PREPARATION OF NANOCRYSTALLINE Bi_2Te_3 VIA MICROWAVE-SOLVOTHERMAL SYNTHESIS AND HOT ISOSTATIC PRESSURE

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• *Nanostructured Bi_2Te_3-based material was prepared by microwave assisted solvothermal method and hot isostatic pressing. Optimal synthesis conditions of the Bi_2Te_3 nanopowder were found. It was established that hot isostatic pressing of nanopowders at temperature of 300°C and pressures of 2, 4, 6 and 8 GPa allowed us to form a homogeneous and dense Bi_2Te_3-based material with average grain size from 60 to100 nm.*

Introduction

Thermoelectric materials are of interest for applications in electrical power generation devices and solid-state cooling due to many attractive properties (long life, no emissions of toxic gases, no moving parts, low maintenance, etc). At present, bismuth telluride based compounds are known to be the most excellent thermoelectric materials for around room temperature applications. The Bi_2Te_3-based alloys are acceptable for some specialized applications, but they are far less so for commercial refrigeration on a large scale. A number of investigations have focused on optimizing the composition, tuning doping with other heavy metals, optimizing device design, etc. in order to improve the thermoelectric properties of Bi_2Te_3-based materials. However, the thermoelectric efficiency of these materials has not improved obviously and the dimensionless figure of merit (ZT) has been approximately 1 for many years.

According to theoretical and experimental investigations, the thermoelectric nanomaterials, such as quantum wells, superlattices, quantum wires, nanograined thin films, bulk nanocomposites demonstrate much higher thermoelectric coefficients than their traditional alternatives [1 – 4].

Bulk nanostructured materials are now considered as one of promising thermoelectric materials. A specific technology should be developed to fabricate nanostructured thermoelectric materials with reproducible and advanced properties.

One of technological approaches is based on two principal stages as follows [5]:

1. Synthesis of nanopowder of thermoelectric material with the desired structure, phase and element compositions, size and shapes of particles, etc.
2. Consolidation of synthesized nanopowder by using pressing and high temperature treatment in order to retain a nanostructure and get a dense sample with high enough mechanical strength and thermoelectric parameters.

In the present work such a kind of technology based on microwave-solvothermal synthesis and hot isostatic pressing was applied to prepare the nanostructured Bi_2Te_3-based material.

Experimental procedure

Bismuth telluride nanopowders have been prepared via microwave-solvothermal synthesis in closed reactor ERTEC (Model 02-02). As is known, compared with the conventional methods, the

microwave assisted heating technique has the advantages of very short time, simplicity and energy efficiency, small particle size of the products, narrow particle size distribution and high purity [6].

Analytical grade Bi_2O_3, TeO_2 and ethylene glycol were used as starting components. A 110 ml teflon-lined stainless-steel autoclave was used and the temperature was regulated by a digital-type temperature-controlled oven. Microwave assisted reactions were conducted in a 300 W microwave oven with a 2450 kHz working frequency.

The ethylene glycol was used both as the solvent and the reducing agent in the reaction. A few routes of synthesis were applied to determine optimal reaction conditions (Table 1). After synthesis, the reaction product, black precipitate, was washed with alcohol and then centrifuged and dried.

The morphology and structure of synthesized powder were characterized by *X*-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer with CuK_α-radiation, transmission electron microscopy (TEM) using a JEM-2010 microscope and scanning electron microscope (SEM) using a Zeiss LEO 1530 microscope.

Synthesized nanopowders were hot isostatically pressed (HIP) at temperature of 300°C during 5 min. Pressures at 2, 4, 6 and 8 GPa were used. The microstructure of consolidated material was then investigated by XRD, SEM and EDAX (energy dispersive *X*-ray microanalysis) using a Quanta 600 FEG scanning electron microscope.

Results and discussion

Phase compositions of the powder samples synthesized under various conditions are collected in Table 1.

Table 1

Parameters and results of microwave-solvothermal synthesis of powders

Reagents	Parameters of synthesis	Phase composition
Ethylene glycol – 60 ml. m (Bi_2O_3) – 4.6 gr. m (TeO_2) – 2.3 gr.	Temperature – 280°C, Pressure – 25 atm. Reaction duration – 100 min.	Bi_2Te_3, Bi, $BiTe$
Ethylene glycol – 60 ml. m (Bi_2O_3) – 4.6 gr. m (TeO_2) – 3 gr.	Temperature – 280°C Pressure – 37 atm. Reaction duration – 45 min.	Bi_2Te_3, Bi, Te
Ethylene glycol – 60 ml. m (Bi_2O_3) – 2.3 gr. m (TeO_2) – 1.5 gr.	Temperature – 250°C Pressure – 30 atm. Reaction duration – 35 min.	Bi_2Te_3, Bi, Bi_4Te_3
Ethylene glycol – 60 ml. m (Bi_2O_3) – 2.3 gr. m (TeO_2) – 2.3 gr.	Temperature – 250°C Pressure – 15 atm. Reaction duration – 50 min.	Bi_2Te_3
Ethylene glycol – 60 ml. m (Bi_2O_3) – 2.3 gr. m (TeO_2) – 2.45 gr.	Temperature – 250°C Pressure – 20 atm. Reaction duration – 35 min.	Bi_2Te_3, Bi_4Te_3

The XRD patterns analysis carried out at room temperature indicates that the microwave-solvothermal synthesis allows us to obtain single-phase powders of Bi_2Te_3 composition (space symmetry group of R-3m) with the following parameters: temperature 250°C, pressure 15 atm., synthesis duration 50 min, Bi_2O_3 to TeO_2 ratio 1:1. The diffraction peaks of the Bi_2Te_3 powder can be

exactly indexed with the standard diffraction planes of hexagonal Bi_2Te_3. This powder synthesized at optimal conditions was used for further study.

Morphology of Bi_2Te_3 powder has been investigated by SEM (Fig. 1). It is established that powder after synthesis consists of agglomerate of particles with the average size of 200 nm. Transmission electron microscopy image in Fig. 2 shows typical morphology of microwave-solvothermally synthesized powders. It is seen that the powder contains nanoparticles with the average size about 30 nm.

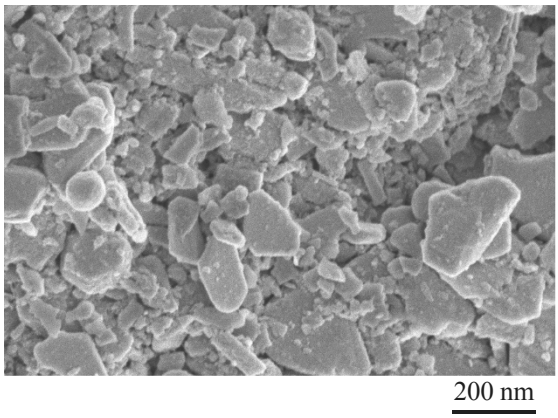

Fig. 1. Morphology of Bi_2Te_3 powder by SEM.

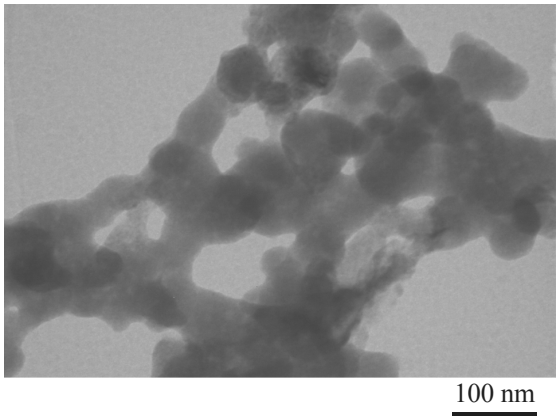

Fig. 2. Nanocrystals of Bi_2Te_3 powder by TEM.

The formation of Bi_2Te_3 hexagonal nanoplates is possibly due to their anisotropic structure. It is known that the Bi_2Te_3 crystal consists of 15 layers stacked along the *c*-axis and presents a combination of three hexagonal layer stacks of the composition in which each set consists of five atoms (Te_1-Bi-Te_2-Bi-Te_1). The bonding within the Te_1-Bi-Te_2-Bi-Te_1 layer is considered to be covalent, while the bonding between the Te_1-Te_1 layers is by van der Waals forces [7].

XRD patterns for the samples consolidated by HIP method at pressures of 2, 4, 6 and 8 GPa are presented in Fig. 3. In contrast with the initial powder, the phase constitution by XRD showed the presence of Bi_2Te_3 (space symmetry group R-3m) and $BiTe$ (P-3m1). So, at high temperature and under high pressure some part of the Bi_2Te_3 phase transforms into the $BiTe$ phase.

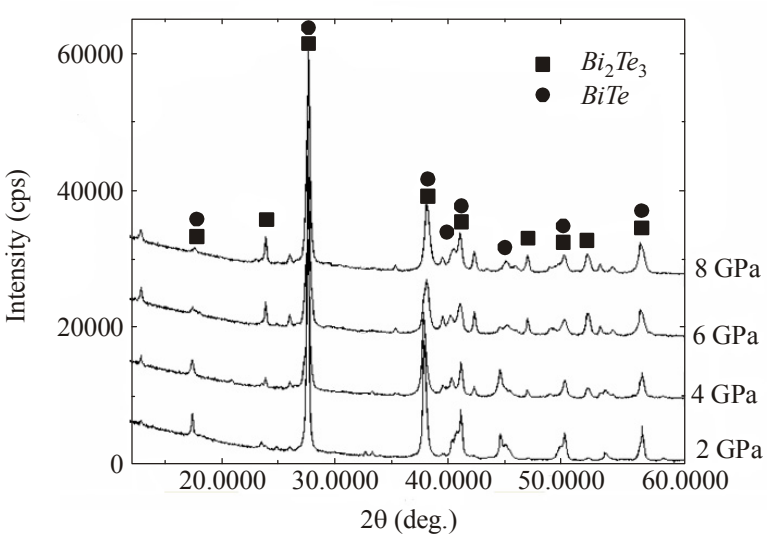

Fig. 3. XRD patterns of the Bi_2Te_3-based materials consolidated by HIP method at temperature of 300°C and pressures of 2, 4, 6 and 8 GPa.

The microstructures of materials consolidated under various HIP pressures are presented in Fig. 4. One can see that consolidated materials have homogeneous porousless nanocrystalline structures. The grain size of material under study is HIP pressure-dependent and the average grain size is varied from 60 to 100 nm.

EDAX experiments confirmed a homogeneous distribution of the *Bi* and *Te* elements within the material. Typical mapping by EDAX for one of the samples under study is shown in Fig. 5.

Preliminary testing of the conducting properties of materials consolidated under various HIP pressures established complex dependences of resistivity, carrier mobility and carrier density on pressure. Further research should be developed to understand the peculiarities of the electrical properties of Bi_2Te_3-based nanostructured materials. Some characteristics of the Bi_2Te_3-based materials are listed in Table 2.

Characterization of the thermoelectric properties of the Bi_2Te_3-based nanostructured materials is in progress now.

Conclusion

Single-phase Bi_2Te_3 plate-like crystals with homogeneous hexagonal morphology were rapidly synthesized using the microwave assisted solvothermal method during 50 min at 250°C and 30 atm. Synthesized nanopowder consists of particles agglomerate with the average size of 200 nm, which comprises crystals of size about 30 nm. HIP compaction of powders at temperature of 300°C and pressures of 2, 4, 6 and 8 GPa formed homogeneous Bi_2Te_3-based material with the average grain size of 60 – 100 nm.

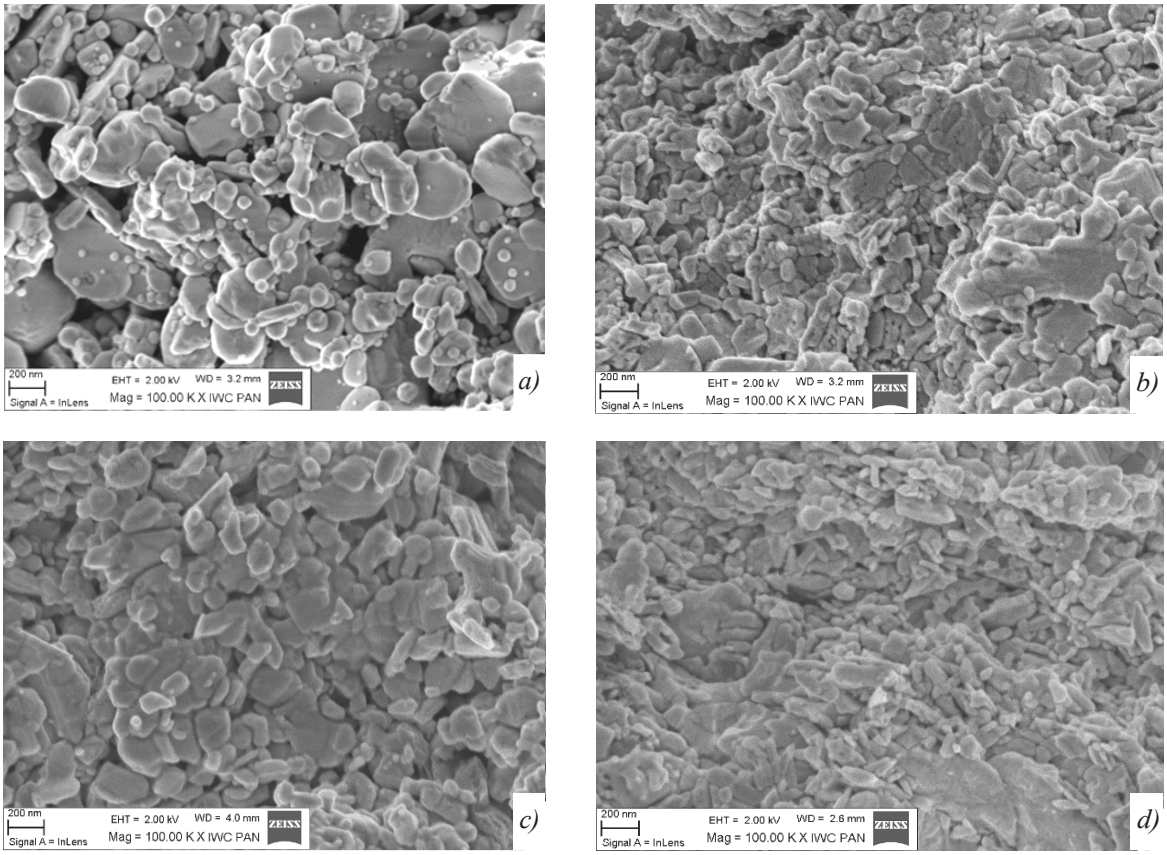

Fig. 4. Microstructure of the Bi_2Te_3-based materials consolidated by HIP method at temperature of 300°C and pressures of 2 (a), 4 (b), 6 (c) and 8 GPa (d).

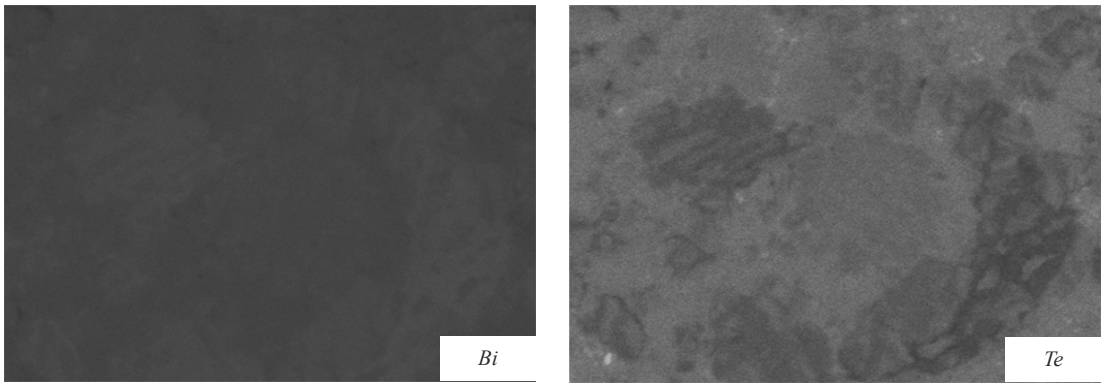

Fig. 5. Typical mapping by EDAX of the Bi_2Te_3-based material consolidated by HIP method at temperature of 300°C at pressure of 2 GPa.

Table 2

Characteristics of the of Bi_2Te_3-based materials

Pressure, GPa	Average grain size, nm	Resistivity, Ω·cm	Carrier mobility, V/(cm^2·s)	Carrier density, 10^{20}, cm^{-3}
2	140	0.0142	1.98	2.23
4	90	0.00199	14.9	2.11
6	120	0.0256	1.54	1.69
8	65	0.0146	1.07	4

Acknowledgements. This work was financially supported by the Ministry of Education and Science of Russian Federation under Contract No 16.552.11.7004.

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Submitted 07.05.2011.