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Projection of the liquidus surface of the Ho-Bi-Te ternary system

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The Ho-Bi-Te ternary system was studied by DTA, X-ray diffraction, and MSA, as well as by measuring microhardness and determining density, congruent triangulation scheme and projection of the liquidus surface, types and coordinates of mono- and invariant equilibria. It is established that this system is triangulated into five pseudo-ternary systems. It was discovered that an incongruently melting ternary compound containing HoBiTe3 is formed in the Ho-Bi-Te ternary system. X-ray phase analysis established that the $HoBiTe_3$ compound crystallises in a tetragonal system with lattice parameters: a = 19.99, c = 13.82 Å, Z = 3. Studying the nature of the interaction of the components of the quasi-binary section Bi_2Te_3-Ho_2Te_3 of the Ho-Bi-Te ternary system, as well as thermoelectric materials formed by combining Bi_2Te_3 with rare-earth tellurides, is of interest from a scientific and practical point of view.

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1. Introduction

The preparation and physicochemical properties of chalcogenides with semiconductor properties have been widely studied. It has been established that, depending on temperature and pressure, various phase transitions are observed in these materials [1-3]. Interesting structural features and magnetic and thermal properties are observed in chalcogenides with anion-anion and cation-cation substitutions. It has been established that the difference in the ionic radii of metal and chalcogen atoms causes serious changes in the crystal structure. Differences in crystal structure are known to affect other physical properties. Therefore, the crystal structure of the synthesized chalcogenide semiconductors requires precise study [4-6]. Theoretical and experimental research is being carried out in this direction. The physicochemical properties observed in new chemistries are predicted by modelling certain chalcogenide semiconductors. Chalcogenide semiconductors can be studied by determining both the crystalline and electronic structure [7-11].

Tellurides of heavy P elements of group V and alloys based on them are promising materials with semiconductor properties such as thermoelectric, and photoelectric. Recent studies have shown that Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 compounds with a layered structure of the tetradymite type and their ternary structural analogues formed in the Ln-B^V-Te system (Ln-lanthanides, B^V-Sb, Bi) are topological insulators [12-16]. In this work, the Ho-Bi-Te ternary system was studied by physicochemical analysis over the entire range of concentrations.

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The Bi_2Te_3-HoTe section [17] belongs to the quasi-binary eutectic type. Eutectic coordinates: 25 mol % HoTe and 830 K.

The paper presents experimental data in the section: Bi_2Te_3-Ho_2Te_3, Bi_2Te_3-Ho_2Te_5, Bi_2Te_3-$HoTe_3$, HoBi-HoTe, HoTe-Bi, Bi_2Te_3-Ho, HoBi-Bi_2Te_3, D-Te (D–HoTe+Bi_2Te_3) in the ratio 60: 40 and the projection of the surface of the liquidus of the ternary system, built based on the results of the study of eight sections of the ternary system.

2. Experimental methods

To synthesize alloys of ternary Ho-Bi-Te systems, the highly pure elements bismuth Bi - 99.9998, holmium - 99.997% and tellurium -99.999% were used.

Samples of metals and tellurium in given ratios weighing 10 g were placed in quartz ampoules, evacuated to a residual pressure of 0.133 Pa, and sealed. Synthesis was carried out in the temperature range of 950–1200 K. Further, the obtained alloys were annealed at 50–60 K below the solidus of the system for 500 h.

After heat treatment, all alloys of the above systems were investigated by differential thermal (DTA) and high-temperature differential thermal (HTTA), X-ray phase (XRD), microstructural (MSA) analyses, as well as by measuring microhardness and determining density.

DTA of alloys was carried out on a Termoksan-2 installation with a heating rate of 5 deg/min. Combined chrome-alumni thermocouples were used, and Al_2O_3 served as the standard. A high-temperature thermograph BDTA and a differential thermocouple W-W/Re were also used; the recording was carried out on a potentiometer with a heating rate of 10 deg/min.

XRF was performed on an X-ray device model D-2 PHASER using CuKα radiation with a Ni filter. The MCA of the alloys of the system was studied, using a MIM-7 metallographic microscope, in the study of the microstructure of the alloys, an etchant with the composition conc. HNO_3:H_2O_2=1:2 etching time 20 s.

The microhardness of the alloys of the system was measured; on a PMT-3 microhardness tester, the error was 2.2–4.3%. The density of the alloys of the system was determined by the psychometric method.

3. Results and discussion

Ternary systems Ho-Bi-Te were studied in the following sections: Bi_2Te_3-Ho_2Te_3, HoBi-HoTe, HoTe-Bi, Bi_2Te_3-Ho_2Te_5, Bi_2Te_3-$HoTe_3$, Bi_2Te_3-Ho, HoBi-Bi_2Te_3, D-Te.

The section Bi_2Te_3-Ho_2Te_3 belongs to the quasi-binary eutectic type (Fig. 1).

In the Bi_2Te_3-Ho_2Te_3 system, with a component ratio 1:1, one ternary compound of the HoBiTe3 composition is formed, melting incongruently at 883 K.

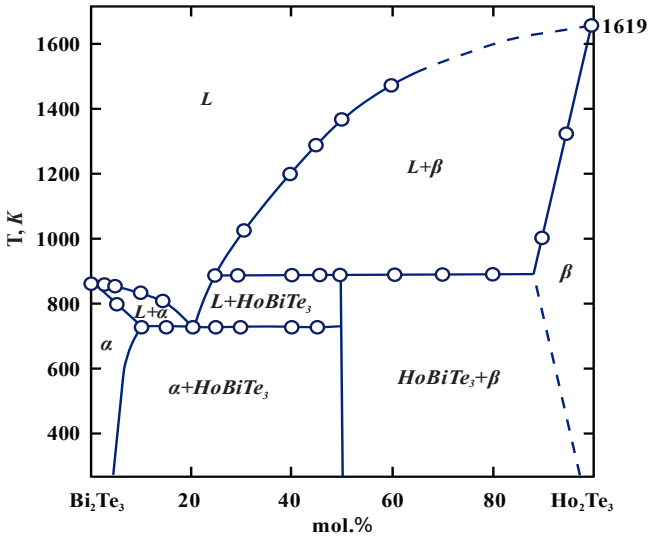

Fig. 1. Phase diagram of the system Bi_2Te_3-Ho_2Te_3.

The joint crystallization of Bi_2Te_3 and Ho_2Te_3 compounds ends at the eutectic point of composition 20 mol. % Ho_2Te_3, temperature 738 K. Based on the initial components, a region of solid solutions was found, which, based on Bi_2Te_3, reaches 5 mol % Ho_2Te_3, and based on Ho_2Te_3 up to -3 mol % Bi_2Te_3. Two-phase alloys (α + $HoBiTe_3$) and (β + $HoBiTe_3$) crystallize in the Bi_2Te_3–Ho_2Te_3 system below the solidus line. According to the results of X-ray phase analysis, it was found that the $HoBiTe_3$ compound crystallizes in a tetragonal syngony with lattice parameters: a = 19.99; c=13.82 Å, Z=3, density $\rho_{puc/}$= 7.30 g/cm^3, $\rho_{X\text{-}ray}$= 7.35 g/cm^3 (Fig. 2).

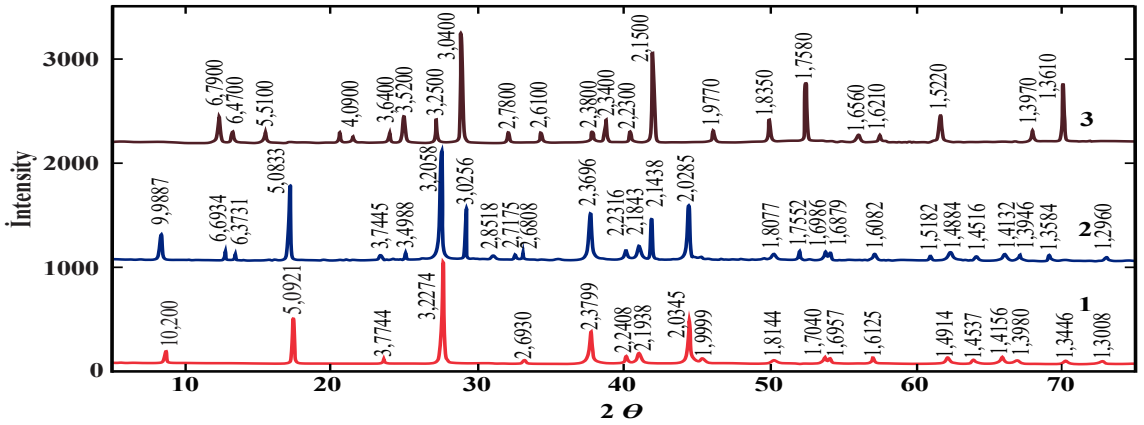

Fig. 2. X-ray diffraction patterns of alloys of the Bi_2Te_3-Ho_2Te_3 system; 1-Bi_2Te_3, 2-($HoBiTe_3$), 3-Ho_2Te_3.

The HoBi-HoTe section is quasi-binary (Fig. 3) and belongs to the eutectic type.

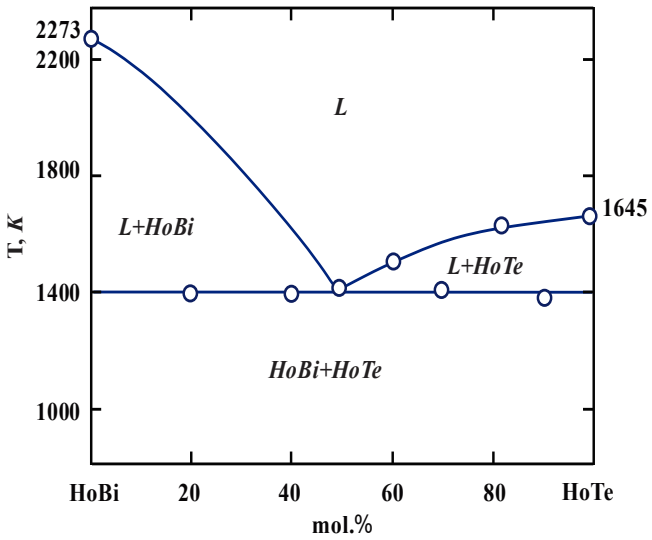

Fig. 3. Phase diagram of the system HoBi-HoTe.

The HoBi and HoTe compounds form a eutectic with a 50 mol % HoTe composition, at a temperature of 1400 K. The liquidus of the HoBi-HoTe system consists of monovariant HoBi and HoTe equilibrium curves.

The Bi-HoTe section is also quasi-binary, of the eutectic type (Fig. 4). A degenerate eutectic is formed between the HoTe and Bi compounds, coordinates: 100 mol % Bi and 544 K. Two-phase alloys (Bi + HoTe) crystallise below the solidus line.

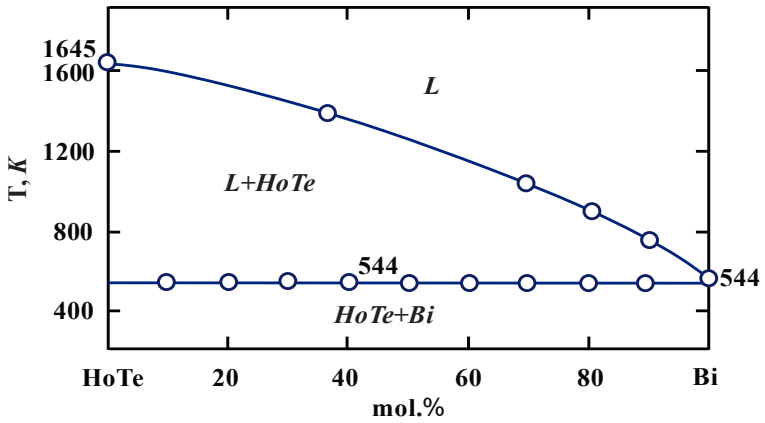

Fig. 4. Phase diagram of the system Bi-HoTe.

The Bi_2Te_3-Ho_2Te_5 section is a partially quasi-binary section of the Bi-Ho-Te ternary system, studied by the methods of physicochemical analysis and a T-x phase diagram was built (Fig. 5). Ho_2Te_5 is formed by a peritectic reaction.

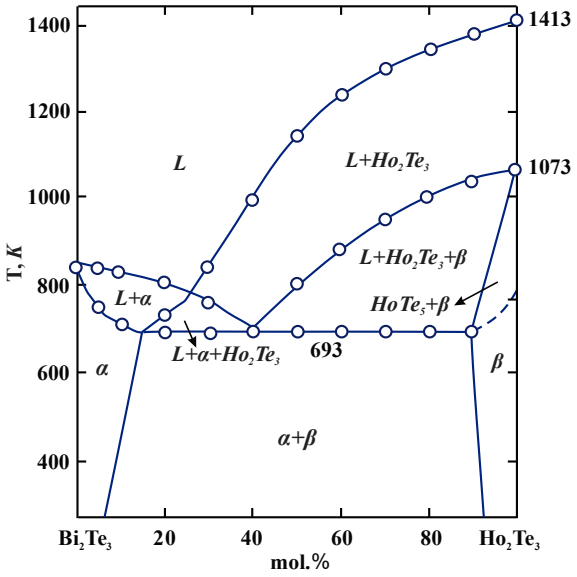

Fig. 5. Phase diagram of the system Bi_2Te_3-Ho_2Te_5.

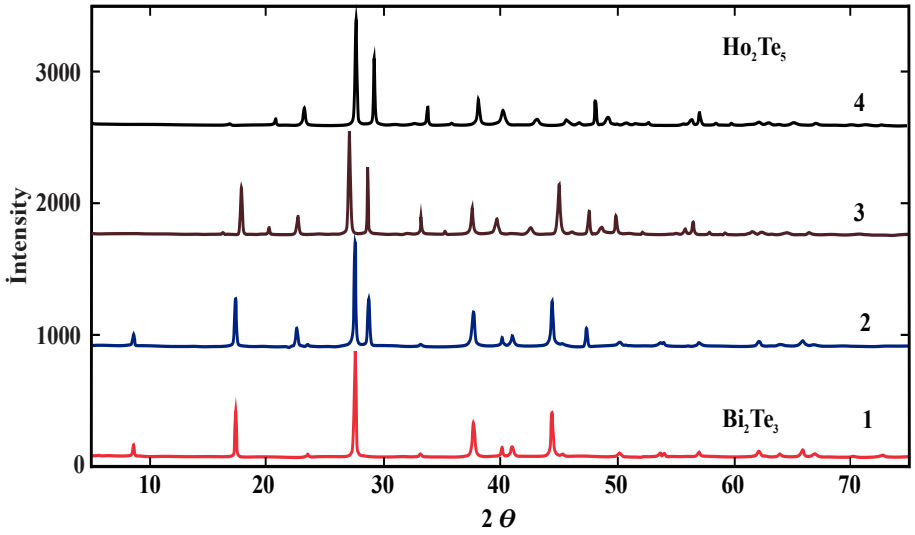

Fig. 6. Diffractograms of alloys of the Bi_2Te_3- Ho_2Te_5 system; 1-Bi_2Te_3, 2-5, 3-50, 4-80, 5-100 mol % $HoTe_3$.

Therefore, the phase diagram of the Bi_2Te_3-Ho_2Te_5 system is partially quasi-binary. Despite this, the system behaves like a stable diagonal of the Bi-Ho-Te ternary system. Solid solutions based on Bi_2Te_3 at room temperature reach up to 6 mol. % Ho_2Te_5, and based on Ho_2Te_5 solid solutions reach up to 8 mol. %.

The physicochemical study of the Bi_2Te_3-$HoTe_3$ system was carried out by the methods of differential thermal (DTA), X-ray phase (XRD), microstructural (MSA), analyses, as well as by measuring microhardness and determining density, and a T-x phase diagram was built (Fig. 7).

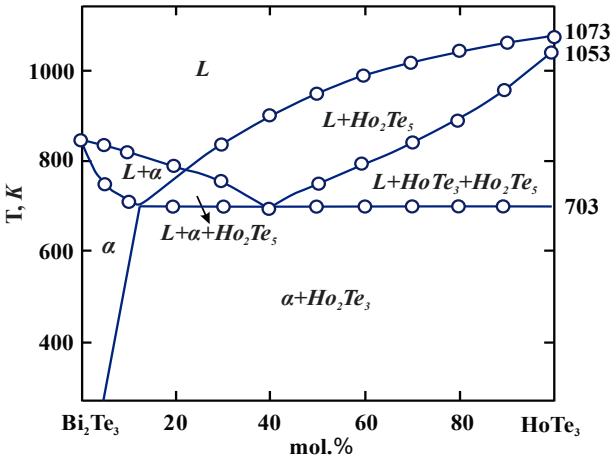

Fig. 7. Phase diagram of the system Bi_2Te_3- $HoTe_3$.

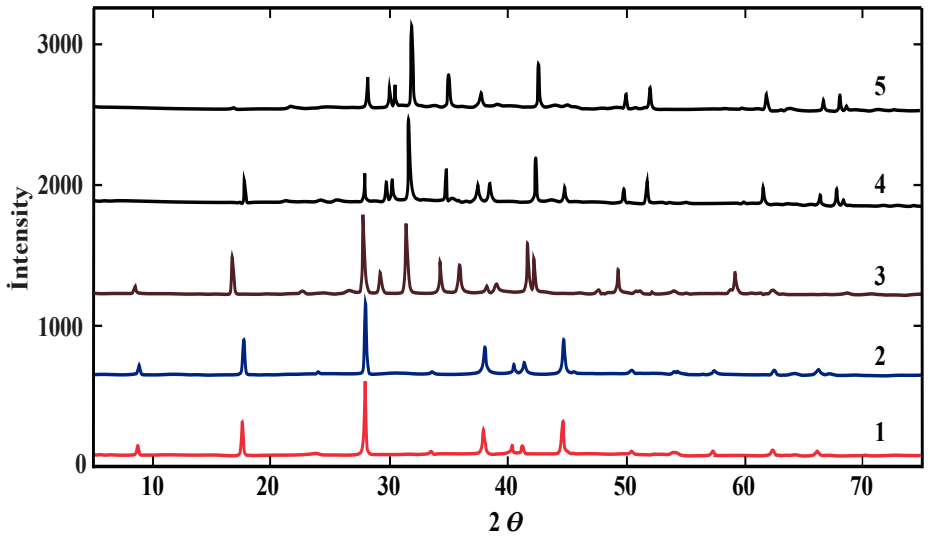

Fig. 8. Diffractograms of alloys of the Bi_2Te_3-$HoTe_3$ system; 1-Bi_2Te_3, 2-5, 3-50, 4-80, 5-100 mol % $HoTe_3$.

It has been established that the Bi_2Te_3-$HoTe_3$ system is a partially quasi-binary section of the Bi-Ho-Te ternary system. Eutectic equilibrium and peritectic transformation occur in the system. Solid solutions based on Bi_2Te_3 at room temperature reach up to 5 mol % $HoTe_3$, and solid solutions based on $HoTe_3$ are practically not found.

X-ray phase analysis of alloys containing 5, 50, and 80 mol % $HoTe_3$ are presented in the form of diffractograms, in Fig.8. Alloys containing 50, 80 mol % $HoTe_3$, two-phase. On the diffraction patterns of these alloys, the diffraction lines consist of the diffraction lines of the initial components. This indicates that the alloys are two-phase. A sample containing 5 mol % $HoTe_3$ is single-phase and belongs to the range of solid solutions based on Bi_2Te_3. Thus, the XRD results are in good agreement with the DTA and MSA data.

The Bi_2Te_3-Ho section (Fig. 9) is non-quasi-binary, it crosses three crystallization fields of the phases formed in the Ho-Bi-Te system. The liquidus curves correspond to primary phase separation, Ho, Ho_5Bi_3, Ho_4Bi_3, HoBi, HoTe, and α. The effects at 500, 450, and 515 K reflect eutectic equilibria in pseudo-ternary systems that cross the cut.

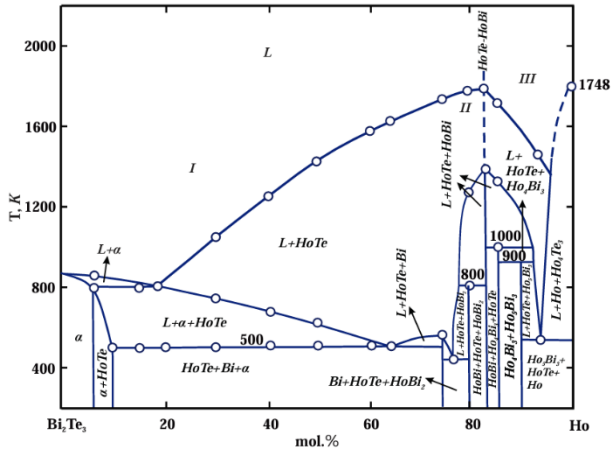

Fig. 9. Phase diagram of the system Bi_2Te_3-Ho.

$$L \xrightarrow{500} HoTe+Bi+б$$

$$L \xrightarrow{450} HoTe+Bi+HoBi_2$$

$$L \xrightarrow{515} Ho_5Bi_3+HoTe+Ho$$

Most of the liquidus is made up of HoTe (20-75 mol % Ho) and Ho_4Bi_3 (85-95 mol % Ho) phases.

The non-quasi-binary section HoBi-Bi_2Te_3 (Fig. 10) crosses two subordinate triangles: HoBi-HoTe-Bi and Bi_2Te_3-HoTe-Bi. The liquidus of the system consists of three branches of primary phase crystallization: L+α (Bi_2Te_3), L+HoTe, and L+HoBi.

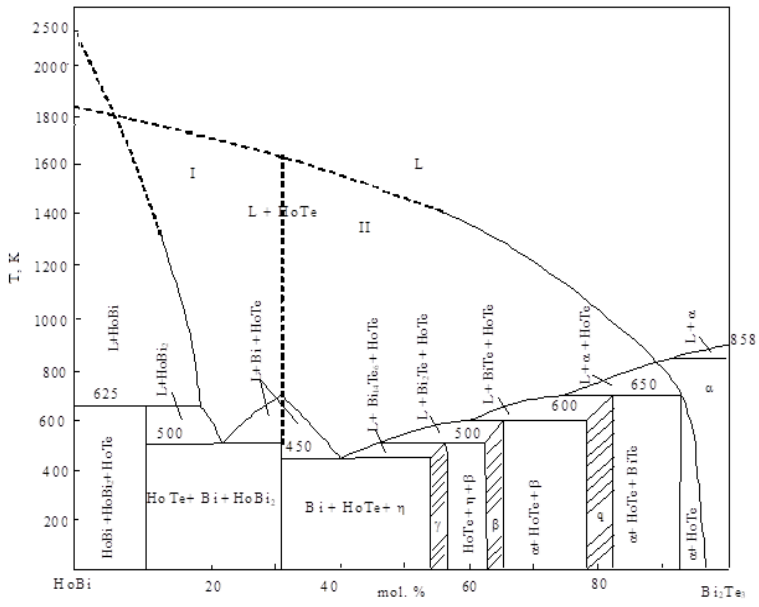

Fig. 10. State diagram of the section HoBi-Bi_2Te_3.

Most of the liquidus is the HoTe phase in the concentration range 10–90 mol % Bi_2Te_3. The following invariant triple eutectic and peritectic processes occur in the system:

in the region of 10–16 mol % Bi_2Te_3 $L \rightarrow HoTe+Bi+HoBi_2$

$L+HoBi \leftrightarrow HoBi_2+HoTe$

in the region of 16–90mol % Bi_2Te_3 $L+Bi_2Te_3 \xrightarrow{650} q(BiTe) + HoTe$

$L+q(BiTe) \xrightarrow{600} в(Bi_2Te) + HoTe$

$L+в(Bi_2Te) \xrightarrow{500} п(Bi_{14}Te_6) + HoTe$

$L \xrightarrow{450} HoTe+Bi+г$

The D-Te section (the alloy ratio D–(HoTe + Bi_2Te_3) 60:40 (Fig. 11) non-quasi-binary crosses two subordinate triangles: Bi_2Te_3-HoTe-Ho_2Te_3 and Bi_2Te_3-Ho_2Te_3-Te. The state diagram of the section has two branches of primary crystallization of Ho_2Te_3 and Te.

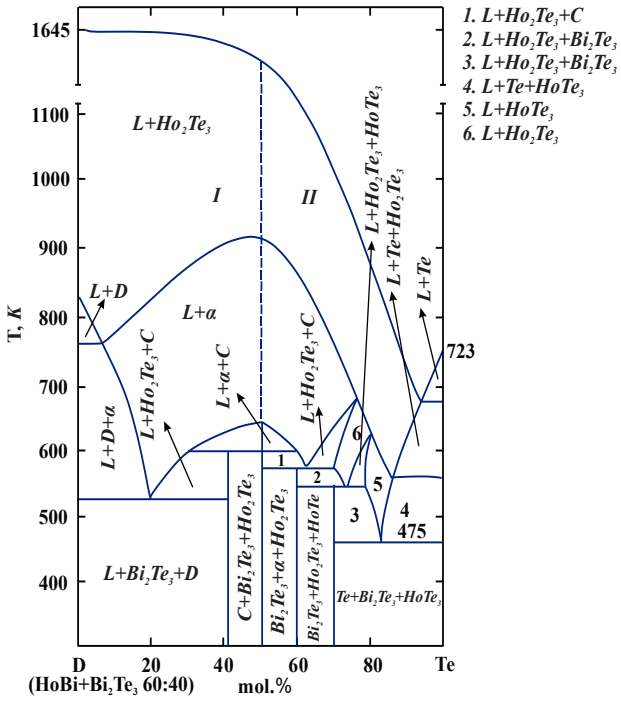

Fig. 11. State diagram of the D-Te section.

It contains data on the following invariant ternary eutectic and incongruent processes:

In the area of 0-50 mol % Te. $L \rightarrow HoBiTe_3(C) + Bi_2Te_3+D$

$L + Ho_2Te_3 \leftrightarrow C+ б$

In the area of 50-90 mol % Te. $L \xrightarrow{475K} Te +Bi_2Te_3 + HoTe_3$

$L + Ho_2Te_3 \xrightarrow{600K} C+ б$

$L + C \xrightarrow{575K} Ho_2Te_5 + б$

$L + Ho_2Te_5 \xrightarrow{525K} HoTe_3 + Bi_2Te_3$

The projection of the liquidus surface of the Ho-Bi-Te ternary system is built based on experimental data of binary systems and using the results of various quasi and non-quasi-binary sections of the Ho-Bi-Te ternary system (Fig.12).

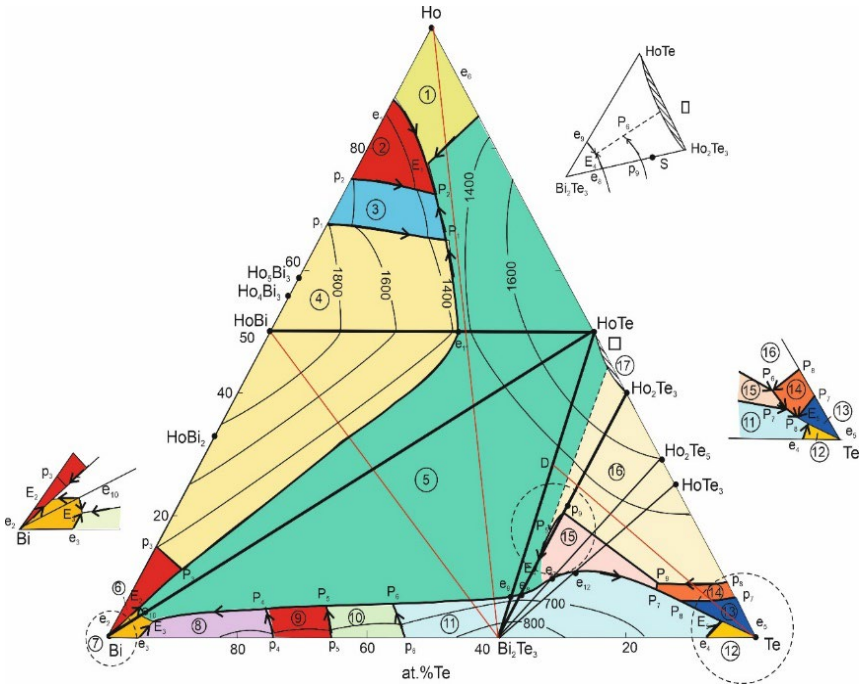

Fig. 12. Projection of the liquidus surface of the Ho-Bi-Te ternary system.

As can be seen from Fig.12 the ternary system Ho-Bi-Te is divided by triangulating cuts into subordinate ternary systems: HoBi-Ho-HoTe, HoBi-Bi-HoTe, HoTe-Bi-Bi_2Te_3, HoTe-Bi_2Te_3-Ho_2Te_3 and Bi_2Te_3-Te-Ho_2Te_3.

The liquidus of the system consists of 16 fields of primary crystallization of phases, separated by 30 monovariant equilibrium curves. The largest region in the diagram is the crystallization field of the HoTe phases (55%), and the smallest α is Bi and Te. There are 13 invariant equilibria in the Ho-Bi-Te ternary system, of which E_1-E_5 are points of triple eutectics, and P_1-P_8 are points of peritectics. Reactions corresponding to invariant equilibria and proceeding in the Ho-Bi-Te ternary system have been established (Table 1).

Table 1. Nonvariant reactions in the Ho-Bi-Te system

Point	**Reactions**	Temperature, K.
E_1	L ↔Ho_5Bi_3+HoTe+Ho	500
E_2	L ↔Bi+HoTe+HoBi	450
E_3	L ↔Bi+HoTe+Bi_4Te_6	515
E_4	L ↔ C +Bi_2Te_3+HoTe	475
E_5	L ↔ Bi_2Te_3+Te+$HoTe_3$	650
P_1	L +HoBi↔Ho_5Bi_3+HoTe	1000
P_2	L +Bi_2Te_3↔BiTe+HoTe	900
P_3	L +BiTe↔Bi_2Te+HoTe	800
P_4	L + Bi_2Te↔Bi_4Te_6+HoTe	415
P_5	L +Ho_2Te_3↔$HoBiTe_3$+ б	600
P_6	L +Ho_2Te_3↔$HoBiTe_3$+ Bi_2Te_3	600
P_7	L +$HoBiTe_3$↔Ho_2Te_5+Bi_2Te_3	575
P_8	L +Ho_2Te_5↔$HoTe_3$+Bi_2Te_3	550

To clarify the coordinates and temperatures, mono- and invariant points of the eutectic and peritectic in the ternary Ho-Bi-Te system, non-quasi-binary cuts were used: Bi_2Te_3-Ho, HoBi-Bi_2Te_3, D-Te (D–HoTe+ Bi_2Te_3). their phase diagrams were studied and constructed. Now consider these non-quasi binary ternary systems.

4. Conclusion

The Ho-Bi-Te ternary system was studied in sections Bi_2Te_3-Ho_2Te_3, HoBi-HoTe, HoTe-Bi, Bi_2Te_3-Ho_2Te_5, Bi_2Te_3-$HoTe_3$, Bi_2Te_3-Ho, HoBi-Bi_2Te_3, D-Te. It has been established that the Bi_2Te_3-Ho_2Te_3, HoBi-HoTe and HoTe-Bi systems, which are quasi-binary sections of the Ho-Bi-Te ternary system, participate in the triangulation of the ternary system. It was found that in the ternary system Ho-Bi-Te an incongruently melting ternary compound with the composition $HoBiTe_3$ is formed. X-ray analysis indicates that the $HoBiTe_3$ compound crystallizes in the tetragonal syngony with lattice parameters: a=19.99; c=13.82 Å, Z=3.

Bi_2Te_3-Ho, HoBi-Bi_2Te_3, D-Te sections are non-quasi-binary sections of the Ho-Bi-Te ternary system. Based on the results of experimental data, as well as using literature data, a projection of the liquidus surface of the Ho-Bi-Te ternary system was constructed. In the ternary system Ho-Bi-Te, 13 invariant equilibrium processes have been determined at triple points E and P, of which five are triple eutectic points E_1-E_5, and eight are triple peritectic points P_1-P_8. The largest crystallization area is occupied by HoTe and HoBi compounds with high melting points.

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