Chapter 3
Effect of Open Die Pressing on the Chemical-Physical Properties of Zn_4Sb_3 Compound

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Abstract Recently, semiconducting intermetallic compounds, belonging to the Zintl phases, have attracted much attention due to their unexpectedly low thermal conductivity, which leads to improved thermoelectric properties. The glass-like thermal conductivity of Zn_4Sb_3, originated in the framework Zn position of its structure, makes this compound one of the most studied phases in the thermoelectric field. The reduction of grain size obtained by the melt spinning process can lead to an improvement of figure of the Merit-ZT but, unluckily, is associated with an increase of material brittleness.

As a prosecution of a previous work, melt-spun samples and powders obtained by a solid-phase synthesis of Zn_4Sb_3 were sintered by Open Die Pressing (ODP) process: with this technique, already used for sintering of nano-powder of chalcogenides, bulk samples with high density and compactness were produced.

Chemical physical properties and the stability of the pure phase Zn_4Sb_3 are investigated after ODP process. All samples were studied in terms of crystal structure, phase composition, thermal stability, mechanical resistance and thermoelectric properties. Preliminary results show the formation of ZnSb phase into the Zn_4Sb_3

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A. Amaldi and F. Tang (eds.), *Proceedings of the 11th European Conference on Thermoelectrics: ECT 2013*, DOI 10.1007/978-3-319-07332-3_3,

matrix after both melt spinning and ODP processes: the effects of time and temperature parameters of ODP process on ZnSb phase formation have also been investigated and thermoelectric properties have been compared for the different conditions.

Keywords Zn_4Sb_3 • Thermoelectric materials • Mechanical processing • Rapid solidification

Introduction

Efficient thermoelectric devices for technological applications require the development of new materials that combine high thermoelectric performance, low cost and chemical stability, in order to make them suitable for different operating conditions [1, 2]. The challenge of thermoelectric materials research is to find compounds with high ZT, in particular in the intermediate- and high-temperature range, in order to improve their capability in wasted heat recovery. The *glass-like* thermal conductivity of some compounds belonging to the Zintl phases makes this class one of the most studied in the thermoelectric field [3]. Particularly the Zn_4Sb_3, originating its good thermoelectric performance from its disordered structure, is one of the most studied intermetallic due to its very low thermal conductivity. Unfortunately, the Zn_4Sb_3, as the main intermetallic compound, presents a very high brittleness [4]. This behaviour is a heavy obstacle for its application in thermoelectric modules.

Here a new approach, aimed to obtain an improvement of the Zn_4Sb_3 mechanical performance, is proposed. The intermetallic, obtained through a simple route, has been processed using Open Die Pressing (ODP) technique [5] starting from both ground bulk material and Melt-Spun (MS) material. ODP has already been successfully applied for fast chalcogenide powder sintering, the main feature of the process being the low temperature involved and the short time required for sintering. Both these factors contribute in preserving a fine structure in the final sample. In this work the results of an investigation carried out on the effects of ODP on microstructural, mechanical, thermal and thermoelectric properties are presented.

Experimental

The intermetallic binary compounds Zn_4Sb_3 were synthesised as bulk samples. A stoichiometric ratio of pure commercial elements (purity 99.999 %), sealed in silica vials under Ar flow, were heated at 750 °C in a muffle furnace, annealed at this temperature for 10 h and spontaneously cooled for 5 h. The material produced was processed following two different paths. In the former the ingot was ground and the powders obtained ODP processed into a Fe sheath. In the latter the material was melt spun [6] and the ribbons obtained were sintered via ODP process again using a Fe sheath as mechanical support for the compaction. The sintering process was

performed at 285 and 290 °C with a sintering time varying from 2 to 10 min. Following both the procedures described, densifications between 98.5 and 99 % of the theoretical value reported in literature [7] were obtained.

A Scanning Electron Microscope (SEM) equipped with Energy-Dispersive X-ray spectroscope (EDX)—EVO 40 (Carl Zeiss) with Pentafet Link (Oxford Instruments)—was used to examine microstructures and determine phase composition. X-ray diffraction (XRD) analysis was used to investigate the phase crystal structures and the lattice parameters. The measurements were performed on bulk or powdered samples using a vertical diffractometer (PANalytical X'Pert Pro model). XRD measurements were also performed at different temperatures, in order to evaluate possible effects on the phase stability in the samples. Data refinement was carried out using Rietveld method by Full Proof Suite software. To evaluate the analytical sample composition, an ICP-AES analysis (Inductively Coupled Plasma-Atomic Electronic Spectroscopy) was performed to support XRD and EDX analyses.

Thermal stability of the samples was investigated by differential scanning calorimetry (DSC) using a power compensation Perkin Elmer Diamond DSC.

Electrical conductivity of the processed samples was measured as a function of the temperature using Van Der Pauw method between 300 and 700 K. In the same range measurements of the Seebeck coefficient have been performed using an MMR Technology system, in order to evaluate the power factor.

Results and Discussions

In Table 3.1 the results of ICP analyses are reported. A change in Zn content at different steps of sample preparation was observed: starting from stoichiometric 4:3 Zn–Sb ratio for as-cast sample, a reduction of this ratio to 1.25 was found after ODP process. This result is consistent and explains the results of other characterizations.

Indeed SEM investigations showed the presence of ZnSb phase into the Zn_4Sb_3 matrix as displayed in Fig. 3.1. The little solubility field of this secondary phase is consistent with the phase diagram [8] considering the Zn content in each sample characterised.

Normalised XRD patterns are reported in Fig. 3.2: Rietveld refinement allowed to obtain lattice parameters, atomic positions and atomic occupancies in the β-Zn_4Sb_3. Results of the analyses were in accordance with cell parameters reported in literature [9, 10], giving lattice parameters *a* and *c*, 1.2228 nm and 1.2424 nm,

Table 3.1 Results of ICP analyses performed on different samples

Sample	Zn (ppm)	Sb (ppm)	Zn:Sb ratio	Zn at. %
Zn_4Sb_3 (th)	–	–	1.33333	57.1
As-cast	10.9	7.85	1.3410	57.3
Melt spun	7.58	5.63	1.3830	58.0
ODP no MS	70.2	47.2	1.2520	55.5
ODP MS	62.3	39.6	1.1836	54.1

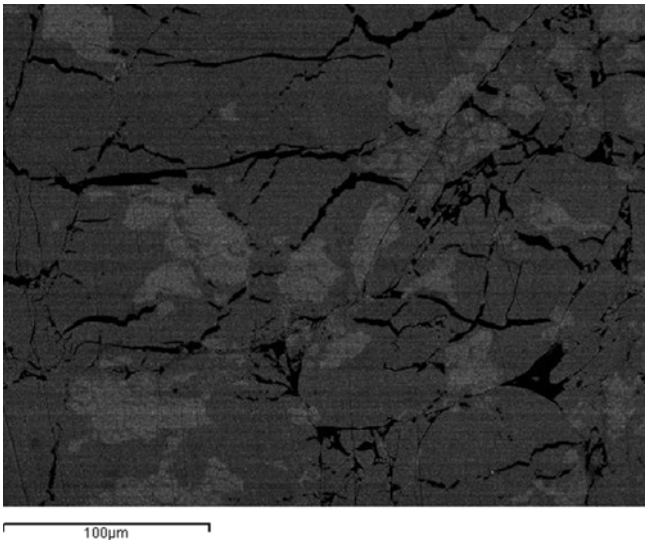

Fig. 3.1 SEM image of ODP sample. The *darker* phase corresponds to Zn_4Sb_3 matrix, the *lighter* one to ZnSb secondary phase

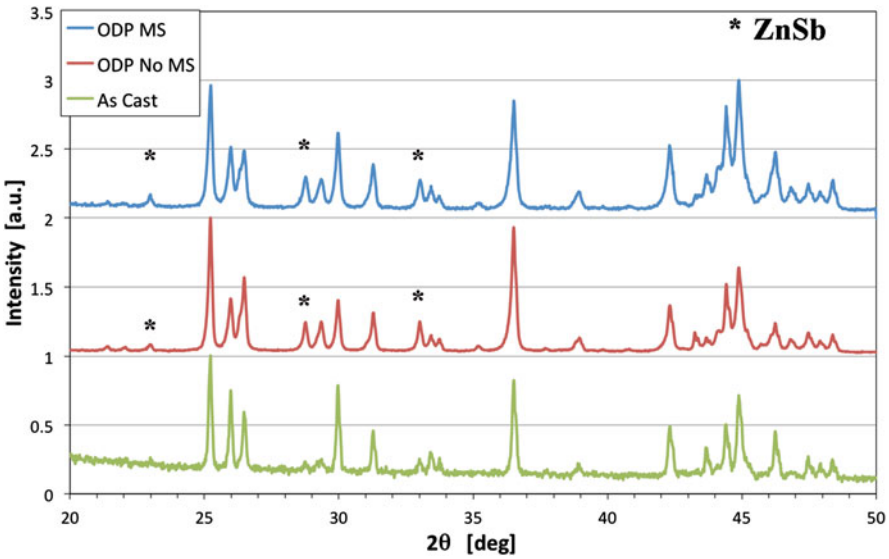

Fig. 3.2 XRD patterns of, starting from the *bottom*, as-cast material, ODP-processed powders and ODP-processed MS ribbons

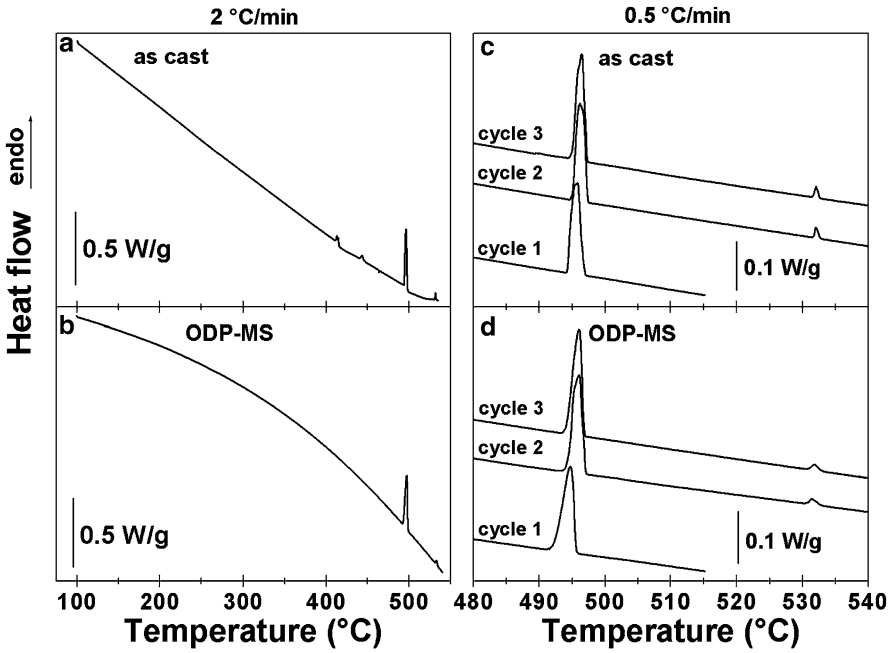

Fig. 3.3 Calorimetric analyses of as-cast (**a**) and ODP samples (**b**) in the range of 100–550 °C. Both measurements were performed at 2 °C/min. Thermal cycling of the same samples is reported in (**c**) and (**d**), respectively, in the range of 480–540 °C: slower rates were used (0.5 °C/min)

respectively. The ODP process resulted to have no significant effect on structural properties of the starting compounds. The two phases already seen with previous analyses were observed: peaks due to the presence of a little amount, estimated in the range of 3–4 %, of ZnSb were identified. XRD performed up to 285 °C displayed no phase evolution in the range of temperatures proper of ODP processing performed on the material.

Calorimetric analyses were performed on the samples up to 550 °C. In order to study the effects of ODP, the starting (Fig. 3.3a, c) and processed (Fig. 3.3b, d) materials were tested.

In the case of the bulk sample, the DSC trace, Fig. 3.3a, shows upon heating a sequence of four endothermic signals: between 409 and 411 °C, around 440, 493, and 532 °C. Each peak can be associated to a corresponding invariant reaction proposed in the equilibrium-phase diagram [8]. However, the two signals at lower temperature (409–411 and 440 °C) are not compatible with the nominal and measured composition, suggesting that the sample is not fully homogeneous. The result can be related to the presence of regions richer in Zn due to local fluctuation of the chemical composition. The two signals at lower temperature disappear in a second DSC heating cycle (not shown here) indicating that the sample became chemically homogeneous after the completion of the first DSC cycle. Repeated heating cycles at 0.5 °C/min on the same sample, Fig. 3.3c, show the reproducibility of the signals at 493 and 532 °C.

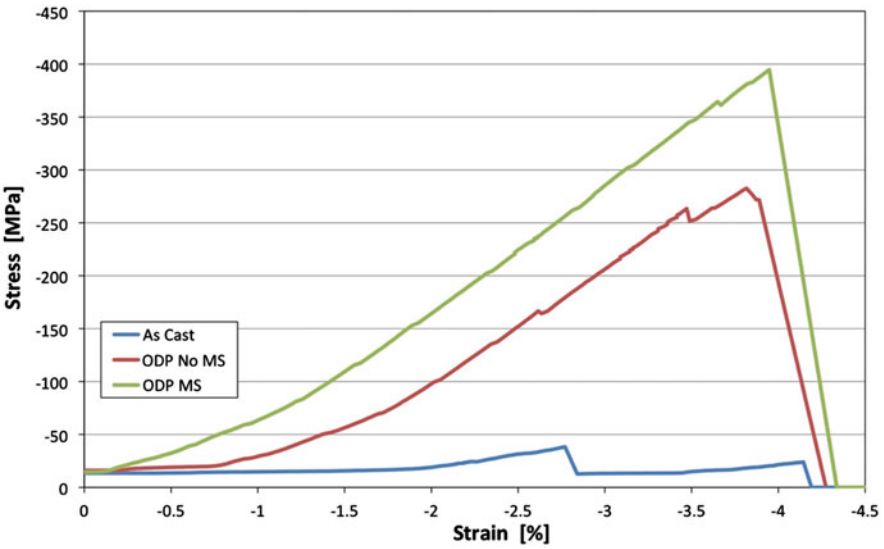

Fig. 3.4 Stress–strain plots in compressive configuration of as-cast, ODP from powders and ODP from MS samples. Sintered material overcomes the limits due to the brittleness of as-cast one

In the case of the ODP sample, the DSC trace, Fig. 3.3b, shows the two expected endothermic signals at 493 and 532 °C, indicating that after ODP processing the sample is already in the equilibrium conditions. Repeated heating cycles at 0.5 °C/min on the same sample show again the reproducibility of the signals at 493 and 532 °C, Fig. 3.3d.

Comparing the DSC traces at 0.5 °C/min, it can be observed that the signal around 532 °C is slightly broader in the ODP sample with respect to the bulk sample. This difference is due to the small variation of composition between the two samples (see Table 3.1) that slightly modify the equilibrium between the phases.

The mechanical behaviour of the samples obtained following the different routes was investigated by stress–strain tests performed in compression in a mechanical test machine (MTS 2/M) at room temperature. Compressive setup was chosen because it better reproduces the most common operating conditions for a material into a basic device (module). Data are reported in Fig. 3.4: the curves correspond to as-cast, ODP of powders and ODP of MS materials. All the samples, as expected, displayed a fragile behaviour with fragile fractures at high strains. The value of fracture load showed a large increase after ODP processing the material: both ODP samples, MS and not, display a maximum load at least eight times greater than the one for original material. MS sample reached the highest value, consistently with the refined structure of starting material. This result suggests that processing the starting material could be helpful in order to overcome the technological limits in the usage of the material represented by its brittleness.

In order to evaluate the effective influence of the ODP process on obtained samples, measurements of electrical resistivity and Seebeck coefficient were carried

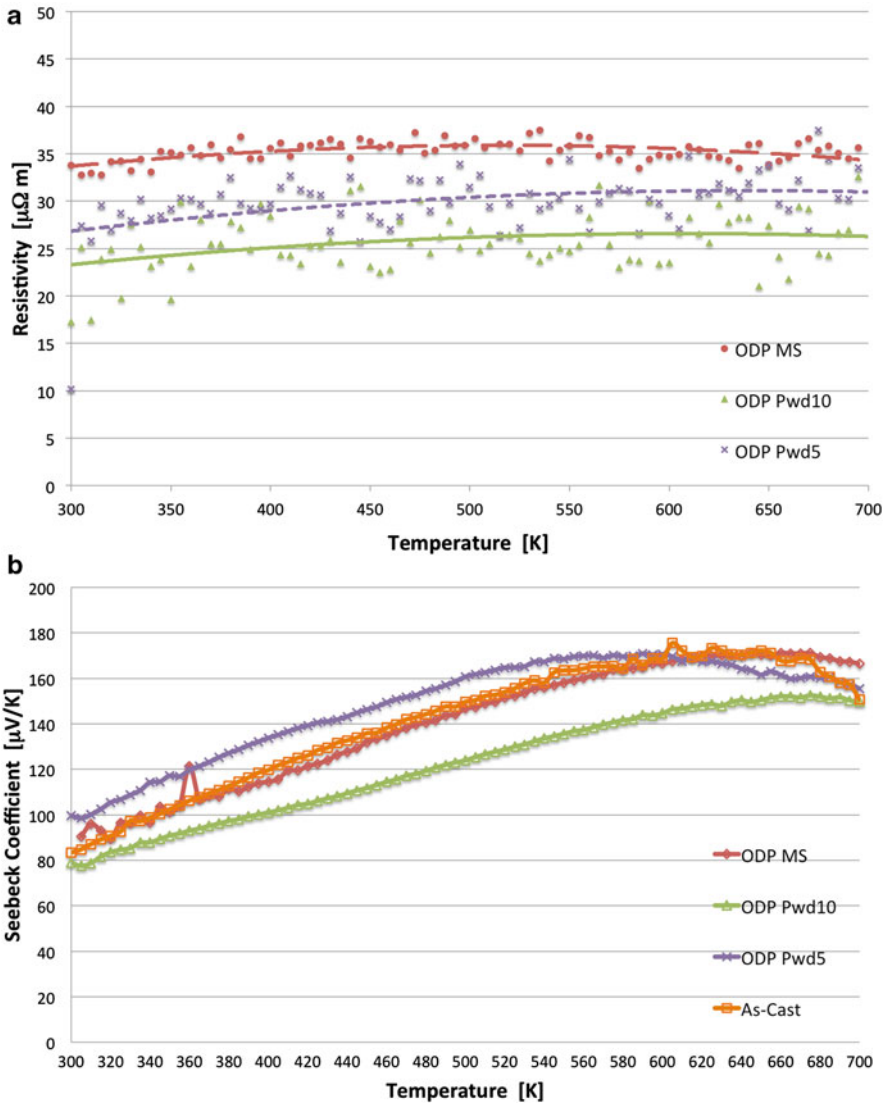

Fig. 3.5 Thermoelectric properties for as-cast and ODP-processed samples. Resistivity (**a**) and Seebeck coefficient (**b**) were measured from 300 to 700 K

out. Results reported in Fig. 3.5 are related to as-cast sample, ODP samples obtained from powders with 5-min and 10-min sintering time (named Pwd5 and Pwd10, respectively) and ODP sample from MS material sintered for 5 min. All the ODP samples were processed and sintered at 285 °C.

The resistivity of ODP-MS samples resulted to be just a bit greater than the one of powdered samples. This effect can be associated to the finer structure of the

sintered material. As expected, a longer sintering time resulted in lower resistivity. The values obtained for as-cast material, here not reported, resulted to be afflicted by the large granularity of the samples obtained from the billet.

The values of the Seebeck coefficient resulted to be lower than the best ones reported in literature: this could be due to the presence of a mix of phases into the final material. As reported in literature the presence of pure Zn and/or ZnSb phase affects the Seebeck value depending on the content of the secondary phases [11, 12]: compared to the pure phase of as-cast sample, the results seem to be similar in all cases.

As a result we can deduce that ODP processing does not clearly affect thermoelectric behaviour of the material: an improvement should be expected in the reduction of thermal conductivity, especially in melt-spun materials, due to the fast sintering process and the low temperatures involved in the ODP process but, up to now, thermal conductivity measurements are still in progress.

Conclusions

Open Die Pressing process was successfully used for the first time to sinter Zn_4Sb_3 compound. The bulk obtained resulted to be fully dense with a sintering time of 5 min at 285 °C: these conditions were such to preserve the microstructure of the sample. Effects of the process have been investigated on melt-spun ribbons, obtaining again good results in terms of densification and thermoelectric properties.

The main result presented in this work is the high improvement in mechanical behaviour of the material after ODP processing: preserving thermoelectric properties of the material, we were able to increase the mechanical resistance of the bulk up to 11 times as respect to the starting as-cast bulk.

Looking for thermoelectric property optimization, further developments are needed in order to reduce the presence of secondary phases in the final material. Moreover, a further refinement of starting powders or a grain refinement of melt-spun ribbons could represent a way to improve mechanical and thermoelectric performances of the ODP-processed samples.

Acknowledgements The authors would like to thank Dr. Gianluca Fiore for the support in the preparation of the rapidly solidified samples by melt spinning, Dr. Francesco Soggia for the ICP-AES analyses, and Dr. Elena Villa and Enrico Bassani for their support in ODP processing and mechanical characterizations.

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