SYNTHESIS AND CHARACTERIZATION
OF Sb_2Te_3-NANOSTRUCTURES

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Abstract
In this work, Sb_2Te_3 nano-materials were prepared by chemical and mechanical methods. Synthetic conditions, structural and morphological characterisation as well as the thermoelectric properties are discussed.

Introduction
Nanostructuring is one of the effective approaches to increase the figure-of- merit of thermoelectric materials. Theoretical work has shown that small, dimensionally-confined materials systems can exhibit figures of merit well in excess of one [i,ii]. Moreover, many studies have shown that the thermoelectric properties can be improved by nanostructuring the materials, such as Bi_2Te_3/Sb_2Te_3 superlattices thin-film thermoelectric materials [iii], PbSeTe based quantum dot superlattice structures [iv] and incorporating nanoscale constituents within bulk materials to form nanocomposites [v,vi].
In this work, we aimed to fabricate nanostructured Sb_2Te_3 by mechanical alloying and hydrothermal synthesis and to study their morphology and thermoelectric properties.

Experimental
Nanostructured Sb_2Te_3 was prepared by both mechanical and chemical methods.
Mechanical Alloying: Sb (5N) and Te (5N) were weighed and loaded into a tungsten carbide bowl with ball-to-material ratio of about 8 for the Sb_2Te_3 preparation. All manipulations were done under nitrogen atmosphere. The ball milling experiments were performed at the speed of 400rpm for different times up to 38hrs. During the first 28hrs of the process, the balls of 10mm in diameter were used while for the rest 10 hrs the balls of 1.6mm in diameter were used. The experiment was stopped several times and some powder was taken out each time for examination. A small amount of the final product was annealed at 673^oK for 36hrs in order to use it as reference in the X-ray diffraction analysis.

Hydrothermal Synthesis: The hydrothermal synthesis was carried out using a modified procedure of a methodology recently reported for the construction of hexagonal nanoplates of Sb_2Te_3 [vii]. In particular the reaction mixture was prepared in a 45 ml Parr reactor inside a nitrogen field glove box as follows: 0.275 mmol of hexadecyltrimethylammonium bromide (CTAB) was dissolved in a mixture of 2.5 mL of distilled water and 20 mL of ethanol. After stirring for 10 min, 2.5 mmol of $SbCl_3$ was added followed by 3.75 mmol of Te powder and 5 mmol of $NaBH_4$. The mixture was stirred for 15 min. The Parr reactor was placed in a furnace at 200^oC for 24hrs. After cooling down at room temperature, a black solid was collected using suction filtration, washed with distilled water and dried in air.
Phase and morphology information of products obtained by the two methods of synthesis were studied by powder X-ray diffraction analysis (PXRD) and by scanning electron microscope (SEM). The Seebeck coefficient was measured on cold

pressed pellets at temperature range of 80-400K.

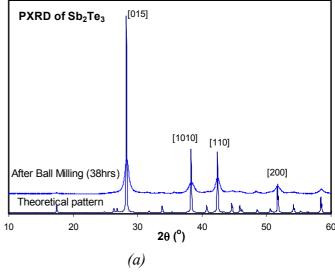**Results and discussion**

Mechanical Alloying
Figure 1a shows the PXRD patterns of the powder after ball milling in comparison to the theoretical of the Sb_2Te_3 phase. The patterns are identical, confirming that the mechanical alloying products correspond to the Sb_2Te_3 phase. Figure 1b shows the [1010] peak of selected ball milled samples. The broadening of the peaks indicates small crystalline size and introduced stress during mechanical alloying process. After annealing, the peaks become sharp indicating that those features are eliminated.

The average grain sizes were estimated using the strongest peak of Sb_2Te_3 [015] with the well-known Scherrer's equation. In this method it is assumed that the broadening is due to the very fine grains and the effect of the lattice strain is not taken into account, therefore the results have some inaccuracy. However, it has been reported [viii] that other methods, where the strain contribution is introduced, can not be successfully applied due to the anisotropic structural features of the material.

Generally, each X-ray diffraction line profile is broadened due to instrumental and physical factors. Therefore, the determination of the pure diffraction line profile is necessary. For our analysis, the Sb_2Te_3 powders were annealed and used as reference in order to get the pure line profile from the experimental profile. The Scherrer's equation is

$$L = \frac{0,9 \cdot \lambda}{\delta(2\theta) \cdot \cos\theta}$$

where $\delta(2\theta)$ is the corrected FWHM and θ is the position of the peak, λ the X-ray wavelength and L the crystallite size.
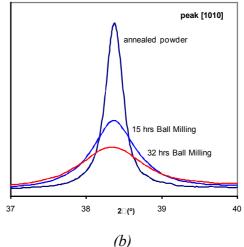

(a)

(b)

Figure 1: (a) Powder X-ray diffraction of powders after ball milling compared to the theoretical pattern. (b) [1010] peak of annealed and ball milled samples.

Figure 2 shows the crystalline size of the mechanical alloyed powders. When balls of 10mm diameter were used, the crystalline size was about 30 nm and it was reduced to 15nm after balls of 1.6mm diameter were used. These values are similar to those achieved elsewhere in the literature [8].
SEM images show the typical morphology of mechanically alloyed powders, see Figure 3. The particles size decreases with ball milling time and after 38hrs is below 1μm. This size corresponds to agglomerates consisting of fine crystals as estimated by PXRD analysis.
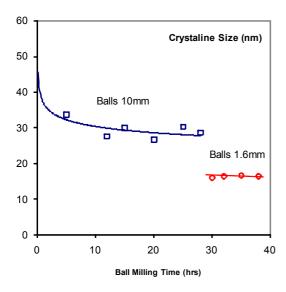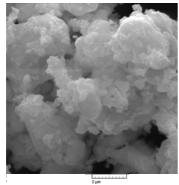
Figure 2: The average grain sizes as

estimated with Scherrer's equation using diffraction peak [015].
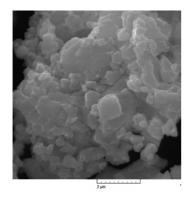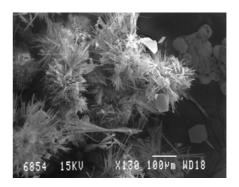

Figure 3: SEM images of mechanically alloyed Sb_2Te_3 after (a) 10hrs and (b) 35hrs.

Hydrothermal Synthesis

The PXRD pattern of the hydrothermal product can be indexed to the rhombohedral Sb_2Te_3 (R-3m) with some extra Te peaks. The morphology of the sample is shown in images of Figure 4. Figure 4a shows a lower magnification image of Sb_2Te_3. Interestingly, the majority of the nanoparticles have a sheaf-shape type. The high magnification image (Figure 4b) demonstrates that the sheaf shaped particles are in the micrometer-scale, with a length of $\sim 200\mu m$.
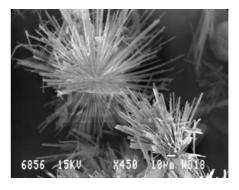

Figure 4: SEM image of the Sb_2Te_3 nanosheaves.

Seebeck Coefficient

In order to study the thermoelectric properties, the Seebeck coefficient was measured for both material prepared by mechanical and chemical methods.

The results from mechanical methods for different ball milling times are shown in Figure 5. The positive values of Seebeck coefficient show that samples are p-type semiconductor materials. The value of Seebeck coefficient of the cold pressed pellets increases with time of milling from ~110 $\mu V/K$ to $130\mu V/K$. These values are higher than those reported for Sb_2Te_3 single crystals and these are ~75 $\mu V/K$ in direction

perpendicular and ~100 µV/K parallel to c-crystallographic axis [ix].

Figure 6 shows the Seebeck coefficient of Sb_2Te_3 prepared by hydrothermal method as a function of temperature. The Seebeck coefficient is much higher than that prepared by mechanical alloying. More work needs to be done, in order to study the properties of more pure material.
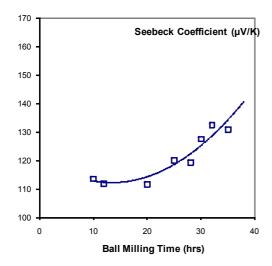

Figure 5:Room temperature Seebeck coefficient of Sb_2Te_3 as a function of milling time.
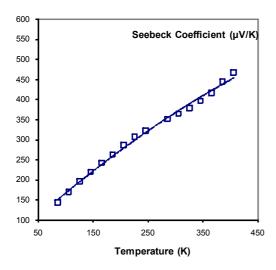

Figure 6: Seebeck coefficient of Sb_2Te_3 synthesized by hydrothermal method as a function of temperature.

Conclusions

Sb_2Te_3 nanostructured materials were fabricated by mechanical and chemical methods. The morphology of the two methods is significantly different since mechanical alloying process resulted particles and hydrothermal method resulted nano-sheaves. The crystalline size was investigated for the mechanical alloyed powders via X-ray diffraction analysis and was found to reach 15nm. The Seebeck coefficient was positive for both cases with the hydrothermal synthesis product showing significantly higher values.

Acknowledgments

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