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Preparation of the $Bi_8Sb_{32}Te_{60}$ solid solution by mechanical alloying

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Bi_2Te_3, Sb_2Te_3 and $Bi_8Sb_{32}Te_{60}$ thermoelectric materials have been prepared by mechanical alloying using a high energy planetary ball mill. The alloy formation was followed by X-ray diffraction (XRD), the morphology by scanning electron microscopy (SEM) and the composition by electron microprobe. The samples of $Bi_8Sb_{32}Te_{60}$ were prepared in a reasonable milling time (less than 8 h) by mechanical alloying of binary alloys (Bi_2Te_3 and Sb_2Te_3). The single phase $Bi_8Sb_{32}Te_{60}$ solid solution obtained presents convenient stoichiometry and good homogeneity in composition.

1. Introduction

Solid solutions formed by Bi_2Te_3 and Bi_2Sb_3 compounds have received considerable attention during the last years due to their great potential for application in electronic refrigeration [1–3]. The most studied $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions involve compounds corresponding to $x = 0.75$. These narrow band-gap semiconductor alloys are among the best *p*-type materials presently available for thermoelectric devices operating at room temperature. Most of the studies relevant to thermoelectric properties have been carried out on single crystals. However, preparation from the melt of homogeneous single crystalline ingots possessing well controlled compositions requires a precise knowledge of the ternary phase diagram [4], which is a difficult task to achieve.

Powder techniques can be advantageously used to study such materials, the cost and the processing periods being considerably lowered by comparison with melt techniques. The pulverized and intermixing elements sintering (PIES) method [5] and the conventional cold pressed method [6] have been successfully applied to the synthesis of bismuth telluride solid solutions. Mechanical alloying, which is alloy formation in the solid phase by means of repeated mechanical impacts during high energy ball milling, is another powerful method for preparing homogeneous compounds for evaluation of their potential for thermoelectric applications, especially when little information is available about the phase diagram or if the growth from the melt is not straightforward [7]. This process has been recently used for the preparation of several conventional thermoelectric materials [8–11] and for new high temperature materials [12].

This paper is devoted to the preparation by mechanical alloying of both the binary Bi_2Te_3 and Sb_2Te_3 compounds and the ternary solid solution $Bi_8Sb_{32}Te_{60}$. Two routes were investigated for processing of the ternary solid solution: mechanical alloying from stoichiometric amounts of Bi, Te and Sb powders in the first approach, and ball milling of stoichiometric amounts of mechanically alloyed Bi_2Te_3 and Sb_2Te_3 compounds in the second approach.

2. Experimental procedure

Mechanical alloying was conducted in a high energy planetary commercial ball mill (Fritsch, pulverisette 5) using 250 ml capacity tungsten carbide vessels. The grinding media were WC balls, 30 mm in diameter. The rotating speed was maintained at 360 r.p.m. and the ball-to-powder charge weight ratio was 50:1. The milling was carried out under wet conditions using n-pentane as the liquid medium. As this solvent is not an oxidant, it does not induce surface modifications in the final powders. The powder-to-liquid weight ratio was 1:6.

Elemental Sb, Te and Bi of high purity (99.999%) of average particle sizes of 3, 5 and 10 mm, respectively, were used in appropriate stoichiometric amounts to perform the mechanical alloying of the binary alloys Bi_2Te_3, Sb_2Te_3 and the directly alloyed ternary compound $Bi_8Sb_{32}Te_{60}$. On the other hand, to obtain ternary alloy from milling of the binary alloys, the binary compounds used were 80 mass % Sb_2Te_3 and 20 mass % Bi_2Te_3. The elemental materials were placed in the vessels under an argon atmosphere in a glove box and kept hermetically sealed during the milling process.

The milling process was carried out for different periods. Alloy formation was followed by X-ray diffractometry (XRD) using a Siemens D 500 diffractometer working in the standard θ–2θ geometry with the $CoK\alpha_1$ radiation. For the analysis, small amounts of powder were taken out of the vessels under Ar atmosphere at regular intervals. The patterns obtained with the powders were compared to those of Bi_2Te_3 and Sb_2Te_3 single crystals crushed to an average particle size of 50 μm, that were processed in our laboratory by the travelling heather method (THM) [4].

Powder morphologies were investigated by scanning electron microscopy (SEM) with a Jeol JMS-820 microscope in the secondary electron image mode.

Homogeneity in composition of cold pressed samples was checked by microprobe analyses performed with a Cameca (Camebax SX 50) probe. About 20 points were randomly taken on the samples. The points were separated either on a large scale (5 mm) or were close to each other (1 μm) in order to verify the homogeneity in composition at both macroscopic and microscopic scales.

3. Results and discussion

3.1. Bi_2Te_3 and Sb_2Te_3 binary alloys

The kinetics of formation of Bi_2Te_3 by mechanical alloying from Bi and Te powders in a stoichiometric ratio was followed by XRD between 30 min and 64 h. Reaction occurs from 30 min of milling and is evident by the disappearance of some Bi and Te diffraction peaks and/or to their displacement towards features corresponding to Bi_2Te_3. Fig. 1 shows the most representative interval of the diffractograms where the transformation of Bi and Te into Bi_2Te_3 as a function of milling time is clearly evident. Peak evolution can be considered as stabilized after 8 h of milling. A shorter milling time (20 min) has been reported by Hasezaki *et al.* [10] who worked with an attritor, under dry conditions. For milling times longer than 8 h, slight displacements of the peaks with respect to the positions of the Bi_2Te_3 peaks are observed (Fig. 1) that can be attributed to small distortions of the cell induced by high energy milling.

Obtainment of a definite Bi_2Te_3 compound is clearly shown by comparison of the diffractograms of a powder milled for 8 h and further annealed for 12 h at 573 K and a crushed Bi_2Te_3 single crystalline material (Fig. 2). All the diffraction peaks can be attributed to Bi_2Te_3 according to the JCPDS files. Annealing leads to peaks that are thinner and more resolved than those obtained in the rough milled powder, due to relaxation of many defects created during the mechanical alloying process and also to an enhancement of the crystallite size. The peaks are, however, located at the same position for annealed and non-annealed samples.

Longer milling times (up to 60 h) lead to the appearance of new diffraction peaks that can be attributed to tungsten carbide, resulting from pollution by the milling material.

Fig. 3 provides examples of the morphologies of Bi_2Te_3, Sb_2Te_3 and $Bi_8Sb_{32}Te_{60}$ obtained after 8 h of milling by the two different synthesis routes. Angular platelet shaped particles as large as 30 μm and about 2 μm in thickness can be seen beside smaller irregular shaped particles themselves constituted of small agglomerated particles. More spherical particles, about 1–2 μm in diameter, seem welded on the platelets as a result of the energetic process. The quasi absence of spherical shaped particles, although generally observed during the mechanical alloying process [13, 14], may be due to the presence of n-pentane, thus conferring better heat dissipation owing to the grinding media. No morphological change was observed as the milling time proceeded, showing a balance between the amount of welding and fracturing.

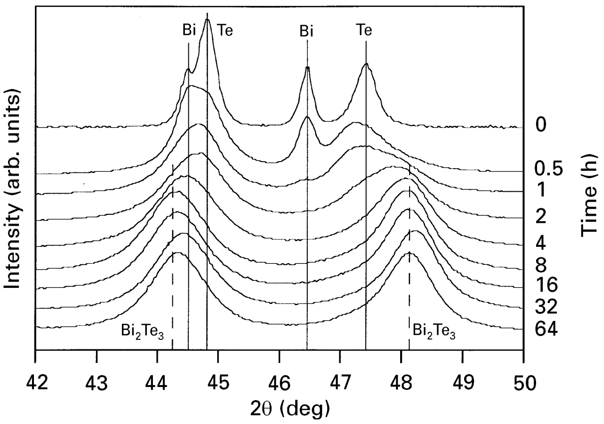

Figure 1 Kinetics of formation of Bi_2Te_3 obtained by mechanical alloying from Bi and Te raw materials in a stoichiometric ratio, followed by XRD. Reaction is achieved after 8 h of milling.

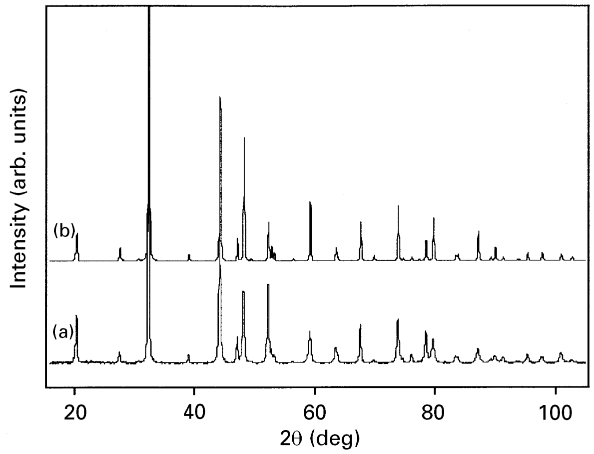

Figure 2 Comparison of X-ray diffractograms obtained on: (a) a Bi_2Te_3 single crystal, and (b) a Bi_2Te_3 powder elaborated by mechanical alloying for 8 h followed by annealing for 12 h at 573 K.

The Sb_2Te_3 compound, isomorphic to Bi_2Te_3, is also obtained after 8 h of milling the raw elements Sb and Te, as shown in Fig. 4. Nevertheless, the morphology (Fig. 3b) is quite different from that of Bi_2Te_3. The majority of particles appear as more or less great thin foils of less than 1 μm in thickness with smaller particles welded onto their surface. This would suggest that Sb_2Te_3 is more ductile than Bi_2Te_3 and, thus, that the powder will plastically deform rather than fracture. Nevertheless, this point would require a more detailed investigation because the mechanical properties of these compounds have not been made clear until now.

3.2. The ternary alloy $Bi_8Sb_{32}Te_{60}$

The $Bi_8Sb_{32}Te_{60}$ compound was prepared by mechanical alloying following two different routes: (i) from

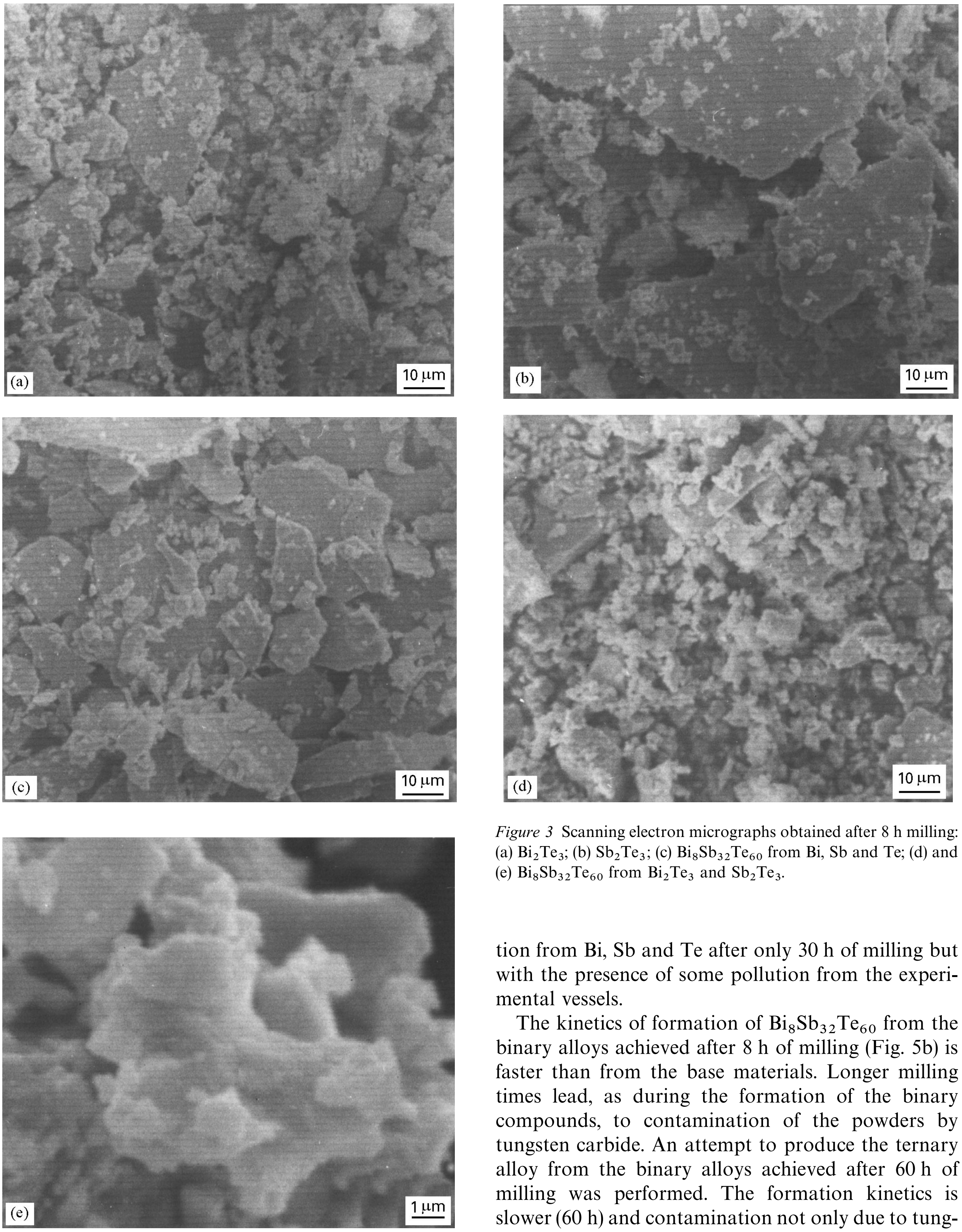

Figure 3 Scanning electron micrographs obtained after 8 h milling: (a) Bi_2Te_3; (b) Sb_2Te_3; (c) $Bi_8Sb_{32}Te_{60}$ from Bi, Sb and Te; (d) and (e) $Bi_8Sb_{32}Te_{60}$ from Bi_2Te_3 and Sb_2Te_3.

the elemental elements Bi, Te and Sb and (ii) from both Bi_2Te_3 and Sb_2Te_3 binary alloys, themselves obtained by mechanical alloying.

The kinetics of formation of $Bi_8Sb_{32}Te_{60}$ from its base materials is very slow (Fig. 5a). Between 20 and 39 h of milling, the three diffraction peaks coming from the base materials disappear while a unique peak appears, in the angular domain considered. Evolution of the peaks is stopped after 60 h of milling whereas Hasezaki *et al.* [10] obtained the ternary solid solution from Bi, Sb and Te after only 30 h of milling but with the presence of some pollution from the experimental vessels.

The kinetics of formation of $Bi_8Sb_{32}Te_{60}$ from the binary alloys achieved after 8 h of milling (Fig. 5b) is faster than from the base materials. Longer milling times lead, as during the formation of the binary compounds, to contamination of the powders by tungsten carbide. An attempt to produce the ternary alloy from the binary alloys achieved after 60 h of milling was performed. The formation kinetics is slower (60 h) and contamination not only due to tungsten carbide appears. In Fig. 6 are overwritten the XRD patterns of a ternary single crystal and those of milled powders obtained from the base materials after 60 h milling and from both binary alloys after 8 h milling. Any peak positions of the powder materials fairly agree with those of the single crystal reference ternary compound. These results show that the ternary solid solution can be obtained more rapidly from its two isomorphic binary alloys than from the elemental elements.

The morphology of the $Bi_8Sb_{32}Te_{60}$ powders differ as a function of their elaboration methods (Fig. 3c and d):

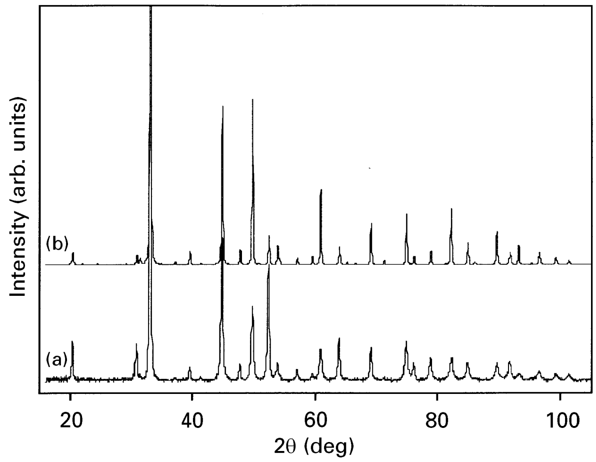

Figure 4 Comparison of X-ray diffractograms obtained on: (a) a Sb_2Te_3 single crystal, and (b) a Sb_2Te_3 powder synthesized by mechanical alloying for 8 h followed by annealing for 12 h at 573 K.

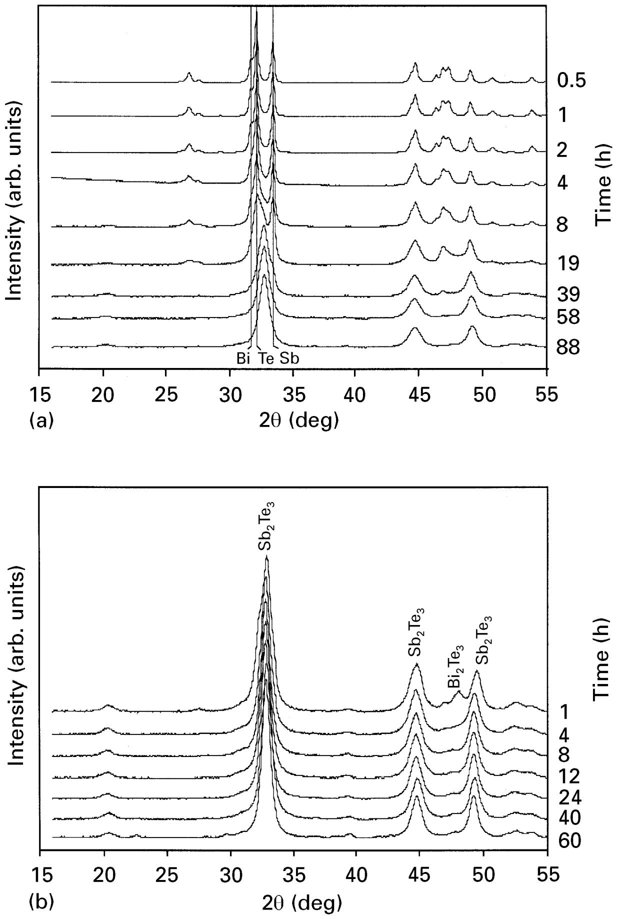

Figure 5 Kinetics of formation followed by XRD of the ternary compound $Bi_8Sb_{32}Te_{60}$ from: (a) Bi, Sb and Te base materials; reaction is achieved after 60 h of milling. (b) Both Bi_2Te_3 and Sb_2Te_3 alloys themselves obtained after 8 h of milling; reaction is achieved after 8 h of milling.

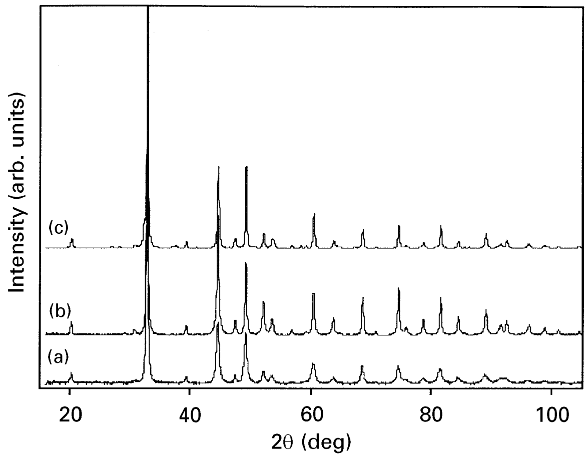

Figure 6 Comparison of X-ray diffractograms obtained on: (a) a $Bi_8Sb_{32}Te_{60}$ single crystal; (b) a $Bi_8Sb_{32}Te_{60}$ powder obtained from Bi, Sb and Te; and (c) a $Bi_8Sb_{32}Te_{60}$ powder obtained from Bi_2Te_3 and Sb_2Te_3.

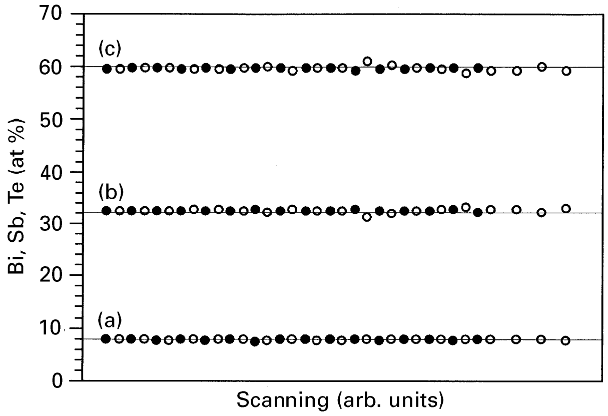

Figure 7 Microprobe analyses performed at several places on cold pressed $Bi_8Sb_{32}Te_{60}$ powders synthesized either via (○) Bi, Sb and Te or via (●) Bi_2Te_3 and Sb_2Te_3. Samples show good compositional homogeneity. (a) Bi, (b) Sb, (c) Te.

the direct route leads to the obtainment of irregular shaped platelets non-homogeneous in size, whereas the morphology of the powders obtained via the indirect route looks like that of Bi_2Te_3. Powders are in a steady state particle size distribution because there is no refinement of the size or agglomeration as the milling time increases. Fig. 3e presents a magnification of a powder particle showing that it is itself constituted of very small irregular shaped particles welded together, some of them less than 300 nm in size.

Microprobe analyses performed on both $Bi_8Sb_{32}Te_{60}$ samples show that the powders present no compositional inhomogeneities on both macroscopic and microscopic scales (Fig. 7). Moreover, the composition that is found is close to the expected composition. Small amounts of oxygen were also detected. Nevertheless, it is mainly located at the surface. Actually, ion bombardment of the surface leads to a decrease of the oxygen signal as observed during secondary ion mass spectrometry depth profiling analyses.

4. Conclusions

The results obtained in this paper show that the synthesis, by high energy ball milling, of alloyed polycrystalline thermoelectric materials, such as Bi_2Te_3, Sb_2Te_3 and their solid solution, was successfully achieved. The powders exhibit the expected compositions and very good homogeneities in composition. The $Bi_8Sb_{32}Te_{60}$ solid solution can be achieved by two different routes, from the elemental elements and from the Bi_2Te_3 and Sb_2Te_3 binary compounds. The second way allows the synthesis in a short time (8 h) of samples with no contamination. Further studies concerning the compaction of the powders and their thermoelectric properties are now under investigation.

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