Fabrication of p-n junctions from conventional nano-sized thermoelectric materials

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Abstract

The technique of laser ablation in a liquid medium has been applied to the synthesis of n-type $(Bi_{0.95}Sb_{0.05})_2(Te_{0.95}Se_{0.05})_3$ and p-type $(Bi_{0.2}Sb_{0.8})_2Te_3$ semiconducting nanopowders which are the best conventional materials currently used for thermoelectric applications at ambient temperature. The nanopowders have been prepared in a cell specificially built-up from laser fracture in water of micron sized nanopowders using a nanosecond Nd:YAG laser working at 532 nm. The obtained powders have been characterized by scanning and transimission electron microscopy and by X-ray diffraction. To test the potentiality of these nano-sized materials, we have fabricated a simple electronic device from them aimed to show that it is possible to create a depletion region in a p-n junction.

Introduction

Thermoelectric materials provided many attractive researches and applications because of their ability of current generation or refrigeration. The principal characteristics for good thermoelectric materials are given through the dimensionless figure of merit *ZT*, where *T* is the absolute temperature and $Z=S^2\sigma/k$. In this equation, S is the Seebeck coefficient, σ the electrical conductivity, and k the total thermal conductivity. Finding more efficient thermoelectric materials corresponds to get materials with higher values of *ZT* than state-of-the-art materials. One of the several ways investigated to achieve a higher figure of merit is to reduce the initial size of the thermoelectric material to low dimensional nano-structures. Nanostructuring leads mainly to a reduction of the lattice thermal conductivity [1-3].

In the field of research with semiconductors, the investigations are focused nowadays on the way to reduce the size of the IC devices to the nano. The external cooling of the electronic components is one obstruction that prevents the size of a device to become smaller. Recently, some groups have investigated the possibility to make an internal cooling device from thermoelectric materials [4,5]. The advantage of an internal cooling device is not only to use less space in a system but also to reduce the cost by suppressing the integration of another external cooling source into the device. The internal cooling device is designed in such a way that the operating current also causes the internal cooling.

In this study, we have synthesed nanopowders of conventional thermoelectric materials to see if such nanopowders can be integrated and used for some applications. They were applied for the simple fabrication of a p-n junction. The method that we choose to synthesize the nanopowders is laser fracture of micron-sized particles in a liquid medium which is a new and simple method. It differs a little bit from laser ablation of bulk materials in a liquid, method that has been previously applied for the preparation of various nano-sized materials [6-8]. The material that we choose for n-type is $(Bi_{0.95}Sb_{0.05})_2(Te_{0.95}Se_{0.05})_3$ and p-type $(Bi_{0.2}Sb_{0.8})_2Te_3$ which are up to now the best conventional thermoelectric materials for room temperature applications.

Experimental

1. Synthesis of the thermoelectric nanopowders

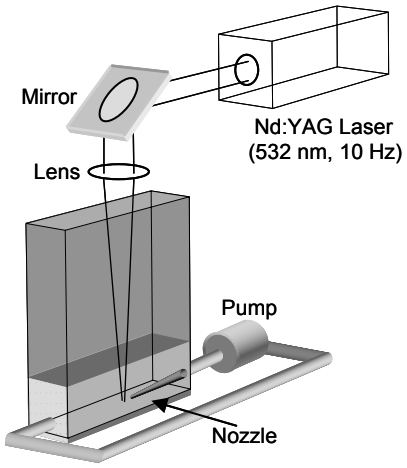

Figure 1. Setup for the synthesis of nanopowders by laser fracture in liquid medium.

The initial raw materials are n-type $(Bi_{0.95}Sb_{0.05})_2(Te_{0.95}Se_{0.05})_3$ and p-type $(Bi_{0.2}Sb_{0.8})_2Te_3$ commercial ingots (5N+) of 18 mm in diameter. Disks of 3 mm in height have been cut and have been further crushed in an agate mortar. The obtained powders have been sieved by 100 μm sieve. These are the initial micron-sized powders exhibiting sizes ranging from 1 to 50 μm. A solution made of 500 mg of these powders and 50 cc of water is put into a special cell designed for yielding higher production rate of nanopowders than the initial cell aimed to produce nano-sized materials from the ablation of a bulk target in liquid [8]. The cell design (Figure 1) is similar to that of a closed chamber but it allows the solution to flow outside and flow back to the chamber continuously by the use of a small pump. This closed loop flow of solution can then be repeatedly hit by a laser beam located at the entrance of the liquid flow in the cell. The flow rate is optimized for a value

of 4 litre/hours. The solution is however injected in the chamber at a higher speed because it travels through a small nozzle and spray inside. The laser beam is focused nearby the solution entrance at a distance of about 5 mm from the nozzle. The solution is hit by the laser beam for 1 hour. The laser used for this work is a pulsed Nd:YAG laser (Continuum Powerlite Precision 8000) working in the second harmonic mode (532 nm) with a repetition rate of 10 Hz. The pulse width is 7 ns. The output energy has been varied from 100 to 400 mJ. The interaction of the laser beam with the liquid medium is a very explosive reaction which causes fluid flushes and consequently a matter loss. This reaction is all the more violent as the energy of the laser beam is high. This is why we limited ourselves to 300 mJ of the laser beam, which corresponds to approximately 250 mJ at the level of the particles (losses of approximately 10% due to two optics (mirror and lens of focusing) and from approximately 7% due to the absorption of the beam by water).

The obtained solution is then filtered and the remaining solution is evaporated at 80 ^{o}C in a beaker on a hot plate for about 1 hour allowing the nanopowders to be finally collected.

The morphology and the size of the powders obtained after laser irradiation of the solution were observed using a scanning electron microscope (SEM, Philips Model XL-30FEG) and a transmission electron microscope (TEM, Philips CM-200) by dropping the resulting solution on a slide for the SEM or a grid covered with a carbon film for the TEM. The drops were dried during 20 min under a lamp. The size distribution of the particles was estimated from the measurement of more than 500 objects on several pictures taken from TEM. The crystallographic structure of the obtained powders was determined by X-ray diffraction (XRD, Siemens D500), by using a Co anticathode. In this case, several drops of solution were deposited onto a glass plate with a drying between each deposition. A thick black layer of nanopowders was obtained for XRD measurements.

2. Fabrication of the p-n junction

A simple process of making a p-n junction was chosen to test the possibility to make an example of semiconductor device (Figure 2). One drop of the solution containing the nanopowders of either p-type or n-type has been dropped on top of a piece of material of opposite type (typical dimensions: 1.5 x 1.5 x 1.5 mm^3) cut in the raw ingots. These assemblies were then heated under air in an oven for periods of 4, 8 or 12 hours at different temperatures raising from 165 to 210°C. The annealing temperature is reached from room temperature in one hour, whatever the final temperature is. After a given annealing duration, the heater was turned off and the samples were let in the oven to cool down slowly.

The two terminals of the p-n junction device have been connected to selected electrodes to avoid the rectifying contact or the Schottky diode effect. The bulk piece has been connected to an aluminum electrode whereas a Ni coated copper wire was fixed to the top of the opposite type nanopowders by silver paste.

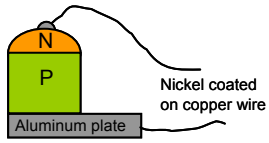

Figure 2. Example of fabrication of a p-n junction made of n-type nanopowders deposited on top of a p-type bulk piece.

3. Measurement of *I-V* characteristics

A simple circuit has been used to measure the *I-V* characteristic curves. The voltage between the junction has been recorded during the application of a constant negative or positive current pulse to the circuit. The constant current pulse-width has been limited to 0.5 second in order to prevent the damage of the fragile structure of our simple p-n junction fabrication due to the temperature gradient near the depletion region, in the forward bias. The maximum current pulses has been limited to 20 mA. During the application of the current pulse, the voltage drop across the p-n junction is always checked during the increasing of the current pulse to be sure that the power at the p-n junction is never greater than 100 mW.

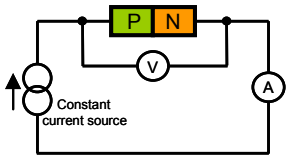

Figure 3. Schematic representation of the circuit setup used for measuring the *I-V* characteristics.

Result and discussions

1. Nano-particles characterization

Initially, we studied the influence of the number of shootings on the quantity of produced nano-particles. A global and fast solution of the result was visualized from a test of sedimentation. We have clearly seen that the more important the number of shoots is, the more the solution becomes black and the less the deposit of particles at the bottom of the container is. The duration of sedimentation increases with the number of shootings and thus the weight and in consequence the size of the particles decrease. The work of fracture of the microparticles under the impact of the laser beam is thus all the more effective. After one hour shooting, the solution appears as an ink, which remains stable during several days (no deposit).

From SEM analyses, we have shown that after the laser treatment, the powders have in general less than 30 nm in diameter.

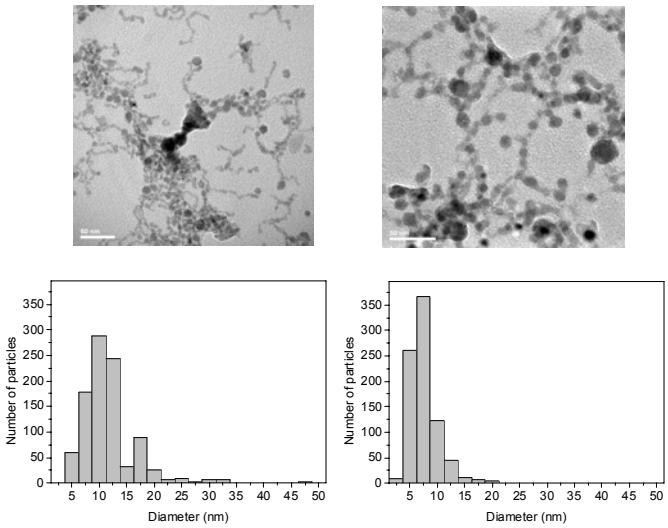

Figure 4. TEM typical images and particle size distributions of n-type and p-type nanopowders (36000 shots, 200 mJ)

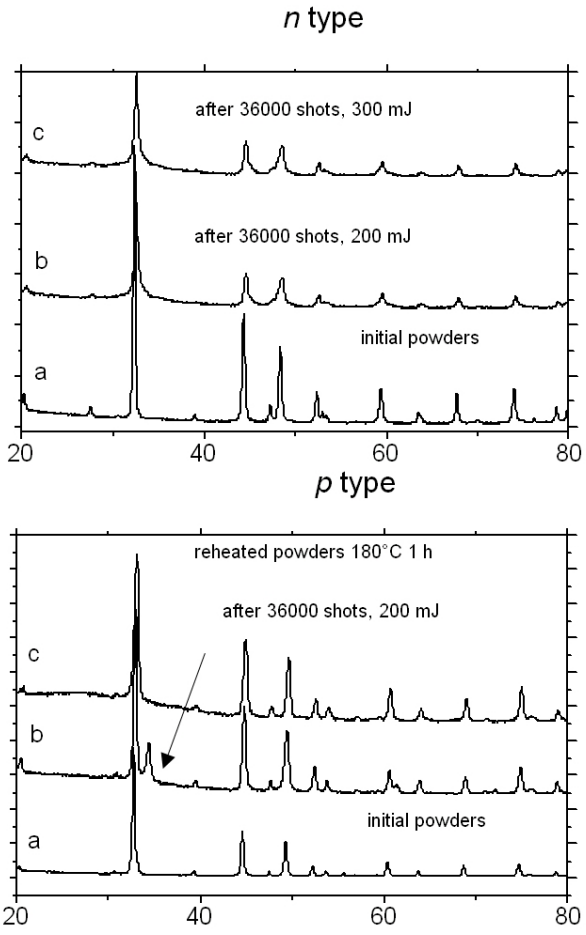

Figure 5. Crystallographic structure of n- and p-type nanopowders (36000 shots, 200 mJ)

TEM has been used to study the shape and the size of the particles. In figures 4a and 4b are the images obtained from TEM and the corresponding size distributions for materials of n-type and p-type, respectively. Whatever the starting material is, the largest particles are present in the form of agglomerates whereas the smallest, which have a diameter of about 5 nm or less, are arranged in the form of chains. The particles are crystallized as shown by electronic diffraction carried out on selected areas. The particles seem globally spherical but are nevertheless all are more or less faceted. This would mean that the particles are not trapped instantaneously in the liquid medium and have time to crystallize according to a preferential orientation. For the n-type material, the distribution in size is relatively narrow (between 2.5 and 25 nm) and the average diameter is of 6 nm. For the p-type material, the distribution is broader (between 2.5 and 50 nm) and the average size is larger (10 nm). These sizes are definitely smaller than those of the powders obtained from ablation in water of a bulk ingot of similar composition for which the average diameter was found equal to 28 nm [8]. These results show that the process of fracture of micron sized powders is definitely more effective than the ablation starting from a bulk material. The processes of light absorption and heat transfer are different for a particle of about 10 µm diameter than for a bulk target.

The nanosized powders were characterized by XRD and the diffraction patterns were compared to those of the initial powders (figures 5a and 5b for materials of n-type and p-type, respectively). The powders obtained are all crystallized. For the n-type material, the nanosized powders exhibit all the diffraction peaks of the initial powders at the same angular positions whatever the output energy of the laser beam (200 or 300 mJ) is. They are however slightly enlargeded for the nanosized powders. For the p-type material, the presence of only one additional peak is noted in the neighborhood of 2 theta = 34°. This peak could neither be attributed to one of simple elements, Bi, Te or Sb, nor to any known compound indexed in the JCPDS files. Thus, as for the powders produced from a bulk material, the achievement of the p-type material is more delicate [8]. Nevertheless, except this peak, all the other peaks of the diffractogram correspond to those of the initial powders. In addition, this peak disappears after a simple heating of one hour under air at 180°C. It would be a non-stable compound perhaps resulting from a reaction with the water dissociated during the process.

2. p-n junction

Figure 6 shows the *I-V* characteristics measured at room temperature of three samples fabricated from various heating durations. From the curves, we can see that the depletion starts to form when the heating fabrication process is longer than 4 hours. We can see that an increase in heating duration leads to a decrease of the onset voltage from 0.6 to 0.3 V and to a faster exponential increase in the forward bias. After a heating duration of 12 h, a nice *I-V* characteristic curve is obtained, showing that it is possible to create a real

p-n junction from the nano-powders. To find the appropriate temperature for making the p-n junction, it has been varied between 100 to 210 °C. The temperature has been limited to 210 °C in order to preserve the stoichiometry/nanosizing of the n-type nanopowders and p-type piece. We observed that for a temperature below 180 °C, it was difficult to have the formation of a p-n junction. The measured break down of reverse bias voltage is around 3.5 V (Figure 7) which implies that low voltage - high current should be applied for the use in reverse bias region.

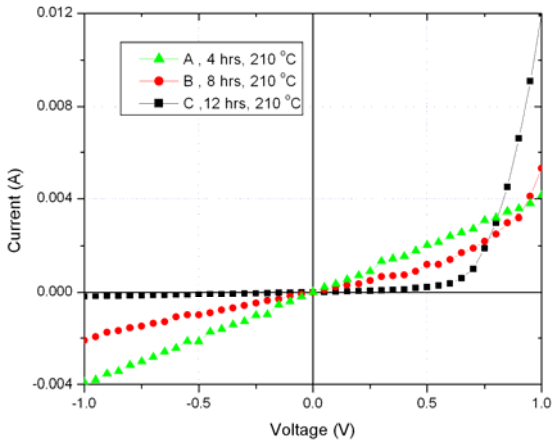

Figure 6 *I-V* characteristic plots of p-n junctions made of n-type nanopowders deposited on top of a p-type piece. Influence of the heating duration.

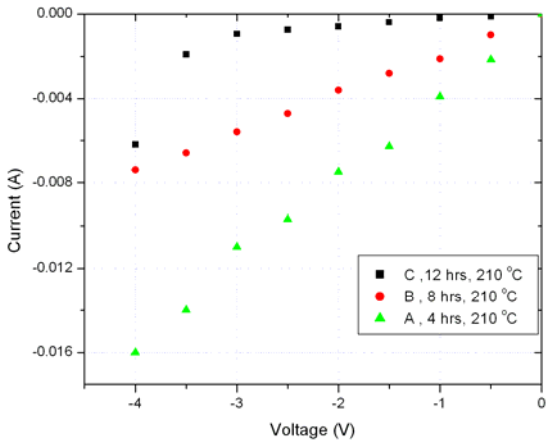

Figure 7 Reverse bias of *I-V* characteristic plots of p-n junctions made of n-type nanopowders deposited on top of a p-type piece. Influence of the heating duration.

Conclusions

We propose here a simple way to synthesize nanosized powders of complex composition $(Bi_{0.2}Sb_{0.8})_2Te_3$ and $(Bi_{0.95}Sb_{0.05})_2$ $(Te_{0.95}Se_{0.05})_3$, obtained from micron sized powders treated by laser irradiation in a liquid medium. Times of synthesis are very short and no further treatment is necessary. The nanosized powders preserve the crystallographic structure of the initial powders, for both n- and p-type materials. This is particularly useful if one wishes to manufacture a thermoelectric module for which it is necessary to have n- and p-type materials having similar thermoelectric and mechanical properties.

The rate of transformation, at the end of one hour of treatment, is quasi total. This last point is particularly interesting since it makes it possible to consider an important production of nano-particles.

A simple p-n junction has been fabricated from the synthesized nano-powders. A depletion region is evidenced that exhibits the good characteristics of a diode. The study and the control of the depletion region can be easily tailored according to this method without need of any complicated or complex set-up and any time consuming. One other major interest of this new kind of devices we fabricated is that they can work as self-temperature cooling devices, since they are made of thermoelectric materials. This is particularly important for diodes, resistors, capacitors and any other semiconductor device.

Acknowledgments

The authors would like to acknowledge the European NoE "Complex Metallic Alloys" for financial support.

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