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ABSTRACT
of the dissertation for the degree of Doctor of Philosophy

LOCAL STRUCTURE AND PHONON SPECTRUM OF As-Ge-Se AND As-Ge-Te GLASSY SEMICONDUCTOR SYSTEMS

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The work was performed at "Physics and electronics of non-crystalline semiconductors" laboratory of the Institute of Physics of the Ministry of Science and Education Republic of Azerbaijan.

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GENERAL DESCRIPTION OF WORK

Relevance of the research topic: Structural properties of non-crystalline semiconductor materials - absence of translational symmetry and long range order (LRO) in the arrangement of atoms, in the regions surrounding the close neighbors of atoms chosen as centers – in the borders of the first coordination sphere, the existence of interatomic correlation in the region of short range order (SRO) inherent in crystals are also characteristic of chalcogenide glass-like semiconductor (CGS) materials.

The results obtained by diffraction methods and also mathematical modeling of the structure show that outside the short range order region, there is a certain order in the arrangement of structural elements covering several spheres of coordination in nanometer-scale space as well. The main facts that prove the existence of those areas called the medium range order (MRO) areas are the first sharp diffraction peaks (FSDP) observed in the distribution curves of the diffraction intensity ($I(Q)$) of X-rays and neutrons and the structure factor ($S(Q)$) obtained from them. At the same time, inelastic scattering of neutrons, low-frequency Raman scattering of light and other experiments prove the existence of a certain order on a nanometer scale - MRO regions.

The important parameters characterizing close order are the average coordination number (Z), which indicates the number of atoms included in the 1st coordination sphere, and the parameter R, which is determined by the ratio of the number of covalent bonds between chalcogen atoms to the number of covalent bonds between other atoms. The change of the first parameter results in the change of interaction of the atoms, and the change of the second parameter results in the threshold-specific change of chemical bonds. According to the existing theories, the first parameter causes a characteristic change of the local structure, and the second parameter causes a change of the chemical bonds, and should be observed by the corresponding changes of the physical properties. The most convenient objects for studying the role of the mentioned short order parameters in controlling the physical properties of substances are

glass-like multicomponent chalcogenides, which consist of elements differing in coordination numbers. According to the 8-N rule, an atom with the number of N (N ≥4) valence electrons creates 8-N chemical bonds - has that number of close neighbors. Coordination numbers of Ge, AS, Se(Te) atoms are 4, 3 and 2, respectively. In other words, it is possible to change the above-mentioned parameters in a wide range in the glassy As-Ge-Se, As-Ge-Te systems with different chemical compositions.

Such a difference in coordination numbers makes it possible to change the glass-like matrix by changing the chemical composition, and to obtain a one-dimensional, two-dimensional, and three-dimensional structured glass-like material. Such changes occurring in the glass-like matrix should be accompanied by changes in physical properties and should allow obtaining information about the correlation between structure and physical properties and clarifying its possible practical application. Another advantage of such CGS systems is that the vitrification area is quite wide.

The perspective of the materials selected for research is also related to the fact that CGS materials have a wide range of practical application areas. The obtain of materials with high sensitivity, high optical refractive index, high optical non-linearity, and chemical stability in the infrared (IR) region has attracted the attention of researchers as an urgent problem recently. This is primarily due to the fact that materials with the mentioned properties are considered promising materials for optoelectronics, fiber optics, nonlinear optical systems, and memory devices. It is possible to make effect on the macroscopic properties and make a certain contribution to the solution of that problem by changing the chemical composition and adding dopants which leads to the modification of the structure of the multicomponent CGS materials.

The object and subject of the research:

The object of the research is $As_8Ge_6Se_{86}$, $As_{16.67}Ge_{8.33}Se_{75}$, $As_{20}Ge_{10}Se_{70}$, $As_{25}Ge_{12.5}Se_{62.5}$, $As_{18.2}Ge_{18.2}Se_{63.6}$, $As_{17}Ge_{28}Se_{55}$, $As_{16.67}Ge_{8.33}Te_{75}$, $As_{20}Ge_{10}Te_{70}$, $As_{25}Ge_{12.5}Te_{62.5}$, $As_{18.2}Ge_{18.2}Te_{63.6}$, and $As_{17}Ge_{28}Te_{55}$ noncrystalline systems, and the subject of the

research is the study of the local structure and phonon spectrum of the mentioned substances.

The purpose and tasks of the research

In As-Ge-Se and As-Ge-Te chalcogenide glassy semiconductors, the regularities of chemical composition dependence of short and medium range order structure, phonon spectrum, optical, electrical and mechanical properties and correlation between near and medium order parameters are discovered.

To achieve this goal:
- As_8Ge6Se_{86}, $As_8Ge_6Se_{86}$, $As_{16.67}Ge_{8.33}Se_{75}$, $As_{20}Ge_{10}Se_{70}$, $As_{25}Ge_{12.5}Se_{62.5}$, $As_{18.2}Ge_{18.2}Se_{63.6}$, $As_{17}Ge_{28}Se_{55}$, $As_{16.67}Ge_{8.33}Te_{75}$, $As_{20}Ge_{10}Te_{70}$, $As_{25}Ge_{12.5}Te_{62.5}$, $As_{18.2}Ge_{18.2}Te_{63.6}$, $As_{17}Ge_{28}Te_{55}$ CGS materials were synthesized by the rotary furnace method;
- The densities of amorphous samples were measured by the pycnometer method;
- $1 \div 10$ μm thick layers of synthesized substances were obtained by the method of thermal volatile in vacuum;
- X-ray diffraction, phonon spectrum (Raman scattering of light), spectral distribution of the optical absorption coefficient in the visible and near-infrared regions of the spectrum were studied;
- The electric field effect on the charge transport process in the sandwich-structured As-Ge-Se and As-Ge-Te layers was studied in the stationary mode.

Research methods:

The methods of X-ray diffraction, Raman spectroscopy, optical spectroscopy and electric field effect on charge transport were used to study the local structure, phonon spectrum and electronic properties of As-Ge-Se and As-Ge-Te non-crystalline substances.

The main provisions submitted to the defense:

1. Correlation distance of local structure parameters of As-Ge-Se and As-Ge-Te layers which differ in chemical composition,

quasi-period in MRO regions, and numerical values of the sizes of nanocavities;

2. Types of structural elements and chemical bonds between atoms that form the amorphous matrix of As-Ge-Se and As-Ge-Te layers and the changes that occur in them depending on the chemical composition;

3. Observation of different areas in graphs of dependence of physical parameters - the density of the substance, the average value of the atomic volume, the coefficients of compaction and compactness, and the cohesive energy of As-Ge-Se system on average coordination number and R parameter and relating it to the existence of flexible, isostatic and high-strain elastic states;

4. Correlating the dependence of the width of the forbidden zone, the cohesive energy, the average value of the bond energy on the Z and R parameters of the As-Ge-Se layers with the presence of a topological and chemical threshold;

5. Correlating the fact that the dependence of the substance density, the average value of the atomic volume, compaction and compactness coefficients on Z and R in the layer with chemical composition of $As_{25}Ge_{12.5}Te_{62.5}$ have an extremum at R=1, Z=2.5 with the occurrence of a 2D→3D transition in the structure of the As – Ge – Te system;

6. From the Te-$Ge_xAs_yTe_{100-x-y}$-Al structure (when Te creates a positive potential on the electrode) with an electric field applied in the straight direction, the charge transport processes occur with monopolar injection currents located below the Fermi level and the holes are controlled by shallow levels;

7. Explanation of the topological properties of amorphous chalcogenides of the N-shaped region, the role of U-centers and the recombination-generation processes of charge carriers, observed in the Volt-Ampere Characteristics of the Te-$Ge_xAs_yTe_{100-x-y}$-Al structure when a negative potential is applied to the Te electrode.

Scientific novelty of the study:

- For the first time, the dependence of the short- and medium-range local structure parameters, phonon spectrum, optical, electrical and mechanical properties of As-Ge-Se and As-Ge-Te thin layers on the chemical composition was studied in complex form;
- Depending on the chemical composition in As-Ge-Se and As-Ge-Te thin films, the changes of the correlation distance, the quasi-period within the MRO region, the compaction and compactness coefficients, the limitations in the numerical values and the average value of the atomic volume were experimentally observed and the obtained results explained based on the cluster model and the theory of topological constraints;
- The types of chemical bonds forming the amorphous matrix of As-Ge-Se and As-Ge-Te layers, the main structural elements were determined, and the changes occurring in them depending on the chemical composition were defined.
- The dependence of the optical width of the forbidden zone, average bond energy, cohesive energy and density of the substance on the average coordination number and the parameter R, which determines the type of chemical bonds, are explained by the presence of topological and chemical thresholds in the investigated CGS systems;
- The changes in the phonon and optical absorption spectra, the optical width of the forbidden zone, the dependence of the average value of the bond energy on the chemical composition were explained based on the basic principles of the chemical bond approximation model, taking into account the presence of local electronic states at the border of the allowed zones;
- The charge transport process from the Te-$Ge_xAs_yTe_{100-x-y}$-Al structure was studied by applying an electric field in two directions (creating a positive and negative potential in the Te electrode) and the obtained results were explained taking into account the topological properties of amorphous

chalcogenides, the role of U-centers and the recombination-generation processes of charge carriers.

Theoretical and practical significance of the study:

The results of the dissertation can be applied in determining the mechanisms of phonon and electronic properties of complex-component chalcogenide glassy semiconductors;

The studied CGS As-Ge-Te system differs from other glass-like materials by its transparency in the range of 3-20 μm wavelength and high optical refractive index value (n~3.5 at 1.55 μm wavelength value). Materials with the mentioned properties are considered promising materials for optoelectronics, fiber optics, non-linear optical systems and memory devices. In the dissertation, the extensive study of the dependence of the mechanical, electrical, and optical parameters of the research areas on the coordination number, which are short range order parameters, and on the R parameter, which characterizes the type of bonds, can be useful in choosing chemical compositions suitable for those application areas.

Approbation and application:

The results of the dissertation were presented at the following scientific conferences:

- International Conference on "Modern Directions in Condensed Matter Physics" (MTCMP-2018, Baku, Institute of Physics) dedicated to the 100th anniversary of Academician H.B. Abdullayev;
- 11th International Conference on Amorphous and Microcrystalline Semiconductors (St. Petersburg, 2018);
- 9th International Conference on "Amorphous and Nanostructured Chalcogenides" (Republic of Moldova, Chisinau, 2019);
- XII International Conference on "Electronic Processes in Organic and Inorganic Materials" (ICEPOM-12, Kamianets-Podilsky, Ukraine, 2020);
- XII International Conference on Amorphous and Microcrystalline Semiconductors (St. Petersburg, 2021).

- Conference on "Physics of Composite Structures" dedicated to Academician M.H.Shakhtakhtinsky's 90th anniversary (Nakhchivan, 2022).
- XIII International Conference on Amorphous and Microcrystalline Semiconductors (St. Petersburg, 2023).

16 scientific works have been published in local and foreign scientific publications on the subject of the dissertation work. 9 of them are articles and 7 are conference materials.

Name of the organization where the dissertation work is done:

The dissertation work was performed at the Institute of Physics of the Azerbaijan National Academy of Sciences.

The structure and volume of the dissertation:

The dissertation is presented in 135 pages, consisting of an introduction, four chapters, conclusions and a bibliographic list of 144 cited literature. There are 24 pictures and 10 tables in the dissertation work. Exculding figures, tables and list of references, introduction consist of 19746, Chapter I 46898, Chapter II 10301, Chapter III 37619, Chapter IV 50423 characters. The results 2620, and the abbreviations and symbols consist of 3716 characters. Thus, total nomber of characters in the dissertasion 171323.

THE MAIN CONTENT OF THE DISSERTATION

In the **introduction**, the relevance of the topic of the dissertation is justified, the purpose of the work, scientific novelty, and practical importance is shown, information about the main provisions to be defended, approbation degree and publications is given, also, the main content of each chapter is briefly explained.

In the first chapter, modern research works related to the obtaining amorphous and glassy substances, their atomic and local structure, and the study of their physical parameters were analyzed. In CGS systems, the presence of long range order (LRO) - that is, the absence of periodicity in the arrangement of atoms, and the presence

of short range order (SRO), that is, the regular distribution of the coordinates of atoms neighboring any atom plays a key role in the formation of properties of non-crystalline substances including As-Ge-Se and As-Ge-Te CGS systems. At the same time, the slight difference of these parameters from the parameters specific to the crystal causes the physical properties to differ sharply from the crystals. At the same time, it should be noted that the existence of the average order structure (MRO) appears as a main problem in the recent scientific literature about the study of amorphous and glassy substances. Average order is the correlation between atoms located at large distances from the radius of the first coordination sphere and a certain regularity in the arrangement of atoms outside the boundaries of the first coordination sphere.

The analysis of the existing literature shows that despite the fact that enough research has been done in this field, it is still important to explain the mechanism of the physical processes occurring in the As-Ge-Se and As-Ge-Te CGS systems and also works need to be done to obtain materials with stable properties that are useful in practice. The selection of the compositions mentioned as the object of research in the dissertation work is related to the numerical difference of valence electrons in the atoms of the elements included in it. The difference in the coordination number of these atoms makes it possible to change the structure of the glassy matrix by changing the chemical composition, that is, to obtain a glassy matrix with a one-, two-, and three-dimensional structure.

Thus, the analysis of existing scientific literature provides certain information about the local structure of CGS materials, the types and physical properties of chemical bonds and structural elements involved in the formation of amorphous matrix. However, the lack of studies devoted to the role of topological properties in the explanation of the physical properties of CGS materials, the lack of studies done on multicomponent objects that allow Z and R to vary in a wider range, creates certain difficulties in obtaining extensive information about the local structure of substances, as well as in clarifying the methods of determining and controlling the mechanism of optical, charge transport and other physical processes, and in this

direction it is necessary to do new researches with a high information capacity.

Thus, the extensive analysis of the scientific literature creates the impression that the research done in the dissertation work can make a certain contribution to the solution of the main problem, both scientifically and practically.

In the **second chapter**, the methods of obtaining amorphous and glassy materials, as well as the synthesis technology of $As_8Ge_6Se_{86}$, $As_{16.67}Ge_{8.33}Se_{75}$, $As_{20}Ge_{10}Se_{70}$, $As_{25}Ge_{12.5}Se_{62.5}$, $As_{18.2}Ge_{18.2}Se_{63.6}$, $As_{17}Ge_{28}Se_{55}$, $As_{16.67}Ge_{8.33}Te_{75}$, $As_{20}Ge_{10}Te_{70}$, $As_{25}Ge_{12.5}Te_{62.5}$, $As_{18.2}Ge_{18.2}Te_{63.6}$, $As_{17}Ge_{28}Te_{55}$ materials selected as the research object, and the methods used in the study of the local structure are explained. Layers with a thickness of $1 \div 10$ μm were obtained by the method of thermal evaporation in a vacuum. Researches were mainly carried out in the D2 PHASER powder diffractometer produced by the German company Bruker, in the Nanofinder-30 three-dimensional confocal laser microspectrograph (Tokyo Instr., Japan), in the SPEKOL 1500 UV-VIS spectrophotometer, and the parameters specific to the samples were calculated with the software corresponding to those methods. Spectral dependences of the optical emission coefficients of the studied thin films were computerized in automatic mode using WINASPEKT package software. Transferring the obtained experimental results to the computer was achieved through the RS-232 interface of the spectrophotometer. Optical studies were performed in the wavelength range $\lambda = 190 \div 1100$ nm and at room temperature. The photometric accuracy of the SPEKOL 1500 spectrophotometer used during the mentioned studies was ~0.01 Å.

The third chapter is devoted to the interpretation of the results obtained from the study of the local structure, topological and mechanical properties of the layers obtained on the basis of CGS As-Ge-Se and As-Ge-Te systems by the methods of X-ray diffraction, Raman spectroscopy and the application of the basic principles of the theory of limits. On the basis of X-ray diffraction experiments, the local structure parameters (quasiperiod and correlation length in the

medium order region) of the As-Ge-Se glassy system were determined.

Also, the dependence of physical parameters (density, packing coefficient, compactness, average value of atomic volume, number of unpaired electrons, cohesive energy) on average coordination number and parameter R, which determines the character of chemical bond between atoms, was determined.

X-ray diffraction curves of As-Ge-Se and As-Ge-Te layers obtained by thermal evaporation in vacuum is shown in Figure 1.
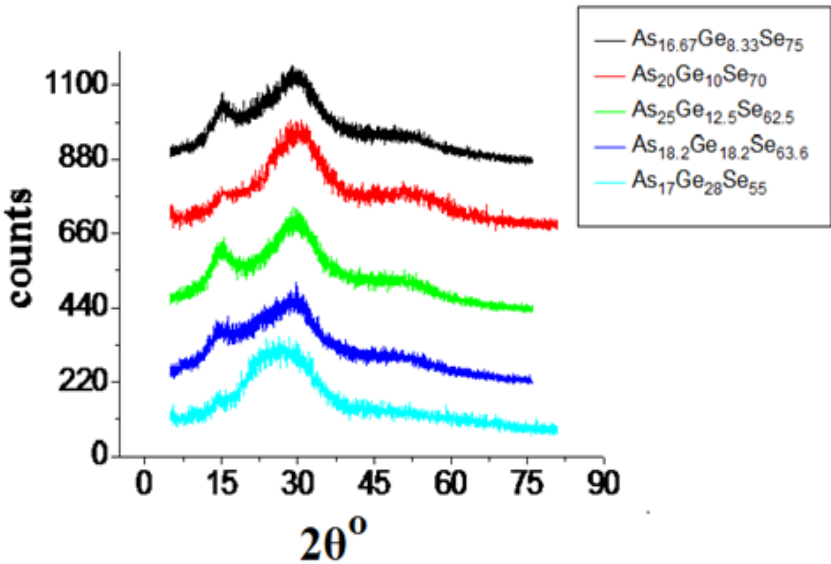
a)
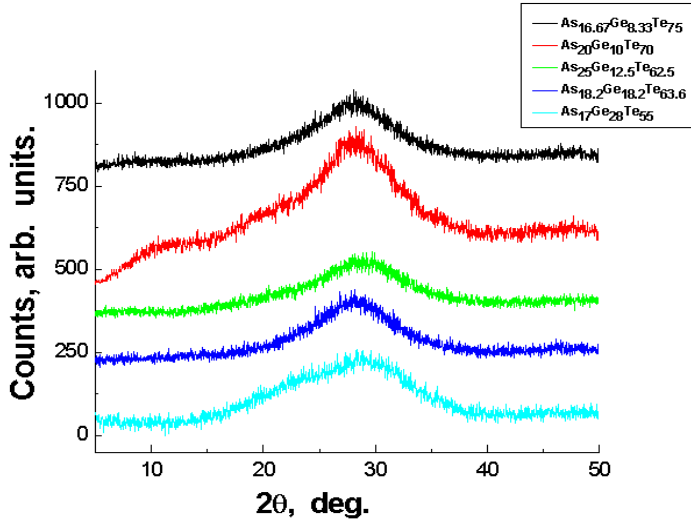
b)

Figure 1. Intensity distribution in X-ray diffraction of As-Ge-Se (a) and As-Ge-Te (b) layers obtained by thermal evaporation in vacuum.

The wide maxima observed in the diffraction pattern prove the amorphous nature of the studied samples. In As-Ge-Se systems, the first sharp diffraction peak (FSDP), which differs from other diffraction peaks due to its anomalous dependence on temperature and pressure typical of most glassy substances, is observed in the X-ray diffraction scattering intensity distribution graph (Fig. 1.a). In the As-Ge-Te system, FSDP is observed only in layers with chemical composition $As_{20}Ge_{10}Te_{70}$ (Figure 1.b). Based on modern points of view about the local structure of non-crystalline substances, it can be concluded that the difference observed in the diffraction pattern of the studied objects is related to the difference in their local structure characteristics. In other words, the observation of FSDP in all studied chemical compositions of the As-Ge-Se system indicates the formation of an medium order range in them. In the As-Ge-Te system, the observation of FSDP in a layer with a chemical composition such

as $As_{20}Ge_{10}Te_{70}$, which corresponds to the value of the average coordination number of 2.4, shows that the medium order range is formed only in that composition. Thus, this experimental fact indicates that the structure of the As-Ge-Te system has a higher degree of disorder. The observation of FSDP only in $As_{20}Ge_{10}Te_{70}$ can be explained by the formation of topological regularity (Z=2,4).

Molecular dynamics or other atomic modeling are usually used to study the structure of amorphous and glassy substances at the molecular level. However, the mentioned methods cannot fully provide the interpretation of the physical processes occurring in them at the microscopic level. According to leading scientists involved in explaining the structure of non-crystalline materials and the physical processes occurring in them at the microscopic level, the improvement of such methods still requires long-term research. However, the theory of topological constraints (TTC), used by researchers recently, has been successfully used to explain the dependence of the physical properties of substances on their chemical composition. This method was successfully used in the presented dissertation.

The chemical and topological order of the amorphous matrix characteristic to materials with a disordered structure is characterized by R parameter and the average coordination number (Z). Therefore, the dependences of the physical parameters characterizing the local structure of the studied substances, especially density (ρ_a), average atomic volume (V_a), packing coefficient ($\varkappa_l$), compactness coefficient (δ_a) on Z (a) and R (b) were investigated. As a final result of the conducted analyses the presence of an extremum(for parameters ρ, $\varkappa$, δ maximum, for V minimum) in the graphs of dependence of the densities, average atomic volumes, packing coefficient, compactness, and cohesive energy of the chemical compositions included in the As-Ge-Se and As-Ge-Te systems on Z and R is associated with the chemical leakage threshold (at values of Z = 2.5; R = 1). And it is shown that this extremum corresponds to stoichiometric $Ge_{12.5}As_{25}Se_{62.5}$, $Ge_{12.5}As_{25}Te_{62.5}$ compositions. The expressions $[0.625(As_{0.4}Se_{0.6})]$ · $[0.379(Ge_{0.333}Se_{0.666})]$, $[0.625(As_{0.4}Te_{0.6})]$ · $[0.379(Ge_{0.333}Te_{0.666})]$ were proposed for the chemical formulas of those compounds. The characteristics of the dependences noted in the

values of Z = 2.5 – 2.55 and R = 1 – 0.998 were considered as the isostatic hard glass state, which forms the transitional phase between the flexible and high-tension hard glass states of the substances of the chemical composition ($As_{25}Ge_{12.5}Se_{62.5}$, $As_{18.2}Ge_{18.2}Se_{63.6}$, $As_{25}Ge_{12.5}Te_{62.5}$ and $As_{18.2}Ge_{18.2}Te_{63.6}$) corresponding to that interval. Compositions (As18.2Ge18.2Se63.6; As17Ge28Se55; As18.2Ge18.2Te63.6; As17Ge28Te55) corresponding to values Z > 2.55, R < 0.998 (As18) correspond to high-tension hard glass.

Raman scattering spectra (phonon spectra) of As-Ge-Se and As-Ge-Te systems are shown in Figure 2 and Figure 3. As can be seen from Figure 2, in the Raman scattering spectrum of the light belonging to the $As_{16,67}Ge_{8,33}Se_{75}$ CGS composition, peaks with a characteristic frequencies of 218, 220, 230, 236, 252 cm^{-1} covering the frequency range of 198-285 cm^{-1} and a dependence with a clear inclination in the range of 265÷285 cm^{-1} and also wide scattering bands located in the range of 178÷198 cm^{-1} were observed. In the spectrum, peaks corresponding to frequencies of 230 cm^{-1} and 252 cm^{-1} were associated with symmetric stretching of $AsSe_{3/2}$ structural elements, vibrations of Se_8 rings and Se-Se-Se chain molecules, respectively. The maximum at 195 cm^{-1} frequency observed in the spectra of all compositions (particularly evident in the spectra of compositions 2 and 6) is associated with the vibration of Ge-Se bonds present in the $GeSe_4$ tetrahedron. The structural elements forming the amorphous matrix of the studied substances, the types of chemical bonds and the changes occurring in them with the variation of the chemical composition were explained based on the basic principles of the chemical bond approximation model. According to the chemical bond aproch model, heteropolar bonds are more likely to form than homopolar bonds, and bonds with higher bond energies are formed first. This process continues until the valence requirements of the atoms are met. It should be noted that the conclusion of the chemical bond approximation model is that in multicomponent chalcogenide glassy systems (for example, in the As-Ge-Se system with a wide range of coordination number) there is a critical component consisting of only heteropolar bonds. From this point of view, it is obtained from the application of the mentioned model that the 4th composition described

in table 1 consists of pyramidal ($AsSe_{3/2}$) and tetrahedral ($Ge[Se_{1/2}]_4$) structural elements composed of energetically favorable heteropolar bonds.

Numerical values of quantity of constraints (N_{co}), R-parameter and average coordination number (Z) for materials with different chemical compositions included in the CGS As-Ge-Se system.

Chemical composition	Z	R	N_{co}
$Ge_6As_8Se_{86}$	2,2	3,58	2,5
$Ge_{8.33}As_{16.67}Se_{75}$	2,33	1,8	2,83
$Ge_{20}As_{10}Se_{70}$	2,4	1,4	3
$Ge_{12.5}As_{25}Se_{62.5}$	2,5	1	3,25
$Ge_{18.2}As_{18.2}Se_{63.6}$	2,55	0,998	3,375
$Ge_{28}As_{17}Se_{55}$	2,73	0,675	3,825

The chemical formula of that substance can be shown as $0.625(As_{0.4}Se_{0.6})$ $0.375(Ge_{0.333}Se_{0.666})$. The formation of the first 3 compositions described in the table includes pyramidal ($AsSe_{3/2}$) and tetrahedral ($Ge[Se_{1/2}]_4$) structural elements consisting of heteropolar bonds, as well as homopolar bonds formed between chalcogen atoms (Se). That is, in this case, the residual Se atoms participate in the formation of bonds between the indicated pyramidal and tetrahedral structure elements, and also create bonds among themselves in the form of ring and chain structures specific to Se. The mentioned structural features were confirmed by the observation of clearly visible maxima corresponding to the vibration of ring (Se_8) ($252 cm^{-1}$) and chain molecules of -Se-Se-Se-…($236 sm^{-1}$) in the Raman scattering spectrum of the light belonging to composition 1 described in table 1. Studies show that the spectrum undergoes a noticeable change with a decrease in the concentration of chalcogen atoms. As a result, the scattering band ($198 \div 285 cm^{-1}$) corresponding to structural elements dominated by covalently linked Se atoms gradually weakens and

disappears. As a result, a new scattering band covering the interval $170 \div 218$ cm^{-1} and a broad maximum with a frequency of ~195 cm^{-1} appear, which is related to the symmetric scattering oscillations of the tetrahedral (Ge[Se$_{1/2}$]$_4$) structural elements. Ge-Se connections with high bond energy (table 1) are more likely to be formed, and therefore, the peak with a frequency of ~195 cm^{-1} belonging to tetrahedral (Ge[Se$_{1/2}$]$_4$) structural elements is more intense in the spectrum. The latter composition, described in Table 1, differs mainly in the presence of residual non-chalcogen atoms. Therefore, due to the high bond energy (Ge-Se), the possible valence requirements of most germanium (Ge) atoms are met and the residual amount of non-chalcogen atoms (As, Ge) mainly forms Ge-As, As-As bonds. Oscillations related to the peaks observed in the frequency range of $170 \div 185$ cm^{-1} in the spectrum are explained by the presence of the mentioned bonds (Ge-As, As-As). As a result of the analysis, it was determined that the scattering band falling in the frequency interval of 198-285 cm^{-1}, the maxima with frequencies of 252 cm^{-1} and 236 cm^{-1} corresponding to the oscillations of ring (Se$_8$) and chain (- Se-Se-Se- ...) selenium molecules were observed in the As-Ge-Se system (Ge$_6$As$_8$Se$_{86}$ and Ge$_{8.33}$As$_{16.67}$Se$_{75}$) with low content of As and Ge. With increasing concentration of As and Ge atoms, those bands and maxima gradually weaken and a new band covering the frequency range of 170-218 cm^{-1} and maxima with frequencies of 195 cm^{-1} and 235 cm^{-1} appear corresponding to the oscillation of Ge(Se$_{1/2}$)$_4$, AsSe$_{3/2}$ structural elements.

As can be seen from Fig. 3, mainly two scattering bands are observed in the spectrum of As$_{16,67}$Ge$_{8,33}$Te$_{75}$ composition. The first scattering band covers the $100 \div 137$ cm^{-1} interval of the spectrum where maxima with frequencies of 121 cm^{-1} and 137 cm^{-1} are observed, and the second scattering band covers the frequency interval of $135 \div 245$ cm^{-1} with a maximum of 153 cm^{-1}. The 121 cm^{-1} frequency maximum observed in the 1st scattering band is associated with oscillations of GeTe$_4$ tetrahedral structure elements (symmetric strain mode of A$_1$- oscillation modes) and at the same time symmetric bending oscillations of pyramidal AsTe$_3$ (A$_1$-oscillation mods) modes.
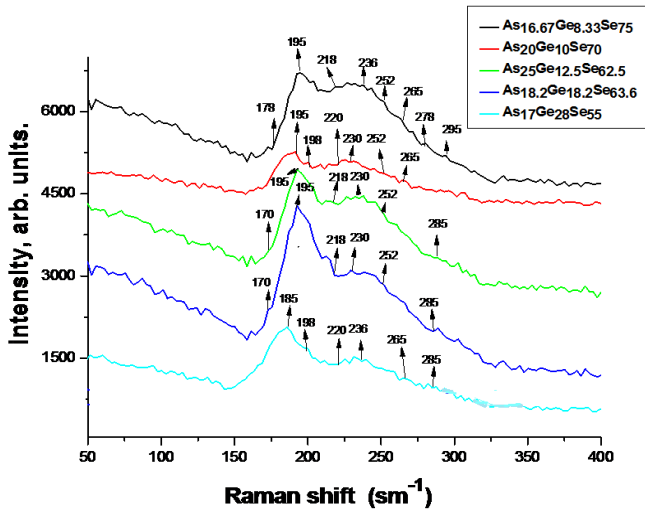
Figure 2. Raman scattering spectra (phonon spectra) of light in the CGS As-Ge-Se system.
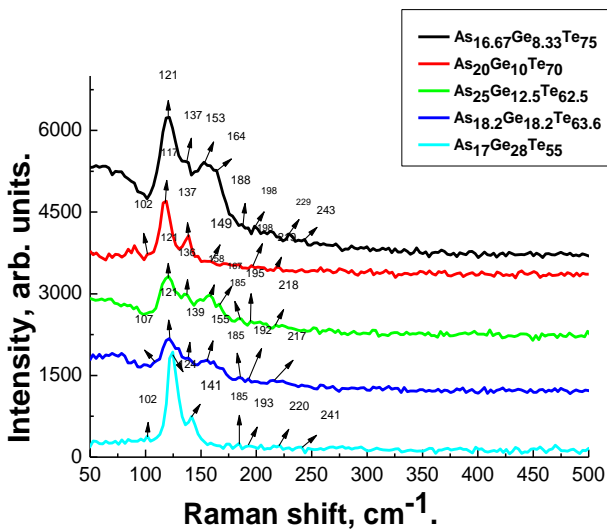

Figure 3. Raman scattering spectra (phonon spectra) of light in As-Ge-Te systems.

The scattering band with maxima covering the frequency range of $136 \div 141$ cm^{-1} observed in all the studied chemical compositions, has a greater intensity in the samples ($As_{16.67}Ge_{8.33}Te_{75}$ and $As_{20}Ge_{10}Te_{70}$ table 3.2.1) with a high atomic percentage of tellurium. This result is mainly associated with the oscillations of irregularly arranged small-sized tellurium chains. A similar result was recorded in amorphous tellurium with a scattering band with a maximum frequency of 157 cm^{-1}. It was shown that the frequency of these oscillations shifts due to the long-range interactions between the tellurium chains. The scattering band related to the maximum observed in the spectrum at the value of frequency 159 cm^{-1} is related to $AsTe_3$ (E-mode) antisymmetric bending vibrations of pyramidal structural elements, as well as A_1-oscillation mode of $GeTe_4$ structural elements characterized by a tetrahedral separation edge or vibrations of disordered Te-Te chains, as in amorphous tellurium. On the other hand, the weak scattering band observed in the frequency range of $185 \div 195$ cm^{-1} of the spectrum is associated with the oscillations of $GeTe_3$ octahedral structural elements. However, in this case, oscillations of structural elements associated with the presence of arsenic (As) atoms are not excluded. If we take into account that the scattering bands observed in the frequency ranges of $185 \div 195$ cm^{-1} and $220 \div 230$ cm^{-1} in the spectrum are related to the partially symmetric (A1-oscillation mode) and antisymmetric valence oscillations (E-oscillation mode) of pyramidal $AsTe_3$ structural elements, it turns out that , with the increase in the concentration of arsenic (As) and germanium (Ge), the maxima observed in the high frequency region weaken or completely disappear. Indeed, in the samples marked with numbers 2, 3, 4 and 5, the intensity of Raman scattering is sharply weakened in the region covering the frequencies of the spectrum $141 \div 230$ cm^{-1}, and that scattering band completely disappears in the last sample. Such changes observed in the spectrum can be explained by the decrease in the relative share of structural elements in which tellurium atoms participate in those chemical compositions.

The reason for the formation of a broad maximum with a frequency of 124 cm^{-1} in the phonon spectrum of $As_{16,67}Ge_{8,33}Te_{75}$,

which has a high atomic percentage of tellurium, is the oscillation of the structural elements and irregularly distributed tellurium chains in which tellurium atoms participate. In $As_{17}Ge_{28}Te_{55}$ with a low atomic percentage of tellurium, the relative share of oscillations of the above-mentioned disordered chains is very small, and as a result, the width of the scattering band is reduced. The narrow-width maximum observed in the spectrum at the frequency of 141cm^{-1} was attributed to the E-oscillation modes of crystalline tellurium (Te). Weak maxima observed in the $102 \div 107$ cm^{-1} frequency range of the Raman scattering spectrum of samples No. 2-5 were also observed in the phonon spectrum of the As-Ge-Se system. This is explained by the high final relative share of oscillations related to As-As and Ge-As connections. The characteristics observed in the phonon spectrum and also other properties observed in electronic processes of the amorphous layers of the studied materials should be explained by the changes in the types of chemical bonds and structural elements that form the amorphous matrix with the change of the chemical composition, based on the basic principles of the chemical bond approximation model. According to the chemical bond approximation model, the stoichiometric compositions corresponding to Z = 2.5 and R = 1 are composed only of heteropolar bonds. In the first and second samples rich in tellurium, along with heteropolar As-Te and Ge-Te bonds, homeopolar bonds are formed (R>1). In compositions with a deficiency of chalcogen atoms (R<1), the concentration of As-As homeopolar bonds is high (the valence requirements of most germanium atoms are completely satisfied because the energy of Ge-Te bonds is high enough). Changes in the types of chemical bonds can be explained by taking into account the basic principles of the chemical bond approximation model. Indeed, the stoichiometric amorphous matrix of $As_{25}Ge_{12.5}Te_{62.5}[0,625(As_{0,4}Te_{0,6})]\cdot[0,379(Ge_{0,333}Te_{0,666})]$ chemical composition is formed from tetrahedral $Ge[Te_{1/2}]_4$ and pyramidal $AsTe_{3/2}$ structural elements from heteropolar bonds. The observation of the oscillation mode (157 cm^{-1}) characteristic of the irregularly located small Te chain in the phonon spectrum of these samples and also the presence of vibration mode (141 cm^{-1}) belonging to

homeopolar Te-Te bonds between pyramidal and octahedral structural elements In samples containing $As_{17}Ge_{28}Te_{55}[0.826(Ge_{0.333}Te_{0.666})]$ · $[0.012(Ge_{0.429}As_{0.571})]$ · $[As_{0.163}]$ indicates that a slight deviation from the chemical approximation model has occurred.

Thus, as a result of the study of the phonon spectrum in the As-Ge-Te system, the main structural elements and types of chemical bonds that form the amorphous matrix of that system have been determined. It was determined that the amorphous matrix of the stoichiometric composition $As_{25}Ge_{12.5}Te_{62.5}$ (R=1) system mainly consists of tetrahedral $Ge[Te_{1/2}]_4$ and pyramidal $AsTe_{3/2}$ structural elements. However, frequencies corresponding to the oscillations of $AsTe_3$-type pyramidal, $GeTe_3$-type octahedral structural elements and Te-Te chemical bonds are also observed in the phonon spectrum. The formation of high-frequency maxima in compositions with an excess of tellurium atoms ($As_{16.67}Ge_{8.33}Te_{75}$, $As_{20}Ge_{10}Te_{70}$) and low-frequency oscillations in compositions with a deficiency of tellurium atoms ($As_{17}Ge_{28}Te_{55}$) indicates a partial deviation from the chemical approximation model.

In the **fourth chapter**, the studies dedicated to clarifying the correlation between the optical and charge transport properties of the As-Ge-Se and As-Ge-Te systems, and the parameters characterizing those properties and close order are explained. As a result of these studies, to determine the optical width of the forbidden zone, the transmission spectra of the samples were studied at high values of the optical absorption coefficient (α), the obtained results are depicted in Figure 4.(a,b) as a dependence of *(αhv)$^{1/2}$* on the photon energy (hv). By experimentally measuring the optical emission spectra and densities of the studied objects and making some calculations, the dependence of both the optical width of the forbidden zone and physical parameters such as cohesive energy, average bond energy, conformation coefficient, the average coordination number (Z) and the R parameter of the compactness of atoms was investigated. It is known that the nature of the zone structure of chalcogenide glasses is associated with p-orbital states of chalcogen atoms. According to the mentioned approach, the valence zone of CGS substances is created

due to lone pair electron (LPE) states, and the conduction zone is created due to antibonding states (σ^*).
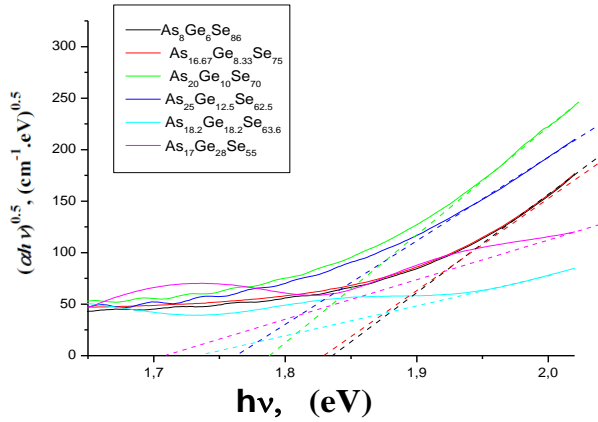
a)
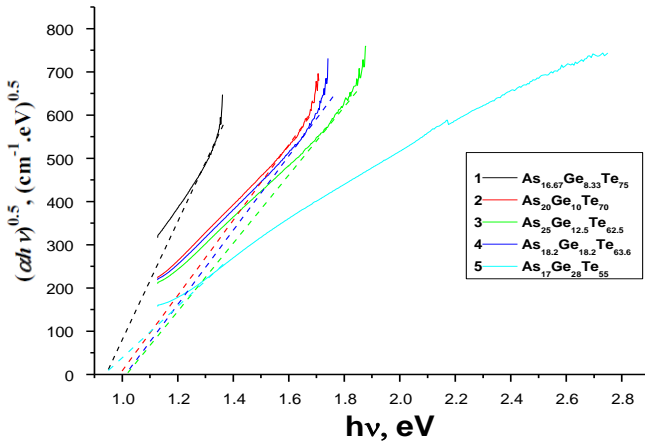
b)

Figure 4.1.1 Optical absorption spectrum of As-Ge-Se (a), As-Ge-Te (b) CGS system

According to this approach, the experimentally determined optical width of the forbidden zone (E_g) σ^* corresponds to the energy distance between the lowest energy state of the states and the upper boundary of the LP states. Therefore, the value of E_g will depend on the result of changes in the mentioned energy states (LP and σ^*). An increase in the coordination number leads to a strengthening of the interaction between atoms. As a result of the mentioned process, the σ^* states are more separated from each other, and thus the lower boundary of the conduction zone shifts downwards, and as a result, the value of E_g decreases (As-Ge-Se). At the same time, the width of the optical forbidden zone (E_g) depends significantly on the changes in the density of the substance, the cohesive energy (the energy required to break all the bonds) and the values of the average bond energy. It was determined that the dependence of the substance density on the average coordination number for samples containing selenium and tellurium has a different character. An increase in Z is accompanied by an increase in the density of the former and a decrease in the density of the latter. This fact shows that short order effects are stronger in selenium-containing substances, and weaker in tellurium-containing substances, and is associated with the fact that selenium has a higher chemical activity than tellurium. As can be seen from the dependence of the cohesive energy (CE) on the values of Z and R (table 4.1.1), the $Ge_{20}As_{10}Se_{70}$ composition with values of Z=2.4, R=1.4 has the most optimal stability. The maximum in values of average bond energy was observed when Z=2.55 (R=0.998), and the analogous result in packing density was observed in case of Z=2.5 (R=1). The regularity of dependence of all parameters (E_g, E_1, CE, E_m, $\varkappa$) on Z and R in the studied substances differs from other areas in the interval Z=2.5÷2.55 (R=0.998÷1). Thus, by applying the Taus method to the spectrum of the optical absorption coefficient of As−Ge−Se and As−Ge−Te CGS systems, the optical width of the forbidden zone was determined for all compositions. Based on the analysis of graphs of dependence of the optical width of the forbidden zone, cohesive energy, experimentally determined density, molar volume, compactness coefficient on the average coordination number and the R parameter characterizing the type of chemical bonds, the possible explanation of the changes in the

width of the forbidden zone was interpreted. The obtained results were explained based on the basic principles of the chemical bond approximation model, taking into account the presence of local states near the boundaries of the allowed zones. The analysis of the mentioned dependencies made it possible to put forward the idea of the existence of both a topological and a chemical leakage threshold in the studied CGS systems. Based on the results of the existing researches, for the $As_{25}Ge_{12.5}Te_{62.5}$ (R = 1, Z = 2.5) composition, the density of matter, packing and compactness coefficients of atoms have a minimum value, and the average atomic volume has a maximum value associated with the 2D→3D structure transition.

In this chapter, the results of the studies devoted to the investigation of the electric charge transport mechanism in the stationary mode from the $Te-Ge_xAs_yTe_{100-x-y}-Al$ structure are explained. Figure 5 shows the room temperature volt-ampere characteristic (VAC) of glassy chalcogenide $Ge_{8.33}As_{16.67}Te_{75}$, $Ge_{10}As_{20}Te_{70}$, $Ge_{12.5}As_{25}Te_{62.5}$.
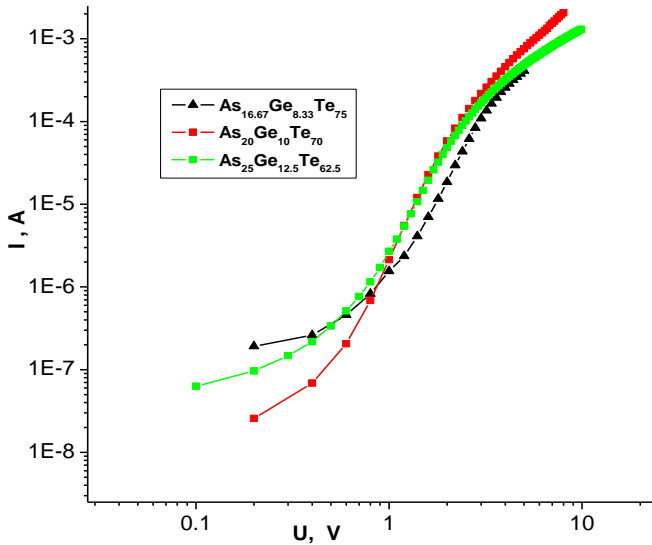
Figure 5. VAC of CGS Ge$_{8.33}$As$_{16.67}$Te$_{75}$, Ge$_{10}$As$_{20}$Te$_{70}$, Ge$_{12.5}$As$_{25}$Te$_{62.5}$ compositions.

When the tellurium electrode is charged with a positive potential, the typical characteristics of the VAC of the Te-$Ge_xAs_yTe_{100-x-y}$-Al system with a sandwich structure are explained by the Pul-Frenkel mechanism, the applying of Fermi-Dirac distribution for the energy distribution of occupied charge carriers and also taking into account the concentration of free and occupied charge carriers (holes) in the Poisson equation. The transition from the area of sharp increase in the current intensity of VAC to the untrapped quadratic law was associated with the decrease of the height of the Coulomb barrier to zero, and the corresponding critical value of the electric field intensity was calculated. The minimum value of the concentration of transport-controlling traps for the $Ge_{12.5}As_{25}Te_{62.5}$-containing CGS material was associated with the improved matrix corresponding to that composition.

Figure 6 shows the VAC measured at room temperature when a negative potential is applied to the tellurium electrode of the Te-$Ge_xAs_yTe_{100-x-y}$-Al sandwich structure.

The legend of the figure:

1 — □ — $As_{16.67}Ge_{8.33}Te_{75}$
2 — ✕ — $As_{20}Ge_{10}Te_{70}$
3 — ● — $As_{25}Ge_{12.5}Te_{62.5}$
4 — ★ — $As_{18.2}Ge_{18.2}Te_{63.6}$
5 — ■ — $As_{17}Ge_{28}Te_{55}$
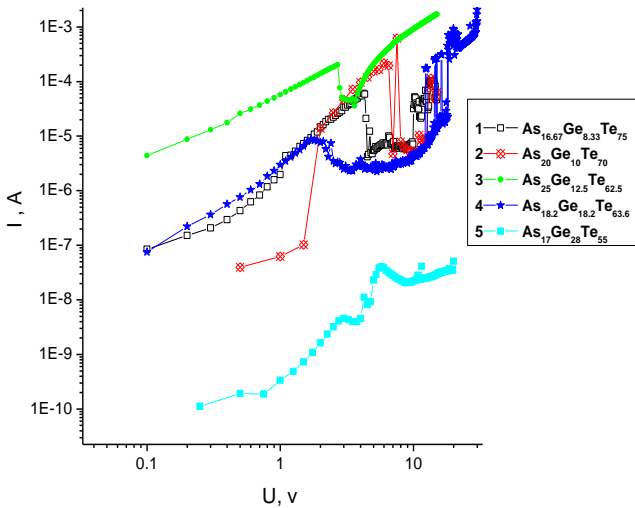
Axes: I, A (vertical); U, v (horizontal)

Figure 6. VAC of the Te-$Ge_xAs_yTe_{100-x-y}$-Al sandwich structure when a negative potential is applied to the tellurium electrode.

As can be seen from Figure 6, in the case of negative potential applied to the tellurium electrode VAC differs sharply from the dependence (Figure 5.) describing the case of positive potential applied to the tellurium electrode. In this case, with an increase in voltage, the linear region of VAC is replaced by a region of non-linear dependence. Finally, starting from the value of the electric field voltage $\sim 5 \times 10^4$ V/cm, the transition of the characteristic to the N-shaped part occurs. It is known that theoretical concepts explaining electronic processes in crystalline substances are mainly based on the periodicity of the structure. However, since there is no long-range order (LRO) in the structure of non-crystalline substances, the explanation of electronic processes with the above-mentioned approach is not convenient. Therefore, to explain the electronic processes in non-crystalline substances, the topological concept is successfully applied, rather than the long-range order of the structure. It is believed that with the further increase of the electric field intensity, the ionization of the U^--centers occurs, and when the concentration of free charge carriers reaches its critical value at a certain critical value of the intensity, their capture by the U^--centers or recombination of electrons and holes occurs. This causes a sharp increase in the resistance of the samples. The instability observed in the form of irregular oscillations in the N-shaped region of VAC is explained by the repeated periodicity of the ionization processes of U^- centers and the capture of charge carriers by those centers. At large values of the applied voltage, the resistance of the samples decreases again, as the probability of the capture of charge carriers decreases sharply. As a result, the N-shaped region formed at values of the field intensity of VAC covering the interval $2 \times 10^4 \div 10^5$ V/cm, was associated with multiphonon thermal-field ionization of the U^- centers and repeated capture of charge carriers by those centers. On the other hand, the instability observed in the N region of VAC in the form of irregular oscillations was associated with the capture of charge carriers by U^- centers and the periodic repetition of the process of ionization of these centers. Also, the decrease in the amplitude of oscillation with the increase in the value of Z is associated with the replacement of low-energy chemical bonds (easily broken) by high-energy bonds.

MAIN RESULTS

1. The observation of FSDP in graphs describing the distribution of intensity in X-ray diffraction for all chemical compositions of the As-Ge-Se system, and for the $As_{20}Ge_{10}Te_{70}$ composition in the As-Ge-Te system, is associated with the presence of an average order region in the distribution of structural elements, and also the correlation length, quasi-period within the average order region, the diameter of the nanocavities were determined and their dependence on the chemical composition was explained by the fact that the chemical activity of selenium is higher than that of tellurium.

2. In the phonon spectrum of samples of As-Ge-Se system with a small amount of As and Ge, frequency maxima corresponding to oscillations of ring (Se_8) and chain (-Se-Se-Se- ...) selenium molecules are replaced by maxima corresponding to oscillations of tetrahedral and pyramidal structure elements with the increase of concentration of these atoms, explained according to the chemical bond approximation model.

3. Observing maxima corresponding to oscillations of tetrahedral and pyramidal structural elements and Te-Te chemical bonds in the phonon spectrum of the sample with stoichiometric composition included in the As-Ge-Te system, presence of high-frequency maxima in compositions with an excess of tellurium atoms, and low-frequency maxima in compositions with a deficiency of tellurium atoms shows that the amorphous matrix of that system partially deviates from the chemical bond approximation model.

4. The dependence of the optical width of the forbidden zone of the As-Ge-Se and As-Ge-Te systems determined by the Taus method on the average coordination number and the parameter R, which determines the type of chemical bond, is associated with the dependence of the average bond energy, cohesive energy, and packing coefficient on the chemical composition. As a result of the analysis of the dependence of the mentioned quantities on Z and R, the presence of topological and chemical thresholds was determined in the investigated CGS systems.

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5. The maximum average atomic volume of the $As_{25}Ge_{12.5}Te_{62.5}$ ($R = 1$, $Z = 2.5$) containing substance and the minimum value of the packing coefficient are related with the occurrence of the 2D $\rightarrow$ 3D transition in the structure of the As-Ge-Te system.
6. The N-shaped region formed at values of the field intensity of VAC covering the interval $2 \times 10^4 \div 10^5$ V/cm is associated with multiphonon thermal-field ionization of U^-- centers and repeated capture of charge carriers by those centers. The instability observed in the form of irregular oscillations in the N-shaped region of VAC was associated with the occupation of charge carriers by U^-- centers and the periodic repetition of the process of ionization of these centers. The decrease of the oscillation amplitude with the increase in the value of Z was explained by the replacement of low-energy chemical bonds (easily broken) by high-energy bonds.
7. Properties such as the N-shaped region observed in the VAC of the Te-$Ge_x As_y Te_{100-x-y}$ -Al system studied in the stationary mode make it possible to recommend these substances as prospective materials for memory elements and transducers.

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