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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

STUDY OF CHEMICAL AND PHASE BEHAVIOUR OF "Nd-B^V-Se (B^V-Sb, Bi) TERNARY SYSTEM THE PASHES

Speciality: 2303.01 – Inorganic Chemistry

Field of science: Chemistry

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GENERAL CHARACTERISTICS OF WORK

Relevance of the topic. As an alternative energy source, the sun is the most basic and inexhaustible source of energy. The development of energy-converting devices from semiconductors based on the complete conversion of this natural energy into electric power has always been in the focus of world scientists working in the field of inorganic materials science. The synthesis of new multifunctional semiconductor materials is of great interest.

The search for multifunctional semiconductor materialsa and the choice of their synthesis mode is based on the properties of raw materials.

Among such materials, the phases obtained based on chalcogenides $B_2^V X_3$(B^V-Sb, Bi; X-Se, Te)-type compounds of arsenic subgroup and neodymium from rare earth elements are of special importance in semiconductor chalcogenides.

The unique physical properties of these compounds allow them to be used in microelectronics as photoelectric and thermoelectric semiconductor materials.

However, the low mechanical resistance in the operating temperature range of these compounds $B_2^V X_3$ and the thermoelectric materials obtained on their basis limits their application.

Therefore, in order to change directionally the properties of new thermoelectric materials based on Sb_2Se_3(Bi_2Se_3), to search for new semiconductor phases with significant electrophysical parameters and establishment of physicochemical bases for their production are expedient and active study of ternary systems consisting of antimony, bismuth and neodymium selenides.

The aims and objectives of research. The aim was to determine the phase equilibrium in Nd-Sb(Bi)-Se systems and to study the newly discovered thermoelectric properties.

In addition, the following specific issues have been resolved to reach the goal set:

- ✓ Study of phase equilibria in Nd-Sb(Bi)-Se ternary systems at all possible consetration and temperature ranges, formation of the their T-x diagrams, as well as liquidus surfaces projections of ternary systems by complex methods of physical and chemical analysis;

- ✓ Individual allocation and study of the properties of compounds formed in Nd-Sb (Bi) -Se ternary systems;
- ✓ Development of a routine for the growing monocrystals of alloys from solid solution field based on ternary-phase and Sb_2Se_3 (Bi_2Se_3) systems;
- ✓ Determination of their applications by studying the electrophysical properties of the newly obtained ternary compounds and samples of solid solutions.

The research methods. The accuracy of the research results based on scientific provisions and ourcomes was determined on element Sb(Bi)-B-4; Nd-Нм-1 (99,34); Se-<<XTr 17-4>>; DTA – up to 1300K temperature on HTP-73 and with an accuracy of ± 5 degrees on the element Termskan-2 pyrometer. Calcined Al_2O_3 and Pt-Pt / Rh thermocouple were used as a reference for DTA. HTDTA was performed on BTA-987 device in helium environment of VCHTU 51-681-75 brand; MIM-7 microscope was used for microstructure analysis, microhardness mesurment was performed on a PMT-3 device according to Vickers; X-ray phase analysis (Bruker XRD D8 Advance was shot with an accuracy of ± 5 K), determination of density, specific thermal conductivity, thermo-electric driving force and measurement of thermal conductivity were conducted based on the application of experimental methods.

The main provisions of the defense.

• Study of phase equilibria in Nd-Sb(Bi)-Se ternary systems by investigation methods in the whole density and temperature range, formation of quasi- and non-quasi-binary sections, liquid surfaces of T-x triple systems, T-x-y diagrams.

• Individual acquisition and study of the properties of ternary phases formed in Nd-Sb(Bi)-Se systems.

• Development of the optimal regime of obtaining samples and single crystals of triple compounds from the solid solution field formed in the systems.

• Study of the homogeneity of the detected triple phases and their application by studying the electrophysical properties.

Scientific innovation of the research. The following results were obtained on Ph.D thesis.

- In the ternary Nd-Sb-Se and Nd-Bi-Se systems, the phase equilibria were systematically studied over the all possible concentration range, and the nature of the physicochemical interactions was determined over a wide temperature range.
- Projection diagrams of different polythermal T-x sections of the studied systems, as well as liquidity surfaces of ternary systems as a whole were formed and equilibrium processes occurring in it were determined.
- The initial crystallization and homogeneity areas of the ternary phases obtained in the Nd-Sb (Bi) -Se triple systems, also based on X-ray phase analysis their crystallographic types and parameters determined.
- As a result of the study of the electrophysical properties of individually obtained new phases, a new thermoelectric material has been proposed that can act as a positive arm of the thermocouple for the manufacture of energy transformers.

Theoretical and practical significance of the research. A new material with a solid solution, $[Bi_2Se_3]_{1-x}\cdot[Nd_2Se_3]_x$ $x\leq0,05$, which can operate in the low temperature field, has a high thermoelectric efficiency and can be used in energy converters obtained according Nd-Bi-Se triple system based on the Bi_2Se_3 compound (AZE Patent Invention i 2017 0053).

The new set of results obtained for the phase equilibria of Nd-Sb(Bi)-Se systems in the dissertation can be used for the development and selection of chemical compounds formed in such systems and their directional synthesis of phases and monocrystalline extraction of alloys of different compositions.

The crystallographic and physicochemical properties of the ternary phases obtained in the studied systems, as well as the built-in state diagrams, are valuable survey data and can be included in the relevant electronic databases and data reference books.

Published works and approbation of the work. 32 scientific works on the topic of the dissertation, including 12 articles (3 articles in foreign scientific journals indexed in international databases, 10 articles - peer-reviewed foreign and republican journals, 20 theses - in conference proceedings) were published and 1 patent was obtained.

Affiliation. The research was performed at Baku State University, the department of General and Inorganic Chemistry

The scope and structure of the work. The dissertation consists of an introduction (3 pages) and five chapters (1st chapter 27 pages, 2nd chapter 12 pages, 3rd chapter 35 pages, 4th chapter 33 pages, 5th chapter 16 pages), main results, 211 citied referances, in total has 153 pages. 105 pages of this total volume are the main text of the work, the rest are graphs and tables. (49 graph) və tables (28 table)

CONTENT OF THE WORK

The **introduction** shows the relevance of the dissertation topic, the purpose of the substantiated work, the scientific innovation and practical significance of the results.

The first chapter provides literature on the characteristics of the synthesis of chalcogenides of lanthanide series elements, neodymchalcogenide systems, lanthanide pnicides, physicochemical and electrophysical properties of stibium and bismuth selenides, as well as the nature of chemical interactions in Ln-B^V-X type three-component systems. This information was used in the planning of experimental studies and the development of their results.

The second chapter devoted to a brief description of methods synthesis methods of compounds and alloys, physical and chemical investigation method. Elemental components with a high degree of purity were used in the synthesis of primary binary and ternary compounds: Sb(Bi)-B-4; Nd-Нм-1 (99,34); Se-<<XTr 17-4>>.

Vacuum melting in quartz ampoules under vacuum conditions (~10^{-3}Pa) has been implemented for the synthesis of samples of polythermic quasi- and non-quasi-binary sections of ternary systems. For this purpose, pre-synthesed and identified binary compounds (ligature) and in some cases elementary components were used.

Current state of physical and chemical investigation of multicomponent systems containing Nd (neodymium) and arsenic subgroup elements was examined and the choice of research objects for the dissertation was substantiated. After the synthesis process, the alloys were heat-treated for 400-500 hours at a temperature 70-80 K below the crystallization temperature. Due to the high-saturated vapor pressure of Se at the melting temperatures of the compounds, the synthesis was carried out in a two-temperature inclined furnace.

The studies were performed using a set of physicochemical analysis methods, including differential-thermal analysis (DTA), high-temperature differential-thermal analysis (HTDTA), X-ray phase analysis, and microstructure analysis, determination of microhardness and pycnometric density.

The dissertation also measured a number of electrophysical properties of alloys, including specific electrical conductivity, thermoelectric driving force (thermo-e.d.f.), and total thermal conductivity.

The third chapter presents the results of chemical interactions in the Nd-Sb-Se system. To clarify the nature of phase formation in the Nd-Sb-Se triple system, let us consider a brief description of the interactions that occur in the binary systems that make up the system and in the internal sections of the triple system:

In the Sb-Se system, the congruent at 863 K containing Sb_2Se_3 is formed with an open maximum of 2: 3 ratio of soluble compounds. In the system, a stratification area is formed by the process of monotectic equilibrium in the area of 17-42.5 at% Se density. Between Sb_2Se_3 and Sb, eutectic crystallizes with a congruent process containing 814 K at 50% soluble Se. In the system, the eutectic on the Se side is twisted.

In the Nd-Se system, binary compounds containing NdSe, Nd_3Se_4, Nd_2Se_3, Nd_4Se_7, $NdSe_{1,9}$ and Nd_3Se_7 are formed. NdSe, Nd3Se4 and Nd2Se3 melt congruent at 2150^0, 1750^0 and 1700^0 C, respectively, while others melt at 1400, 1210 and 1110 ^{0}C. In the system, a continuous solid solution between Nd_3Se_4 and Nd_2Se_3 is formed in the area of 57.14-60 at% Se concentration. Eutectic is irritated by selenium. Eutectic crystallizes between Nd and NdSe and between NdSe and Nd_3Se_4. Coordinates of eutectic: 3; 54 at% Se, 1040 ^{0} and 1750 ^{0}C.

Four binary antimony, NdSb, $NdSb_2$, Nd_4Sb_3, Nd_5Sb_3 are formed. Of these, mono antimonide is formed at 2080^0 C, with an open maximum, and the remaining antimonides are obtained by peritectic conversion reactions, respectively:

$$M+NdSb \leftrightarrow Nd_4Sb_3 \ (1800^0\ C)$$

$$M+ Nd_4Sb_3 \leftrightarrow Nd_5Sb_3 \ (1690^0\ C)$$

In the system, eutectic crystallizes on the stibium side at 3 at% Nd and 600^{0}C, and on the neodymium side at ~ 4 at% Sb and 9550C.

In the Nd-Sb system, four individual compounds are obtained: Nd_5Sb_3, Nd_4Sb_3, NdSb, and $NdSb_2$. The system produces eutectic that melts at 955^0 and 600^{0}C, respectively, at 5 and 95 at% Sb.

The $\underline{Sb_2Se_3\text{-}Nd_2Se_3}$ system is quasi-binary, and a process of peritectic conversion with a nonvariant equilibrium at 865K forms the $NdSbSe_3$ compound in a 1: 1 ratio of components in the system.

$M+ Nd_2Se_3 \leftrightarrow NdSbSe_3$ (865 K)

Liquidus consists of primary crystallization curves of three phases: α-phase, $NdSbSe_3$ and β-phase. The initial crystallization of the α-containing phase in the concentration range of 0-15 mol% Nd_2Se_3, the compound containing $NdSbSe_3$ in the concentration range of 15-30 mol% Nd_2Se_3 and the β-containing phase in the concentration range of 30 ÷ 100 mol% Nd_2Se_3 occurs by monovariant equilibrium process.

Eutectic crystallizes at 755 K 15-mol% Nd_2Se_3. It was found that 5-mol% of solid solution based on Sb_2Se_3 and 2.5 mol% of solid solution based on Nd_2Se_3 are formed at room temperature (Figure 1).

The $\underline{Sb_2Se_3\text{-}Nd_3Se_4}$ system is quasi-binary. The state diagram of the system corresponds to the V-type Rosebom diagram, which forms a limited solid solution, and is a simple eutectic type. At 795 K, 15 mol% Nd_3Se_4 crystallizes, and a 3 mol% solubility field is formed in the solid phase based on Sb_2Se_3.

$$M \leftrightarrow \alpha(Sb_2Se_3)+\beta(Nd_3Se_4)$$

In order to determine the area of solid solution based on Sb2Se3 in the system, 10 samples of 1 mol% were synthesized.

The $\underline{Sb_2Se_3\text{-}NdSe}$ system is a simple eutectic-type quasibinar cross section of the Nd-Sb-Se ternary system. The eutectic content corresponds to a concentration of 30-mol% NdSe and crystallizes at 825 K. An 8-mol% solubility area at 300 K based on Sb2Se3 is formed in the system. M↔α+NdSe (825 K)

At the point of eutectic, a process of nonvariant equilibrium occurs:

A small composition of 1.0 mol% around Sb2Se3 was prepared and synthesized, thermally treated at 500K, 700K and 800K, and after immersion in ice water, the microstructures were studied with the help of a MIM-8 microscope, resulting in a solution boundary. The solubility decreased to 15 mol% at room temperature and 8 mol% NdSe at room temperature. Thus, the system we studied is of simple eutectic type and is a quasibinar cross section of the Nd-Sb-Se system.

The Sb-NdSe system is a simple eutectic-type quasibinar cross section of the Nd-Sb-Se ternary system. The coordinates of the eutectic are 10 mol% NdSe and 823 K. The liquidity of the system is limited by the initial crystallization curves of the Sb and NdSe components.

NdSe-NdSb is a simple eutectic type. No solution has been determined based on the initial components. In the system, eutectic crystallizes with 50-mol% NdSe and at 1600 K.

Thus, based on the results of RFA and MQA, it can be concluded that the NdSb-NdSe system is of the simple eutectic type and is a quasi-binary cross section of the triple system.

The Sb_2Se_3-NdSb is a non-quasibinar cross section of the Nd-Sb-Se ternary system that intersects the area of a two-dimensional triangle (figure 2). To clarify the nature of phase formation in the Nd-Sb-Se triple system, the Sb_2Se_3-NdSb system was studied over the entire concentration range.

The liquid surface of the system Sb_2Se_3-Sb-NdSe (1) and NdSb-Sb-NdSe (2) consists of three-phase crystallization curves: M+NdSb, M+NdSe və M+α triple eutectic crystallizes at 785 K with a 4-phase equilibrium reaction with a triangle of (1).

M↔α+NdSe+Sb

(2) $NdSb_2$ binary compound and triple eutectic crystallize in the

subtripe triangle.

$$M \leftrightarrow NdSe+Sb+NdSb_2 \ (700K)$$

$$M+NdSb \leftrightarrow NdSb_2+NdSe \ (950K)$$

An area of 2-mol% NdSb solid solution based on Sb_2Se_3 is formed in the system.

$NdSbSe_3$-Se is quasibinary system. Only one subordinate Sb_2Se_3-Nd_2Se_3 –Se intersects the area of the triangle. In the system, at 865, 800, 750, 650 K, the corresponding $NdSbSe_3$, Nd_4Se_7, $NdSe_2$ və Nd_3Se_7 compounds are on side of the triangle.

$$M+Nd_2Se_3 \leftrightarrow Nd_4Se_7 + Sb_2Se_3 \ (800 \ K)$$

$$M+ Nd_4Se_7 \leftrightarrow NdSe_{1,9} + Sb_2Se_3 \ (750 \ K)$$

$$M+ NdSe_{1,9} \leftrightarrow Nd_3Se_7 + Sb_2Se_3 \ (650 \ K)$$

In the system, the triple eutectic shrinks and crystallizes at 493K.

$$M \leftrightarrow S+Nd_3Se_7+Se$$

The projection of the liquidus surface of the Nd-Sb-Se triple system is based on the literature data of the initial binary systems and the results obtained from the studied internal polythermal sections.

According to the order of triangulation, the triple system is divided into 6 sub-triangles with five quasibinar sections (figure 3).

The surface of the triple system consists of an initial crystallization area of 16 phases bounded by 27 monovariant curves.

The system has 13 nonvariant equilibrium processes, six of which are triple eutectic (E_1-E_6) and seven are triple peritectic (P_1-P_7) (table 1).

An isothermal line at 200 K is drawn on the liquidus surface of the system, which fully controls the flow of nonvariant curves.

Sb-NdSb-NdSe subordinate triangle. The surface of this triangle is intersected by the non-quasibinar section Sb_2Se_3-NdSb. Here, a triple peritectic (P_4) and eutectic (E_1) process with a four-phase equilibrium reaction in the presence of a liquid phase takes place.

$$(P_4) \quad M+NdSb \leftrightarrow NdSb_2 +NdSe \ (950 \ K)$$

$$(E_1) \ M \leftrightarrow NdSb_2 +Sb + NdSe \ (700 \ K)$$

2. Sb-Sb_2Se_3-NdSe intersects the Sb2Se3-NdSb polythermal section of the surface of the subordinate triangle system. Only a triple eutectic equilibrium reaction occurs here.

(E_2) M↔Sb+NdSe+ Sb_2Se_3 (785 K)

3. Sb_2Se_3-NdSe- Nd_3Se_4 subsystem: In the system, the process ends in triple eutectic. The coordinates of the triple eutectic (E_3) were determined experimentally by synthesizing additional samples and DTA.

(E_3) M↔Sb_2Se_3+NdSe+ Nd_3Se_4 (775 K)

4. Subordinate system Sb2Se3- Nd3Se4 - Nd2Se3: The coordinates of the triple eutectic and peritectic in the system were determined experimentally based on the results of DTA.

(P_7) M+Nd_2Se_3 ↔$NdSbSe_3$+α (Nd_3Se_4 + Nd_2Se_3) (850 K)

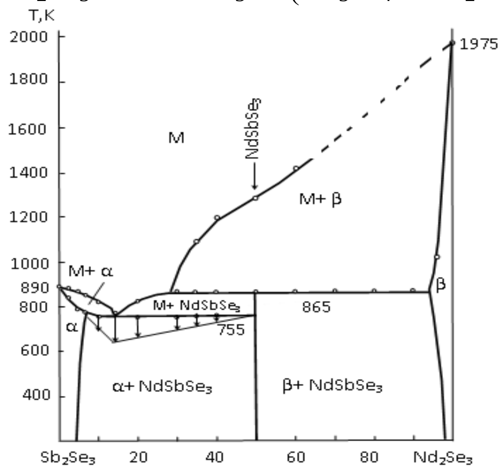

Figure 1. State diagram of the Sb_2Se_3-Nd_2Se_3 system

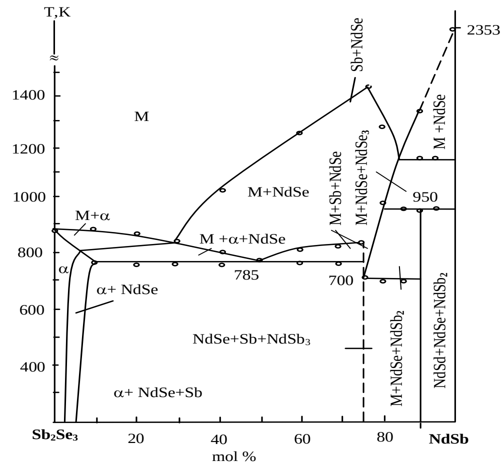

Figure 2. State diagram of the Sb_2Se_3-NdSb system

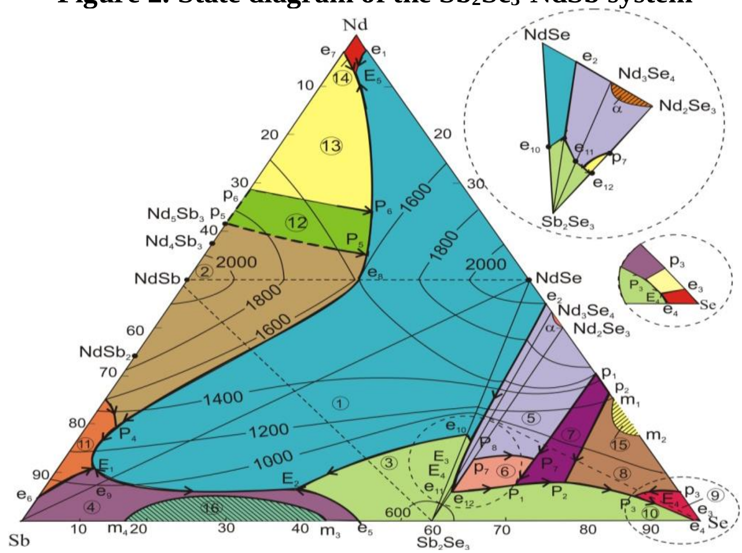

Figure 3. Projection of the liquid surface of the Nd-Sb-Se triple system. Areas of primary crystallization:
1-NdSe 2-NdSb 3-Sb_2Se_3 4-Sb 5-α(Nd_3Se_4+Nd_2Se_3) 6-S($NdSbSe_3$) 7-Nd_4Se_7 8-$NdSe_2$ 9- Nd_3Se_7 10-Se 11-$NdSb_2$ 12-Nd_4Sb_3 13- Nd_5Sb_3 14-Nd 15- stratification 16- stratification

Table 1

Nonvariant equilibria of the Nd-Sb-Se system

Points	Equlibria	Temperature,K
e_1E_6	M↔αNd+NdSe	1873-975
e_7E_6	M↔αNd+ Nd_5Sb_3	1228-975
P_6p_6	M ↔ Nd_5Sb_3+Nd_4Sb_3	2073-1150
P_5p_5	M ↔ Nd_4Sb_3+NdSb	1963-1210
P_6E_6	M↔ Nd_5Sb_3+NdSe	1150-975
P_5p_6	M↔ Nd_4Sb_3+NdSe	1210-1150
P_4p_4	M↔ NdSb+$NdSb_2$	1925-950
$P_5e_8P_4$	M↔ NdSb+NdSe	1210-1850-950
P_4E_1	M↔ $NdSb_2$+ NdSe	950-700
e_6E_1	M↔Sb+ $NdSb_2$	903-700
$E_1e_9E_2$	M↔Sb+ NdSe	700-723-785
e_5E_2	M↔Sb+ Sb_2Se_3	814-785
$E_2e_{10}E_3$	M↔ Sb_2Se_3+ NdSe	785-825-775
e_2E_3	M↔ NdSe+ α(Nd_3Se_4+ Nd_2Se_3)	1600-775
$E_4e_{12}P_8$	M↔ Sb_2Se_3+S ($NdSbSe_3$)	680-755-710
$E_3e_{11}E_4$	M↔ Sb_2Se_3+α	775-795-680
P_8E_4	M↔ S($NdSbSe_3$)+α	850-680
P_1p_7	M↔ α+ Nd_4Se_7	1400-850
P_7p_1	M↔ S($NdSbSe_3$)+ Nd_4Se_7	850-800
P_2p_2	M↔ Nd_4Se_7+$NdSe_{1,9}$	1200-750
P_1p_2	M↔ Nd_4Se_4+ Sb_2Se_3	800-750
P_2p_3	M↔ $NdSe_{1,9}$+ Se	750-650
P_3p_3	M↔ $NdSe_{1,9}$+ Nd_3Se_7	1158-650
P_3E_5	M↔ Sb_2Se_3+Nd_3Se_7	650-493
P_7p_7	M↔S($NdSbSe_3$)+ α	865-845
e_3E_5	M↔ Se+ Nd_3Se_7	shrinking
E_4E_5	M↔ Se+ Sb_2Se_3	shrinking
E_1	M↔$NdSb_2$+Sb+NdSe	700
E_2	M↔Sb+NdSe+ Sb_2Se_3	785
E_3	M↔ Sb_2Se_3+NdSe+α	775
E_4	M↔ Sb_2Se_3+S+α	680

e_{12}	**M↔ Sb+ Nd_2Se_3+ Sb_2Se_3**	**shrinking**
E_6	**M↔NdSe+α-Nd+ Nd_5Sb_3**	**975**
P_1	**M+ Nd_2Se_3↔ Nd_4Se_7+ Sb_2Se_3**	**800**
P_2	**M+ Nd_4Se_7↔ $NdSb_{1,9}$+ Sb_2Se_3**	**750**
P_3	**M+ $NdSb_{1,9}$↔ Nd_3Se_7+ Sb_2Se_3**	**650**
P_4	**M+ NdSb↔ $NdSb_2$+ NdSe**	**950**
P_5	**M+NdSb↔ Nd_4Sb_3+NdSe**	**1270**
P_6	**M+ Nd_4Sb_3↔ Nd_5Sb_3+ NdSe**	**1150**
P_7	**M+ Nd_2Se_3↔S+α**	**850**

The fourth chapter presents the results of phase formation in the Nd-Bi-Se system. To clarify the nature of the phase equilibrium in the Nd-Bi-Se system, let us look at the general characteristics of the interactions occurring on the sides and inside sections of the system.

The Nd-Bi system is characterized by the formation of binary compounds containing $NdBi_2$, NdBi, Nd_4Bi_3, Nd_5Bi_3 and Nd_2Bi. Of these compounds, only the NdBi compound melts the congruent at 2175 K, and the rest is obtained by peritectic equilibrium reactions. In the system, eutectic crystallizes at 85 mol% Nd and melts at 1175 K. On the other hand, eutectic is narrowed (544 K).

In the Nd-Se system, compounds containing NdSe, Nd_3Se_4, Nd_2Se_3 and Nd_4Se_7, $NdSe_2$, Nd_3Se_7 are formed. Of these, NdSe, Nd_3Se_4 and Nd_2Se_3 are congruent, the rest are incongruent. In the system, in the area of 57.2-60% Se, an uninterrupted solid solution is formed between Nd_3Se_4 and Nd_2Se_3. On the Nd side, the eutectic crystallizes at 5 horsepower Se and 1315 K, but the eutectic on the selenium side is 494 K.

In the Bi-Se system, a stratification area is formed in the range of 87-90 at% Se. The system produces a compound containing Bi_2Se_3 that melts at 979 K, and other compounds with BiSe and Bi2Se melt at 891, 790 K, respectively. The BiSe compound forms a solubility area in the range of 48-58% Bi. The eutectic is bi-lateral. In the system, stratification occurs in the area of 3-30 at% Bi.

The Bi_2Se_3-Nd_2Se_3 system is a quasibinar section of the Nd-Bi-Se ternary system. In the system, the $NdBiSe_3$ compound is formed at

995 K by a peritectic equilibrium reaction of the components in a 1: 1 ratio:

$M+\beta\text{-}Nd_2Se_3 \leftrightarrow NdBiSe_3$ (995K)

At the eutectic point of the system, the following nonvariant equilibrium process takes place:

$M \leftrightarrow \alpha\ (Bi_2Se_3) + NdBiSe_3(S)$ (815 K)

The liquidity of the system consists of the initial crystallization area of the three components. The following monovariant equilibrium processes occur in the initial crystallization curves: $M \leftrightarrow \alpha$; $M \leftrightarrow S$ and $M \leftrightarrow \beta$.

The solid of the system consists of four fields based on Bi2Se3 and Nd_2Se_3, single-phase, α and β phases, α + S and S + β two-phase fields.

Thus, it was determined that the system is a quasi-binary section of the Nd-Bi-Se triple system and is of eutectic type.

Projection of the liquid surface of the Nd-Bi-Se ternary system

In the $\underline{Bi_2Se_3\text{-}Nd_2Se_3}$ All alloys of the Bi_2Se_3-Nd_3Se_4 system have been studied by complex methods of FKA. Two endothermic effects were observed in the thermograms of the alloys. This makes the system simple eutectic. This system, eutectic crystallizes at 815 K with 20-mol% Nd_2Se_3. The area of solid solution based on Bi_2Se_3 was 13-mol% at euthetic temperature, 8 mol% Nd_2Se_3 at room temperature, 2 mol% Bi_2Se_3 at 300 K on the basis of Nd_2Se_3.

The $\underline{Bi_2Se_3\text{-}Nd_3Se_4}$ system is a quasi-binary section of the Nd-Bi-Se triple system and is a simple eutectic type. The coordinates of the eutectic that crystallize in the system are 25-mol% Nd_3Se_4 and 860K.

The $\underline{Bi_2Se_3\text{-}NdSe}$ system is quasi-binary. In the system, eutectic crystallizes at 30 mol% NdSe and at 800 K. Based on Bi_2Se_3, the room temperature increased by 7 mol% to eutectic temperature (800 K) and became 12 mol% NdSe.

<u>NdSe-Bi</u> is quasibinary system. The eutectic in the system is 98 mol% Bi shrinking at 538 K.

$M \leftrightarrow NdSe+Bi$

The area of solution based on the components in the system is practically not defined.

Thus, it was determined that the NdSe-Bi system is a simple eutectic type and is a quasibinar cross section of the Nd-Bi-Se system.

NdSe-NdBi is a quasibinar section of the Nd-Bi-Se triple system. In the system, eutectic crystallizes with 40-mol% NdSe content and melts at 1800 K.

The NdBi-Se system is a non-quasi-binary section of the Nd-Bi-Se triple system that intersects the area of a five-dimensional triangle. Chemical interactions in the system are complex. In the system, at 1275, 600, 585, 700, 645, 610, 550 K, $NdBi_2$, Bi_3Se_2, Bi_2Se_3, $NdBiSe_3$, Nd_4Se_4, $NdSe_2$ and Nd_3Se_7 compounds are obtained by four-phase peritectic equilibrium reactions, respectively. At 500, 535, and 650 K, the triple eutectic crystallizes respectively. In a V-shaped system, the triple eutectic crystallizes on selenium at 494. NdBi and NdSe compounds occupy the largest crystallization area in the system.

Bi_2Se_3-Nd is also non-quasi-binary, intersecting the area of a three-dimensional triangle. In the field of Bi_2Se_3-Bi-NdSe (1), NdSe-Bi-NdBi (2) və NdSe-Nd-NdSe (3) subordinate systems, BiSe, Bi_3Se_2, $NdBi_2$, Nd_4Bi_3, Nd_5Bi_3 and Nd_2Bi compounds formed in binary systems on the sides of the ternary system at 620, 585, 1075, 1275, 1125, 1065K, respectively, reflected their 4-phase peritectic conversion reaction.

In the system, the triple eutectic crystallizes in the following nonvariant equilibria.

$M \leftrightarrow Bi+NdSe+Bi_3Se_2$ (525 K) $M \leftrightarrow NdSe+NdBi_2+Bi$ (510 K)

$M \leftrightarrow NdSe+Nd_2Bi+Nd$ (650 K)

The NdBi-NdSe system is quasibinar and simple eutectic type. Eutectic crystallizes at 60 mol% NdSe and at 1800 K in the system,.

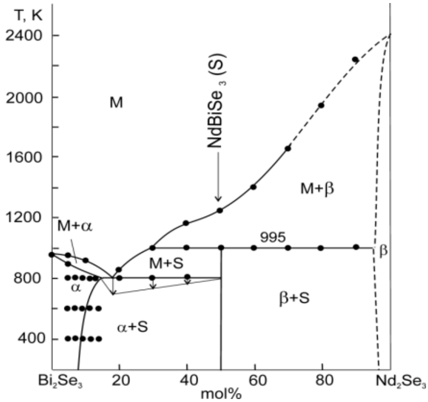

Figure 4. State diagram of the Bi_2Se_3-Nd_2Se_3 system

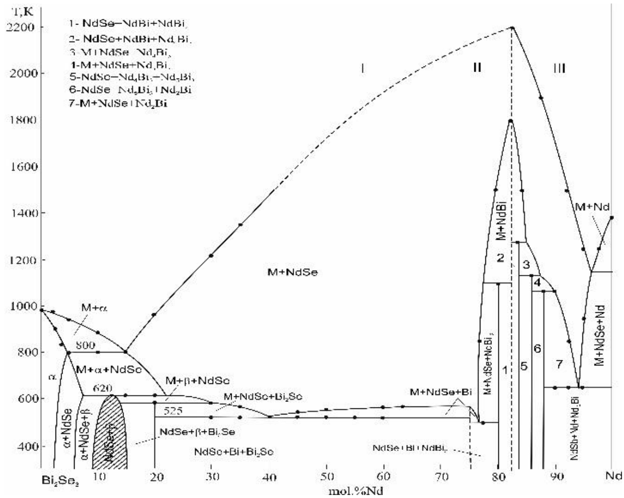

Figure 5. State diagram of the Bi_2Se_3-Nd system

The projection of the liquid surface of the Nd-Bi-Se triple system is based on the results of the studied internal sections and the literature data of binary systems (Figure 7).

It is determined that the system is divided into 6 sub-triangles with five quasi-cross sections:

NdSe-Nd-NdBi, NdBi-Bi-NdSe, NdSe-Bi- Bi_2Se_3, NdSe- Bi_2-Se_3-Nd_3Se_4, Nd_3Se_4-Bi_2Se_3- Nd_2Se_3 və Nd_2Se_3 –Se- Bi_2Se_3.

The liquid surface of the triple system is divided into the initial crystallization area of 20 phases bounded by 35 monovariant curves.

Coordinates of equilibrium reactions occurring at 35 mono-variable and 16 non-variable points in the system has been identified (table 1).

Six of the nonvariant equilibria are triple eutectic (e_9, E_1-E_5), and 10 are peritectic (P_1-P_{10}). The largest crystallization area in the system is occupied by the NdSe phase (~ 50-mol%). There is a narrow stratification in the system.

Based on the projection obtained by the Nd-Se of the system from the surface of the ternary system, one isotherm is drawn by every 200 K.

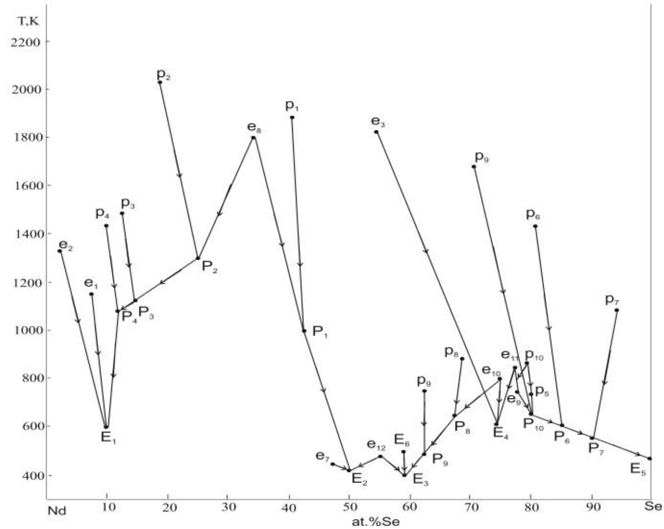

Figure 6. Nd-Se side projection of monovariant curves

We consider it expedient to dwell briefly on the chemical interactions that occur in each subordinate system below:

1. The NdSe-Nd-NdBi system is characterized by nonvariant points E_1, P_2, P_3, P_4. The main crystallization fields in this field are NdSe (1), NdBi (2), Nd_4Bi_3 (3), Nd_5Bi_3 (4), Nd_2Bi (5) and Nd (6).

The following four-phase nonvariant equilibrium reactions occur in the following triangle:

$M+NdBi \leftrightarrow Nd_4Bi_3 + NdSe$ (P_2)

$M+ Nd_4Se_3 \leftrightarrow Nd_5Se_3 + NdSe$ (P_3)

$M+ Nd_5Se_3 \leftrightarrow Nd_3Bi + NdSe$ (P_4)

$M \leftrightarrow NdBi+Nd+NdSe$ (E_1)

<u>2. NdSe-Bi-NdBi </u>The area of this subsystem consists of the crystallization areas of the components NdBi (2), NdSe (1), $NdBi_2$ (7) and Bi (8). The following four-phase nonvariant equilibrium reactions occur in the presence of liquid in the system:

$M+NdBi \leftrightarrow NdBi_2+NdSe$ (P_1)

$M \leftrightarrow NdBi_2+NdSe+Bi$ (E_2)

3. The following equilibrium processes occur in the NdSe-Bi-Bi_2Se_3 system:

$M+ Bi_2Se_3 \leftrightarrow BiSe+NdSe$ (P_8)

$M+BiSe \leftrightarrow Bi_3Se_2+NdSe$ (P_9)

In this part of the ternary system, the main crystallization area is occupied by the NdSe (1) phase.

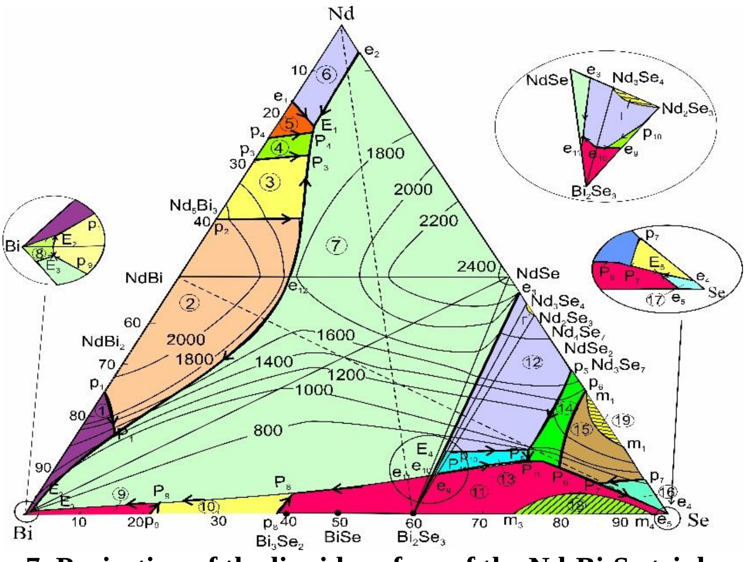

Figure 7. Projection of the liquid surface of the Nd-Bi-Se triple system 1-$NdBi_2$, 2-NdBi, 3-Nd_4Bi_3, 4-Nd_5Bi_3, 5-Nd_2Bi, 6-Nd, 7-NdSe, 8-Bi, 9-Bi_2Se, 10-BiSe, 11-Bi_2Se_3, 12-α(Nd_3Se_4+Nd_2Se_3), 13-S ($NdBiSe_3$), 14-Nd_4Se_7, 15-$NdSe_{1,9}$, 16-Nd_3Se_7, 17-Se, 18, 19, 20- layering.

4. The $NdSe$-Bi_2Se_3- Nd_3Se_4 system is characterized by only a triple eutectic (E_4) equilibrium process:

$$M \leftrightarrow NdSe + Bi_2Se_3 + Nd_3Se_4 \ (E_4)$$

5. In the system Nd_3Se_4-Nd_2Se_3-Bi_2Se_3 triple eutectic is intertwined (e_9). Here the process of equilibrium of nonvariant peritectic (P_5) and twisted eutectic (e_9) takes place:

$$M + Nd_2Se_3 \leftrightarrow NdBiSe_3 \ (3) + \alpha \ (P_5), \quad M \leftrightarrow S + \alpha + Bi_2Se_3 \ (e_9)$$

In this area of the system, the continuous solid solution area α (Nd_3Se_4 + Nd_2Se_3) (20) formed between Nd_2Se_3 and α-Nd_3Se_4 is reflected.

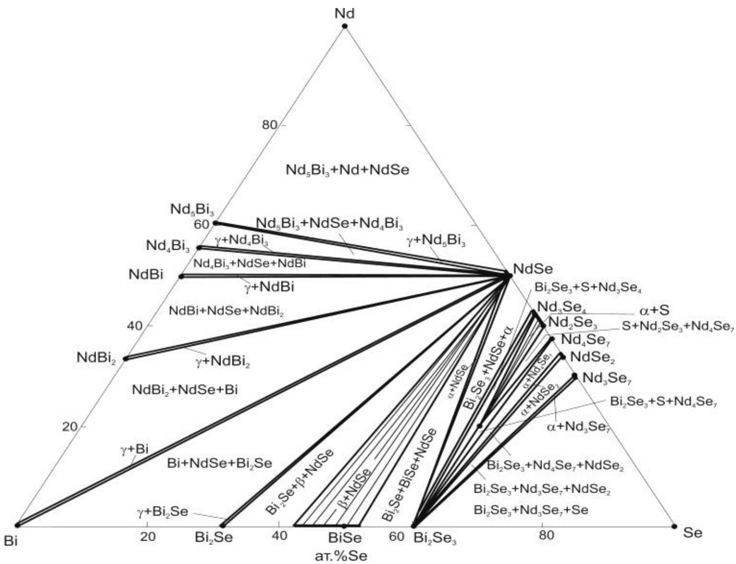

Figure 8. Isothermal cross section of the Nd-Bi-Se triple system at 300K

6. The triple system Nd2Se3-Bi2Se3-Se is characterized at nonvariant points E5, P5, P10, P6, P7. The following nonvariant equilibrium reactions occur at these points.

$M + Nd_2Se_3 \leftrightarrow Nd_4Se_7 + \alpha$ (P_5)
$M + Nd_4Se_7 \leftrightarrow NdSe_2 + Bi_2Se_3$($P_6$)
$M + NdSe_2 \leftrightarrow Nd_3Se_7 + Bi_2Se_3$($P_7$)
$M \leftrightarrow Nd_3Se_7 + Bi_2Se_3 + Se$ (E_5)

This is reflected in the area stratification areas of the subordinate triangle (19) and (18). Based on the projection of the liquidus surface of the Nd-Bi-Se triple system and the nature of the binary compounds formed on the inside and sides of the triple system, a diagram of its isothermal cross section at 300 K was constructed (Figure 8). As can be seen from the figure, the sub-solid of the Nd-Bi-Se triple system consists of 27 parts. Fifteen of them are three-phase and twelve are two-phase.

Table 2

Nonvariant equilibria of the Nd-Bi-Se system

Points	**Equlibria**	**Temperature,K**
1	**2**	**3**
e_1E_1	$M \leftrightarrow Nd + Nd_2Bi$	**1860-650**
e_2E_1	$M \leftrightarrow Nd + NdSe$	**1070-650**
p_2P_2	$M \leftrightarrow NdBi + Nd_4Bi_3$	**1600-1275**
p_3P_3	$M \leftrightarrow Nd_4Bi_3 + Nd_5Bi_3$	**1250-1125**
p_4P_4	$M \leftrightarrow Nd_5Bi_3 + Nd_2Bi$	**1250-1065**
p_1P_1	$M \leftrightarrow NdBi + NdBi_2$	**1875-1075**
P_4E_1	$M \leftrightarrow Nd_2Bi_3 + NdSe$	**1065-650**
P_3P_4	$M \leftrightarrow NdSe + Nd_5Bi_3$	**1125-1065**
P_2P_3	$M \leftrightarrow NdSe + Nd_4Bi_3$	**1275-1125**
$P_1e_{12}P_2$	$M \leftrightarrow NdSe + NdBi$	**1075-1800-**

		1275
e_7E_2	**M↔Bi+ $NdBi_2$**	**544-525**
P_1E_2	**M↔ $NdBi_2$+NdSe**	**1075-525**
$E_2e_8E_3$	**M↔Bi+NdSe**	**510-538-510**
P_8P_8	**M↔Bi_2Se_3+NdSe**	**891-620**
P_9P_9	**M↔Bi+ Bi_2Se_3**	**745-585**
P_9E_3	**M↔ Bi_2Se+NdSe**	**585-510**
$P_8e_{11}E_4$	**M↔ Bi_2Se_3+NdSe**	**610-860-650**
e_3E_4	**M↔ Nd_3Bi_4+NdSe**	**1825-650**
$E_4e_{10}P_{11}$	**M↔ Bi_2Se_3+α**	**650-800-700**
$P_{11}P_{10}P_5$	**M↔ α+$NdBiSe_3$(S)**	**600-995-645**
$P_{11}e_9$	**M↔ Bi_2Se_3+S**	**700-815**
e_9 P_{10}	**M↔S+ Bi_2Se_3**	**815-700**
P_5P_{10}	**M↔S+Nd_4Se_7**	**1675-700**
P_5P_5	**M↔ α+ Nd_4Se_7**	**1675-645**
$P_{10}P_6$	**M↔ Nd_4Se_7+ Bi_2Se_3**	**700-610**
P_6P_6	**M↔ Nd_4Se_7+$NdSe_2$**	**1425-610**
P_7P_7	**M↔ $NdSe_2$+ Nd_3Se_7**	**1158-550**
P_6P_7	**M↔ $NdSe_2$+ Bi_2Se_3**	**610-550**
P_7P_5	**M↔ Nd_3Se_7+ Bi_2Se_3**	**550-495**

e_4E_5	$M \leftrightarrow Se + Nd_3Se_7$	shrinking
e_5E_5	$M \leftrightarrow Se + Bi_2Se_3$	shrinking
e_2E_1	$M \leftrightarrow Nd + NdSe$	1315-650
E_1	$M \leftrightarrow Nd + Nd_2Bi + NdSe$	650
E_2	$M \leftrightarrow Bi + Bi_3Se_2 + NdSe$	525
E_3	$M \leftrightarrow NdBi_2 + NdSe + Bi$	510
E_4	$M \leftrightarrow NdSe + Nd + Nd_3Bi$	650
e_9	$M \leftrightarrow Bi_2Se_3 + S + \alpha$	815
E_5	$M \leftrightarrow Se + Bi_2Se_3 + Nd_3Se_7$	shrinking
P_1	$M + NdBi \leftrightarrow NdBi_2 + NdSe$	1075
P_2	$M + NdBi \leftrightarrow Nd_4Bi_3 + NdSe$	1275
P_3	$M + Nd_4Bi_3 \leftrightarrow NdSe + Nd_5Se_3$	1125
P_4	$M + Nd_5Se_3 \leftrightarrow Nd_3Bi + NdSe$	1065
P_5	$M + Nd_2Se_3 \leftrightarrow Nd_4Se_7 + \alpha$	645
P_6	$M + Nd_4Bi_7 \leftrightarrow NdSe_2 + Bi_2Se_3$	610
P_7	$M + NdSe_2 \leftrightarrow Nd_3Se_7 + Bi_2Se_3$	550

P_8	**M+ $Bi_2Se_3 \leftrightarrow BiSe+NdSe$**	**620**
P_9	**M+BiSe$\leftrightarrow$ $Bi_2Se+NdSe$**	**585**
P_{10}	**M+ $Nd_2Se_3 \leftrightarrow S+\alpha$**	**700**

Based on the phase diagrams of the systems, the methodology and synthesis conditions of the obtained triple systems and phases with variable composition were developed.

Indirect synthesis conditions of the $NdSbSe_3$ compound have been developed.

The temperature conditions for the cultivation of single crystals by the CGCR (chemical gas carrier reaction) method of $NdSbSe_3$ compound were also determined and needle shaped single crystals were obtained.

The stoichiometric composition of the obtained single crystals was determined by chemical analysis. Based on the results of X-rays diffraction of $NdSbSe_3$ and $NdBiSe_3$ compounds obtained in the systems, the crystal lattice constants, types of structure, density and microhardness were determined (table 3).

Table 3

Some physicochemical and crystallographic properties of ternary compounds

Compound	$T_{formation}$, K	Syngonia	Lattice parameters	Lattice parameters,Å			Density, g/cm^3		H_μ, MPa
				A	B	C	$\rho_{rent.}$	ρ_{pik}	
$NdSbSe_3$	865	rhombic	Sb_2Se_3	12,77	14,08	5,82	6,0	6,20	1170
$NdBiSe_3$	995	“-“	“-“	13,79	14,32	6,12	6,42	6,48	1250

<u>The fifth chapter</u> presents the results of the study of the electrophysical properties of monocrystals of ternary phases obtained in the studied systems.

There is a great need for clean and special pure ingredients in modern technology, semiconductors, microelectronics, optical generators, power converters, etc. Special pure substances are obtained from alloys in several ways. In the research, the conditions for obtaining single crystals of solid solution alloys based on $Bi_2^V Se_3$ were developed using the Bricman-Stockbarger method.

These include zonal melting or Pfann, Chochralski and Bricman-Stockbarger methods, which show that the substance crystallizes in a single crystal at the same time. The basis of these methods is the different solutions of the additive in the liquid and solid phase in equilibrium. The method of solid solution alloys on the basis of B_2 ^ VSe3 using the Breeckman-Stockbarger method. The conditions for the acquisition of nokris-tals have been developed.

The Bricman-Stockbarger method is available in two variants: horizontal and vertical. The simplest and most widespread is the vertical option. The heating furnace in the unit consists of 2 different temperature zones (T_1, T_2). The heaters must be hermetic, keep the temperature stable, and be resistant to mechanical vibrations and shocks. The temperature of the upper zone (T_1) should be higher than the melting temperature of the substance T = 70-80 K, and the temperature of the lower zone (T_2) should be lower than the crystallization temperature of the substance T = 70-80 K.

In the Bricman method, the crystallization rate of the alloy varies between 10 ÷ 1 mm / h. The lower the rate of crystal formation, the higher its quality. The crystallization zone is vertical and horizontal.

The Bricmen method uses quartz ampoules as containers. The ampoule is filled with polycrystalline substance, deaerated at a pressure of 10-3 Pa, and the mouth is closed with a source of oxygen gas. To prevent the formation of a large number of crystallization centers during the crystallization process, the tip of the ampoule should be thinly pointed, ie conical. The cooling process is carried out by means of a moving mechanism that allows large-scale crystallization. When a single crystal is grown in this way, a purification process takes place at the same time, and the additive atoms accumulate at the end of the single crystal.

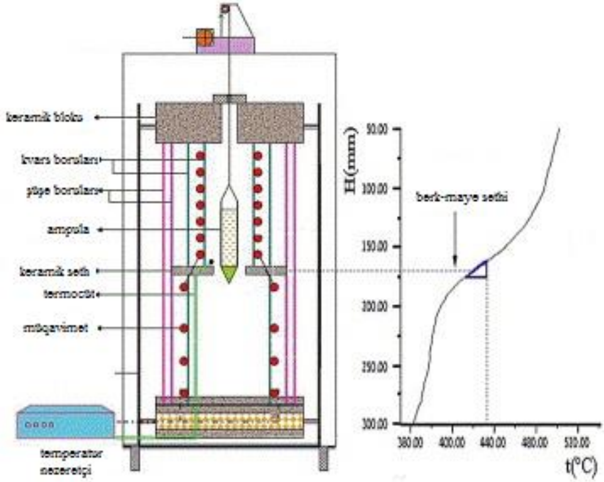

Figure 9. Device used for single crystal cultivation (a), general view of its furnace and graph of temperature distribution in the furnace (b)

Optimal temperature conditions and oven speed were determined as a result of repeated experiments. Single crystals of solid solution alloys containing $[Sb_2Se_3]_{1-x}$ $[Nd_2Se_3]_x$ and $[Bi_2Se_3]_{1-x}$ $[Nd_2Se_3]_x$ (where $x \leq 0.05$) were obtained by the above method.

The single crystals of single crystals were determined by drawing a laueogram from different parts. The obtained single crystals had a metallic luster and brittle properties.

In the studied systems, electrophysical properties such as, the thermo-e.d.f., electrical conductivity and thermal conductivity of solid solutions based on $B_2^VSe_3$ (B^V-Sb, Bi) and in the temperature range of 300-850 K were measured.

Based on the results obtained, it was determined that all samples in the studied temperature range have semiconductor properties.

In order to study the electrophysical properties of $[Sb_2Se_3]_{1-x}$ $[Nd_2Se_3]_x$ solid solutions; Samples of x = 0.01; 0.03; 0.05 were synthesized, thermally processed and specially sized, and the temperature dependence of electrical conductivity (σ) and thermoelectric driving force (α) was studied (Figure 5).

As the amount of Nd_2Se_3 in Sb_2Se_3 enhances, the electrical conductivity increases by about two orders.

960 μV/°C (for Sb_2Se_3) decreases to 615 μV/°C (for alloys).

The specific conductivity in alloys starts at ~ 350 K.

The ΔE_T of the samples in the field of special conductivity was calculated.

While ΔE_T = 1.20 eV in Sb_2Se_3, the content of 5 mol% Nd_2Se_3 increased to 1.46 eV.

Based on thermo-e.d.f values, it was determined that Sb_2Se_3 and alloys based on it have an "n" type conductivity.

The electrophysical properties of alloys containing $[Sb_2Se_3]_{1-x}$ $[NdSe]_x$ ($x \leq 0,05$) were studied and it was determined that the value of electrical conductivity of the samples increases depending on the NdSe concentration. This is most likely due to the enhancement of mobility and density of the carriers. The $\sigma \sim f(T)$ dependence of the samples can be divided into two areas: low temperature from ~ 300K to ~ 400 K and high temperature 400 K> above. In the field of specific conductivity, the ΔE_T of the samples was calculated and it was determined that Sb_2Se_3 and solid solutions based on it vary in the range ΔE_T =1.20÷1.35 eV.

The main reason for the increase in ΔE_T in the field of Sb_2Se_3 and solid solution based on it can be explained by the fact that in the field of concentration of 0÷5 mol% NdSe (Nd_2Se_3) the defects in the structure of Sb_2Se_3 are filled. As a result, the statistical distribution of the degree of localization of electrons between the defects and selenium atoms in the crystal lattice of Sb_2Se_3 increases, which leads to an increase in ΔE_T, respectively. Since the thermal conductivity of solid solution alloys has been studied, the thermoelectric efficiency of alloys can be inferred from the formula $Z=\frac{\alpha^2\sigma}{\chi}$ and the value of $\alpha^2\sigma$. Maximum value of a $\alpha^2\sigma$ at 700 K for the $(Sb_2Se_3)_{0,97}$ $(Nd_2Se_3)_{0,03}$ composition is $5,65 \cdot 10^{-4}$ B^2 (Om·M·K^2).

Thus, based on this value, it can be said that the material has thermoelectric properties. Materials obtained based on Sb_2Se_3 can be used as a negative arm of the thermocouple.

Thermoelectric properties of solid solutions based on Bi_2Se_3

were measured at low temperatures.

Bi_2Se_3-based thermoelectric materials, which can operate at low temperatures, have a short service life due to their low mechanical strength and resistance to aggressive environments. Therefore, the electrophysical properties such as electrical conductivity (σ) and thermal e.d.f., thermal conductivity (χ) of alloys containing $[Bi_2Se_3]_{1-x}$ $[Nd_2Se_3]_x$ $x \leq 0,1$ (α) was studied at the 100÷500K temperature range and the results obtained are given in Table 4.

Table 4

Thermoelectric properties of solid solution samples based on n-Bi_2Se_3 inNd_2Se_3-Bi_2Se_3 system

composition mol% Nd_2Se_3	α, μV/°C			$\sigma, 10^3 om^{-1} cm^{-1}$			χ 10^{-3}V/cm °C			Z ,10^{-3}/°C		
	100K	300K	500K	100K	300K	500K	100	300	500	100	300	500
0,05	68	118	82,2	1,55	3,95	2,69	14,2	19,52	16,41	0,65	2,30	0,88
0,10	75	123	100	2,55	5,94	3,93	17,3	29,48	18,2	1,12	3,28	2,24
0,15	73	103	110	4,24	3,92	3,50	35,1	24,85	17,22	0,72	1,81	2,56
0,20	50	98	116	3,73	3,22	2,01	23,31	19,75	16,12	0,44	1,59	1,68
0,25	45	90,1	125	6,32	2,41	1,01	23,42	19,80	15,61	0,42	1,10	1,17

0,50	31	68,3	95,5	2,59	1,59	0,89	8,2	11,51	5,82	0,36	0,67	1,31
1,00	29	62,1	76,3	1,02	1,01	0,43	13,25	14,18	7,41	0,18	0,28	0,34

As can be seen from Table 4, the thermoelectric parameters of the material containing (99.95 ÷ 99.00) mol% (Bi_2Se_3), (0.05 ÷ 0.10) mol% Nd_2Se_3 are stable in the operating temperature range of 100-400 K. By adding Nd2Se3 to Bi_2Se_3, a new material containing $[Bi_2Se_3]_{1-x} \cdot [Nd_2Se_3]_x$ $x \leq 0{,}1$, which can operate in the low temperature field, was obtained (Patent Invention i2017 0053).

KEY FINDINGS

1. A new data set on phase equilibrium in Nd-Sb (Bi) -Se triple systems has been obtained, which provides a scientific basis for obtaining a new class of perspective semiconductors based on three-component chalcogenides composed of REMs and VA group metals.
2. In order to obtain a complete picture of the phase equilibria in Nd-Sb(Bi)-Se systems, the area density of 50-57.2 at% Se of the Nd-Se binary system was reworked and determined that the $Nd_{3-x}Se_x$ continuous a solid solution area is formed.
3. In Nd-BV-Se (BV-Sb, Bi) ternary systems, the phase equilibria and the nature of the phase formation have been studied over a wide temperature and concentration range. For the first time, T-x state diagrams of polythermal sections and T-x-y state diagrams of three-dimensional systems were constructed on 14 polytermic sections (9 of them are quasibinar, 5 are non-quasi-binary).
4. In the studied Nd-Sb-Se and Nd-Bi-Se systems, it was determined that the liquidus surface of the systems consists of the initial crystallization area of 35 phases bounded by 59 monovariant curves, and in both systems the largest crystallization area is occupied by the NdSe phase. In order to follow the equilibrium processes occurring in the solid phase in

the studied triple systems, their isothermal sections were formed at 300 K.

5. In the studied systems, the optimal conditions for obtaining single crystals of the alloys containing $[Sb_2Se_3]_{1-x}[Nd_2Se_3]_x$ and $[Bi_2Se_3]_{1-x}[Nd_2Se_3]_x$ were obtained from the solid solution field based on $B_2^V Se_3$ by the Bricman-Stockbarger method, and the reaction the single crystals of the $NdSbSe_3$ compound obtained by the CGCR method were selected. T_1=700 K, T_2=600 K, duration 36 hour.
6. The conditions for the synthesis and formation of compounds containing $NdSbSe_3$ and $NdBiSe_3$ obtained in the Nd-B^V-Se ternary system were determined by both direct ampoule method and indirect synthesis methods. Based on the results of X-ray analysis, their lattice parameters and structure types were determined by the powder method and it was shown that both compounds crystallize in a similar type of Sb_2Se_3 in rhombic syngony: $NdSbSe_3$ *a*= 12,77; *b*= 14,68; *c*=5,82 A^0, ρ_{pik}=6,20 q/sm^3, ρ_{ren}=6,38 q/sm^3; $NdBiSe_3$ *a*=13,79; *b*=14,32; *c*=6,12 A^0, ρ_{pik}=6,42 q/sm^3, ρ_{ren}=6,48 q/sm^3;
7. The electrophysical properties of $NdSbSe_3$ and $NdBiSe_3$ compounds and solid solutions based on $Bi_2^V Se_3$ obtained in Nd-Bi^V-Se triple systems in the temperature range of 300-850 K were studied and it was determined that they are promising semiconductor materials with thermoelectric properties. As a result of the study of the electrophysical properties of samples containing $[Bi_2Se_3]_{1-x}[Nd_2Se_3]_x$ in the temperature range of 100-500 K, a thermoelectric material based on Bi_2Se_3 that can work in a low temperature area of 100-300 K was obtained. (Z=1,12 $\cdot 10^{-3}$ deg^{-1}, Z=3,28 $\cdot 10^{-3}$ deg^{-1} (patent № İ 2017 0053).

The main results of the thesis are published in the following publications.

1. Ганбарова Г.Т., Садыгов Ф.М., Ильяслы Т.М., Исмаилов З.И. Исследование химического взаимодействия в системе Sb_2Se_3-NdSe, Journal of Qafqaz University Chemistry and biology Volume 1, Number 2 2013 s 158-160
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