Preparation of nano-sized Bi$_2$Te$_3$ thermoelectric material powders by cryogenic grinding

Xiaozong Chen$^a$, Leifeng Liu$^b$, Yuan Dong$^a$, Lianjun Wang$^{a,*}$, Lidong Chen$^c$, Wan Jiang$^{a,*}$

$^a$State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, 2999 people of North Road, Shanghai 201620, PR China
$^b$Department of Materials and Environmental Chemistry, Stockholm University, SE-106 91 Stockholm, Sweden
$^c$Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, PR China

Received 19 November 2011; accepted 29 March 2012
Available online 13 June 2012

Abstract A novel method for rapid preparation of Bi$_2$Te$_3$ nano-sized powders with an average particle size of about 70 nm was developed. A starting powder mixture consisting of Bi$_2$Te$_3$ coarse particles of ~5 mm was ground using cryogenic grinding in the liquid nitrogen. For comparison, the conventional high-energy ball milling was used to prepare the Bi$_2$Te$_3$ nano-sized powders. Sintering properties of as-prepared powders was investigated by spark plasma sintering (SPS). The effects of the preparation procedure on the crystallinity, morphology and structure were examined by X-ray diffraction (XRD) and transmission electron microscopy (TEM). It was found that Bi$_2$Te$_3$ was not transformed into a non-equilibrium amorphous phase or decomposed during the cryogenic grinding process, and as-prepared nano-powders possessed excellent sinterability. This technique might also be applicable to other thermoelectric materials.

1. Introduction
Thermoelectric (TE) material with the function of the direct solid-state conversion between thermal and electrical energy has received enormous attention in the past twenty years because of its potential on the application of eco-friendly energy, cooling and space energy source [1,2].

In the TE family group, Bismuth telluride (Bi$_2$Te$_3$) and its alloys, discovered by Loeffe in the early 1960s, are the most widely applied TE materials over the temperature range 200–400 K, due to the high TE performance [3]. The Bi$_2$Te$_3$ crystal has a hexagonal structure that consists of quintuple atomic layer series in the order of Te(1)-Bi-Te(2)-Bi-Te(1)
along the c-axis [4,5]. Since Te$^{(1)}$–Te$^{(1)}$ layers are weakly bonded by the van der Waals forces, this crystal can easily cleave on the basal plane resulting in some difficulties for large-scale application [6].

Since the American scientist Dresselhaus [7–9] put forth the issues that low-dimension and nanostructure can significantly enhance the thermoelectric performance in 1990s, a lot of work has been done to fabricate the nanoparticles [10–16] and nanocomposites [17–19] by many researchers. Among those, a simple approach employing ball-milling of bulk BiSbTe alloy and subsequent hot pressing has been reported to be effective for producing the nanoparticles with average grain size of 20 nm [10]. This method is also cost-efficient, which means that it is promising in large-scale application. However, the conventional grinding inevitably generates a large amount of heat that causes the lattice distortion and the breaking-down of chemical bonds, making the material amorphous or decomposed [20]. Thus, it is desirable to further develop a method which can be used to produce the nanoparticles and at the same time introduce fewer amorphous phase and decomposition.

Cryogenic grinding (CG) is always called “Mill of last resort”. Since the cryogenic medium, always the liquid nitrogen, provides an extremely low temperature of $-195.6$ °C and an inert atmosphere, it prevents the amorphous transition and decomposition of the substance [21–24]. Meanwhile, the low temperature provided by cryogenic precooler is below the brittle point of most materials, which makes the grinding process more efficient. Therefore the cryogenic grinding is considered as the best milling method for these hard grinding samples and the substances susceptible to oxidation and volatile.

In this paper, both cryogenic grinding and conventional high-energy ball milling (HEBM) were employed for grinding N-type Bi$_2$Te$_3$ particles. The microstructure feature of Bi$_2$Te$_3$ powder after the CG and HEBM was investigated and compared.

2. Materials and methods

The starting material of N-type Bi$_2$Te$_3$ zone-melted ingots was from a commercial supplier (Shenhe Thermo-Magnetics Co. Ltd., Shanghai, China). The ingots were crushed into coarse particles of $\sim$5 mm by steel mortar. Then the coarse particles

![XRD patterns](image).

**Fig. 1** XRD patterns of (a) the ingots and the particles CGed for different times and (b) the particles after 12 h, 24 h, 36 h and 60 h HEBM.
were milled to fine powder by either cryogenic grinding or high-energy ball milling.

The crushed sample was grinded by a CG machine (SPEX SamplePrep 6770 Freezer/Mill, TECH-Knowledge International Co., California, USA). The sample and a magnetically driven impactor were inserted into a closed grinding vial immersed in liquid nitrogen and precooled to make Bi$_2$Te$_3$ below its brittle point. The grinding was performed for a few minutes at the speed of 10–12 cycles per second. During the process, the grind was paused every 2 h to collect a small amount of the powder for analysis and post treatment.

The same crushed sample was also milled in a HEBM machine (Model GN-2, Shenyang Science Equipment Factory, Shenyang, China) at the speed of 480 rpm using a steel vial. The steel vial was sealed in a glove box under argon atmosphere. The as-prepared Bi$_2$Te$_3$ nano-powders were sintered using spark plasma sintering (SPS, Dr. Sinter 725, Sumitomo Coal Mining Co., Japan). The nano-powders were loaded into cylindrical carbon dies with an inner diameter of 10 mm. The heating rate was controlled in the range of 70 $^\circ$C/min, and the pressure was set at 60 MPa. The final temperature was selected at 390 $^\circ$C for a dwelling time of 5 min, respectively.

The as-prepared powders were analyzed by X-ray diffraction (XRD) with Cu Kα radiation at 40 kV and 100 mA. The particle morphology and microstructure observation were performed by transmission electron microscopy (TEM). After sintering, the surfaces of samples were ground to remove the graphite layer. The densities of consolidated specimens were obtained using the Archimedes immersion method with deionized water as the immersion medium. The theoretical densities of the specimens were calculated according to the rule of mixtures. Microstructural observation was conducted using a scanning electron microscope (FE-SEM: JSM-5600LV, JEOL, Japan).

3. Results and discussion

The XRD patterns of uncrushed Bi$_2$Te$_3$ ingots and the grinded samples by CG for different time are shown in Fig. 1(a). The diffraction peaks cited from the database of binary Bi$_2$Te$_3$ (PDF#15-0863) were plotted at the bottom of the figure with vertical lines. The strong peaks of (0 0 3), (0 0 6) and (0 0 15) in the pattern of raw ingots indicate the existence of texture in the material. The texture disappeared as the ingots were grinded into fine powder, which made those peaks weakened dramatically. Owing to the hugely anisotropic structure with lattice parameters $a=0.438$ nm and $c=3.049$ nm [4], and Te–Te layers are weakly bonded by the van der Waals forces along with $c$-axis, the resistance of the Bi$_2$Te$_3$ ingots to shear on non-basal planes is much greater than that on basal planes [5]. During milling process, much more dislocations occurred.

![Fig. 2](image-url)  
**Fig. 2** Low-resolution TEM images of the particles CGed for (a) 3 h, (b) 6 h, (c) 10 h and (d) 15 h with the corresponding electron diffraction pattern and high-resolution TEM images of the particles after (e) 10 h and (f) 15 h CG.
on the basal plane than those occurred on the non-basal plane leading to the break-down of the long-range lattice order in the direction of c-axis [6], which is also confirmed in the high resolution TEM image, as shown in Fig. 2. As a result, the XRD reflections of the basal plane weakened and even disappeared.

The reflections were weakened and broadened severely until the milling time of 10 h, which indicated the continuous decrease in crystal size. The XRD pattern of 15 h milling had the similar peak width and intensity as the 10 h milling one, indicating that the further milling beyond 10 h made no more changes on the crystal size. After 15 h extensive milling under CG, no extra peak or peak shift can be found in the XRD pattern, indicating that no phase transition happened during the milling. Moreover the background of pattern after 15 h milling was still flat and low. This means that the CG process successfully restrained the generation of amorphous phase and chemical decomposition.

Fig. 1(b) shows the XRD patterns of Bi₂Te₃ powder after different HEBM time (the increment between any adjacent XRD pattern remains in line with Fig. 1(a)). It can be found that all the characteristic peaks of HEBMed powder coincided well with those of Bi₂Te₃ and the shape of peaks keeps unchanged with the increase of the HEBM time (60 h), indicating that the Bi₂Te₃ particles display ductility performance just like metal and are hard to grind to nanoparticles. This can be seen obviously in the TEM image in Fig. 3. In addition, it is inevitable to introduce an amount of impurities after long time ball milling.

The microstructures of Bi₂Te₃ particles after CG for different times are shown in TEM images in Fig. 2. The low resolution TEM images of 4 h and 6 h CGed sample (Fig. 2a and b) show that the average particle size remains about 200 nm, and varies barely before the 6h. However, as the grinding continued, the average particle size decreased obviously from the 6 h. The TEM images of 10 h and 15 h CGed sample (Fig. 2c and d) show that the average particle size decreases dramatically to about 70 nm. Interestingly, the results of high resolution TEM (Fig. 2e and f) clearly reveal the existence of ~10 nm nanocrystals in different orientation inside of particles. The further grinding will not decrease the particle size significantly. This means that the major break-down process occurred from 6 h to 10 h, and the particle size reaching the minimal size of about 70 nm maintained even prolonging the grinding time. The selected-area electron diffraction (SAED) pattern (Fig. 2c, inset) confirms the crystal structure of Bi₂Te₃. In the high resolution TEM image, the lattice frame of nano-sized Bi₂Te₃ particle can be clearly observed. As marked in the image, the distance of 0.322 nm indicates crystal plane of [0 1 5].

Fig. 3a–c show the TEM images of high-energy ball milled Bi₂Te₃ powder for milling periods of 12 h, 24 h and 36 h, respectively. The average size of the Bi₂Te₃ powders remained unchanged at about 500 nm with the increasing milling time from 12 h to 36 h, which indicates that high-energy ball milling cannot break down the micron powders. In the Bi₂Te₃ ingots, the Te and Bi atoms are connected by a strong bond, either covalent or mixed covalent and ionic [5], and Te–Te layers are weakly bonded by the van der Waals forces [6], and hence, the Bi₂Te₃ alloy micron particles possess weak ductility performance by the distortion and slippage of grain boundaries and defects, and are hard to be grinded further. Therefore, after the milling time of 12 h it is impossible to obtain much finer particles with longer ball-milling time, but it may be inevitable to introduce impurities and generate amorphous phase.

In the early time of 1920, Griffith has set up the Griffith breaking theory (GBT), which attributed the macroscopic break-down of material to the microscopic crack extension [24]. On the basis of GBT, we present a two-step breaking model to study Bi₂Te₃ grinding process in the present
In the CG process, two dramatic break-down of the particles occurred, as shown in the schematic diagrams of Fig. 4a. Before the grinding, the particle size of coarse Bi$_2$Te$_3$ particles was about 5 mm. A large amount of microcracks in the coarse grains and the aforementioned hugely anisotropic structure accelerate crack extension. As a result, at the initial stage of CG, the average particle size decreased rapidly to about several hundred microns at the impact load within a short time, as shown in the front part of Fig. 4a. A serious brittle fracturing of the powders occurred in the first period just like the general milling. As is well known, the capacity of the grain distortion and dislocation slip decreases sharply at ultralow temperature. Since in the present study the cryogenic medium adopted was the liquid nitrogen (−195.6 °C) in the CG process, the defects of the micron Bi$_2$Te$_3$ particles formed new microcracks slowly under the severe cyclic load of 1200–1400 beats per minute, and then further crack extension occurred during long time cycles. Finally, the micron Bi$_2$Te$_3$ particles broke down into small sized powders. This break-down mode could be named as fatigue fracture in this period, as shown in the latter part of Fig. 4a.

Fig. 4b shows the changes of particle size with milling time at two breaking model. Both of the general breaking model and the two-step breaking model present brittle fracture within a short grinding time. In the general milling process, with the increase of grinding time, a large part of the heat generated during milling process makes the Bi$_2$Te$_3$ particles easily to be distorted as well as the slip of the grain boundaries and dislocations, and hence there is no second breaking down process compared with cryogenic grinding.

In order to investigate the sintering behavior of Bi$_2$Te$_3$ powders prepared by cryogenic grinding and high-energy ball milling, spark plasma sintering was used to densify as-prepared Bi$_2$Te$_3$ powders at 390 °C for a dwelling time of 5min. Fig. 5 shows FE-SEM image for typical fracture surface of bulk samples prepared by SPS at 390 °C, respectively. It is easy to find that there are two distinct types of grains: one is ball shape and the other is laminate shape. It was observed that the average grain sizes of the two bulk samples fabricated at the same sintering temperature of 390 °C were obviously different, and the grain size of bulk sample using HEBM (b) powders is many times larger than that using CG powders (a). It is suggested that the cryogenic grinding is conducive to obtain the finer nanoparticles, and then to form uniform nanocomposite.

![Fig. 4](image_url)

Fig. 4  (a) Schematic of the break-down from micron to millimicron during the CG process. (b) Milling time dependence of average particle size of the CG samples as compared with that of the HEBM sample.

![Fig. 5](image_url)

Fig. 5  FE-SEM image of bulk samples using (a) 10 h CG powders and (b) 60 h HEBM powders as precursors at sintering temperature of 390 °C.
4. Conclusions

1) Bi₂Te₃ nano-sized powders with an average particle size of about 70 nm were successfully prepared by a cryogenic grinding (CG) in the condition of liquid nitrogen. The Bi₂Te₃ powders showed great stability during GC process, and no phase transformation or amorphous state was observed to take place even after milling for 15 h. The two-step breaking model of Bi₂Te₃ powders was proposed to explain the CG process.

2) Compared with high-energy ball milling (HEBM), spark plasma sintering (SPS) showed that cryogenic grinding (CG) can produces much finer and good sinterability Bi₂Te₃ powders.

3) This investigation presents a promising method to prepare thermoelectric material nanopowders. And this method may be used to fabricate other metal nanopowders with a similar manner.

Acknowledgments

Foundation item: Projects (10JC1400500) supported by the Shanghai Committee of Science and Technology, “Shu Guang” project supported by Shanghai Municipal Education Commission and Shanghai Education Development Foundation (no. 11SG34), Projects (NCET-10–0323) supported by the Commission and Shanghai Education Development Foundation item: Projects (10JC1400500) supported by the Shanghai Committee of Science and Technology, ‘Shu Guang’ project supported by Shanghai Municipal Education Commission and Shanghai Education Development Foundation (no. 11SG34), Projects (NCET-10–0323) supported by the Commission and Shanghai Education Development Foundation.

References