Structural Transformations in (Bi, Sb)₂Te₃ Solid Solutions Grown by Spark Plasma Sintering

D I Bogomolov, V T Bublik, A A Ivanov, M V Voronov, M G Lavrent'ev, V P Panchenko, Yu N Parkhomenko, and N Yu Tabachkova

1National University of Science and Technology (MISIS), 119049, Leninsky pr. 4, Moscow, Russia
2National Research Center «Kurchatov Institute», 123182, Akademika Kurchatova pl., 1, Moscow, Russia
3State Scientific-Research and Design Institute of Rare-Metal Industry "Giredmet" JSC, 119017, B. Tolmachevsky per., 5-1, Moscow, Russia
4RMT Ltd, Warshavskoe shosse, 46, 115230, Moscow, Russia
5Prokhorov General Physics Institute RAS, 119991, Vavilova st. 38, Moscow, Russia

E-mail: ntabachkova@gmail.com

Abstract. We have studied the dependence of the thermoelectric properties of the bulk (Bi,Sb)₂Te₃ material on the temperature of spark plasma sintering (SPS). For analysis of the experimental results we took into account the regularities of structure formation in the material. The average crystallite size decreases with an increase in the SPS temperature to above 400 °C. Transmission electron microscopy showed that at above 400 °C the bulk and boundaries of the initial grains that are several micrometers in size contain a large number of nanosized grains (approx 10 – 20 nm) having the same composition. We show that the dependence of the thermoelectric properties of the material on SPS temperature correlates with changes in the fine structure of the material which is controlled by the redistribution of the intrinsic point defects. Our results suggest that, along with the well-known nanostructure formation processes, there is one more high-temperature self-organizing process of the formation of the nanostructural material based on the redistribution and change in the form of occurrence of the nonequilibrium point defects. This information can be used to broaden the possibilities of controlling the properties of the bulk thermoelectric material on the basis of (Bi,Sb)₂Te₃.

1. Introduction

In spite of the absence of any material practical results in the field, there is a persistent interest to the works dealing with the growth of bulk nanostructural materials on the basis of (Bi,Sb)₂Te₃ with a high thermoelectric figure of merit, and the announced values of the thermoelectric figure of merit of the bulk material become even higher every year, e.g. $ZT = 1.4$ [1] and $ZT = 1.8$ [2].

Different aspects of the current status of works dealing with bulk nanostructural materials and the outlook of their development were reviewed in earlier works [3 - 6]. Most authors obtained the material by planetary ball milling followed by powder compaction using hot pressing [4]. In some works the powder was obtained by melt spinning [7, 8], and compaction was achieved using the method of spark plasma sintering [8].

The origins of the growth of the thermoelectric figure of merit ($ZT$) in p-type conductivity antimony and bismuth chalcogenide based materials obtained by pressing of nanopowders remain
unclear. There is no definitive opinion as to whether the growth of ZT is caused by intragranular processes related to the large number of defects formed during milling and powder pressing or by the effect of grain boundaries. The prevailing opinion is that in nanostructural specimens, phonon scattering at grain boundaries is stronger than electron scattering, and therefore the thermal conductivity of these materials declines faster than their electrical conductivity [9 - 13]. However, comparison of the free path lengths of electrons and phonons with grain sizes does not confirm this viewpoint [14].

The aim of this work is to study the physical formation processes of the structure and properties of the (Bi,Sb)2Te3 solid solutions. In the present work compacting bulk nanostructured materials on the basis of solid solutions (Bi, Sb)2Te3 are obtained by the spark plasma sintering method (SPS), which has a number of advantages over the traditional method of hot pressing [15]. We studied the electrical conductivity, Seebeck coefficient, thermal conductivity and thermoelectric figure of merit of the material at room temperature as functions of the composition of the solid solution and sintering temperature. For analysis of the experimental results we took into account the regularities of structure formation in the material.

2. Experimental

Powders of (Bi,Sb)2Te3 solid solutions were obtained from the synthesized material of the respective composition. The raw materials were Bi (99.999), Sb (99.999) and Te (99.999). The material was synthesized by direct smelting of the components in soldered quartz ampoules. The synthesized ingots were mechanically treated in a protective atmosphere in a high-energy planetary ball mill.

The compacted specimens were obtained by spark plasma sintering in an SPS - 511S (SPS Syntex) plant. Before spark plasma sintering the powder was compacted to cold-pressed tablets which were further transferred to the SPS plant. All the operations with the powder were carried out in a glove box in a protective atmosphere with humidity and O2 content control. The O2 concentration in the atmosphere was maintained at below 10 ppm with the aim of avoiding powder oxidation.

The specimens sintered in graphite molds were 3 to 10 mm in thickness and 20 mm in diameter. The sintering temperature was 250 to 550 °C, the pressures were 50 MPa or higher, and the process duration was 5 min. The structure of the powders and the sintered material was studied using X-ray diffraction on a Bruker D8 instrument using CuKα radiation. The cleave surface morphology of the sintered specimens was examined in secondary electrons under a JSM - 6480LV scanning electron microscope. The structure of the specimens was also studied by transmission electron microscopy under a JEM 2100 electron microscope.

The thermoelectric properties of the bulk materials were studied at room temperature using the Harman method for 2.5×2.5×4 mm3 sized specimens [16]. An essential feature of the Harman method is that the thermoelectric figure of merit (ZT), by analogy with the Seebeck coefficient (α) and the electrical conductivity (σ), is determined directly from the experimental data, while the thermal conductivity (κ) is calculated using the formula $Z = \frac{\alpha^2 \sigma}{\kappa}$. The electrical conductivity and the thermal conductivity were measured for the same specimen in the direction perpendicular to the compression direction.

The temperature dependences of the thermoelectric properties of the material in the 30 - 150 °C range were measured for different specimens cut out from one tablet. The electrical conductivity and the Seebeck coefficient were measured on a ZEM 3 instrument for 2.5×2.5×10 mm3 sized specimens in the direction perpendicular to the compression direction. The temperature conductivity DT was measured using the laser spark method in an LFA 457 plant. In order for the measurements to be also in the direction perpendicular to the compression direction we cut the 10×10×2.5 mm3 sized specimens along the compression direction. The heat capacity Cp was measured for 0.7×2×4 mm3 sized specimens on a DSC - 404C instrument. The density d of the specimens was measured using the Archimedes method. The thermal conductivity was calculated using the formula $\kappa = DT \times Cp \times d$. 
3. Results and Discussion

Taking into account the availability of literary data on (Bi,Sb)\(_2\)Te\(_3\) based nanostructural bulk materials having a wide range of compositions and aiming at correction and optimization of the material composition, we studied almost the entire practically used range of compositions of the p-type conductivity (Bi,Sb)\(_2\)Te\(_3\) solid solution. The maximum thermoelectric figure of merit was observed in the Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) composition material. Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) proved to be the optimum composition for the (Bi, Sb)\(_2\)Te\(_3\) based single crystal materials. The shift of the composition seems to originate from the differences in the structure and technology of the specimens. An increase in the concentration of holes with a decrease in the Bi content is caused by an increase in the concentration of the antistructural defects of the metal in the Te sites which are the main acceptors. This, in turn, is caused by the fact that the formation energy of the Sb\(_{Te}\) antistructural defect is lower than that of Bi\(_{Sb}\).

We studied the thermoelectric properties of the Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) composition specimens as a function of SPS temperature in the 250 – 550 °C range. The maximum thermoelectric figure of merit at room temperature is observed for the sintering temperature range 450 °C – 500 °C, and then the efficiency decreases slightly. The results are presented in Fig. 1.

![Thermoelectric Properties of Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) as Functions of SPS Temperature](image)

**Figure 1.** Thermoelectric Properties of Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) as Functions of SPS Temperature: (a) Electrical Conductivity, (b) Seebeck Coefficient, (c) Thermal Conductivity and (d) Thermoelectric Figure of Merit

Figure 2 shows electrical conductivity, Seebeck coefficient, thermal conductivity and dimensionless thermoelectric figure of merit ZT for Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) composition specimens obtained by SPS at 450 °C. The maximum ZT = 1.25 is in the range 90 – 100 °C. For SPS at 500 °C the maximum ZT = 1.28 is at approx. 80 – 90 °C. The slight difference in the σ, α and κ values at room temperature between Figs. 1 and 2 is due to the different measurement techniques, although the ZT values are almost identical for both techniques.
As the properties of the bulk material depend largely on its structure at the micro- and nano-levels, we studied the structure of the specimens at different specimen preparation stages, from the powder to the sintered bulk material.

X-ray diffraction and transmission electron microscopy showed that the powder particles of the (Bi,Sb)₂Te₃ solid solution obtained from the synthesized material were single-phase and inherited the composition of the source material. The average size of the powder particles as determined from the transmission electron microscopy data was approx 10 nm which agreed with the average crystallite size as determined from the broadening of the X-ray lines.

The inheritance of the nanostructural state in the compacted specimens is a serious problem associated with the negative effect of the recrystallization processes that lead to grain coarsening. Figure 3 shows secondary electron images of the cleave surfaces of specimens obtained using SPS at different temperatures in the 250 – 400 °C range.

Figure 2. (a) Electrical Conductivity and Seebeck Coefficient, (b) Thermal Conductivity and Thermoelectric Figure of Merit ZT for BiₓSb₁₋ₓTe₃ Solid Solution Obtained by SPS at 450 °C

Figure 3. Cleave Surface Images of Specimens Obtained Using SPS at Different Temperatures: (a) 250 °C; (b) 300 °C; (c) 350 °C; (d) 400 °C
At sintering temperatures of 350 and 400 °C the grains grow to several microns in size and acquire facets, this process indicating intense recrystallization. A fine grained structure without cleave surface faceting is typical for specimens sintered at a lower temperature.

X-ray diffraction study of the phase composition and the fine structure of the compacted (Bi,Sb)2Te3 specimens showed that all the specimens obtained using SPS were single-phase. The composition of the solid solution was controlled based on the lattice parameter. The crystallite sizes were determined from the broadening of the diffraction lines as a function of the SPS temperature. With an increase in the SPS temperature the average crystallite size grows monotonically. The maximum crystallite size was observed at 400 °C. However, with a further increase in the SPS temperature the crystallite size decreased and became even smaller than in the specimens obtained at an SPS temperature of 250 °C.

To have a more complete view of the structure of the specimens obtained at different SPS temperatures we examined the specimens using transmission electron microscopy (TEM). Figure 4 shows typical light-field images of the structure of the (Bi,Sb)2Te3 solid solutions for different sintering temperatures.

![TEM Images of the Structure of (Bi,Sb)2Te3 Solid Solutions Obtained at Different Sintering Temperatures](image)

For sintering at 250 °C the grains are already by one order of magnitude greater than the initial powder particles and continue growing with an increase in the sintering temperature to 400 °C. An essential feature of the specimens sintered in the temperature range from 250 to 350 °C is the scatter of the grain sizes; this scatter decreases for a sintering temperature of 400 °C. According to transmission electron microscopy data, the specimens sintered at 400 °C have a larger number of intergrain joints that are close to the equilibrium state (Fig. 4c), and the internal structure of the grains is more perfect, this fact being in agreement with the abrupt growth in the crystallite size. For a sintering temperature of 450 °C the pattern of the transmission electron microscopy images changes dramatically. The structure of the specimens contains a large number of nanosized grains (~10 – 20 nm) located predominantly in the grain bulk (Fig. 4d). However, the total volume of the new nanosized grains is not large. The crystallite sizes are smaller for this sintering temperature.
For a sintering temperature of 500 °C the number of new grains increases significantly, the grains being larger in size and well-faceted (Fig. 4e). The bulks of the “old” grains contain grains of different sizes that are newly generated and have had sufficient time for growth during sintering. Sometimes the newly grown small grains occupy the entire volume of the “old” grains. The total volume of these grains is substantially greater than for a sintering temperature of 450 °C. The structure of the specimens sintered at 500 °C contains pores the sizes and number of which are far greater than for sintering at 450 °C. For a sintering temperature of 550 °C the newly grown small grains occupy the entire volume of the “old” grains and form a new structure consisting of relatively large grains (Fig. 4f).

Based on the results of our TEM studies we suggested the following mechanism of structural changes. At a sintering temperature of 250 °C, collective recrystallization proceeds under the conditions of an insufficient mobility of the defects. For sintering at 300 – 400 °C the grains continue to grow, and their structure contains relatively large twins. With an increase in the mobility of the defects, a new structural change occurs, i.e. repeated recrystallization (at 450 °C). The formation of new grains in the structure proceeds faster than the growth of the old grains. The overall density of the defects including the twins decreases. The new centers of repeated recrystallization precipitate at the grain boundaries, at dislocation defects, and in the grain bulk, probably, at the subgrains. Thus, the regularity revealed in the course of this study will allow one to obtain structures with different grain sizes in the 450 – 500 °C range, depending on the development of repeated recrystallization. However, the key questions are the origin of the new grains and the cause of their formation. Unlike collective recrystallization the motive force of which is a decrease in the length of the grain boundaries, the cause of the formation of small grains in the bulk of large ones is most probably a decrease in their bulk energy. The similarity of the elemental compositions of the new and the “old” grains suggests that the cause of repeated recrystallization is a decrease in the energy of the intrinsic defects in the grain bulk. In a dislocation-free material, these defects can be intrinsic point defects. Then one can hypothesize that the newly forming grains have a lower concentration of intrinsic point defects compared to the “old” grains.

The high concentration of point defects in the bulk material can be associated with their formation in the particles of the initial powder as a result of crushing in a high-energy ball mill. Then the initiation of repeated recrystallization requires an inhomogeneous distribution of the concentration of the intrinsic point defects at the nanosize level. The formation of these local inhomogeneities in SPS specimens may have various origins. First, the nanoparticles of the powder with different sizes may have initially different concentrations of point defects, and these concentrations are inherited during compaction. Secondly, the density of the pulse current in the specimen during sintering in a spark plasma discharge may also have local inhomogeneities that inevitably cause an inhomogeneous temperature distribution. Then the annealing of the intrinsic point defects during sintering proceeds at different temperatures in different areas, resulting in the formation of local areas with different point defect concentrations.

Repeated recrystallization causes a redistribution of the intrinsic point defects in the bulk of the grains. As this process has a diffusion nature, recrystallization proceeds intensely at high sintering temperatures under the conditions of higher defect mobility. Metastable point defects may either migrate towards the grain boundaries or form clusters in the bulk of the grains. The pores in the specimen structure observed using electron microscopy for specimens sintered at 450 – 550 °C suggest that the intrinsic point defects have a vacancy nature. Thus, most probably all the structural changes described above are caused by the redistribution of the intrinsic point defects during specimen sintering.

One cannot however ignore another theoretically possible origin of repeated recrystallization in heavily anisotropic materials among which there is the Bi2Te3—Sb2Te3 solid solution. In these materials the grain boundary energy depends strongly on the grain boundary orientation. The grain boundary energy is the lowest for a grain boundary close to the cleavage plane. Under the conditions of heavily anisotropic growth rates of individual grains, the grain boundaries forming during
recrystallization may acquire a specific configuration for which a decrease in the boundary energy can be achieved by the growth of one grain at the expense of the other in the direction in which the growth rate is low. With an increase in temperature, recrystallization may proceed not only by increasing the grain growth rate in the low growth rate direction but also as a result of the formation of differently oriented precipitates having lower grain boundary energies.

We will now dwell upon the possible correlation of the thermoelectric properties of the material obtained using SPS at different temperatures with the respective structural changes. An increase in the electrical conductivity with an increase in the sintering temperature (Fig. 1a) can result from two factors.

On the one hand, at low SPS temperatures (at least below 250 °C) the specimens are insufficiently sintered which is evidenced by a low relative density that grows with an increase in SPS temperature. The maximum density of 99.5% of the theoretical parameter is achieved at a sintering temperature of 400 °C. With a further increase in the sintering temperature, beginning from 450 °C, the density of the material decreases to 99.0% due to the formation of pores in the material. As the SPS temperature increases to 350 – 400 °C the fraction of grain boundaries with high electrical resistivities decrease. On the other hand, an increase in the electrical conductivity with an increase in the SPS temperature can be associated with the redistribution and change in the form of occurrence of the nonequilibrium point defects.

At SPS temperatures of below 400 °C, the thermal conductivity of the material grows as a result of an increase in the contribution of the electrons (Fig. 1 c). However, at sintering temperatures of above 400 °C, i.e. in the range in which repeated recrystallization takes place, the thermal conductivity of the material decreases. This decrease in the thermal conductivity combined with the continuing increase in the electrical conductivity of the material can only be accounted for by a decrease in the lattice (phonon) heat conductivity.

4. Conclusions
We studied the structure of the (Bi,Sb)2Te3 based solid solution as a function of SPS temperature. The average crystallite size decreases with an increase in the SPS temperature to above 400 °C. Transmission electron microscopy showed that at above 400 °C the bulk and boundaries of the initial grains that are several micrometers in size contain a large number of nanosized grains (approx 10 – 20 nm) having the same composition. This observation suggests that the formation of the nanosized grains is an early stage of repeated recrystallization that leads to the fragmentation of the initial grains and hence a decrease in the crystallite sizes.

We showed that the SPS temperature dependence of the thermoelectric properties of the (Bi,Sb)2Te3 based material correlates with the structural changes taking place in the material. The formation of nanosized pores and grains is a result of the agglomeration of the nonequilibrium intrinsic point defects (vacancies and antistructural defects).

Our experimental results suggest that, along with the well-known nanostructure formation processes, there is one more high-temperature self-organizing process of the formation of the nanostructural material based on the redistribution and change in the form of occurrence of the nonequilibrium point defects. This information can be used to broaden the possibilities of controlling the properties of the bulk thermoelectric material on the basis of (Bi,Sb)2Te3.

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