Preparation of BiSbTe based nano-particles by pulsed laser ablation in solution

C. Candolfi, A. Thiam, B. Lenoir, A. Dauscher
Laboratoire de Physique des Matériaux, UMR 7556, Ecole Nationale Supérieure des Mines de Nancy, Parc de Saurupt, 54042 Nancy cedex, France
dauscher@mines.inpl-nancy.fr

Abstract

Laser ablation of bulk targets in a liquid media has been applied to prepare nano-sized powders of multi-components semiconducting materials, namely n and p-type Bi,Sb,Te,Se solid solutions, the best conventional materials for thermoelectric applications at room and moderated temperature. The influence on the composition and the size of the nano-particles formed has been studied as a function of many parameters such as the wavelength, the laser energy fluence, the speed of laser scanning on the target, the laser frequency, the liquid nature and its volume. The powders have been characterized by X-ray diffraction, electron microprobe analyses, scanning electron microscopy, and transmission electron microscopy. Stoichiometric, crystallised nano-sized n-type powders have been successfully achieved. The production of the p-type material remains however to be improved.

Introduction

Nano-structured materials are of great interest for improving the thermoelectric properties. Actually, thermoelectric figures of merit largely higher than those of the corresponding bulk materials have been reported in Bi_2Te_3/Sb_2Te_3 superlattices [1] and PbSeTe/PbTe quantum dot superlattices [2], opening interesting perspectives in the field of thermoelectric cooling and generation.

The preparation of nano-structured bulk materials goes through the necessary step of the synthesis of nano-sized powders. The control of the grain size, the chemical composition, the microstructure and the surface state of nano-powders is essential for the optimization of their properties. The usual techniques for producing nanoparticles include mechanical milling of solid materials, solution chemistry and vapour-phase synthesis. Quite recently, laser ablation of solids in a liquid media appeared as a new way to produce nano-particles. Advantages of this colloid preparation method compared to chemical synthesis are simplicity of the procedure and absence of chemical reagents in solution. This technique has been applied to the synthesis of nano-powders of many materials, especially of metals like silver [3-9] and gold [3,7,10-12] that exhibit particular optical properties at a small scale. Some attempts have been performed with semiconductors like CdS [13], ZnSe [13], and Si [3].

This paper reports the preliminary results we obtained concerning the preparation by pulsed laser ablation in a liquid media of nano-sized n-type $(Bi_{0.95}Sb_{0.05})_2(Te_{0.95}Se_{0.05})_3$ and p-type $(Bi_{0.2}Sb_{0.8})_2Te_3$ powders. These materials were selected because they are the current most performant conventional thermoelectric materials for near room temperature applications.

Experimental procedure

In our experimental set-up, the laser beam produced by a *Q*-switched Nd:YAG laser with wavelength λ = 1064 or 532 nm, pulse width τ = 10 ns, repetition rate R = 2, 5 or 10 Hz is conducted via optical means on a bulk target placed in a liquid media contained in a glass vessel. A lens (f = 300 mm) placed above the ablation cell allows the beam to be focused. During ablation, the laser beam was scanned following a crenel-like form by the way of micrometric motorized x,y tables allowing homogeneous ablation over the whole target. The rate of displacement was fixed to r = 0.5 or 2 mm/s.The density of energy, F, was varied between 1 and 20 J/cm^2 by changing the output energy E. The number of shots, n, was in the range 1-36000.

Three different solvents were selected as the liquid media: water, ethanol and n-heptane. The overall height of liquid, H, was 1 or 2 cm. During the ablation process, the liquid was stirred with a magnetic stirrer to prevent agglomeration on the top of the target and so to maximum avoid further interaction of the formed particles with the laser beam. The powders were collected for characterization after further evaporation of the solvent.

The targets present themselves in the form of discs of 25 mm in diameter and 3 mm in thickness. They were cut from polycrystalline ingots provided by the society 5N+ (Montreal, Canada). The compositions given by the manufacturor are $(Bi_{0.95}Sb_{0.05})_2(Te_{0.95}Se_{0.05})_3$ and $(Bi_{0.2}Sb_{0.8})_2Te_3$ for the n and p targets, respectively.

For all the characterizations needing a significant amount of powder material, the experiments were conducted in the following conditions: λ = 1064 nm, R = 5 Hz, r = 2 mm/s, n = 18000, H = 1 cm. These conditions will be called standard conditions.

The crystallographic structure was determined by X-ray diffraction (XRD) using the $CoK_{\alpha 1}$ radiation. The chemical composition and chemical homogeneity were estimated from electron probe micro-analyses (EPMA) in the wavelength dispersive mode. The mean composition was obtained from about 15 ponctual analyses selected for their mass fitting close to 100. The powders were tamped in a resin. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to evaluate the morphology and size of the powders. For the SEM analysis, a drop of solution taken from the decanted part rich of particles was directly deposited on the SEM holder and dried under an IR lamp. For the TEM analyses, a drop of solution taken in that case from the stirred solution (in order to minimize the particles superposition) was deposited directly on a carbon covered cupper microscopy grid.

Results and discussion

Our first objective was to produce enough particles for their physico-chemical characterization. Different experimental parameters showed great influence on the amount of ablated material. This amount was determined by the difference of mass of the non-ablated target and the ablated target after a given number of shots. The height of solvent of 2 cm was to high to produce any ablation, particularly in ethanol, certainly due to too great absorption of the laser beam by the liquid media. Another important parameter was the repetition rate, as shown in Fig.1. For R = 2 Hz, the mass ablated increases

quite linearly with number of laser shots whereas for 5 Hz, the the ablation kinetic decreases after about 10000 shots, corresponding to a concentration of about 70 $\mu g/cm^3$. The particles present in the solution absorb part of the incident beam, leading to a decrease of the ablation at the target surface. Another phenomena appears for R = 10 Hz. Curiously, the yield is lower than for 5 or 2 Hz. This is certainly due to the higher overlapping between two consecutive shots (about 80 %, 50 % and none for R = 10, 5 and 2 Hz, respectively). The decrease of powder production at 10 Hz is even more clearly evidenced when the scanning rate is lower (90 % overlapping for r = 0.5 mm/s). These results made us choose the repetition rate of 5 Hz for our further experiments.

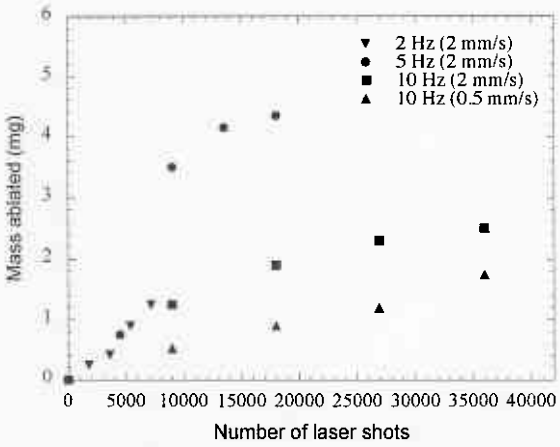

Figure 1 Influence of number of laser shots on the mass ablated for different laser frequencies R and scanning rates r (n-type, 532 nm, water, 2.6 J/cm^2).

Working in the IR spectral domain rather than in the visible allowed us to work at higher densities of energy at the target surface. Increasing F results in an increase of powder production (Fig.2). The change in kinetic ablation regime appeared also at a higher concentration (~ 220 $\mu g/cm^3$) with IR irradiation. The wavelength of 1064 nm was therfore selected.

The production of p-type particles exhibit higher initial ablation yield, but seems to saturate quite more rapidly (Fig. 2).

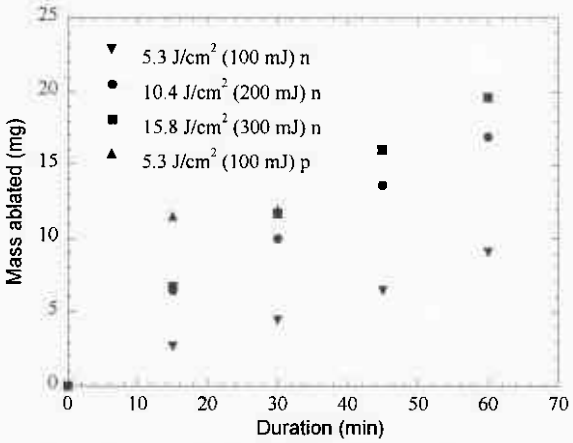

Figure 2 Influence of ablation duration on the mass ablated for different densities of energy F (n-type, water, standard conditions).

The standard conditions were then applied to produce n and p particles. Influence on the crystallographic structure of the output energy and liquid media was studied.

In Fig.3 and Fig.4 are illustrated the influence of the output energy for n and p-type powders produced in water, respectively. The n-type powders are crystallised and the X-ray diffraction patterns exhibit the four main peaks detected in the corresponding target, for quasi all the energies (Fig. 3). It is a unique phase, except for E = 100 mJ for which the peak near $2\theta = 31°$ is not single. For the other energies, this peak is quite large, certainly due to the presence of an amorphous oxide phase. This oxide phase could arise from the decomposition of water at the target-laser beam interface and to further interaction of the oxygen species with the ionized particles species ejected from the target. In ethanol, the n-particles are also crystallised and single phase. However, the peak enlargment at $2\theta = 31\text{-}32°$ is less pronounced while ethanol could decompose like water. In n-heptane, the powders produced where multi-phases, whatever E was. It is intersting to note that we never obtained the chemical composition of the target at $\lambda = 1064$ nm when working in the gas phase for the preparation of Bi_2Te_3 thin films by pulsed laser deposition [14].

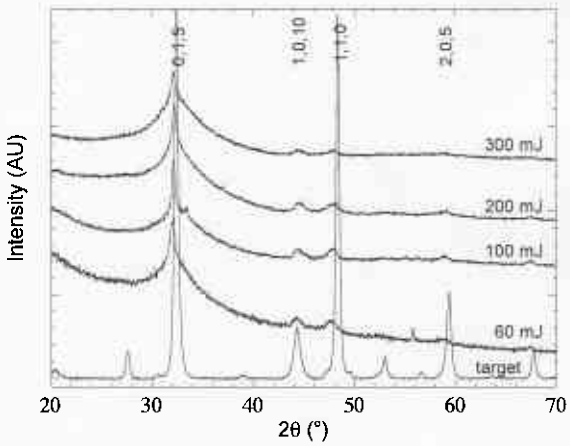

Figure 3 X-ray diffraction patterns of n-type materials: target and powders prepared at different output energies in water (standard conditions).

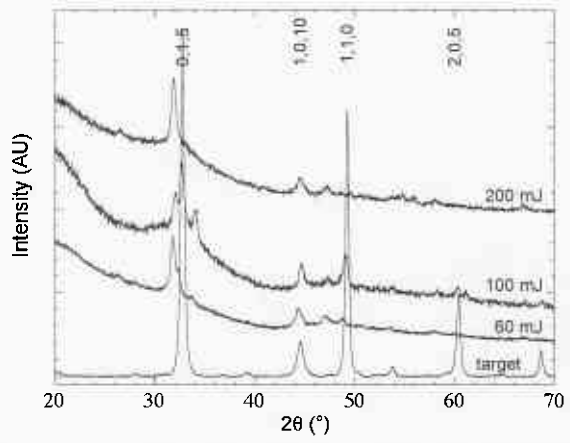

Figure 4 X-ray diffraction patterns of p-type materials: target and powders prepared at different output energies in water (standard conditions).

The p-type powders produced were all crystallised, but they were never single phase neither in ethanol nor in n-heptane. In water, single phases are obtained but they are different from that of the target (Fig.4).

The chemical composition and homogeneity was checked by EPMA for selected samples. One must note that as the analysis pear is about 1 μm^3, the analysis takes into account a large number of particles. Moreover, as the material was not sintered, there are a lot of voids that were filled by the resin. The results are compared to those obtained with the targets analysed under similar conditions (table 1). The chemical composition of the n-powders are not dependent on the energy of the laser beam. They exhibit a small excess of bismuth to the detriment of tellurium with regard to the target, but these compositions are close to the most performant n-type solid solution $(Bi_{38}Sb_2)_2(Te_{58}Se_2)_3$. The p-type powders prepared in water are of same composition as the target, whereas some deviation can be seen in n-heptane, but again we are close to the best p-type material $(Bi_8Sb_{32})_2Te_3$. So even if the powders are multi-phases, the mean chemical composition reflects generally the composition of the target (n-type/water/300 mJ, p-type whatever the experimental conditions are).

	Bi	Te	Sb	Se
n-target	36.5	59.4	2.2	1.9
n-powders water, 100 mJ	38.2	58.2	1.8	1.8
n-powders water, 300 mJ	38.7	57.8	1.6	1.9
p-target	7.6	60.8	31.3	-
p-powders water, 60 mJ	8.0	60.8	31.3	-
p-powders n-heptane, 60 mJ	8.5	61.6	29.9	-

Table 1 Atomic percentage of the different elements present in the target and the powders as determined by EPMA (standard conditions for the powders).

The dispersion of the chemical compositions according to the analysis points and with regard to that of the target is reported in Fig. 5.

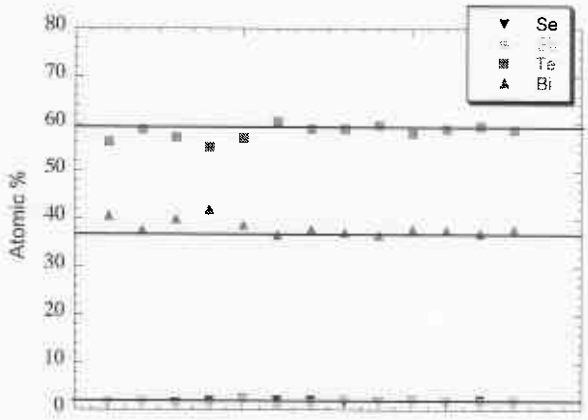

Figure 5 EPMA results of n-type powders produced in water at 100 mJ (standard conditions).

The influence of the solvent, the output energy and the wavelength on the morphology and size of the n and p-type particulates has been investigated. All these parameters lead to great differences. Fig.6 provides examples of n-type powder morphologies obtained by SEM in the three different liquid media. In water , the particles look strongly agglomerated and like cauliflowers. Their shape is either spherical or facetted. They are quite uniform in size. The size distribution was determined from TEM (Fig.7). The mean particle size deduced from this counting is 28 nm, value that is in agreement with that found by using the Scherrer's formula on the main diffraction peak (35 nm). This means also that in water, it

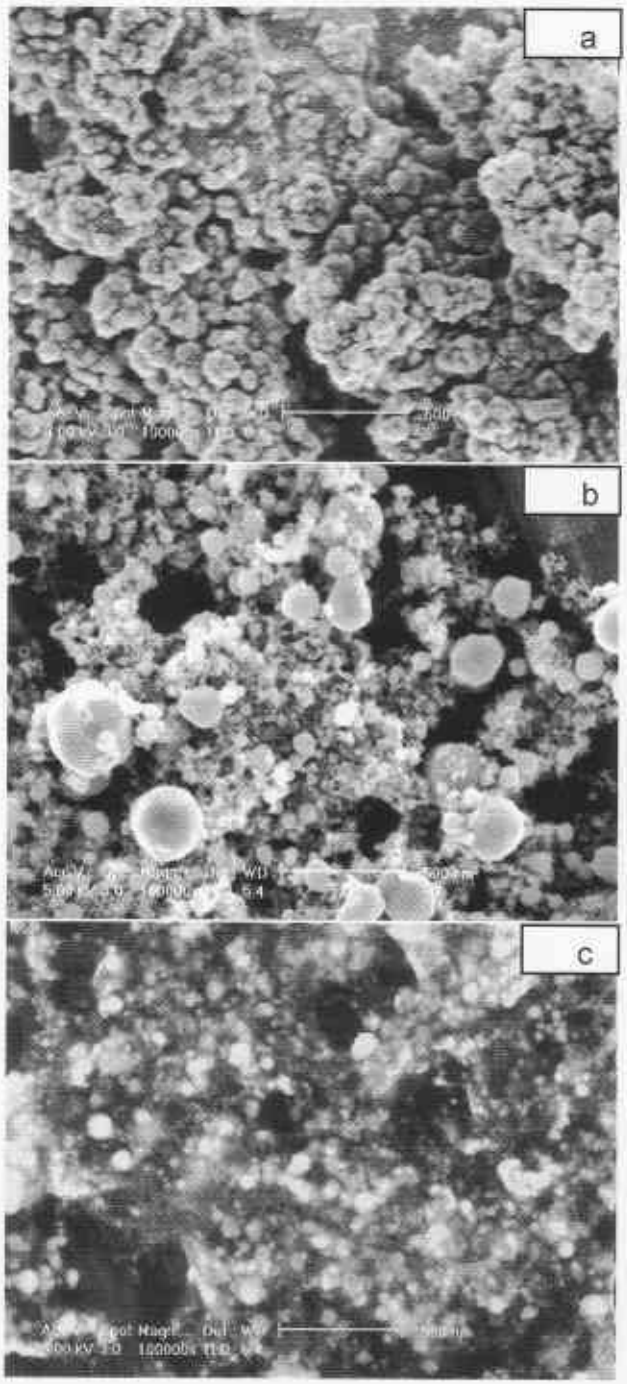

Figure 6 SEM images of n-type nano-powders produced at 100 mJ in: a) water, b) ethanol, and c) n-heptane (standard conditions).

seems no fracture of the particulates to occur after longer ablation durations (TEM: 200 shots, SEM: 18000 shots). Selected area diffraction patterns show the particles are crystallised. The diffraction rings could be attributed to d-spacing of the $Bi_{1.8}Sb_{0.2}Se_{0.15}Te_{2.85}$ compound (JCPDS file n°00-049-1714).

In ethanol, the size ditribution is broader. Some very large particulates are obtained (> 200 nm). This could result from the presence of two different ablation regimes, especially at the beginning of ablation where highly energetic bubbles are formed, together with a plasma regime. The more exothermic regime would result in the expulsion of the largest particles.

In n-heptane, the particles seem smaller than in water. They look embedded in a sort of matrix that has also been observed on the TEM images. It has not been identified yet.

The solvent effect seems less evident with the p-type particles.

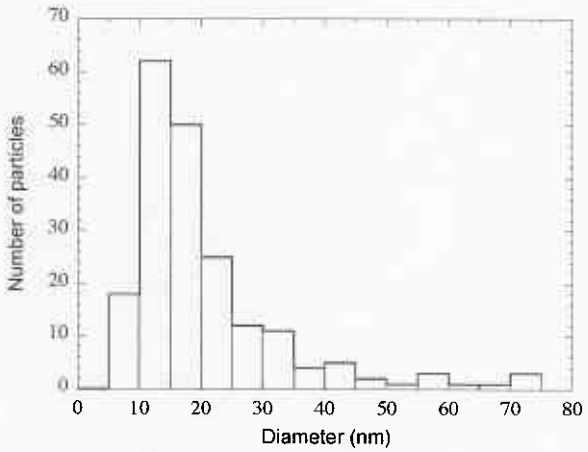

Figure 7 Size distribution deduced from TEM micrograph images of n-type particles produced at 100 mJ in water (200 shots, other standard conditions).

Lower output energies lead to smaller particles. Working in the visible range rather than in the IR also lead to a decrease of the mean particle size.

Conclusions

We have shown that pulsed laser ablation in a liquid media is an efficient and simple technique to prepare nano-sized powders. Single phase n-type $(Bi_{0.95}Sb_{0.05})_2(Te_{0.95}Se_{0.05})_3$ nano-particles of fairly similar composition than the target have been successfully synthesized in water and ethanol. The preparation of a p-type single phase $(Bi_{0.2}Sb_{0.8})_2Te_3$ revealed to be more delicate, may be because of the differences in absorption coefficients and probably different interaction with the solvent.

The influence of a lot of parameters has been investigated. The wavelength acts mainly on the saturation limit of absorption in the solution, the composition and the particles size. The solvent plays a role in the crystallographic phase achieved, the size of the particules and their aptitude to agglomeration. Finally, the output energy is important in what concerns the ablation yield, the crystallographic phase and the particles size. So, by tuning all these parameters, we should be able to produce high quality nano-sized thermoelectric particles.

Acknowledgments

We would like to thank Dr X. Devaux for his help in the MET analyses.

References

1. R. Venkatasubramanian et al., Nature, 413 (2001) 597.
2. T. C. Harman et al., Science, 297 (2002) 2229.
3. S. I. Dolgaev et al., Appl. Surf. Sci, 186 (2002) 546.
4. C. H. Bae et al., Appl. Surf. Sci., 197-198 (2002) 628.
5. T. Tsuji et al., Appl. Surf. Sci, 202 (2002) 80.
6. T. Tsuji et al., Appl. Surf. Sci, 206 (2003) 314.
7. A. V. Simakin et al., Appl. Phys. A, 79 (2004) 1127.
8. A. Pyatenko et al., Appl. Phys. A, 79 (2004) 803.
9. R. A. Ganeev et al., Optics Comm., (2004), available on line.
10. G. Compagnini et al., J. Appl. Phys., 94 (2003) 7874.
11. A. V. Kabashin et al., J. Appl. Phys., 94 (2003) 7941.
12. F. Mafuné et al., Chem. Phys. Lett., 372 (2003) 199.
13. K. V. Anikin et al., Chem. Phys. Lett., 366 (2002) 357.
14. A. Dauscher et al., Thin Solid Films, 280 (1996) 61.