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Research Article

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Phase Formation and Properties of Phases in the Yb-As-Se Ternary System

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Abstract The character of chemical interaction in the Yb-As-Se ternary system was investigated by complex methods of physical-chemical analysis. The regions of the primary crystallization of the initial and obtained phases were detected. A number of physical-chemical, crystallochemical and chemical properties of the obtained phases were studied. All of the compounds obtained are prospective semiconductors with mixed chemical bonds.

Keywords phase diagram, ternary system, Yb-As-Se, glasses, semiconductors

Introduction

The simplicity of technology and determined high photosensitivity greatly increased application of chalcogenide glasses in optic electronics. It was of interest to give them a new property by introduction of the magnetic ion – a rare earth element into their composition. To solve the set problem, phase equilibrium in the Yb-As-Se ternary system has been investigated.

To find out the complete nature of chemical interaction in the Yb-As-Se ternary system together with the sections studied before, the following sections were investigated: $YbAs_4Se_7$-Se, As_2Se_3-Yb_3Se_4, As_2Se_3-Yb_2Se_3 and AsSe-Yb_2Se_3 [1-3]. Earlier in the Yb-As-Se system three congruent $YbAs_4Se_7$, $Yb_3As_4Se_9$, $YbAsSe_3$ and incongruent compounds were found.

Experiment

The alloy synthesis of the system was carried out in a rotary oven from As_2Se_3, $YbAs_4Se_7$, AsSe, Yb_2Se_3, Yb_3Se_4 and from ITM-1 Ytterbium and B-4 selenium elements. The synthesis consisted of preliminary holding at 650 K during 3-4 hours and the following heating to the required synthesis temperature. The initial components of sections are described in [1-3].

The plot of the phase diagrams of the sections mentioned above was constructed. The alloys synthesized before and after annealing were investigated by the methods of differential-thermal analysis (DTA), high-temperature differential thermal analysis (HDTA), X-ray diffraction analysis (XRDA), microstructural analysis (MSA) and determination of microhardness and density. DTA was carried out using two-coordinate self-recoding PDC-021 unit at the heating rate 9°/min, high-temperature VDTA-8_{2M} unit with Pt\Pt-Rh thermocouple. XRDA was carried out with the help of DROM-3 unit with CuKα emission. MSA was carried out using the metallographic microscope MIM-7. Density was determined by picnometric weighing (bottle method) using toluene as a filler. Microhardness was measured with the help of PMT-3 microhardness meter with a loading of 10g.

Results and conclusions

The section $YbAs_4Se_7(S_1)$-Se (fig.1) passes 2 determinate triangles $YbAsSe_3(S_3)$-As_2Se_3-S_1 and S_3-As_2Se_3-Se.

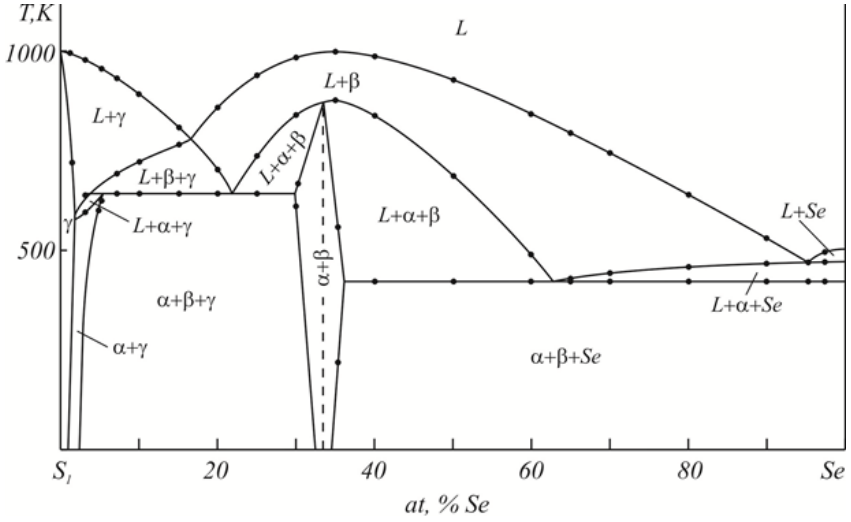

Figure 1: Phase diagram of the $YbAs_4Se_7(S_1)$-Se system

The largest liquidus part of the section S_1-Se 16,0-95,5 at.% is formed by the primary crystallization of β solid solutions on S_3 basis; while the smallest part, 96,5 - 100 at.% - by the region of primary crystallization of selenium. The region L+γ, where γ-solid solution is based on S_1, occupies the intermediate part.

In the section, there are the following three-phase regions with participation of the liquid phase L+ α + β, L+ γ +α, L+ γ + β, L+ β + Se.

The region of primary crystallization L+ β, as well as, the region of secondary crystallization L+ α + β relate to both triangles intersected by the section.

In the system, the following peritectic reactions take place:

1) in the triangle S_3-As_2Se_3-S_1: L+ α + β ↔ α + γ
2) in the triangle S_3-As_2Se_3-Se: L+ β ↔ α +Se

The section As_2Se_3-Yb_3Se_4 (fig. 2) crosses over 4 dependent triangles As_2Se_3-S_1-S_3, S_1-S_3-S_2 ($Yb_3As_4Se_7$), S_2-S_3-Yb_2Se_3, S_2-Yb_2Se_3-Yb_3Se_4.

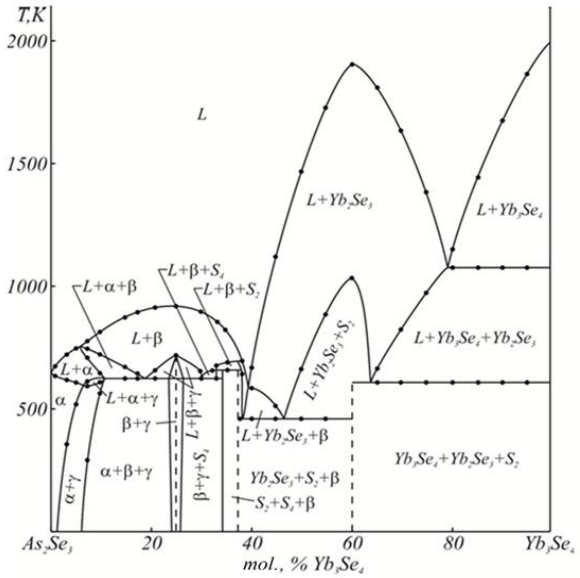

Figure 2: Phase diagram of the As_2Se_3-Yb_3Se_4 system

The liquidus of the section consist of 4 fields of primary crystallization of phases: L+ Yb_2Se_3, L+ β, L+ Yb_3Se_4, L+ α(As_2Se_3); 8 fields of secondary crystallization L +α+ γ, L+ α + β, L+ β + γ, L+ β + S_4, L+ β + S_2, L+ Yb_3Se_4+ Yb_2Se_3. It is noteworthy that the field of primary crystallization L+ β is in three, but that of L+ Yb_2Se_3 is in two dependent triangles.

Alloys of the section from 1,1 mol.% Yb_3Se_4 to 5,8 mol.% Yb_3Se_4 crystallize as α +γ, 24,5-25,5 mol.% Yb_3Se_4 as β + γ, alloys 0-1,1 mol.% Yb_3Se_4 crystallize as α solid solutions correspondingly.

In the region from 5,8 to 24,5 mol.% Yb_3Se_4 a tertiary crystallization α + β+ γ takes place, for the alloys with concentration 24,5-32,6 mol.% Yb_3Se_4 the following eutectic reaction L+ β ↔ β+ γ+ S_4 takes place. The lowest eutectic horizontal of the section – 465 K is within concentrations from 37.5 mol.% Yb_3Se_4 to 60,0 mol.% Yb_3Se_4 and the corresponding eutectic reaction is Yb_2Se_3+L ↔ β + S_2+ Yb_2Se_3. Alloys 32,6-37,5 mol.% Yb_3Se_4 of this section crystallize according to the peritectic reaction L+ β + S_2↔ β + S_2+ S_4 alloys with concentrations from 60-100 mol.% crystallize in the form of mixture Yb_3Se_4+ Yb_2Se_3+ S_2.

The section AsSe-Yb_2Se_3 (fig.3) intersects three dependent triangles of system Yb-As-Se, namely AsSe-S_2-YbSe, YbS_3-S_2-Yb_3Se_4, Yb_3Se_4–S_2-Yb_2Se_3.

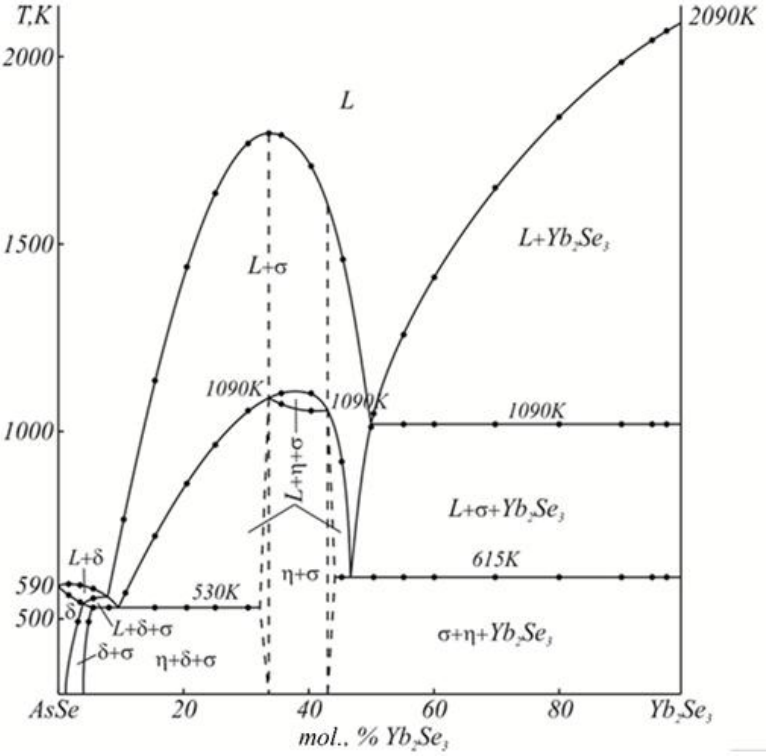

Figure 3: Phase diagram of the AsSe-Yb_2Se_3 system

The phase L+Yb_2Se_3 (42,9-100 mol.% Yb_2Se_3) forms the largest part of liquidus of the section. The phase L+ σ, which is in three dependent triangles at once is almost commensurable with it. The liquidus region formed by δ solid solutions in comparison with that based on σ solid solution is only within the range 0-7,3 mol.%Yb_2Se_3. There are three regions of secondary crystallization: L+δ+σ, L+σ+η, L+ σ +Yb_2Se_3.

Crystallization of alloys 42,9-100 mol.% Yb_2Se_3 takes place according to the eutectic reaction L+ δ ↔ σ + Yb_2Se_3.

The alloys of a triangle YbSe-S_2-Yb_3Se_4 crystallize into a mixture consisting of two solid solutions η +δ. The eutectic horizontal η+σ+δ is the lowest eutectic in the system AsSe-Yb_2Se_3 – 530 K. Alloys of the system to 0,5 mol.% Yb_2Se_3 crystallize as σ solid solution, but in the region 0,5-4,3 mol.% Yb_2Se_3 the alloys solidify into a mixture σ+δ.

The ternary system was triangulated by using data of methods of physical chemical analysis of quasi-binary systems. The indicated system is divided by the triangulating secants into 14 dependent triangles AsSe-Yb_2Se_3-S_2, As_2Se_3-S_1-S_2, AsSe-As_2Se_3-S_1, As_2Se_3-S_1-S_3, S_2-Yb_2Se_3-Yb_3Se_4, S_3-Yb_2Se_3-Se, S_3-As_2Se_3-Se, YbAs-AsSe-As, YbAs-YbSe-Yb_4Se_3, Yb_4Se_3-YbSe-Yb, S_2-S_3-Yb_2Se_3, S_1-S_2-S_3, S_2-YbSe-Yb_3Se_4, S_3-Yb_2Se_3-Se.

On the basis of literature and experimental data, the projection of liquidus surface of the system Yb-As-Se (Fig.4) was plotted.

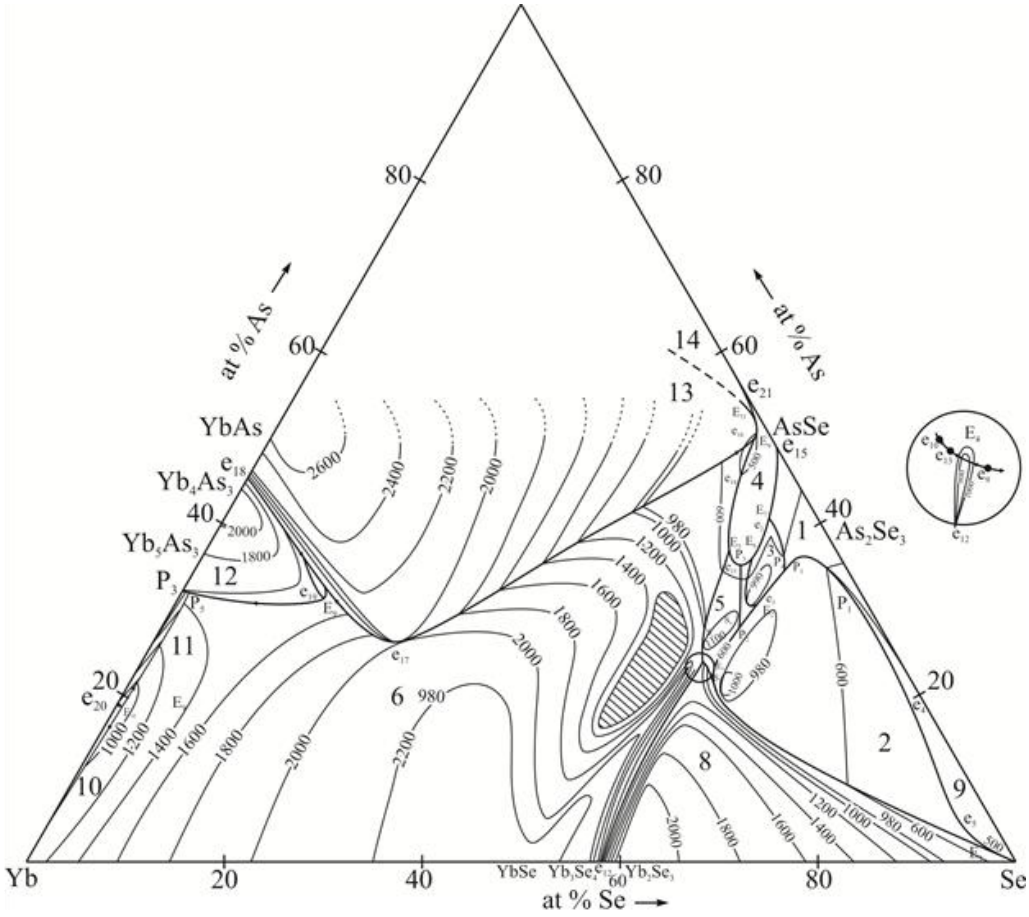

Figure 4: Liquidus projection of the Yb-As-Se system with isothermal lines

The liquidus of the system consists of 3 fields of primary crystallization of phases: 1-α, 2-β, 3-γ, 4-δ, 5-η, 6-σ, 7- S_4, 8- Yb_2Se_3, 9- Se, 10-Yb, 11- Yb_5As_3, 12- Yb_4Se_3, 13- YbAs and As.

Due to the high partial pressure of arsenic vapours the subordinate *triangle* YbAs-As-AsSe was not studied, therefore, the boundary of the regions YbAs and As was not set. As a result, the regions of these phases coincide in the diagram. In the system Yb-As-Se, the character of mono- and non-variant progresses was studied. The characteristic points, their coordinates and reactions taking place in Yb-As-Se system are given in tables 1,2.

Table 1: Coordinates of double and ternary eutectic and peritectic points in the Yb-As-Se system.

№	Point symbol	Co-ordinate of a point. at.%		
		Yb	As	Se
1	**2**	**3**	**4**	**5**
1	e_1	5.5	35.5	58.9
2	e_2	4.9	40.3	54.8
3	e_3	10.5	31.5	58.5
4	e_4	-	20.0	80.0
5	e_5	4.2	4.2	91.7

6	e_6	12.5	30.0	57.5
7	e_7	19.2	22.5	58.1
8	e_8	21.0	19.0	60.0
9	e_9	19.7	23.5	56.8
10	e_{10}	19.3	24.6	56.1
11	e_{11}	10.9	35.3	53.7
12	e_{12}	41.7	-	58.2
13	e_{13}	19.6	24.0	56.2
14	e_{14}	5.5	44.5	50.5
15	e_{15}	-	46.0	54.0
16	e_{16}	1.5	48.5	50.0
17	e_{17}	50.0	25.0	25.0
18	e_{18}	56.1	43.9	-
19	e_{19}	55.0	30.0	15.0
20	e_{20}	64.2	35.8	-
21	e_{21}	-	55.0	45.0
22	p_1	4.0	36.0	60.0
23	p_2	13.4	29.5	58.0
24	p_3	58.9	41.9	-
25	E_1	2.1	0.6	97.2
26	E_2	11.7	30.1	58.2
27	E_3	19.9	22.1`	58.0
28	E_4	20.1	23.5	56.4
29	E_5	11.2	36.6	52.9
30	E_6	8.7	36.0	55.2
31	E_7	4.4	40.4	55.5
32	E_8	2.9	48.5	48.5
33	E_9	54.4	32.2	13.3
34	E_{10}	64.0	35.9	0.3
35	P_1	0.8	32.8	66.4
36	P_2	15.1	26.6	58.3
37	P_3	10.3	35.0	54.7
38	P_4	6.6	34.4	59.0
39	P_5	52.3	47.4	1.5

Table 2: The character of proceeding of monovariant and nonvariant processes in the Yb-As-Se system

№	Curve symbol	The nature of chemical interaction	Temperature, K
1	p_1P_4	$L+\beta\leftrightarrow\alpha$	870→630
2	e_3P_4	$L\leftrightarrow\gamma+\beta$	720→630
3	P_4e_1	$L\leftrightarrow\alpha+\gamma$	630→590
4	P_1e_4	$L\leftrightarrow\alpha$+Se	420→415
5	p_1P_1	$L+\beta\leftrightarrow\alpha$	870→415
6	e_5P_1	$L\leftrightarrow\beta$+Se	470→415
7	e_3 E_2	$L\leftrightarrow\gamma+\beta$	720→635
8	e_7 P_2	$L\leftrightarrow\eta+\beta$	690→635
9	p_2P_2	$L+\eta\leftrightarrow S_4$	1000→665
10	e_6 E_2	$L\leftrightarrow S_4+\gamma$	870→635
11	P_2E_2	$L\leftrightarrow S_4+\beta$	660→635
12	e_7E_3	$L\leftrightarrow\eta+\beta$	690→465

13	e_9E_3	$L\leftrightarrow Yb_2Se_3+\eta$	1050→465
14	e_8E_3	$L\leftrightarrow Yb_2Se_3+\beta$	750→465
15	$e_{12}E_4$	$L\leftrightarrow \delta+Yb_2Se_3$	1250→615
16	e_9E_4	$L\leftrightarrow Yb_2Se_3+\eta$	1070→615
17	$e_{13}E_4$	$L\leftrightarrow\eta+\delta$	1050→615
18	$e_{14}E_5$	$L\leftrightarrow\sigma+\delta$	550→530
19	$e_{11}E_5$	$L\leftrightarrow\eta+\sigma$	540→530
20	$e_{10}E_5$	$L\leftrightarrow\delta+\eta$	1090→530
21	$e_{11}P_3$	$L\leftrightarrow\eta+\delta$	540→470
22	p_2P_3	$L+\eta\leftrightarrow S_4$	1000→470
23	$e_6\ E_6$	$L\leftrightarrow S_4+\gamma$	870→450
24	P_3E_6	$L\leftrightarrow\delta+S_4$	470→450
25	$e_2\ E_6$	$L\leftrightarrow\delta+\gamma$	540→450
26	$e_2\ E_7$	$L\leftrightarrow\delta+\gamma$	540→490
27	$e_{15}E_7$	$L\leftrightarrow\delta+\alpha$	545→490
28	e_1E_7	$L\leftrightarrow\gamma+\alpha$	590→490
29	$e_{10}\ e_{13}$	$L\leftrightarrow\eta+\delta$	1090→1070
30	$e_{14}E_8$	$L\leftrightarrow\sigma+\delta$	550→407
31	$e_{16}E_8$	$L\leftrightarrow YbAs+\delta$	520→407
32	$e_{17}E_8$	$L\leftrightarrow YbAs+\sigma$	2000→407
33	$e_{17}E_9$	$L\leftrightarrow\sigma+YbAs$	2000→1370
34	$e_{18}E_9$	$L\leftrightarrow YbAs+Yb_4Se_3$	1620→1370
35	$e_{19}E_9$	$L\leftrightarrow\sigma+Yb_4Se_3$	1450→1370
36	$e_{19}E_5$	$L\leftrightarrow Yb_4As_4+\delta$	1450→1438
37	p_3P_5	$L+Yb_4Se_3\leftrightarrow Yb_5Se_3$	1685→1438
38	P_5E_{10}	$L\leftrightarrow Yb_5Se_3+\delta$	1438→856
39	$e_{20}E_{10}$	$L\leftrightarrow Yb_5Se_3+Yb$	880→856
40	YbE_{10}	$L\leftrightarrow Yb+\delta$	1097→856
41	SeE_{10}	$L\leftrightarrow Se+\delta$	490→470
42	E_1	$L\leftrightarrow Se+\beta+Yb_2Se_3$	470
43	E_2	$L\leftrightarrow\beta+\gamma+S_4$	640
44	E_3	$L\leftrightarrow\eta+\beta+Yb_2Se_3$	690
45	E_4	$L\leftrightarrow\eta+Yb_2Se_3+\delta$	615
46	E_5	$L\leftrightarrow\sigma+\delta+\eta$	530
47	E_6	$L\leftrightarrow\delta+\gamma+S_4$	450
48	E_7	$L\leftrightarrow\alpha+\gamma+\sigma$	490
49	E_8	$L\leftrightarrow\sigma+\delta+YbAs$	407
50	E_9	$L\leftrightarrow\sigma+YbAs+Yb_4As_3$	1370
51	E_{10}	$L\leftrightarrow\sigma+Yb+Yb_5As_3$	856
52	P_1	$L+\beta\leftrightarrow\alpha+Se$	420
53	P_2	$L+\eta\leftrightarrow S_4+\beta$	660
54	P_3	$L+\eta\leftrightarrow S_4+\sigma$	470
55	P_4	$L+\beta\leftrightarrow\gamma+\alpha$	630
56	P_5	$L+Yb_4As_3\leftrightarrow Yb_5As_3+\sigma$	1438

Conclusion

The largest liquidus region of the Yb-As-Se ternary system is formed by σ solid solution on the basis of YbSe and Yb_4Se_3 (49.5 wt.% of Yb-As-Se triangle) the smallest one falls within 3 regions: S_4, Yb_5Se_3, Yb (0.2 wt.% of Yb-As-Se triangle). The glasses occupy 1.88 wt.% of triangle's total area.

The glasses are not dissolved in mineral acids, as HCL and H_2SO_4, but they are well dissolved in concentrated nitric acid and alkali, as well. The values of such properties of glasses as softening temperature, density and microhardness grow with increase of the concentration of Yb in the composition of glasses.

The detected glasses are p-type semiconductors and their electroconductivity rises with growing ytterbium concentration. Both metallic Yb and its chalcogenides, probably, form polarons of small radius and transition into trivalent state is not excluded, conductivity in this case is realized at the account of jumps of charge carriers between ions of different valency and this favours the increase of electroconductivity [4-6].

On the basis of AsSe, As_2Se_3, S_1, S_2, S_3, YbSe, Yb_3Se_4 the regions of solid solutions have been discovered.

References

[1]. P.G. Rustamov, T.M. Ilyasov, L.A. Mamedova. (1985) Phase diagrams and phase properties of the systems As_2Se_3-SmSe and As_2Se_3-Sm_2Se_3. Journal of the Less Common Metals, v.110, iss.1-2, p.195-197.

[2]. T.M. Ilyasly, R.F. Abbasova, Adıgüzel Vedat, Necefoğlu Hacali. (2015) Study of semiconductor systems of Ln-As-X type (Ln=Sm,Yb,Eu; X=S,Se,Te). İnternational Semiconductor Science Technology Conference (ISSTC) May 11-13. Kuşadası Turkey s.74.

[3]. T.M. Ilyasly, R.F. Abbasova, S.M. Veysova. (2016) Semiconductor phases of ternary systems of Ln-As-X type (Ln= Sm, Yb, Eu; X= S, Se, Te) Chemical Senses. Issue 9 (2), November. V. 41, p.985 – 999.

[4]. G. Gangadhar Reddy, A. Ramakanth. (1990) On the semiconductor-metal transition in a model for mixed valence systems. Journal of Physics and Chemistry of Solids. Volume 51, Issue 6, Pages 515-522

[5]. E.Sh. Hajiyev. (2006) The crystallization kinetics of the $YbAs_2S_4$ amorphous films. Fizika. v.XII, N 4, p. 41-42

[6]. R. Ali-zade, E. Efendiyev, E. Hajiyev. (1999) Determination of partial coordinate number of atoms in amorphous Yb-As-S(Se,Te) systems. J. of Physics. 23, 493 – 496.