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THE METASTABLE PHASE Bi_2Te_3-*m* OBTAINED DIRECTLY FROM THE SEPARATE ELEMENTS

A Bi_2Te_3-m metastable phase has been obtained from the stoichiometrically mixed separate elements (Bi and Te) by the HPHT- treatment and mechanical alloying methods. Structure of the new phase has been clarified by Rietveld refinement. The density and hardness of the samples have been measured. The homogeneity of initial and metastable phases was investigated by the scanning electron microscopy (SEM). The temperature region of Bi_2Te_3-m stability was defined by the differential scanning calorimetry. The thermoelectric properties of Bi_2Te_3-m have been measured.
Key words: pressure-induced phase transition, *X*-ray diffraction, thermoelectric material, mechanical alloying.

Introduction

The bismuth telluride is widely used as a base material in the thermoelectric cooling systems and converters of heat into electric energy at room temperatures, so the investigation of its properties is highly important. Recently, pressure dependencies of the electrical resistance, thermal conductivity, and thermal power (Seebeck coefficient) [1, 2, 3] along with the resistance and the Hall coefficient [4] of Bi_2Te_3 have been studied up to 10 GPa. An experimental study has been carried out up to 29 GPa in diamond anvil cells [5, 6, 7], where reversible pressure-induced phases have been found; the experimental data have been confirmed by theoretical calculations [7]. The structures and bulk properties of the new phases [3, 5] were investigated. The fascinating electronic properties of Bi_2Te_3 were detected. For example, the electronic topological transition in Bi_2Te_3 under the high pressure was observed [8], the structural phase transition of Bi_2Te_3 from normal to superconductive state was found [9]. The atomic structure of the latter phase was determined by particle-swarm optimization method [10].

Earlier Bi_2Te_3 metastable phase has been observed after HPHT-treatment at a pressure $P > 6$ GPa and temperature $T > 800$ °C [11]. Here we investigated the formation of this phase from separate elements (*Bi* and *Te*) in stoichiometric proportion using quenching at high pressure and high temperatures. We studied the stability, structural and thermoelectric properties of the metastable phase at ambient conditions. The authors of [11] denoted the discovered phase as Bi_2Te_3 II, but this notation was later used for another pressure-induced phase [6], then we labeled this phase as Bi_2Te_3-*m* (metastable).

Experiment

Previously the Bi_2Te_3-*m* metastable phase was obtained from the initial compound of Bi_2Te_3 (I) [11]. In order to increase the thermoelectric figure of merit, it was suggested to synthesize the Bi_2Te_3-*m*

metastable phase directly from the initial elements under pressure. Bismuth and tellurium (Aldrich: *Bi* 99.999 %, *Te* 99.999 %) were taken as initial elements. The *Bi* and *Te* ingots taken in stoichiometric proportion were crushed and rubbed in a mortar. We synthesized the metastable high-pressure-phase from these materials by a rapid quenching after the electrical current thermoresistive heating of the "anvil with cavity" high-pressure apparatus [12]. The sample cooling rate was ≈ 60 °C/min, and pressure reduction rate in the reaction cell ≈ 1 GPa/min.

Mechanical alloying (MA) was used to obtain the new phases of Bi_2Te_3 with a higher figure of merit (*ZT*), but at lower pressures [13, 14] using an AGO-2U planetary mill. In order to avoid possible contamination of treated materials by oxygen and water vapor, all the procedures with the mixtures were carried out in a glove box filled with argon of purity not less than 0.1 ppm. A stoichiometric mixture of powders of bismuth and tellurium was placed in the mill's drums. The tungsten carbide balls WC6 of diameter 10 mm, weight 6.2 g, were used as the milling bodies for generation of higher pressures and temperatures during collision of balls.

The appearance of Bi_2Te_3-*m* metastable phase was determined by comparing the diffractograms of Bi_2Te_3-*m* and Bi_2Te_3 (I). A Bi_2Te_3-*m* diffractogram obtained after quenching at 7.7 GPa and 700 °C from the original Bi_2Te_3 (I) alloy was taken as a standard of the new phase. The *X*-ray powder diffraction patterns were obtained by using ARL X´TRA powder diffractometer (*Cu-Kα* radiation) equipped with a solid-state (*Si(Li)*) semiconductor detector.

Thereby, the samples were obtained in three different ways:

1. Processing of a stoichiometric *Bi* and *Te* mixture under the 7.7 GPa pressure and 700 °C temperature in a hydraulic press.
2. Mechanical alloying of a stoichiometric *Bi* and *Te* mixture at mill's speed of rotation 1090 rot./min and 1 hour holding time.
3. Sintering of the mechanically alloyed Bi_2Te_3 (I) powder under the 5.5 GPa pressure at 600 °C.

Results and discussion

Diffractograms of the metastable phase Bi_2Te_3-*m* are shown in Fig. 1.
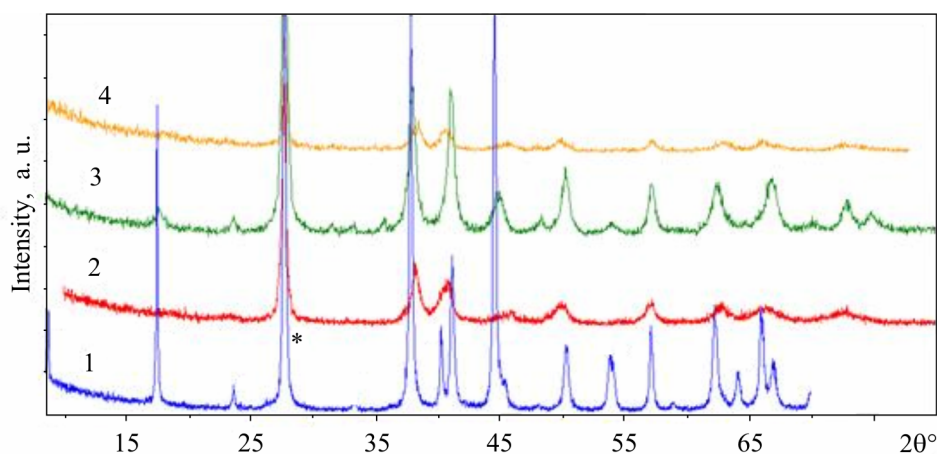

Fig. 1. X-ray diffractograms of Bi₂Te₃-m obtained by three different ways. 1) initial Bi₂Te₃ (I);
2) Bi₂Te₃-m obtained by the 1ˢᵗ method; 3) mixture of Bi₂Te₃ (I) and Bi₂Te₃-m obtained by the 2ⁿᵈ method;
4) Bi₂Te₃-m obtained by the 3ʳᵈ method. No appearance of Bi₂Te₃ (I) in patterns (2) and (4) was found.
Only one strongest peak (about 2θ ~ 28°) of the initial phase coincides with peak
*of new phase (marked by asterisks *).*

While using the 1-st and 3-rd method, the Bi_2Te_3-*m* outcome was 100 %. We can conclude that it is a new phase, because the peaks change their positions and intensity. After MA (the 2-nd method), we can conclude that there is a mixture of the initial and metastable phases in the planetary mill drums (Fig. 1, No 3), because the reflections corresponding to the Bi_2Te_3 (I) lose their intensity (in comparison with an initial phase diffractogram), but peaks of the metastable phase start appearing (in comparison with diffractograms 2 or 4). The Rietveld analysis showed that 20 – 30 % of the first phase in the metastable phase transforms after mechanical alloying. The diffraction peaks of the sample obtained by the 3-rd method were broad, i.e. the coherent region is very small (50 nm). The new phase of Bi_2Te_3-*m* is not a mechanical mixture of two elements, because the diffractograms have no separate peaks of bismuth and tellurium.
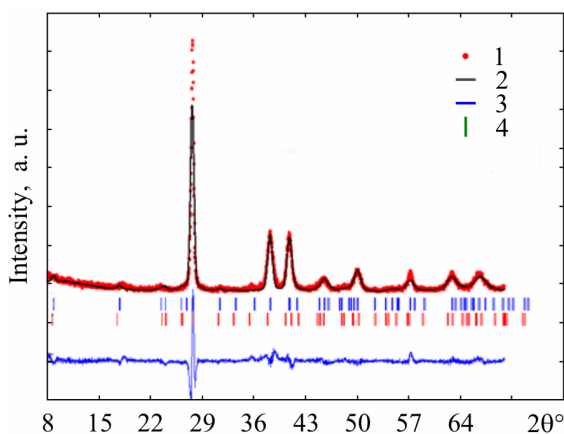
Cell parameters of the initial and metastable phases are shown in Table 1. The difference in volumes is 0.6 %.

Table 1

Parameters of Bi₂Te₃ (I) and Bi₂Te₃-m

Phase	Space group	a, Å	c, Å	V, Å³	ρ, g/cm³
Bi_2Te_3 (I)	$R\bar{3}m$	4.40	30.44	509.28	7.834
Bi_2Te_3-*m*	$R3m$	4.42	29.84	503.87	7.962

By the Rietveld fit method (FullProf software [15]), the unit-cell-parameters and the tellurium and bismuth coordinates were refined. Two – phased simulation was carried on, the contribution of the initial and metastable phases was 6.2 % and 93.8 %, respectively. The factor of the reliability of the structure determining is $R_{Bragg} \sim 10$ % calculated by the positions of diffractional reflections (Fig. 2).

Fig. 2. Results of Rietveld analysis of two – phased Bi₂Te₃ pattern.

The *Te – Te* distance changes dramatically (from 4.54 Å to 3.15 Å) (Table 2) and become closer to the covalent bond *Te – Te* (sum of covalent radii of *Te*, 2.74 Å), which testifies the strengthening in the covalent bond of the metastable Bi_2Te_3-*m* modification.

Microhardness of the new metastable phase was measured and equals to (1.5 ± 0.2) GPa, which is almost identical with the hardness of the initial phase (H = 1.7 GPa).

The thermal properties of Bi_2Te_3-*m* were studied by a DSC 800° scanning calorimeter (PerkinElmer). The measurements were carried out during heating at a 20 °C/min speed in the 50 ÷ 380 °C temperature range. When heated, the release of heat was found (Fig. 4 *a* "First run"

curve) after 80 °C (exothermic effect), the intensity of which increases with the temperature rise up to 230 °C. The exothermic effect gradually reduces after 230 °C. "Second run" (Fig. 3) curve shows that there is no exothermic effect in the sample and Bi_2Te_3 (I) is stable at these temperatures. It means that Bi_2Te_3-m phase is stable up to 80 °C and the reverse transition stops at 230 °C.

Table 2

Coordinates of the atoms and distances between them in Bi_2Te_3 (I) and Bi_2Te_3-m

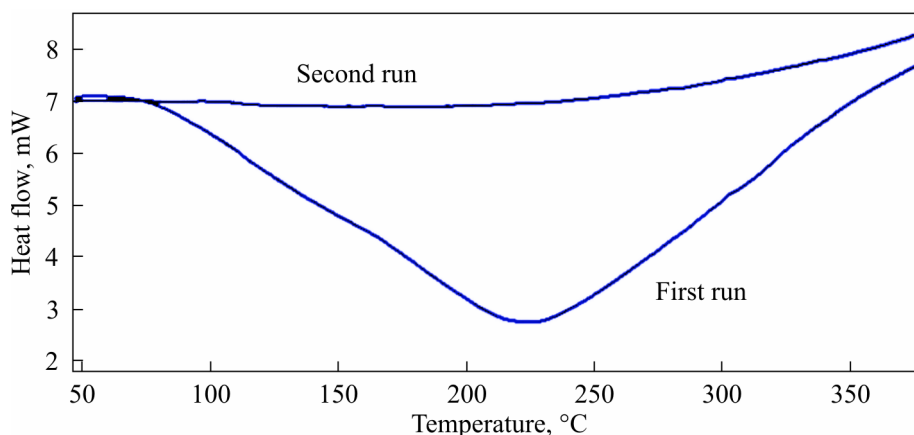| Phase	Element	x	y	z	Ionic radius, Å	Covalent radius, Å	Atomic radius, Å	Atoms	Distances, Å
Bi_2Te_3 (I)	Bi_1	0	0	0.40	1.60	1.46	1.70	$Bi_1 - Te_1$	3.07
	Te_1	0	0	0.79	1.40	1.37	1.60	$Te_2 - Te_2$	3.65
	Te_2	0	0	0				$Bi_1 - Te_2$	3.26
Bi_2Te_3-m	Bi_1	0	0	0.20				$Bi_1 - Bi_2$	3.15
	Bi_2	0	0	0.59				$Bi_1 - Te_1$	3.36
	Te_1	0	0	0.79				$Bi_2 - Te_2$	3.32
	Te_2	0	0	0				$Te_3 - Te_2$	3.15
	Te_3	0	0	0.39				$Te_3 - Te_1$	3.21

Fig. 3. The reverse Bi_2Te_3-m → Bi_2Te_3 (I) transition.

The Seebeck coefficient (α), electric conductivity (σ) and thermal conductivity (κ) were measured by the Harman method (direct method for obtaining the figure of merit (*ZT*) of a material) [16] (Table 3). The significant decreasing of the *ZT* coefficient in Bi_2Te_3-m (*n*-type sample) was obtained.

Table 3

The thermoelectric properties of Bi_2Te_3-m and Bi_2Te_3 (I)

(All data is given at temperature 300 K)	Bi_2Te_3 (I)	Bi_2Te_3-m
α, μV/K	(274 ± 14)	(72 ± 4)
σ, 1/(Ω·cm)	(1100 ± 60)	(850 ± 40)
κ, W/(m·K)	(1.45 ± 0.07)	(2.06 ± 0.1)
Z, (10⁻³1/K)	(1.8 ± 0.2)	(0.25 ± 0.03)

We can conclude that the Bi_2Te_3-*m* metastable phase appears during the high-pressure – high-temperature treatment. The MA process only activates the phase transition, because the pressure created by planetary mill is not enough for a complete transformation. Additives of Bi_2Te_3-*m* could both increase and decrease the thermoelectric power of the bulk materials, because *ZT* is not an additive value. During the phase transition, the symmetry changes (the center of symmetry is lost), a layered structure is retained. The phase transition also changes the alternation of the atomic layers (-*Bi-Te-Te-Te-Bi*-). It should be noted that Bi_2Te_3-*m* is stable at normal conditions and has rhombohedral structure in contrast with the pressure – induced reversible phases of Bi_2Te_3 obtained *in situ* at room temperatures [5, 6, 7]. Such a low value of *ZT* in Bi_2Te_3-*m* could be explained by increasing of the covalent bonding between *Te* atoms.

Conclusions

A Bi_2Te_3-*m* metastable phase was obtained by a direct high-pressure – high-temperature synthesis of the separate elements mixed stoichiometrically at 7.7 GPa and 700 °C. Pre-MA of the Bi_2Te_3 (I) powder allows to fabricate a compact material with a 100 % Bi_2Te_3-*m* outcome at a lower pressure 5.5 GPa and temperature 600 °C. This phase is stable under normal conditions and differs from all the other pressure-induced phases of Bi_2Te_3 obtained by authors of [5-7]. The Bi_2Te_3-*m* structure was refined; the positions of the atoms in the metastable structure were determined. The hardness (1.7 GPa) of Bi_2Te_3-*m* is the same as the Bi_2Te_3 (I) values within the limits of experimental error. The volume change is 0.6 %, i.e. metastable phase is denser than initial phase. The Bi_2Te_3-*m* phase is stable up to 80 °C at the atmospheric pressure. The value of figure of merit of the metastable phase is lower than that of the initial one and equals to $(0.25 \pm 0.003) \cdot 10^{-3}$ K. The new phase is characterized by semimetal properties, which could lead to decreasing in *ZT* coefficient.

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