Baku State University Journal of Chemistry and Material Sciences, 2024, v. 1 (4), p.34-39

journal homepage: http://bsuj.bsu.edu.az/en
https://doi.org/10.30546/209501.201.2024.1.04.035

PHASE FORMATION IN THE TRINARY SYSTEM Nd-Bi-Te ACCORDING TO THE SECTION Bi_2Se_3-Nd_2Se_3

Gunel Ganbarova, Fuad Sadigov, Zakir Ismayilov, Rahila Mirzayeva, Zivar Hasanova
Baku State University, Baku, Azerbaijan

Received: 13 november 2024
Accepted: 12 december 2024
Published: 24 december 2024

Chemical interaction in the Bi_2Se_3- Nd_2Se_3 system was studied by methods of physicochemical analysis (differential thermal analysis, X-ray phase analysis, microstructural analysis, microhardness measurement and density determination).
Based on the analysis results, a phase diagram of the Bi_2Se_3- Nd_2Se_3 system was constructed.
It has been established that the Bi_2Se_3- Nd_2Se_3 section is a quasi-binary section of the Nd-Bi-Te ternary system and belongs to the eutectic type.
In the system, a solid solution area of 8 mol % Nd_2Se_3 is formed at room temperature based on Bi_2Se_3.The solid solution area was determined by microstructural analysis, to be 13 mol % at the eutectic temperature 813K and 8 mol % Nd_2Se_3 at room temperature.
From the phase diagrams it is evident that in the Bi_2Se_3- Nd_2Se_3 section a new ternary incongruent-melting compound of the composition $NdBiSe_3$ is formed by a peritectic reaction at a temperature of 995K with a component ratio of 1:1.
According to the results of X-ray phase analysis, it was established that the $NdBiSe_3$ compound crystallizes in the rhombic syngony with the lattice parameters:
a =13,79; b=14,32; c=6,12 Å, Z=8, density pycnometric =6,42g/cm^3, X-ray density g/cm^3.

Key words: system, alloy, analysis, phase, temperature, diagram, eutectic

---

INTRODUCTION

The efficiency of the production of new technology devices is inextricably linked with the development of semiconductor materials science [1-3]. At present, to meet the demand for semiconductor electronics, radio electronics and automation using known elementary or binary semiconductors does not always satisfy the requirements of technology, therefore, an intensive search for complex materials with a favorable combination of properties is given [4-6]. The study of a complex of electrophysical properties that make it possible to reveal the existence of various new phases in semiconductor systems, to determine the methods and conditions for synthesis, as well as the growth of perfect single crystals and their introduction into various sectors of the national economy, is of great importance [7-9]

Therefore, the study of chemical interaction in the Ln-Bi-Te (Ln-La, Ce, Sm, Tm, Er, Ho) system is of interest in connection with the use of rare earth elements in switching thermoelements based on Bi_2Te_3 [10-14].

EXPERIMENTAL

The following starting materials were used in the synthesis of Bi_2Se_3- Nd_2Se_3 alloys: Bi grade B-4, neodymium with a purity of 99-99.9%, Te grade Te-A2. The alloys were synthesized by direct alloying of the Bi_2Se_3 and Nd_2Se_3 components using the ampoule

E-mail address: zakir-51@mail.ru

method in the temperature range of 900-1150 °C, followed by slow cooling with the furnace switched off. In order to achieve an equilibrium state, the samples were annealed at 500 °C for 140 hours.

To study the Bi_2Se_3- Nd_2Se_3 system, 20 samples were prepared, the compositions of which are shown in Table 1.

Samples of the system were synthesized from Bi_2Se_3 and Nd_2Se_3 ligatures in graphitized quartz vials, evacuated to a pressure of 10-3 Pa. The vial was shaken regularly to ensure complete interaction. After synthesis, the alloys were annealed at 900 K for two weeks to homogenize them.

After heat treatment, it was determined that samples with a content of up to 65 mol % Nd_2Se_3 had a compact metallic luster, while the rest were porous.

All alloys were tested for their resistance to various reagents. It was determined that the alloys were resistant to air, water, and organic solvents, but were decomposed by mineral acids and alkalis.

The investigation of this system was carried out by the methods of physical and chemical analysis: differential thermal (DTA), X-ray phase (RFA), microstructural (MSA), as well as determination of density and measurement of microhardness.

Differential thermal analysis alloys of the system were carried out on a TERMOSKAN-2 device with an accuracy of 3-5°C, a chromel-alumel thermocouple, and calcined Al_2O_3 served as the standard. Heating rate of 9 degrees/min. X-ray phase analysis was performed on an X-ray instrument of the D2 PHASER model through the use of CuKα radiation with a Ni filter. The micro-structural analysis of alloys was carried out using an MIM-8 microscope. In the study of alloy microstructure, an etchant of composition 1 N HNO3 + HF = 2:1 was used, the etching time was 20 s. The microhardness of the phases was measured on a PMT-3 instrument with an accuracy of 5 %, and the density of the samples was determined by the pycnometric method.

RESULTS AND DISCUSSIONS

Based on the results of differential thermal analysis, the heating effects obtained in the thermograms are endothermic and reversible.

Thermograms of refractory samples were taken in a high-temperature pyrometer in graphite crucibles weighing 0.1 g in an argon atmosphere, under vacuum conditions, using a W-W/Re thermocouple. The amount of selenium was taken in excess to maintain the stoichiometric composition. The thermograms of the alloys show that the observed heating effects are endothermic and reversible. The results of differential thermal analysis are given in Table 1.

The diffractograms obtained as a result of X-ray phase analysis of the alloys were compared. It was found that the reflections obtained in the diffractogram of samples containing 7 mol% Nd_2Se_3 correspond to the reflections of the Bi_2Se_3 compound. This indicates that an 8 mol% solubility zone is formed in the system based on Bi_2Se_3 at room temperature. All reflections in the diffractogram of the sample containing 2 mol% Bi_2Se_3 correspond to the reflections of Nd_2Se_3.

In the compound , Bi_2Se_3 the coordination number of the Bi^{3+} ion is 6 and the radius (Bi^{3+})=1.030, whereas in Nd_2Se_3, the coordination number of Nd^{3+} is also 6.

Table 1. Results of DTA and microhardness of alloys of the Bi_2Se_3-Nd_2Se_3 system

№	Composition, mol %		Thermal heating effects, K	Microhardness, MPa		
	Bi_2Se_3	Nd_2Se_3		Bi_2Se_3	$NdBiSe_3$	Nd_2Se_3
1	100	0	980	850	-	-
2	99	1	875,980	860	-	-
3	98	2	860,970	910	-	-
4	97	3	835,975	960	-	-
5	95	5	815,835	980	-	-
6	93	7	825,845	970	-	-
7	90	10	815,840	980	-	-

8	85	15	815,825	not measured	-	-
9	80	20	815,820	eutectic	eutectic	-
10	75	25	815,875	-	-	-
11	70	30	815,975	-	-	-
12	60	40	815,995,1100	-	not measured	-
13	55	45	815,995,1200	-	1250	-
14	50	50	995,1215	-	1250	-
15	45	55	995,1310	-	1250	-
16	40	60	995,1485	-	1240	-
17	30	70	995,1615	-	not measured	2360
18	20	80	995	-	-	-
19	10	90	995	-	-	-
20	0	100	2010	-	-	2360

(Nd^{3+}), and the ionic radius is 0.995Å. The closeness of the ionic radii of the cations indicates that a substitutional solid solution is formed as a result of the replacement of Bi atoms with Nd atoms in the Bi_2Se_3 compound.

The reflections observed in the diffractogram of the sample corresponding to the 50 mol % Nd_2Se_3 content in the system are completely different from the reflections of Bi_2Se_3 and Nd_2Se_3 and are new, and a melting compound containing $NdBiSe_3$ is formed in the system with a 1:1 ratio of components.

MQA of polished and surface-polished alloys showed that samples with 0-8; 50 and 98-100 mol % Nd_2Se_3 contents were single phase, while the remaining alloys were two-phase. MQA results (Fig. 1) confirm the results of XRF.

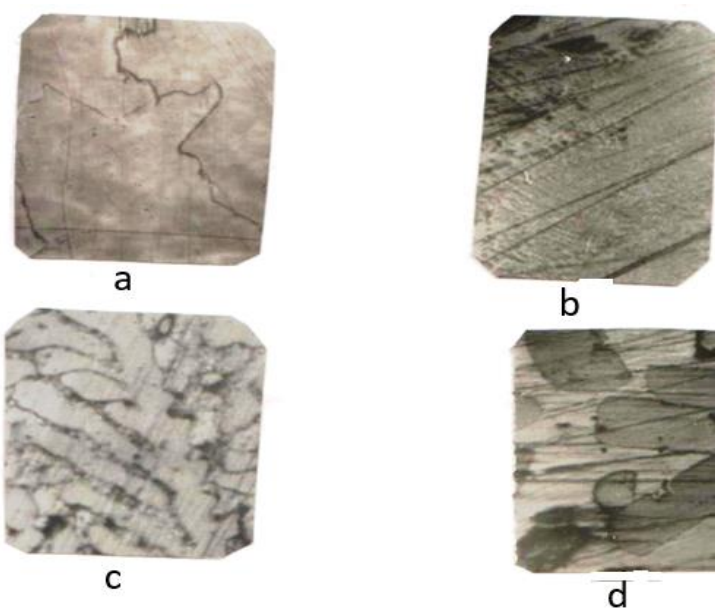

Fig.1. Microstructure of some alloys from the Bi_2Se_3-Nd_2Se_3 system. a-6 mol % Nd_2Se_3; b-20 mol % Nd_2Se_3; c-50 mol % Nd_2Se_3; d-60 mol %

As a result of measuring the microhardness of the alloys, three groups of different values were obtained. 850-980 MPa corresponds to solid solutions based on Bi_2Se_3, 1250 MPa to a phase containing $NdBiSe_3$, and 2360-2380 MPa to a solid solution based on Nd_2Se_3. Based on the results of differential thermal analysis, X-ray phase analysis, and microstructural analysis, a phase diagram of the Bi_2Se_3-Nd_2Se_3 system was constructed (Figure 2).

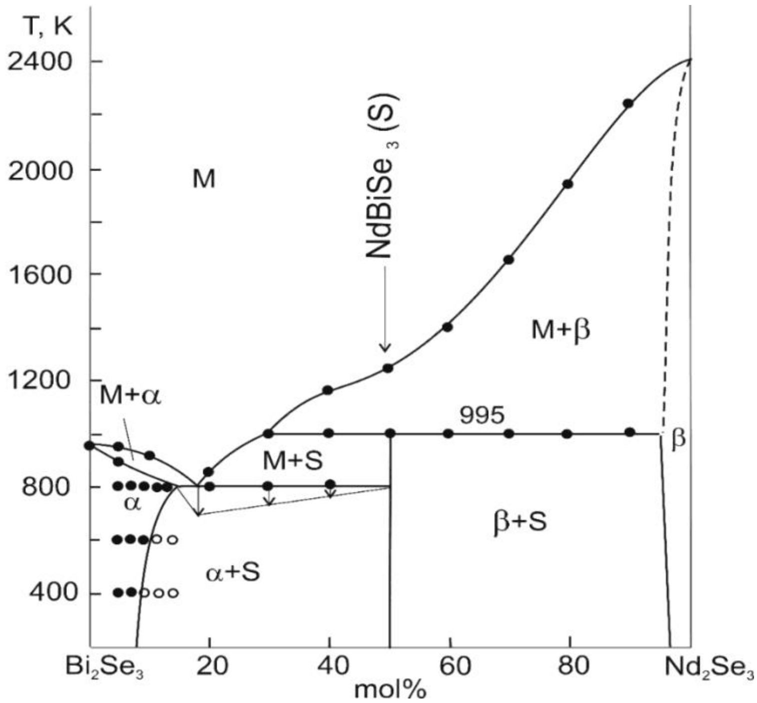

Fig. 2. State diagram of the Bi_2Se_3 - Nd_2Se_3 system

As can be seen from the figure, the phase diagram of the system is quasi-binary. This is explained by the fact that although three components are involved in the interaction in the system, only two-phase alloys crystallize below the solidus. In the system, a compound containing $NdBiSe_3$ is formed at 995 K by a peritectic reaction of the components in a 1:1 ratio.

P = M+β- (Nd_2Se_3)↔ $NdBiSe_3$ (S) (995 K)

The $NdBiSe_3$ compound co-crystallizes with solid solution components formed by the starting components below the solidus in the system.

In the system, a solid solution area of 8 mol % Nd_2Se_3 is formed at room temperature based on Bi_2Se_3. To determine the boundary of the solid solution area, small percentage samples based on Bi_2Se_3 were synthesized and thermally treated at 400,600,700,800 K for 200 hours, respectively, and quenched in ice water. The solid solution area was determined by microstructural analysis, to be 13 mol % at the eutectic temperature and 8 mol % Nd_2Se_3 at room temperature.

In the system based on Nd_2Se_3, a ~2 mol % Bi_2Se_3 solid solution region is formed at 300 K. In the Bi_2Se_3 - Nd_2Se_3 system, a eutectic containing 20 mol % Nd_2Se_3 crystallizes at 815 K. The location of the eutectic was determined by constructing a Tamman triangle.

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

M ↔α (Bi_2Se_3)+$NdBiSe_3$(S) (815 K)

The liquidus of the system consists of the initial crystallization region of the three components. The following monovariant equilibrium processes occur in the initial crystallization curves: M↔α; M↔ S and M↔β.

The solidus of the system consists of four domains: a single-phase domain based on Bi_2Se_3 and Nd_2Se_3, α and β phases, and a two-phase domain of α+S and S+β.

Thus, it was determined that the system is a quasi-binary cross-section of the Nd-Bi-Se ternary system and is of eutectic type. In the system, an incongruent compound with a $NdBiSe_3$ content of 50 mol % Nd_2Se_3 is formed, a solid solution region of 8 mol % Nd_2Se_3 on the Bi_2Se_3 basis at room temperature, and ~2 mol % Bi_2Se_3 on the Nd_2Se_3 basis.

The compound containing $NdBiSe_3$ formed in the Bi_2Se_3- Nd_2Se_3 system was again obtained from $BiCl_3$, $NdCl_3$ compounds by indirect synthesis method, and after thermal treatment, the crystallographic properties of the compound were studied by the powder method of X-ray diffraction. The interplanar spacing (d), hkl and line intensity (I) of the compound are given in Table 2.

Table 2. X-ray phase analysis results of the $NdBiSe_3$ compound

I	$d_{təc.}$, Å	$d_{hes..}$, Å	$1/d^2_{təc.}$	$1/d^2$, hes.	hkl
16.3	4,7700	4.7700	0,0439	0,0439	300
16.8	4,6204	4.6204	0,0473	0,0473	030
2.4	4,2094	4,3602	0,0564	0,0526	211
20.5	3,7020	3,6707	0,0730	0,0740	301
11.9	3,5792	3,5806	0,0781	0,0780	040
100.	3,0603	3,0603	0,1068	0,1068	002
21.9	2,9182	2,9111	0,1174	0,1180	112
8.2	2,8016	2,8060	0,1276	0,1270	150
32.2	2,3959	2,3870	0,1742	0,1755	060
24.9	2,3166	2,3166	0,1863	0,1848	042
34.8	2,2427	2,3262	0,1988	0,1965	260
18.4	2,0920	2,0911	0,2285	0,2287	052
8.0	2,0671	2,0606	0,2340	0,2355	621
17.4	1,9060	1,9035	0,2753	0,2760	352
1.7	1,8528	1,8490	0,2913	0,2925	313
4.8	1,8025	1,8045	0,3078	0,3071	323
4.5	1,7283	1,7239	0,3348	0,3365	800
5.5	1,6609	1,6593	0,3625	0,3632	801
6.5	1,5413	1,5399	0,4209	0,4217	091

It was determined that the NdBiSe3 compound crystallizes in the rhombic system, the lattice parameters are a = 13.79; b = 14.32; c = 6.12 Å, Z = 8, the pycnometric density is 6.42 g/cm3, and the X-ray density is 6.48 g/cm3.

CONCLUSION

As a result of physical and chemical methods of research on the ternary system Nd-Bi-Te, a diagram of the state of the bisecting system Bi_2Se_3-Nd_2Se_3 was created. It is established that the section Bi_2Se_3-Nd_2Se_3 is a quasi-binary section of the ternary system Nd-Bi-Te and belongs to the eutectic type.

A new ternary compound of composition NdBiSe3 was discovered in the system. The compound NdBiSe3 can be used as a promising thermoelectric material in the manufacture of thermoelectric energy converters.

REFERENCES

[1] Goltsman, B.M.; Kidinov, V.A. and Smirnov, I.A. Semiconductor thermoelectric materials based on Bi_2Te_3 **1972**, 320 p., https://www.scirp.org/reference/referencespapers?referenceid=824182

[2] Yarembash, E.I. and Eliseev, A.A. Chalcogenides of rare earth elements. Moscow: *Nauka*, **1975**, 275 p., https://ouci.dntb.gov.ua/en/works/4y18JXB4/

[3] Sadygov, F.M.; Jafarova, E.K.; Babanly, M.B. et al., Character of phase formation in Sb_2Se_3(Bi_2Se_3)-TmSe systems, *Zh. Inorg. Chemistry*, **2002,** .47(10), p.1713-1717, https://www.researchgate.net/publication/282684424_Character_of_phase_formation_in_the_Sb2Se3Bi_2Se3-TmSe_systems

[4] Sadygov , F.M.; Ilyasly ,T.M.; Nasibova, L.E. and Aliev, I.I. Physico-chemical study of the Sb_2Se_3-Nd_2Se_3system, *Zh. Inorg. Chemistry*, **2013**, vol. 58, N9, pp. 1253-1256, https://doi.org/10.58351/2949-2041.2023.4.4.030

[5] Sadygov , F.M., Mamedova ,S.G., Babanly ,M.B., Ilyasly, T.M. Phase equilibria in the Ce-Sb-Se system along the Sb_2Se_3-Ce_2Se_3 section, *Zh. Inorg. Chemistry*, **2001**, vol. 46(8), pp. 1382-1383, https://www.researchgate.net/publication/286684177_Phase_Equilibria_in_the_Ce-Sb-Se_System_along_the_Sb2Se3-Ce2Se3_Join

[6] Jeffrey, S. and Eric S. T. Complex Thermoelectric Materials, *Nature Materials* , **2008,** 7, pp.105-114, https://doi.org/10.1038/nmat2090

[7] Sadygov, F.M.; Ilyasly, T.M.; Ganbarova, G.T.; Zlomanov, V.P. and Aliev, I.I. Physical and chemical study of the Sb_2Se_3-Nd_2Se_3system, *Inorg. Mater.,* **2017**, vol. 53 (7), pp. 681-685, https://link.springer.com/journal/10789/volumes-and-issues/53-7

[8] Rustamov, P.G. and Aliev, O.M., Eypullaev et al. Chalcolanthanates of rare elements, M: *science*, **1988**, 284 p., https://www.scirp.org/reference/referencespapers?referenceid=420836

[9] Chih-hao, L.; Hsin-jay, W. and Sinn-Wen, C. Liquidus Projection of the Ternary Bi-Sb-Te, *Thermoelectric Material System*, **2013**, https://doi.org/10.1007/s11661-013-1883-8

[10] Goltsman, B.M., Kudinov, V.A., Smirnov, I.A. Semiconductor thermoelectric materials based on Bi_2Te_3 M: science, **1972**, pp.320, https://www.scirp.org/reference/referencespapers?referenceid=824182

[11] Fang, W.; Hongzhang, S.; Jianfeng, J. and Xing, H.Effects of Ce, Y, and Sm doping on the thermoelectric properties of Bi_2Te_3 alloy, Progress in Natural Science: Materials International, 2013, 23(4), pp. 408-412, https://doi.org/10.1016/j.pnsc.2013.06.007

[12] Imamalieva, S.Z.; Mashadiyeva, L.F.; Zlomanov, V.P. and Babanly, M.B. Phase equilibria in the Tl_2Te-YbTe-Te system. Inorganic Materials 2015, 51(11), pp.1237-1242,https://doi.org/10.1134/S0020168515110035

[13] Wu, F.; Song, H.; Jia , J. and Hu, X. Effects of Ce, Y, and Sm doping on the thermoelectric properties of Bi_2Te_3 alloy. *Progress in Natural Science: Materials International*, **2013**; 23(4): pp.408-412, https://doi.org/10.1016/j.pnsc.2013.06.007

[14] Lyakisheva N.P., State diagrams of double metallic systems. M.: Engineering, 1997, v.2, 1023 p. https://www.scirp.org/reference/referencespapers?referenceid=1293741