TECHNOLOGY OF OBTAINING GLASSES FROM As-S-Se-Te-I SYSTEM

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Abstract — *In this paper we present the technology of obtaining glasses from complex, five-component system $(As2S_3)_x(AsSe_{0.5}Te_0.5I)_{100-x}$ with x=100; 95; 90; 85; 80; 75; 70; 65; 50; 30; 10 and 0 mol%. Glasses were obtained from elemental components with cascade heating and air quenching. The amorphous character all of the samples were controlled by X-ray diffraction on powdered targets and by polarization microscope. The density of all synthesized samples was determined by Archimedes's method. It was modeled analytical form of dependence of density versus As_2S_3 content or $AsSe_{0.5}Te_{0.5}I$ content.*

1. INTRODUCTION

A series of different applicative characteristics of binary systems of chalcogenides As-S, As-Se and As-Te would be remained and improved by structure combination introducing two or even three chalcogenides elements into the system. In addition, introducing halogen elements in material leads to the changes in structure, i.e. the chain-structure transforms in to space-defined or layer-chain-structure. [1]

Considering the fact that, varying the components relation in their compositions, during synthesizes of glassy and amorphous materials, in general case, leads to desired characteristics of materials. This so-called the effect of structural-technological modification, gives great possibility in an area of practical application of glassy materials. [2]

In the last decades, the range of forming of glassy state was studied in many of binary (A^V-B^{VI}, $A^{IV}-B^{VI}$; A^{IV} -Si, Ge, Pb; A^V - As, Sb, Bi; B^{VI} - S, Se, Te), ternary (M-A^V-B^{VI}, $A^V-B^{VI}-C^{VI}I$; M - element from Periodic table, $C^{VI}I$ - Cl, Br, I), quaternary (M-$A^V-B^{VI}-C^{VI}I$) [3,4] and some fivecomponents systems like $A^{IV}-A^V-B^{VI}(1)-B^{VI}(2)-C^{VI}I$ [5,6,7].

The state diagram in system As-S is shown in Pict. 1. In the range of glass formation, As_2S_3 and As_2S_5 structural units are formed. These glasses have layer structure, while in As_2S_3, As-atoms are connected with three S-atoms by strong covalent bonds. [2]
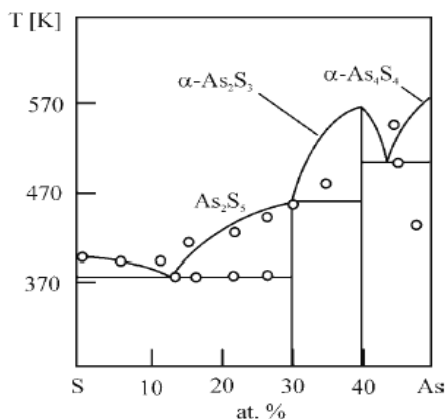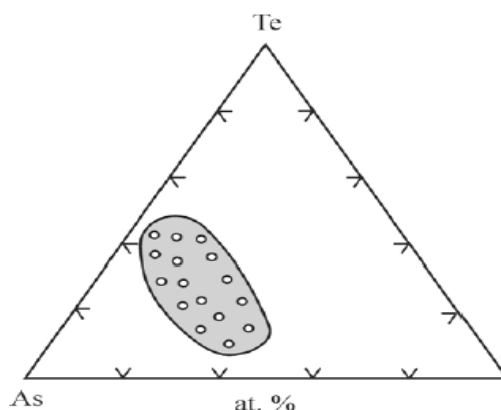
PICTURE 1. THE STATE DIAGRAM IN SYSTEM AS-S

The ranges of glass formation in As-Se-I and As-Te-I systems are shown on Pict. 2 and Pict. 3 [2, 8].
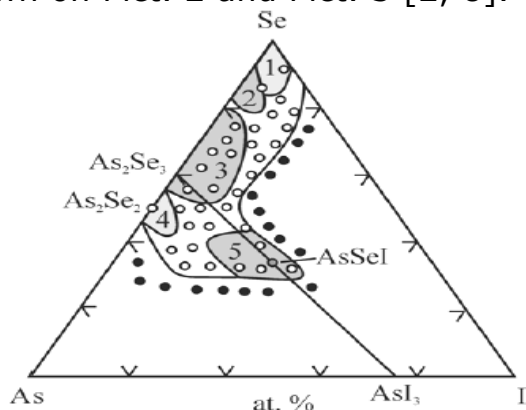
PICTURE 2. THE GLASS-FORMING REGION IN AS-SE-I SYSTEM

PICTURE 3. THE GLASS-FORMING REGION IN AS-TE-I SYSTEM

Glasses from the As-Se-I system have small crystallization ability. Introducing iodine into two-components glasses and also, increasing selenium content, leads to forming three-components structural units $AsS_2/2I$, while the $(-Se-)_n$ chain are reduced. Greater glass forming ability of melts from As-Se-I system is connected with forming more chain ($AsS_2/_2I$, $(-Se-)_n$ type) and layer ($AsS_3/_2$ and $AsSe_5/_2$) structure. Increasing the atomic weight in S»Se—»Te order, leads to "island-character" area of glass forming in the As-Te-I.

Systematic investigations of the process of glass formation, chemical interaction, and formation of glass structure in the As-S, As-Se, As-Te, As -B^{VI}-I, as well as, in the Ge-As-S(Se)-I [9] systems have indicated that in the As-S-Se-Te-I system, could exist significant glassy range. Starting from the fact that replacing S with Se and Te, contribute increasing electrical conductivity and increasing the values of the refractive index, as well as, the fact that introducing I into As_2S_3 contribute better thermodinamical characteristics, $(As_2S_3)_x(AsSe_0.5Te_0.5I)_{100-x}$ system was chosen. This chosen cut is the most optimal one from the point of view of relevant physical properties for technological application.

2. EXPERIMENT

Elementary components of extremely high purity (99,9999 %) have been used for glass synthesis. The masses were measured by the Mettler scale B-6 with accuracy of +510" g. The process itself has been carried out in quartz ampullae's, first washed in chrom-sulphur acid, distilled water, then in alcohol, and after dried in furnace at 500 °C for 5 to 6 h. After such a treatment ampullae's were filled with elementary components, vacuum scaled up to 133-10"^{3} Pa and then welded by oxygen-acetylene flame.

The synthesis was carried out in furnace with manual adjuster and automatically maintains temperature. As the initial components show essential differences in melting temperatures (they range from 113,5 °C for I up to 452 °C for Te) synthesis have been carried out according to the following procedure. Ampullae's filled with elementary components were initially heated in the furnace at a heating rate of v=50 °/h up to 250 °C, and kept at that temperature for 6 to 8 h. Further heating up to 450 °C was the same rate. Samples were kept 6 to 8 h under this condition, and afterwards the temperature was increase to 750 °C. In order to carry out homogenization, melts were kept at maximal temperature for 18 h.

The successive heating and holding the system for several hours at constant temperature determined in advance, permitted completion of the melting process of the starting high purity elementary components (As, S, Se, Te, I), and successive formation of particular structural units. For example, on the first temperature plateau iodine and sulphur interacted with other initial components, the second temperature plateau enabled forming binary compounds As_2S_3, As_2Se_3, AsI_3.

It is necessary subsequently to cool the system gradually down to 10 to 30 °C below the softening point of given glass material, and to keep it at that temperature for about 5 to 6 h in order to obtain favorable optical characteristics. Cooling of the five components melts were achieved by the procedure of in alumina (Al_2O_3) powder. The ampullae's with AsSe0.5Te0.5I sample from the maximal temperature of the synthesis has been cooled by putting the melt in cold water. The fast cooling rate should enable that the structure of solid sample obtained would be analogous melt structure at maximal temperature of the synthesis.

This heating procedure caused a decrease in the pressure of iodine and sulphur vapors, which react with telluric and arsenic during the period of constant temperature, which prevents the ampullae's breaking during the period of synthesis. The melting temperatures for binary and ternary compounds (for example AsI_3, As_2S_3, As_2Se_3, As_2Te_3, AsSI, AsSeI, AsTeI, ...) appearing in the five-component system As-S-Se-Te-I were taken into account while selecting these synthesis conditions.

The amorphous character of synthesized samples was controlled by X-ray diffraction on powdered samples. It was used a high-voltage

generator SEIFERT ID 3000 with cooper anticathode whose radiation is monochromatized by nickel filter and diffractometer system PHILIPS PW 1373-PW 1965/50 with proportional counter as detector. The optical controll of amorphous was carried out by polarization microscopy MIN-8. The samples were prepared in a form of parallelepiped 4x4x1 mm. The density of samples was determined by Archimedes's method.
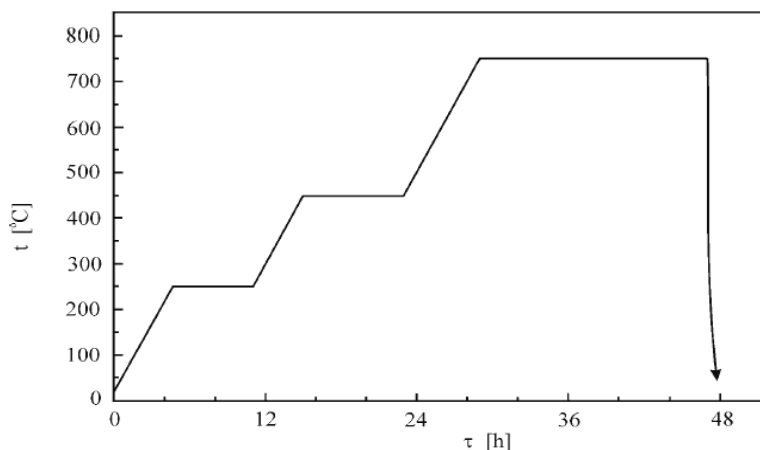
3. RESULTS AND DISCUSSION

The temperature regime of the synthesis is shown on Pict. 4 and Pict. 5.
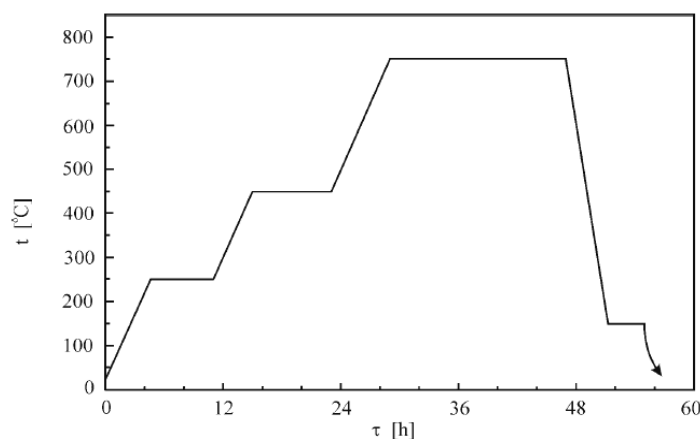
PICTURE 4. THE TEMPERATURE REGIME OF THE SYNTHESIS
OF THE GLASSES IN AS-S-SE-TE-I SYSTEM

All synthesized samples have metallic shine, shell break, and dark-red or dark-gray colors. Pict. 6 illustrate the results of the diffraction at the room temperature on the investigated samples. The absence of diffraction maximums, which characterizes the crystalline phase, confirms the amorphous nature of all investigated samples. It was established by means polariyation microscopy that the samples demonstrate optical homogenous and completely amorphous characteristics. In Table 1. are shown values of density of investigated glasses.


PICTURE 5. THE TEMPERATURE REGIME OF THE SYNTHESIS
OF THE GLASSES IN AS-SE-TE-I SYSTEM
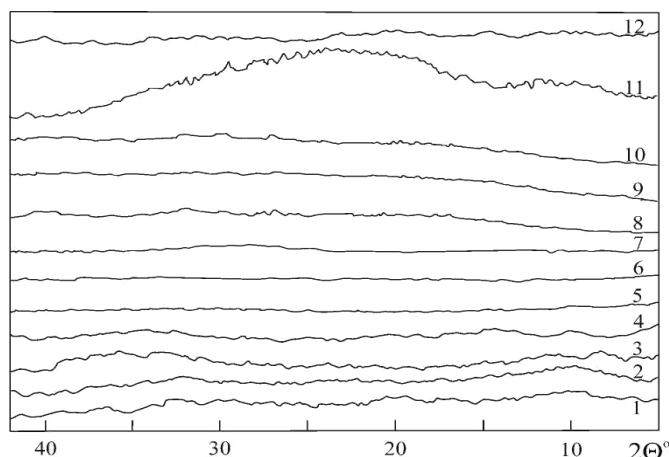
PICTURE 6. DIFFRACTOGRAMS OF $(As2S_3)_x(AsSeo.5Teo.5l)ioo-x^a$ TROOM
TEMPERATURE: 1) x=0; 2) x=10; 3) x=30; 4) x=50; 5) x=65; 6) x=70;
7) x=75; 8) x=80; 9) x=85; 10) x=90; 11) x=95; 12) x=100.

TABLE 1. THE DENSITY OF THE GLASSY SAMPLES
IN THE $(AS_2S_3)_X(ASSEO5TEO5L)IOO-X$ SYSTEM

mol % $AsSe_{0.5}Te_{0.5}I$	$\rho\ [kg/m^3]$
0	3201 ± 3.2
5	3300 ± 2.6
10	3379 ± 2.9
15	3509 ± 4.3
20	3603 ± 2.7
25	3630 ± 3.5
30	3737 ± 1.1
35	3852 ± 2.2
50	3960 ± 6.8
70	4220 ± 4.6
90	4478 ± 7.5
100	4783 ± 9.3
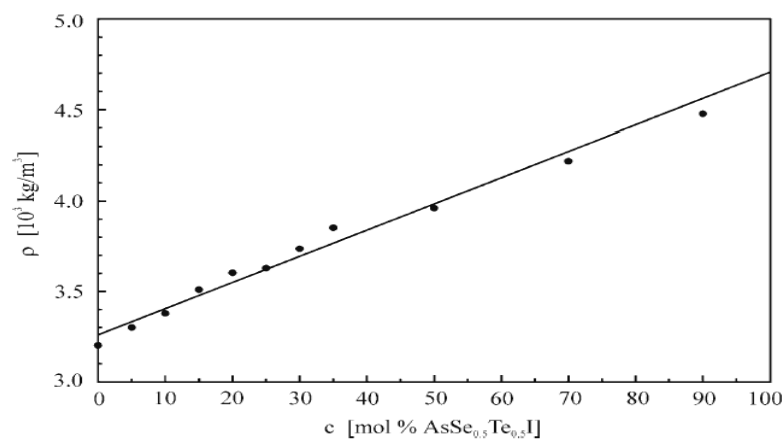
PICTURE 7. THE DENSITY OF THE INVESTIGATED GLASSES
VERSUS MOLAR CONTENT OF AsSe0.5Te0.5I

The functional dependance of the sample density versus its content is shown on Pict.7. As it seen on Pict.7. the sample density linear increasing with decreasing (AsSe0.5Te0.5I) content, which characterized solid solutions. The corresponding analytical form of this term would be as follows:

$$P = 3.262 + 0.0145\ c$$

where c is AsSe0.5Te0.5I content (mol %). This model gives practical possibility to calculate a density of any sample from the $(As_2S_3)x(AsSeo.5Teo.5l)1oo-x$ system.

4. CONCLUSION

This paper presents the elements of technology of obtaining glasses from complex, five-component As-S-Se-Te-I system. The study was carried out on the cut $(As_2S_3)_x(AsSeo.5Teo.5l)1oo-x$ with x=100; 95; 90; 85; 80; 75; 70; 65; 50; 30; 10 and 0 mol %. In view of the previous results obtained in the synthesis [10], the objective was to study in detail the process of their synthesis, which proceeds in several stages. Successive heating and holding the system for several hours at a constant temperature determined in advance, permitted completion of the melting process of starting high-purity elementary components (As, S, Se, Te, I), and successive formation of particular structural units. The amorphous phase of materials was verified by X-ray diffraction on powdered samples and by polarization microscopy. The obtained sample density linear increased with decreased (AsSe0.5Te0.5I) content.

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