic vacuum to remove free oxygen and other impurities, then graphitized and sealed under high dynamic vacuum ( $5 \cdot 10^{-6}$  mbar) and subsequently heated to 973 K with a rate of 100 K/h. During a holding time of 30 minutes the tube was vigorously stirred. After a standstill 5 minutes the tube was quenched with water. Afterwards an annealing for 100 and 1000 h was performed at a temperature of 713 K.

The diffusion couple was made using a pure ZnSb material, whose synthesis was well described elsewhere [3], and tellurium (5N Alfa Aesar). The materials were polished first with water followed by diamond solutions (3  $\mu\text{m}$ , 1  $\mu\text{m}$  and 1/4  $\mu\text{m}$ ) using SiC abrasive paper (roughness 800, 1200, 2400, 4000). The materials were cleaned in ethanol and put in contact inside a graphite crucible by means of steel springs. Before sealing the crucible under argon atmosphere in a glove box (19 ppm  $\text{H}_2\text{O}$ ; 30ppm  $\text{O}_2$ ) titanium was added as oxygen getter.

For the XRD analysis the materials were sieved at 20  $\mu\text{m}$  and investigated by XRD with a copper anode ( $K_{\alpha 1} = 1.54056 \text{ \AA}$  and  $K_{\alpha 2} = 1.54439 \text{ \AA}$ ) in the range of  $2\theta$  from 20 to  $60^\circ$  using a PANalytical Philips X'pert apparatus. The first XRD scans were performed with the classical Bragg-Brentano reflection geometry. In order to prevent preferential orientations, a spinner was used, with a step size of  $0.0080^\circ 2\theta$ .

The morphological analysis of the samples was performed under dynamic vacuum between  $10^{-6}$  and  $10^{-9}$  MPa with a scanning electron microscope FEI Quanta 200, with a resolution of 3 nm and an accelerating voltage of 30kV for secondary electrons. The resolution for the backscattered electrons was 4 nm. Quantitative analysis of the compositions was performed by microprobe (EPAM) with a CAMECA SX-100 equipped with five EDS sensors. The acceleration voltage was 20 kV for a focusing of the beam of 10 nA and a 2 minute counting time.

The Seebeck coefficient microprobe scanning was performed under vacuum on the cross section of one pellet using the transient measuring successor of the Potential-Seebeck Microprobe (T-PSM) at DLR. During the T-PSM measurement the sample surface is touched by an initially notheated tungsten carbide tip with a radius of curvature of 12  $\mu\text{m}$ . The tip carries a laser-welded type-T thermocouple and builds the apex of a fiber optical cable. The sample is mounted within a sample holder on an encoder controlled x-/y-motion stage from Micos (type: LS-110 52 VSS43 HV LIA) with nm resolution. A second thermocouple of same kind is attached to the sample, which is kept at room temperature during scanning by a passive heat sink. Once the tip settles onto the sample surface, the thermocouples form two independent thermoelectric measurement circuits, which are fed to differential pre-amplifier from Elsys Instruments (EL-LNA2) with high gain/bandwidth (100/5 MHz) and low input noise ( $< 6\mu\text{Vrms}$ ). The amplifier outputs are connected to a TransCom transient recorder (MF-Instruments) with a high sampling rate (max. 80 MHz/channel). Once the cold tip

contacts the sample surface, a vertical z-axis actuator sets a reproducible tip pressure by a control loop with a force sensor from ALTHEN GmbH (type: 31E-001N5-30b), which ensures the necessitated high repeatability of thermal contact resistance between the tip and the sample during scanning. In order to measure the local Seebeck-coefficient, a laser pulse generates a local temperature gradient in a microscopic sample volume in the vicinity of the tip. The principle evaluation of generated thermovoltages is described in [32]. The uncertainty of the measured Seebeck coefficient is  $< 10\%$  for the T-PSM and is determined against the reference value of an iron disilicide bulk reference material [33] with a certified uncertainty of the homogeneity of  $2.4 \mu\text{V/K}$ , which corresponds to  $1.4\%$  of the expectation value at room temperature. Within the limits of local resolution the ability to resolve differences in thermopower remains unaffected from the absolute accuracy, yielding distinguishable Seebeck contrasts around  $1\text{-}2\%$  [34]. While the predecessor PSM offered a lateral resolution of maximal  $10 \mu\text{m}$  [31], the T-PSM resolves the local Seebeck coefficient on a length scale of  $1\text{-}3 \mu\text{m}$  by a fast data acquisition during the transient process of laser-induced thermal excitation of the sample volume.

### **3. Results and discussion**

#### **a. Preliminary study**

##### **i. Ternary diagram**

The ternary diagram of the Zn-Sb-Te system has yet to be studied. The only existing data takes three binary diagrams and optimizations with the Calphad method for Zn-Sb, Zn-Te and Sb-Te into account [36-38]. It is thus possible to obtain a theoretical ternary diagram based on the projection of the binary diagrams, using the Calphad method and the Thermocalc software. The isothermal projection at  $500 \text{ K}$  is shown in figure 1. Apparently ZnTe, which

has a lower enthalpy of formation (-59.7 kJ mol<sup>-1</sup>) [39], compared to ZnSb (-7.5 kJ mol<sup>-1</sup>) [40], is involved in all the equilibria. However, it is worth noting, that this model does not include the possibility of Te-doping of the different phases.

## ii. DFT calculations: Tellurium

### 1. Formation enthalpy of the pure compounds

Since no consistent experimental reports on the Te- doping are available and in order to get insights to the behavior of this ternary system the formation enthalpies of pure ZnSb and binary tellurides were calculated, see Table 1 (lines 4-7).

In a first step, the formation enthalpy of the pure ZnSb phase has been calculated. Using the conditions given in paragraph 1, one obtains -3.06 kJ/mol (of atoms). This result is similar to previous DFT calculations using GGA [41], [42], [43] as presented in Table 1. However, calculated values are significantly lower than the experimental results.

Calculation of formation enthalpy of the Te-rich phases Sb<sub>2</sub>Te<sub>3</sub> (*R-3m*, hR15, prototype Bi<sub>2</sub>Te<sub>3</sub>) and ZnTe (*F-43m*, cF8, prototype ZnS) revealed similarity between DFT and experimental values from [44] for the Sb<sub>2</sub>Te<sub>3</sub>, whereas for ZnTe the calculated value was found to be lower than the assessment of Feutelais et al. [45]. For these two phases results of this work are similar to previous DFT calculations [42],[43].

**Table 1 : enthalpy of formation (in kJ/mol (of atoms)) of binary phases**

Phase	Space group, Pearson symbol,	DFT (This work)	DFT (literature)	Experiment or Calphad

	prototype			assessment
Zn	P6 <sub>3</sub> /mmc , hP2, Mg	0	0	0
Sb	R-3m, hR6, As	0	0	0
Te	P3 <sub>1</sub> 21, hP3, Se	0	0	0
ZnSb	Pbca, oP16, C2dSb	-3.06	-3.34 [41]; -3.28 [42]; -2.80 [43]	-7.55 ± 1 [46]; -6.4 ± 0.6 [47]; -37.2 ± 5 [48]
Sb <sub>2</sub> Te <sub>3</sub>	R-3m, hR15, Bi <sub>2</sub> Te <sub>3</sub>	-12.63	-12.35 [42]; -12.45 [43]	-10.4 [44]
ZnTe	F-43m,cF8, ZnS	-45.22	-45.44 [42]; -45.15 [43]	-59.9 [44]
Sb <sub>2</sub> O <sub>3</sub>	Pccn, oP20, Sb <sub>2</sub> O <sub>3</sub>	-145.0	-152.3 [42]; -170.8 [43]	-141.95 [49]
TeO <sub>2</sub>	P4 <sub>1</sub> 2 <sub>1</sub> 2, tP92, TeO <sub>2</sub>	-115.5	-129.2 [42]; -145.6 [43]	-108 [50]
ZnO	P6 <sub>3</sub> mc, hP4, ZnO	-152.4	-162.1 [42]; -173.5 [43]; -166.9 [51]	-175 [52]

## 2. Stability of the defects

The formation energy of ZnSb with one or several defects has been calculated and compared to the enthalpy of formation of a multi-phased reference state composed of pure elements and binary phases in order to predict the most probable phase. The difference between these two energies will be referred to as  $\Delta E$  in the paper.

Considering only the Zn-Sb system Jund et al. [41] have shown Zn vacancies ( $V_{Zn}$ ) as most probable defects in ZnSb, since, other defects (antisites, Sb vacancies ( $V_{Sb}$ ) or interstitial defects) have higher formation energies. Here, the formation enthalpy of a ZnSb system containing one Zn vacancy (63 Zn atoms + 64 Sb atoms) has been calculated. This value is compared to the enthalpy of formation of a mixture between pure ZnSb and Sb (since adding a Zn vacancy shifts the global composition to the Sb-rich part of the Sb-Zn phase diagram). As can be seen in table 2 (line 1), in this case, at 0K,  $\Delta E$  is positive and small. This result is in agreement with the results of Jund et al. [41] showing a positive formation energy for Zn vacancies of 0.8 eV/defect. Thus, since the value of  $\Delta E$  in table 2 is small, at higher temperature, entropic effects could stabilize this defect as assumed in the thermodynamic assessment of the Sb-Zn phase diagram of Liu et al. [36].

Considering the case of the tellurium doping it has been shown previously by Niedziolka [23], that from an energetical point of view, Te atoms can substitute Sb atoms. Performing corresponding calculations this word confirms a Te substitution of Sb at high temperature, table 2 (line 2). Moreover, this Te substitution can also occur together with the presence of vacancies ( $V_{Zn} + Te_{Sb}$ : Table 2, line 3).

**Table 2: Enthalpy of formation (in kJ/mol (of atoms)) of ZnSb with several defects and difference in energy with the enthalpy of formation of the multi phased region according to the global composition given by the formula of the 2\*2\*2 ZnSb supercell + defects . Possible defects are in bold face.**

Defect	Formula	Multi phased domain	$\Delta_f H$	$\Delta_f H$ (multi	$\Delta E$

			(formula)	phased)	
$V_{zn}$	$Sb_{64}Zn_{63}$	$Sb+ZnSb$	-2.48	-3.04	<b>0.56</b>
$Te_{sb}$	$Sb_{63}Zn_{64}Te_1$	$ZnSb+ZnTe$	-2.98	-3.73	<b>0.75</b>
$V_{zn} + Te_{sb}$	$Sb_{63}Zn_{63}Te_1$	$ZnSb+ZnTe+Sb$	-2.79	-3.7	<b>0.92</b>
$O_{sb}$	$O_1Sb_{63}Zn_{64}$	$Sb+ZnSb+ZnO$	-5.55	-5.39	<b>-0.16</b>
$O_i$	$O_1Sb_{64}Zn_{64}$	$Sb+ZnSb+ZnO$	-4.53	-5.35	<b>0.82</b>
$O_i + O_{sb}$	$O_2Sb_{62}Zn_{64}$	$Zn+ZnSb+ZnO$	7.24	-7.72	<b>0.48</b>
$V_{zn} + O_i$	$O_1Sb_{64}Zn_{63}$	$Sb+ZnSb+ZnO$	-0.81	-5.34	4.53
$V_{zn} + O_{sb}$	$O_1Sb_{63}Zn_{63}$	$Sb+ZnSb+ZnO$	-2.56	-5.38	2.82
$O_{sb} + O_i + V_{zn}$	$O_2Sb_{63}Zn_{63}$	$Sb+ZnSb+ZnO$	-3.66	-7.67	4.01
$O_{sb} + Te_{sb}$	$O_1Sb_{62}Zn_{64}Te_1$	$ZnSb+Zn+ZnO+ZnTe$	-3.67	-6.05	2.37
$O_i + Te_{sb}$	$O_1Sb_{63}Zn_{64}Te_1$	$ZnSb+Sb+ZnO+ZnTe$	-4.33	-6.00	1.67
$O_{sb} + Te_{sb} + O_i$	$O_2Sb_{62}Zn_{64}Te_1$	$ZnSb+Sb+ZnO+ZnTe$	-5.05	-8.31	3.26
$V_{zn} + Te_{sb} + O_i$	$O_1Sb_{63}Zn_{63}Te_1$	$ZnSb+Sb+ZnO+ZnTe$	-4.08	-6.00	1.92
$V_{zn} + Te_{sb} + O_{sb}$	$O_1Sb_{62}Zn_{63}Te_1$	$ZnSb+Sb+ZnO+ZnTe$	-3.57	-6.05	2.47
$V_{zn} + Te_{sb} + O_i +$ $O_{sb}$	$O_2Sb_{62}Zn_{63}Te_1$	$ZnSb+Sb+ZnO+ZnTe$	-4.86	-8.33	3.47

## b. Microstructural characterization:

Among the few results available on Te- doping of ZnSb none clearly mentioned a solubility limit of Te into the ZnSb phase. Kostur et al. [12, 19] demonstrated the formation of ZnTe and Sb for Te concentrations of 0.07 at. %. The amount of the two phases increases with the amount of tellurium introduced. Ueda et al. [11] reported a doping up to 2.06 at% Te without the formation of ZnTe. Our calculations predict a possible doping of ZnSb with 0.78 at% Te. In order to determine the influence of the Te concentration on the formation of the different phases and on the thermoelectric behavior of the ZnSb materials, three samples have been experimentally studied:  $\text{Zn}_{0.5}\text{Sb}_{0.5-x}\text{Te}_x$  with  $x = 0.001, 0.005$  and  $0.01$ .

### i. DRX analysis

The Rietveld refinement carried out on the powder diffractogram for the composition  $\text{Zn}_{0.5}\text{Sb}_{0.49}\text{Te}_{0.01}$  after 100 hours of annealing is shown in Figure 2. The  $\chi^2$  profile factor is 13.2. Two phases are highlighted. Quantification by the Rietveld method gives a mass composition of 99.93% ZnSb and 0.07% ZnTe. Substitution of antimony by tellurium in the ZnSb structure does not allow to obtain a better profile factor. There was no evidence of changes in the volume of the unit cell, which remains similar to that determined for ZnSb (see Table 3).

The X-ray diffraction pattern shows the presence of ZnTe for  $x=0.01$ . Thus, one cannot conclude on a doping of ZnSb by tellurium. In the case of the two other compositions, ZnTe is not found in the diffraction pattern.

**Tableau 3: Cell parameters determined for  $\text{Zn}_{0.5}\text{Sb}_{0.49}\text{Te}_{0.01}$  after annealing.**

	a (nm)	b (nm)	c (nm)	V (nm <sup>3</sup> )	
ZnSb:Te	0.6202	0.7743	0.8089	0.3885	This work
ZnSb	0.6202	0.7743	0.8100	0.3890	This work
ZnSb	0.6203	0.7740	0.8097	0.3889	[53]

## ii. Optical and Scanning electron microscopy analyses:

The observation by optical microscopy suggests for all samples the presence of ZnTe (Figure 3a). Indeed, ZnTe crystals are easily recognizable due to their characteristic red color [54].

This result is confirmed by the SEM/EDS analysis: figure 3 b) shows the analysis of the upper part of a section of an  $\text{Zn}_{0.5}\text{Sb}_{0.499}\text{Te}_{0.001}$  ingot after annealing. One can observe the presence of cracks and macropores (1), as well as the presence of antimony (2). The presence of antimony can be explained by a slight deviation to the targeted stoichiometry. Small crystals of about 1 mm in diameter (having darker shade of grey) are visible in area 3. The EDS analysis identified these crystals as ZnTe. In all ingots ZnTe crystals are located at the edge or in the upper part of the ampoule. No evidence of other phases than ZnSb and Sb can be found in the core of the ingot figure 3 c).

By highlighting the ZnTe phase at the edge of the ingot, the SEM and optical microscopy analyses suggest the solubility limit of Te in ZnSb to be  $< 0.001$  at %. However the doping of the ZnSb phase could not be evaluated due to the small difference in the EDS spectra of tellurium and antimony.

## iii. Electron probe microanalysis

Figure 4 presents the atomic distribution of Te, Sb and Zn determined by EPMA for the composition  $Zn_{0.5}Sb_{0.49}Te_{0.01}$  after annealing. The brighter areas are, the more atoms of the corresponding elements are contained. Three regions are visible: area 1 with lowest antimony content but high Te and Zn content. The “needle” shaped area 2 with small amount of Te, and the area 3 with negligible Te content. The quantitative EPMA analysis of the marked areas is reported in table 3, confirming area 1 to correspond to ZnTe. The area 2 is then identified as tellurium doped ZnSb and the area 3 as undoped ZnSb. The same behavior has been observed for the two other compositions with a tellurium doping of ZnSb reaching 0.5 at. %.

**Table 2 : Quantitative WDS analysis performed on the areas labeled in figure 4.**

Area	At.% Te	At. % Sb	At. % Zn
1	$50.2 \pm 0.68$	$0.65 \pm 0.08$	$49.15 \pm 0.37$
2	$0.47 \pm 0.06$	$49.65 \pm 0.84$	$49.88 \pm 0.37$
3	0	$50,54 \pm 0.84$	$49.46 \pm 0.37$
Detection limit	0.09	0.14	0.5

From the results obtained, it appears that the system is out of equilibrium. Indeed for all the compositions three phases ZnSb, ZnTe and  $Zn_{0.5}Sb_{0.5-x}Te_x$  can be found. Since these three phases cannot be plot on the tie line between ZnSb and ZnTe in the Zn-Sb-Te phase diagram, they should not be found together in a system at equilibrium. In order to reach equilibrium, a 1000 h annealing, instead of the 100 h previously used, was carried out for a sample with 0.1 at. % Te. Again needle shaped areas with bright spots can be seen in the tellurium distribution micrograph determined by EPMA (Figure 5). The quantitative analysis confirms ZnSb, ZnTe and  $Zn_{0.5}Sb_{0.5-y}Te_y$  within this sample. Furthermore, it appears that the doping (y value in the

formula) reaches 0.5 at. % Te for all the compositions regardless of the annealing time. These results lead us to investigate the corresponding doping mechanism.

#### iv. Doping mechanism determination:

##### 1. Influence of the thermal treatment

As mentioned earlier, the sample kept liquid for 30 min before quenching, and subsequent annealing for 100h or 1000h at 723 K yields the same phases and doping level. The influence of the thermal treatment is further evaluated by analyzing a sample of  $\text{Zn}_{0.5}\text{Sb}_{0.49}\text{Te}_{0.1}$  after having been quenched in water. As for the annealed sample, ZnTe crystals can easily be found at the edge of the ingot. On the micrograph in figure 6, ZnSb,  $\text{Zn}_4\text{Sb}_3$  and Sb, are identified by EDS respectively as the main phase, the needle shaped dark gray phase and the white gray phase.

From the thermodynamic database used to plot the isothermal section, a calculation based on the Scheil-Gulliver model is realized (Figure 7). This model is based on an infinite diffusion in the liquid, which allows changes in its composition and zero diffusion in the solid phases. This model predicts the phases expected after a rapid solidification process such as quenching. It is worth noting that ZnTe is present at 973 K in a solid state. The second phase which is formed for this composition is then  $\text{Zn}_4\text{Sb}_3$ . With the formation of  $\text{Zn}_4\text{Sb}_3$  the antimony content in the liquid increases. ZnSb is then formed, and at the end, the pure Sb phase appears. This calculation, even though it does not take into account a possible doping of the different phases, reproduces quite well the observed results.

The presence of  $\text{Zn}_4\text{Sb}_3$  results from the finite value of the quenching rate. Figure 8 shows the micrographs of three alloys of composition  $\text{Zn}_{0.5}\text{Sb}_{0.49}\text{Te}_{0.1}$  quenched with different rates. The slowest cooling rate is obtained by cooling the quartz tube in the oven, the

intermediate speed by quenching it in air and the highest speed by water quenching. These micrographs illustrate that the higher the cooling rate the smaller the  $Zn_4Sb_3$  formation. This result contradicts the one obtained by Kostur et al. [12]. These authors stated higher formation of  $Zn_4Sb_3$  in the solidified ingot was received with fastest cooling rates. Nevertheless, our observation is more consistent with the phase diagram.

The needlelike shape observed for the minority phase ( $Zn_4Sb_3$ ) during rapid quenching is commonly observed in the case of intermetallic compounds [18]. There is a change of shape in the case of a slower cooling, and a shift towards a lamellar structure is observed. The elemental distribution micrographs of the material after water quenching determined by EPMA, (Figure 9) highlights the presence of ZnTe (1), ZnSb (2) Sb (3) and  $Zn_4Sb_3$ : Te (4). The quantitative analysis in Table 3 confirms the tellurium doping of  $Zn_4Sb_3$  up to 0.34 at %. Similar results are obtained for other quenching rates. This result is in agreement with the DFT calculations made by Faghaninia et al. [21]. These authors predicted a favorable formation enthalpy for the antisite defect  $Te_{Sb}$  in  $Zn_4Sb_3$ . Furthermore, Li et al [55] reported successful attempts of tellurium doping of  $Zn_4Sb_3$  even if no EDS/WDS results were presented in their study.

**Table 3 : Quantitative WDS analysis performed on the areas in figure 9.**

Area	at. % Te	at. % Sb	at. % Zn
1	$50.47 \pm 0.84$	$0.51 \pm 0.8$	$49.02 \pm 0.3$
2	$0.01 \pm 0.06$	$50.58 \pm 0.8$	$49.40 \pm 0.3$
3	$0.03 \pm 0.06$	$98.57 \pm 0.8$	$1.40 \pm 0.08$

4	$0.32 \pm 0.06$	$44.23 \pm 0.8$	$55.45 \pm 0.3$
Detection limit	0.07	0.14	0.5

Thus, it appears that the coexistence of ZnTe, with doped and undoped ZnSb in the same material results from the formation of ZnTe in the melt and of doped Zn<sub>4</sub>Sb<sub>3</sub> during the quench. Indeed, after quenching ZnTe needle shaped doped Zn<sub>4</sub>Sb<sub>3</sub> regions have been observed in the sample. Katayama et al. [56] reported a Kirkendall effect in the Zn-Sb system, a signature of the higher diffusion rate of zinc in this system. One can assume that the same is true for the Zn-Sb-Te system. Then, the diffusion of zinc during the annealing associated with the reaction between Zn<sub>4</sub>Sb<sub>3</sub> and Sb lead to the formation of ZnSb. With this mechanism it is assumed that there is no tellurium diffusion during the annealing. The identification of the Te diffusion in ZnSb during the annealing process of a partially doped ingot can be difficult. Indeed the change in the size of the needles is mainly induced by the quenching and is thus not relevant to perform this identification.

## 2. Tellurium diffusion: ZnSb-Te diffusion couple

In order to verify the assumption of the low diffusion rate of tellurium into ZnSb, a diffusion couple made with ZnSb and tellurium has been annealed for 30 days at 673 K. The temperature was limited by the melting point of tellurium (722 K). We decided to work 50 K below this temperature to avoid the formation of the liquid phase. The welding between the two materials presents no mechanical strength: once the spring was removed, the materials

did not stick together. This is a clue of the low diffusion rate of the species in this system. Figure 10 presents a SEM image of the interfacial area on the ZnSb side. Many cracks and porosities are visible in this area. Up to now the WDS analyses were focused only on the amount of zinc, antimony and tellurium. In the present case previous EDS measurements showed the presence of an oxidized phase at the interface, so the WDS quantification of oxygen was carried out as well. Nevertheless the surface to be analyzed does not fulfill all the criteria for quantitative WDS analysis. Moreover quantification of oxygen, which is a light element, is difficult. Thus, the WDS analyses in the interfacial area presented in this part have to be considered with caution. Nevertheless, they demonstrate the presence of at least four phases, (Table 4), that can be identified as:

In area 1: a ZnSb phase which is slightly oxidized, the oxygen level being similar to the one generally neglected during EDS analyses of the pure material.

In area 2: antimony containing zinc and oxygen.

In area 3: a mixed oxide of zinc and antimony containing no tellurium.

In area 4: zinc oxide containing antimony and tellurium.

**Table 4 : Quantitative WDS analysis performed on the areas in Figure 10.**

Area	at. % Te	at. % Sb	at. % Zn	at. % O
1	$0 \pm 0.04$	$49.44 \pm 0.75$	$47.21 \pm 0.4$	$3.35 \pm 0.03$
2	$0.02 \pm 0.04$	$94.35 \pm 0.75$	$2.54 \pm 0.04$	$3.09 \pm 0.03$

3	$0.04 \pm 0.04$	$39.92 \pm 0.75$	$32.68 \pm 0.4$	$27.36 \pm 0.03$
4	$3.04 \pm 0.04$	$10.63 \pm 0.75$	$41.15 \pm 0.4$	$45.18 \pm 0.03$
Detection limit	0.04	0.08	0.02	0.04

No further investigation of the exact nature of the phase in area 3 has been performed.

However, it is worth noting that the stoichiometry does not approach that reported for the mixed oxides [57]. The assumption of a phase identified as ZnO solubilizing antimony and tellurium, (area 4) may be supported by the results available in the literature on doping of ZnO by antimony and tellurium [58-60].

Even if these results are partial due to the oxidation of the interfacial area between ZnSb and tellurium no evidence of tellurium diffusion into ZnSb has been revealed by this experiment. However, WDS analysis on the ZnSb side showed a slight oxidation of the sample (usually detected by EDS) but neglected in our case [61]. In the overall process of synthesis, the limited diffusion rate of tellurium into ZnSb leads to the formation of the needle shaped areas of doped ZnSb. However, one cannot exclude the influence of other mechanisms that can limit the spread of tellurium such as segregation defects or impurities in the grain boundaries which delimit the ZnSb / Zn<sub>4</sub>Sb<sub>3</sub> interface. The influence of impurities has also to be considered when looking at the results available in the literature. Muller et al [62] and Abou-Zeid et al. [20, 63] reported the influence of oxygen on the thermoelectric properties of tellurium doped ZnSb single crystals. Indeed, during the material preparation, the use of hydrogen is compulsory to obtain n-type material. The antimony has to be purified under hydrogen and the mixture of the element has to be melted under the same atmosphere.

Moreover, stored in air at room temperature the Seebeck coefficient of tellurium doped n-type single crystals ( $S=-790 \mu\text{V.K}^{-1}$ ) decreases (in norm) to  $-400 \mu\text{V.K}^{-1}$  after 14000 h.

The experimental results on single crystals and the non-diffusion of tellurium into slightly oxidized ZnSb, motivated in this work the investigation of the influence of oxygen on the relative stability of the phases in the Zn-Sb-Te-O system.

## **c. DFT Calculations: oxygen**

### **i. Formation enthalpy**

The method used for Te and Zn vacancies (see section ii) was also used to investigate the influence of oxygen on the stability of the phases.

The enthalpy of formation of the main oxides ZnO ( $P6_3mc$ , hP4, prototype ZnO),  $\text{TeO}_2$  ( $P4_12_12$ , tP12, prototype  $\text{TeO}_2$ ) and  $\text{Sb}_2\text{O}_3$  ( $Pccn$ , oP20, prototype  $\text{Sb}_2\text{O}_3$ ) have been calculated. The values for  $\text{TeO}_2$  and for  $\text{Sb}_2\text{O}_3$  are similar to the experimental data reported by Itkin and Alcock [50] for  $\text{TeO}_2$  and by Aspiala et al. [49] for  $\text{Sb}_2\text{O}_3$ . In contradiction, our calculation (table 2) underestimates the enthalpy of formation of ZnO. For these three oxides, we obtain similar results than previous calculations [42],[51] even if the values reported in the open database of the Materials Project [43] are systematically more negative.

If a global agreement is obtained for most of the phases, the formation enthalpies of all phases containing Zn are underestimated with the selected pseudo potentials. For ZnSb and ZnO calculations with different Zn pseudo potentials were performed in this work (considering 18 or 20 valence electrons). For ZnSb, the obtained enthalpy of formation varies from  $-2.90$  to  $-3.68$  kJ/mol (of atom) whereas for ZnO it ranges from  $-151.50$  to  $-153.71$  kJ/mol (of atom).

However, accurate quantitative values of the formation enthalpies of all the binary phases is not in the focus for this work, since energies obtained within the same theoretical description are compared.

## ii. Defect stability

This part will focus on the stabilization effect due to the main defects or to oxygen impurities, which could affect the thermoelectrical properties of pure ZnSb or Te-doped ZnSb.

As previously mentioned even during the synthesis of the pure ZnSb phase with great care, it is not possible to totally avoid the presence of oxygen. This is why oxygen defects in the structure have been considered. For this study two kinds of oxygen defects were taken into consideration: interstitial O atoms and substitution of Sb by an oxygen atom on the Sb site.

The formation enthalpy of the combination of these two defects with or without a zinc vacancy was calculated likewise (Table 2 line 4-12).

If the value of  $\Delta E$  is highly positive for the combinations vacancies/interstitials, vacancies /substitutions and substitutions/interstitials/vacancies, this is not the case for the other defects. Especially, one can see that for oxygen substitution on the Sb site,  $\Delta E$  is negative which means that, even at 0K, oxygen could spontaneously enter the crystal structure of ZnSb. DFT calculations of this work also show interstitial oxygen may also exist at higher temperature, especially in combination with the  $Sb_O$  substitutional defect.

Similarly to what occurs in the pure non-doped ZnSb phase, cases with oxygen, Zn vacancies and/or tellurium have been considered. As shown in table 3, independently of the configuration, tellurium and oxygen cannot coexist in the ZnSb crystal.

These results provide an explanation to the observed behavior for the studied sample but also for the results obtained by Abou-zeid *et al.*[20, 63]. Indeed according to calculations in this

work, the presence of oxygen in the system prevents the doping of ZnSb by tellurium.

Furthermore the limited diffusion of tellurium into ZnSb observed here may arise from the presence of oxygen defects in the structure preventing the formation of tellurium defects.

However the influence of the  $O_{Sb}$  substitutional defect on the thermoelectric properties has not yet been evaluated.

#### **d. Local Seebeck coefficient determination**

Referring to the literature [9, 27, 28] and to Niedziolka's [23] calculations, doping of ZnSb may lead to a n-type semiconductor. Nevertheless the macroscopic analysis of the Seebeck coefficient by means of a ZEM3 apparatus or by the "hot tip" method on the annealed ingot revealed that the Te doped sample is p-type. However, from a metrological point of view averaging effects can hide the information on effectively n-type polarity of the doped regions. The T-PSM method allows a spatially resolved analysis of the Seebeck coefficient. The reproduction of the true sign of thermopower is given on length scales down to 1-3  $\mu\text{m}$  but in absence of eddy currents, which are driven in case of inhomogeneously distributed Seebeck coefficients. Given the expansion of Te-doped areas in the annealed samples, the T-PSM analysis should permit to evaluate the effectiveness of the doping. The presence of Te-doped areas in the annealed samples was demonstrated by analyzing the microprobe results. This study is done in several steps: First a PSM measurement was conducted on the polished surface of the ingot. Afterwards the ingot was characterized by scanning electron microscopy to locate the PSM-scanned area. Finally a region close to the analyzed area is characterized by microprobe.

The figures 11 and 12 show respectively the T-PSM + SEM analysis and the atomic repartition of the elements (EPMA) in the sample containing 1 at. % Te after water quenching and 100 h annealing. The EPMA analysis was performed on an area directly adjacent to the zone analyzed by T-PSM since the surface is deteriorated after the PSM analysis.

Three areas are highlighted in figure 11 (left panel):

- area (1) displays a Seebeck coefficient varying between  $-60$  and  $180 \mu\text{V.K}^{-1}$ , which corresponds to visible holes and cracks on the images of the secondary and backscattered electrons .
- area (2) shows a homogeneous Seebeck coefficient value close to  $40 \mu\text{V.K}^{-1}$ . These zones correspond to the antimony visible in the backscattered electrons image.  $40 \mu\text{V.K}^{-1}$  is consistent with the value of the Seebeck coefficient reported in the literature for pure antimony [64].
- area (3) has a Seebeck coefficient around  $380 \mu\text{V.K}^{-1}$ . This value is coherent with the range of the Seebeck coefficient observed for pure ZnSb [3, 7, 9]. In this area one can distinguish needle shaped regions (identified by arrows in figure 11), on which the Seebeck coefficient is lower and takes a value around  $280 \mu\text{V.K}^{-1}$ . These zones correspond to the Te-doped needles described previously (figure 5). The lateral resolution for measuring the Seebeck coefficient by this method is around  $1-3 \mu\text{m}$ . The needles having an approximate dimension of  $25 \times 300 \mu\text{m}^2$ , it is actually possible to analyze them by this method. According to this analysis it appears that the doping with tellurium has little influence on the value of the Seebeck coefficient of ZnSb. The change of sign observed in the case of single crystals doped with tellurium is not visible here. However, the donor effect of tellurium is confirmed.

## 4. Conclusion

In this study we have first presented our first principles calculation results about the tellurium doping of ZnSb. These results are in good agreement with previous calculations presented in the literature and with experimental data on monocrystalline doped ZnSb materials.

However, the experimental validation of the predicted n-type behavior of the doped material was unsuccessful. In fact the doped polycrystalline material was not composed of a single phase. We showed the coexistence of tellurium doped ZnSb, zinc telluride ZnTe and undoped ZnSb. The mechanism leading to the formation of these phases has been determined: ZnTe is formed in the melt due to its high melting point and stability. During the quench, tellurium doped  $\text{Zn}_4\text{Sb}_3$  is the first phase formed. Its formation is associated with an increase of the antimony content in the melt and so it is followed by the formation of ZnSb and finally Sb when the temperature reaches the eutectic temperature. During the annealing, the doped  $\text{Zn}_4\text{Sb}_3$  regions become doped ZnSb regions due to the zinc diffusion. On the contrary, the tellurium diffusion in this system appears to be extremely limited. Additional DFT calculations allowed us to determine that oxygen may play an important role in the stability of tellurium defects and we showed that the presence of oxygen prevents tellurium doping of ZnSb. These calculation results are consistent with the results obtained in the literature about monocrystalline doped materials. Finally, local Seebeck coefficient measurements showed that the tellurium doped ZnSb areas exhibit a slight decrease of the Seebeck coefficient suggesting a donor-like behavior of tellurium defects in ZnSb. However since the doped areas are rather spatially limited in the material, it keeps a p-type conductivity.

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1. [Access date 2016; URL:[https://www.nasa.gov/feature/goddard/2016/climate-trends-continue-to-break-records.](https://www.nasa.gov/feature/goddard/2016/climate-trends-continue-to-break-records)]
2. D. Narducci, *Do we really need high thermoelectric figures of merit? A critical appraisal to the power conversion efficiency of thermoelectric materials*. Appl. Phys. Lett., 2011. **99**(Copyright (C) 2016 American Chemical Society (ACS). All Rights Reserved.): p. 102104/1-102104/3.
3. R. Pothin, R.-M. Ayrat, A. Berche, F. Rouessac, P. Jund, *Interest of the differential thermal analysis on the characterization of a thermoelectric material: ZnSb*. Journal of Alloys and Compounds, 2016. **657**: p. 358-365.
4. X. Song, P.H.M. Böttger, O.B. Karlsen, T.G. Finstad, J. Taftø, *Impurity band conduction in the thermoelectric material ZnSb*. Physica Scripta, 2012. **2012**(T148): p. 014001.
5. L. Bjerg, B.B. Iversen, G.K. Madsen, *Modeling the thermal conductivities of the zinc antimonides ZnSb and Zn<sub>4</sub>Sb<sub>3</sub>*. Physical Review B, 2014. **89**(2): p. 024304.
6. K. Berland, X. Song, P.A. Carvalho, C. Persson, T.G. Finstad, O.M. Løvvik, *Enhancement of thermoelectric properties by energy filtering: Theoretical potential and experimental reality in nanostructured ZnSb*. Journal of Applied Physics, 2016. **119**(12): p. 125103.
7. Q. Guo, S. Luo, *Improved thermoelectric efficiency in p-type ZnSb through Zn deficiency*. Functional Materials Letters, 2015. **08**(02): p. 1550028.
8. D.-B. Xiong, N.L. Okamoto, H. Inui, *Enhanced thermoelectric figure of merit in p-type Ag-doped ZnSb nanostructured with Ag<sub>3</sub>Sb*. Scripta Materialia, 2013. **69**(5): p. 397-400.
9. R. Pothin, R. Ayrat, A. Berche, D. Granier, F. Rouessac, P. Jund, *Preparation and properties of ZnSb thermoelectric material through mechanical-alloying and Spark Plasma Sintering*. Chemical Engineering Journal, 2016. **299**: p. 126-134.
10. K. Valset, P.H.M. Böttger, J. Taftø, T.G. Finstad, *Thermoelectric properties of Cu doped ZnSb containing Zn<sub>3</sub>P<sub>2</sub> particles*. Journal of Applied Physics, 2012. **111**(2): p. 023703.
11. T. Ueda, C. Okamura, Y. Noda, K. Hasezaki, *Effect of Tellurium Doping on the Thermoelectric Properties of ZnSb*. Journal of the Japan Institute of Metals, 2010. **74**(2): p. 110-113.
12. T.A. Kostur, V.I. Psarev, *The effect of tellurium additions on the crystallization and electrical characteristics of the ZnSb compound*. Soviet Physics Journal, 1969. **12**(1): p. 88-91.
13. P.H.M. Böttger, K. Valset, S. Deledda, T. Finstad, *Influence of Ball-Milling, Nanostructuring, and Ag Inclusions on Thermoelectric Properties of ZnSb*. Journal of Electronic Materials, 2010. **39**(9): p. 1583-1588.
14. J. Sottmann, K. Valset, O. Karlsen, J. Taftø, *Synthesis and Measurement of the Thermoelectric Properties of Multiphase Composites: ZnSb Matrix with Zn<sub>4</sub>Sb<sub>3</sub>, Zn<sub>3</sub>P<sub>2</sub>, and Cu<sub>5</sub>Zn<sub>8</sub>*. Journal of Electronic Materials, 2013. **42**(7): p. 1820-1826.
15. K. Valset, X. Song, T.G. Finstad, *A study of transport properties in Cu and P doped ZnSb*. Journal of Applied Physics, 2015. **117**(4): p. 045709.
16. L.V. Prokofieva, P.P. Konstantinov, A.A. Shabaldin, D.A. Pshenai-Severin, A.T. Burkov, M.I. Fedorov, *Doping and defect formation in thermoelectric ZnSb doped with copper*. Semiconductors, 2014. **48**(12): p. 1571-1580.
17. A.A. Shabaldin, L.V. Prokof'eva, P.P. Konstantinov, A.T. Burkov, M.I. Fedorov, *Acceptor Impurity of Copper in ZnSb Thermoelectric*. Materials Today: Proceedings, 2015. **2**(2): p. 699-704.
18. A.A. Shabaldin, L.V. Prokof'eva, G.J. Snyder, P.P. Konstantinov, G.N. Isachenko, A.V. Asach, *The Influence of Weak Tin Doping on the Thermoelectric Properties of Zinc Antimonide*. Journal of Electronic Materials, 2015: p. 1-4.
19. N.L. Kostur, V.I. Psarev, *Electrical properties of doped single crystals of ZnSb*. Soviet Physics Journal, 1967. **10**(2): p. 21-23.
20. A. Abou-zeid, G. Schneider, *Te-Doped n-Type ZnSb*. physica statu solidi (a), 1971. **6**: p. K101-K103. .
21. A. Faghaninia, C.S. Lo, *First principles study of defect formation in thermoelectric zinc antimonide, β-Zn<sub>4</sub>Sb<sub>3</sub>*. Journal of Physics: Condensed Matter, 2015. **27**(12): p. 125502.

22. J-H Zhao , E-J Han , T-M Liu W. Zeng *First Principles Study on the Electronic Properties of Zn<sub>64</sub>Sb<sub>64-x</sub>Te Solid Solution (x = 0, 2, 3, 4)* Int. J. Mol. Sci. 2011, 12, 3162-3169
23. K. Niedziolka, *Improving the thermoelectric properties of materials via numerical simulations. The case of zinc antimonides.* Thèse de Doctorat, Université Montpellier 2. 2014.
24. G. Kresse, J. Furthmüller, *Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set.* Computational Materials Science, 1996. **6**(1): p. 15-50.
25. G. Kresse, J. Furthmüller, *Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set.* Physical Review B, 1996. **54**(16): p. 11169-11186.
26. G. Kresse, D. Joubert, *From ultrasoft pseudopotentials to the projector augmented-wave method.* Physical Review B, 1999. **59**(3): p. 1758-1775.
27. P.E. Blöchl, *Projector augmented-wave method.* Physical Review B, 1994. **50**(24): p. 17953.
28. J.P. Perdew, K. Burke, M. Ernzerhof, *Generalized gradient approximation made simple.* Physical review letters 1996. **77**(18): p. 3865.
29. A. Zunger, S.H. Wei, L.G. Ferreira, J.E. Bernard, *Special quasirandom structures.* physical review letters, 1990. **65**(3): p. 353-356.
30. A. Van de Walle, P. Tiwary, M. De Jong, D. Olmsted, M. Asta, A. Dick, D. Shin, Y. Wang, L.-Q. Chen, Z.-K. Liu, *Efficient stochastic generation of special quasirandom structures.* Calphad, 2013. **42**: p. 13-18.
31. H. Putz, K. Brandenburg, C.S. Pearson's Crystal Data, *Database for Inorganic Compounds.* CD-ROM software version, 2007. **1**.
32. P. Ziolkowski, G. Karpinski, D. Platzek, C. Stiewe, E. Müller, Proceedings 25th International Conference on Thermoelectrics (2006),
33. P. Ziolkowski, C. Stiewe, J. de Boor, I. Druschke, K. Zabrocki, F. Edler, S. Haupt, J. König, E. Müller, *"Iron Disilicide as High-Temperature Reference Material for Traceable Measurements of Seebeck Coefficient Between 300 K and 800 K"*, Journal of Elec. Materi. (2016). doi:10.1007/s11664-016-4850-5
34. P. Ziolkowski, G. Karpinski, T. Dasgupta, E. Müller, *"Probing thermopower on the microscale"*, Phys. Status Solidi A (2013).]
35. D. Platzek, G. Karpinski, C. Stiewe, P. Ziolkowski, C. Drasar, E. Müller. *Potential-Seebeck-microprobe (PSM): measuring the spatial resolution of the Seebeck coefficient and the electric potential.* in *Thermoelectrics, 2005. ICT 2005. 24th International Conference on.* 2005. IEEE.
36. Y. Liu, J.-C. Tedenac, *Thermodynamic modeling of the Cd-Sb-Zn ternary system.* Calphad, 2009. **33**(4): p. 684-694.
37. A. Haloui, Y. Feutelais, B. Legendre, *Experimental study of the ternary system Cd · Te · Zn.* Journal of Alloys and Compounds, 1997. **260**(1-2): p. 179-192.
38. C. Guo, C. Li, Z. Du, *Thermodynamic re-modeling of the Sb-Te system using associate and ionic models.* Journal of Electronic Materials, 2014. **43**(11): p. 4082-4089.
39. R.F. Brebrick, *High Temperature Thermodynamic Properties of ZnTe (s).* Journal of Phase Equilibria and Diffusion, 2011. **32**(6): p. 525-536.
40. E.K. Arushanov, *Crystal growth, characterization and application of II V compounds.* Progress in Crystal Growth and Characterization, 1986. **13**(1): p. 1-38.
41. P. Jund, R. Viennois, X. Tao, K. Niedziolka, J.-C. Tédénac, *Physical properties of thermoelectric zinc antimonide using first-principles calculations.* physical Review B, 2012. **85**(22): p. 33.
42. OQMD. [Access date May 2016; URL:[http://oqmd.org/.](http://oqmd.org/)]
43. Material project. [Access date May 2016; URL:[https://materialsproject.org/.](https://materialsproject.org/)]
44. G. Ghosh, *The Sb-Te (antimony-tellurium) system.* Journal of phase equilibria, 1994. **15**(3): p. 349-360.
45. Y. Feutelais, A. Haloui, B. Legendre, *A thermodynamic evaluation of the Te-Zn system.* Journal of phase equilibria, 1997. **18**(1): p. 48-61.

46. W.M. W. Oelsen, Mitt. K.W., Inst. Eisenforsch. Dusseldorf, 1937. **19**: p. 1-26.
47. T.A. Stolyarova, Russ. Met, 1979. **6**: p. 61-62.
48. M.P.M. S.A. Shchukarev, Yu.P. Sapozhnikov, Zhur. Obshchet. Khim, 1956. **26**: p. 304-307.
49. M. Aspiala, D. Sukhomlinov, P. Taskinen, *Determination of standard thermodynamic properties of Sb<sub>2</sub>O<sub>3</sub> by a solid-oxide electrolyte EMF technique*. Solid State Ionics, 2014. **265**: p. 80-84.
50. V.P. Itkin, C.B. Alcock, *The O-Te (oxygen-tellurium) system*. Journal of phase equilibria, 1996. **17**(6): p. 533-538.
51. P. Erhart, K. Albe, A. Klein, *First-principles study of intrinsic point defects in ZnO: Role of band structure, volume relaxation, and finite-size effects*. Physical Review B, 2006. **73**(20): p. 205203.
52. H. Wriedt, *The O–Zn (Oxygen-Zinc) system*. Journal of phase equilibria, 1987. **8**(2): p. 166-176.
53. Y. Mozharivskiy, A.O. Pecharsky, S. Bud'ko, G.J. Miller, *A promising thermoelectric material: Zn<sub>4</sub>Sb<sub>3</sub> or Zn<sub>6-δ</sub>Sb<sub>5</sub>. Its composition, structure, stability, and polymorphs. structure and stability of Zn<sub>1-δ</sub>Sb*. Chemistry of Materials, 2004. **16**(Copyright (C) 2014 American Chemical Society (ACS). All Rights Reserved.): p. 1580-1589.
54. I.C. Avetissov, E.N. Mozhevitina, A.V. Khomyakov, R.I. Avetisov, A.A. Davydov, V.P. Chegnov, O.I. Chegnova, N.V. Zhavoronkov, *Homogeneity limits and nonstoichiometry of vapor grown ZnTe and CdTe crystals*. CrystEngComm, 2015. **17**(3): p. 561-568.
55. W. Li, L. Zhou, Y. Li, J. Jiang, G. Xu, *Thermoelectric properties of hot-pressed Zn<sub>4</sub>Sb<sub>3-x</sub>Te<sub>x</sub>*. Journal of Alloys and Compounds, 2009. **486**(1–2): p. 335-337.
56. K. Masatake, K. Hara, J. Osugi, *Layer growth of ZnSb phase in the Zn-Sb diffusion couple at high pressure*. Review of Physical Chemistry of Japan, 1977. **47**(1).
57. B.L. Zhu, C.S. Xie, A.H. Wang, D.W. Zeng, M.L. Hu, W.Y. Wang, *Electrical conductivity and gas sensitivity of Zn–Sb–O thick films*. Materials Research Bulletin, 2004. **39**(3): p. 409-415.
58. J.C. Fan, K.M. Sreekanth, Z. Xie, S.L. Chang, K.V. Rao, *p-Type ZnO materials: Theory, growth, properties and devices*. Progress in Materials Science, 2013. **58**(Copyright (C) 2015 American Chemical Society (ACS). All Rights Reserved.): p. 874-985.
59. A. Iribarren, P. Fernández, J. Piqueras, *Cathodoluminescence study of Te-doped ZnO microstructures grown by a vapour–solid process*. Journal of Materials Science, 2008. **43**(8): p. 2844-2848.
60. F. Jamali-Sheini, R. Yousefi, M.R. Mahmoudian, N. Ali Bakr, A. Sa'aedi, N. Ming Huang, *Facile synthesis of different morphologies of Te-doped ZnO nanostructures*. Ceramics International, 2014. **40**(6): p. 7737-7743.
61. D. Eklof, A. Fischer, Y. Wu, E.W. Scheidt, W. Scherer, U. Haussermann, *Transport properties of the II-V semiconductor ZnSb*. Journal of Materials Chemistry A, 2013. **1**(4): p. 1407-1414.
62. H.-G. Müller, G. Schneider, *Elektrische Transportgrößen von n-und p-ZnSb*. Zeitschrift für Naturforschung A, 1971. **26**(8): p. 1316-1322.
63. A. Abou-zeid, G. Schneider, *Various Donors in n-ZnSb and the influence of sample treatment*. Z.Naturforsch 1975. **30a**: p. 381-382.
64. G.A. Saunders, C. Miziumski, G.S. Cooper, A. Lawson, *The seebeck coefficients of antimony and arsenic single crystals*. Journal of Physics and Chemistry of Solids, 1965. **26**(8): p. 1299-1303.

## Supporting information

The measurements of the electrical conductivity and the Seebeck coefficient were performed using a ZEM 3 (ULVAC-RIKO, Inc., Japan) apparatus in the range of temperature from 300 to 600K. The pellets were cut into 10 mm x 2 mm x 2mm parallelepipeds. The contacts were checked with I-V plots and each sample underwent two cycles of measurements. Since the results for both cycles are identical and for a better understanding of the results only the second one is shown here.

