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NANOSTRUCTURAL THERMOELECTRIC MATERIALS OBTAINED BY SOLVOTHERMAL SYNTHESIS AND HOT ISOSTATIC PRESSURE

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Abstract. 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 400°C and pressures of 2, 4, 6 and 8 GPa allowed us to form homogeneous and dense Bi_2Te_3-based material with average grain size from 60 to 100 nm.

Keywords: solvothermal synthesis, bismuth telluride, nanostructural thermoelectric materials.

1. 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 of the composition, tuning doping with other heavy metals, optimizing device design, etc in order to improve thermoelectric properties of the 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, superlattice, quantum wires, nanograined thin films, bulk nanocompo- sites demonstrate much higher thermoelectric coefficients than their traditional alternatives [1-4].

Bulk nanostructured materials are now considered as one of perspective thermoelectric materials. A specific technology should be developed to fabricate nanostructured thermoelectric materials with reproducible and advanced properties. One of technological approach is based on two principal stages as follows [5]:

- Synthesis of initial nanopowder with desired structure, phase and element compositions, size and shapes of particles, etc.

- Consolidation of synthesized nanopowder by using the pressing and high temperature treatment in order to retain a nanostructure and fabricate dense sample with high enough mechanical strength and thermoelectric parameters.

In present work such a kind of technology based on microwave-solvothermal synthesis and hot isostatic pressing was applied to prepare the bulk nanostructured Bi_2Te_3-based material. As it 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 products, narrow particle size distribution and high purity [6].

2. Experimental procedure

Bismuth telluride nanopowders have been prepared via microwave-solvothermal synthesis in closed reactor ERTEC (Model 02-02).

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

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

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

Table 1

Parameters and results of microwave-solvothermal synthesis of powders

Reagents	Parameters of synthesis	Phases
Ethylene glycol – 60 ml., m (Bi_2O_3) - 4.6 gr. m (TeO_2) – 2.3 gr.	Temperature – 280 °C, Pressure – 25 atm., Duration of reaction – 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., Duration of reaction – 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., Duration of reaction – 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., Duration of reaction – 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., Duration of reaction – 35 min.	Bi_2Te_3, Bi_4Te_3

Synthesized nanopowders were hot isostatically pressed (HIP) at temperature of 400 °C during 5 min by using a toroidal press. Powder for compaction was placed in graphite matrix with hexagonal BN powder as media to spread isostatic pressure to the object under pressing. Pressures equal to 2, 4, 6 and 8 GPa were used.

Microstructure of consolidated material was then investigated by XRD and SEM using the Zeiss LEO 1530 scanning electron microscope. EDAX (Energy Dispersive X-ray Microanalysis) method was used to study the element distribution within samples under consolidation.

Electrical conductivity, σ, of the consolidated samples was also measured by four-probed method at room temperature.

3. Results and discussion

It was established that phase composition of material after synthesis is strongly dependent on synthesis conditions and ratio of initial reagents. Phase compositions of powder samples synthesized at various conditions are collected in Table 1.

One can see that all of five technological routes allow us to prepare the desired Bi_2Te_3 phase, but for routes №1, 2, 3 and 5 the Bi_2Te_3 phase is coexisting with other parasite phases (BiTe, Bi_4Te_3, Bi, Te). Single phase Bi_2Te_3 powder could be prepared via route №4. This powder synthesized at optimal conditions was used for further study.

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

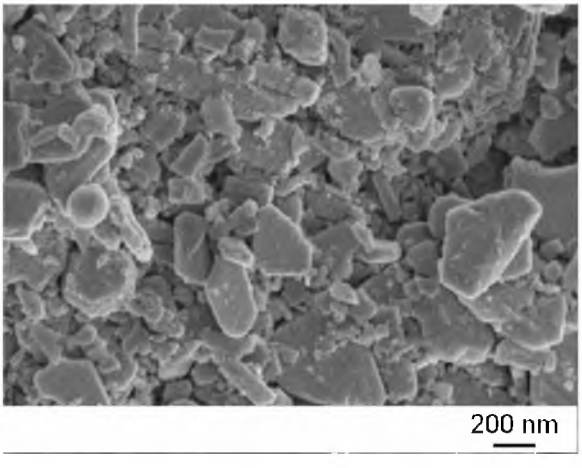

Fig 1. Morphology of the Bi_2Te_3 nanopowder by SEM.

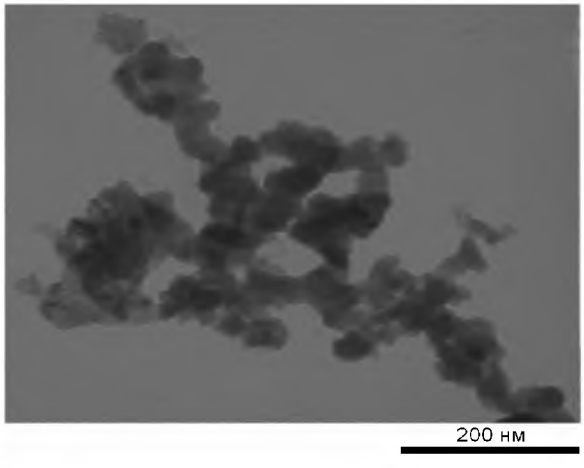

Fig. 2. Nanocrystals of the Bi_2Te_3 powder by TEM.

Bulk material cylindrical form with sizes of 5x5 mm was then prepared by HIP-consolidation. A few specific features were found at research of consolidated material:

- In contrast with initial powder, the phase composition extracted from XRD patterns showed presence of Bi_2Te_3 (space symmetry group $R\text{-}3m$) and BiTe ($P\text{-}3m1$). So, at

high temperature and under high pressure, some part of the Bi_2Te_3 phase transforms into the BiTe phase.

- Consolidated materials have dense, homogeneous and porousless nanocrystalline structures (Fig. 3). Grain size, d, of the material under study is the HIP-pressure-dependent one and the average grain size is changed from 60 to 100 nm (Fig. 4).
- EDAX experiments confirmed the homogeneous distribution of the Bi and Te elements within the material.

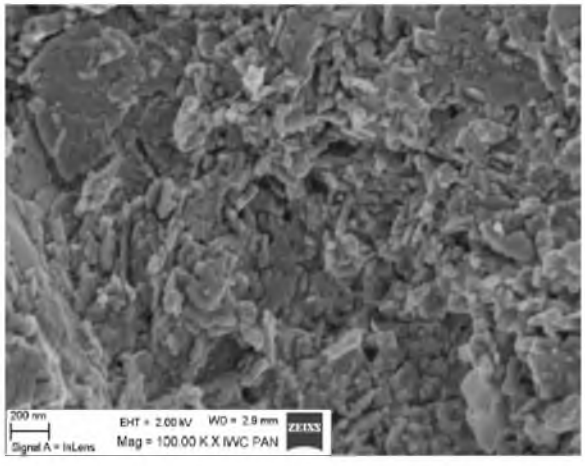

Fig. 3. Microstructure of the Bi_2Te_3-based materials consolidated by the HIP method at temperature of 400°C and pressures of 8 GPa

According to the theoretical consideration [7], electrical conductivity of bulk thermoelectric Bi2Te3 material should be depressed when grain size is decreasing. This behavior is attributed to carriers mobility decrease owing the carriers scattering by grain boundaries. The $\sigma(d)$ dependence is shown in Fig. 5. For the grain sizes of 100, 85 and 60 nm (corresponding HIP-pressures are 2, 6 and 8 GPa) experimental points are in agreement with the theoretical prediction. But electrical conductivity is maximal the sample with d=80 nm ($P = 4$ GPa). It is obvious that to explain the change of electrical conductivity versus the HIP-pressure other physical mechanisms besides grain size change should be taken into account. In particularly, carriers concentration and defect structure in volume materials can also change during the hot isostatic pressure.

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

4. Conclusion

Single-phases Bi_2Te_3 plate-like crystals with homogeneous hexagonal morphology were rapidly synthesized using by the microwave assisted solvothermal method in 50 min at 250°C and 30 atm. Synthesized nanopowder consists of particles agglomerate with average size of 200 nm which consists of crystals with size about 30 nm. HIP compaction of powders at

temperature of 400 °C and pressures of 2, 4, 6 and 8 GPa formed homogeneous Bi_2Te_3-based material with average grain size is of 60-100 nm. Electrical conductivity of samples under study shows the complex dependence of the grain size (HIP-pressure).

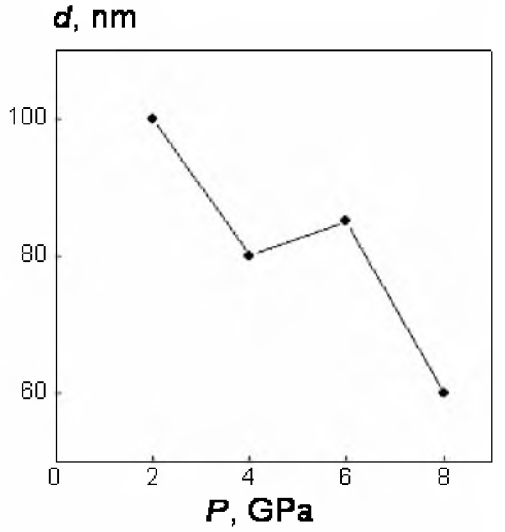

Fig. 4. The $d(P)$ dependence for the Bi_2Te_3-based materials consolidated by the HIP method

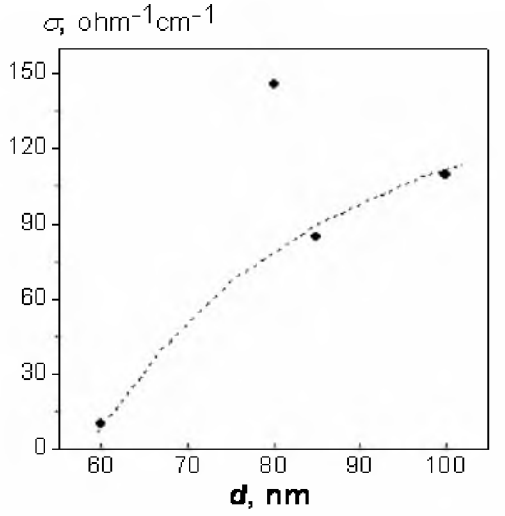

Fig. 5. The $\sigma(d)$ dependence for the Bi_2Te_3-based materials consolidated by the HIP method

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ПОЛУЧЕНИЕ И СВОЙСТВА НАНОСТРУКТУРНЫХ ТЕРМОЭЛЕКТРИЧЕСКИХ МАТЕРИАЛОВ МЕТОДАМИ СОЛЬВОТЕРМАЛЬНОГО СИНТЕЗА И ГОРЯЧЕГО ИЗОСТАТИЧЕСКОГО ПРЕССОВАНИЯ

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Аннотация. Сольвотермально-микроволновым способом синтезирован наноразмерный порошок теллурида висмута, состоящий из пластинок неправильной формы со средним размером $\sim$ 30 нм. Были установлены оптимальные условия получения однофазного порошка Bi_2Te_3. Наноразмерный порошок был консолидирован методом горячего изостатического прессования при температуре 400 °C и давлениях 2, 4, 6 и 8 ГПа. В результате были получены плотные химически однородные наноструктурные материалы со средним размером зерна 60-100 нм, зависящим от давления прессования. Удельная электрическая проводимость консолидированных материалов, измеренная при комнатной температуре, имеет экстремальную зависимость от среднего размера зерна.

Ключевые слова: сольвотермальный синтез, теллурид висмута, наноструктурные термоэлектрические материалы.