

THE STRUCTURE AND PHYSICAL PARAMETERS OF CHALCOGENIDE GLASS-LIKE SEMICONDUCTORS OF SYSTEM As- Ge – Se

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The parameters of local structure (correlation length and quasi-period in average order region) are defined by carrying out of experiments by X-ray beam diffraction and density of glass-like systems As – Ge – Se. The dependence of physical parameters (density, packing coefficient, compactness, molar volume average value, lone pair electron number, cohesion energy) on average coordination number and R parameter defining the bond character between atoms is established. The compositions corresponding to chemical percolation threshold and also compositions in which the glass state is flexible, highly-stressed and isostatically stressed are established using results of Phillips-Torp and Tichy theories.

Keywords: X-ray beam diffraction, coordination number, cohesion energy.

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INTRODUCTION

The chalcogenide glass-like semiconductors (ChGS) outperform other functional materials in their unique electronic properties used for applications [1 -6]. They are transparent in wide spectral region, have high photosensitivity, optical nonlinearity, high value of refraction index and also they differ from other materials by technological process simplicity at preparation of different details on their base and chemical stability [7 -9]. Advantage of ChGS also is caused by wide region of glass formation, possibility of unlimited doping and chemical composition variation that allows us to change the structure and obtain the material with optimal parameters [1,10- 12]. However, the successful realization of applied tasks requires the obtaining of material with predicted properties and optimal parameters necessary for concrete purpose.

It is known, that macroscopic properties of non-crystalline materials are controlled by micro-structure peculiarities, i.e. short-range order and average one in atom disposition. The change of parameters of short-range and average orders, in particular, coordination number, length and type of chemical bonds, relative part of heteropolar and homeopolar bonds, correlation length and etc. can be achieved by change of chemical composition that should be reflected on structure and electron properties [13 – 14]. ChGS are characterized by existence of structural elements forming the amorphous matrix and also by existence of free volume appearing at technological processes of sample preparation [15 – 22]. The change of chemical composition should lead to change of free volume part in sample that also should influence on electron properties. Thus, the correlation between structure and properties can be established and the possibility of expansion of given material application regions can be revealed by complex investigation of peculiarities of local structure and physical properties.

The investigation of local structure and physical parameters of ChGS of As – Ge – Se system is the goal of the present work. The numerical values of correlation length, quasi-period in average order region, packing coefficient, compactness, average value of atomic volume, average coordination number, limitation number,

cohesion energy are obtained using X-rays diffraction method and density measurement. The choice of the given composition as investigation object is caused by the fact that element atoms including into the given composition differ by the number of valency electrons. According to rule 8-N (atom with N-valency electrons, $N \geq 4$) forms 8-N bonds, i.e. has the 8- N neighbors) the coordination numbers of Ge, As and Se atoms are 4,3 and 2 correspondingly. Such difference in coordination number value allows us to change the glass matrix structure changing chemical composition, i.e. to obtain the glass with both one-, two- and three-dimensional structures. Such change in amorphous matrix should be accompanied by changing of electron properties that allows us to obtain the information on correlation between structure and electron properties and reveal the possibilities of their application.

EXPERIMENT TECHNIQUE AND SAMPLE PREPARATION

Synthesis of ChGS of As – Ge – Se system is carried out in the following sequence: especially pure elementary substances in required atomic percentages are filled into quartz ampoules from which air is evacuated to pressure 10^{-4} millimeter of mercury. After that ampoules are heated up to ~ 900 °C temperature during 3 hours and kept about 12 hours at this temperature. The synthesis is carried out in revolver to supply of sample homogeneity and cooling is carried out in switching off mode. The films by different thickness used in investigations are obtained by thermal evaporation with rate $0,2 \div 0,4$ μ /sec on glassy substrates in vacuum at pressure 10^{-4} millimeter of mercury.

The density (ρ) of investigated ChGS of As-Ge-Se systems is measured by Archimedes principle with use of liquid (water) and it is calculated using the following formula:

$$\rho = \left[\frac{w_0}{(w_0 - w_L)} \right] \rho_L \quad (1),$$

where w_0 and w_L are material heights in air and liquid (in water). Liquid (water) density ρ_L at room temperature is

1gr/cm³. The measurement accuracy isn't less than ± 0.02gr/cm³.

The investigations of aggregate state, local structure of synthesized substances and evaporated films are carried out by X-ray structural analysis on power diffractometer D8 ADVANCE (Bruker, Germany) in mode 40kV, 40mA, 0 < 2θ < 80°. The diffraction pictures are analyzed using the special program Evaluation for the definition of such parameters of diffraction maximum as their square, amplitude, scattering angle 2θ and full width at half maximum ΔQ (FWHM).

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

The intensity curves of X-ray beam diffraction in thermally evaporated films of As-Ge-Se system with different content of composite elements are shown in fig.1. The wide maximums observed in diffraction picture evidences on their amorphism. As it is seen from the figure corresponding to intensity distribution of X-ray diffraction of investigated ChGS as to majority of glasses [22 – 26] the so-called first sharp diffraction peak (FSDP) differing from other ones by anomalous dependence on temperature and pressure is observed.

FSDP characteristics defined from graph (fig.1) and calculated with the help of scattering vector Q₁ (Q₁ = 4π sin θ/λ, wavelength of X-rays λ= 1,54056Å,) corresponding to FSDP position and ΔQ

are shown in table 1. Using the given data of FSDP the local structure parameters are defined by formula:

$$d = 2\pi/Q_1 \tag{1}$$

$$L = 2\pi/\Delta Q \tag{2}$$

where **d** parameter either is called as repetitive distance defining the structural unit sizes or the distance between layers [32 – 34], or as quasi-period of density fluctuation [32 – 34]; L is correlation length, i.e. area size in which the density fluctuation periodicity is maintained. The values of the given parameters are also shown in table 1. As it is seen from the table ΔQ and **d** values increase and L decreases with the increase of relative part of As and Ge atoms in As-Ge-Se system. Increase of d is probably connected with high value of atomic radius of As and Ge atoms in comparison with Se atoms. Increase of ΔQ and decrease of L evidence on disorder degree increase at such change in chemical composition.

The existence of free volumes in amorphous materials is the recognized fact by all investigators interesting by the given region. The definition of parameter numerical values connected with given structure peculiarities plays the important role in both understanding of electron process mechanism taking place in them and establishment of the regions of their application.

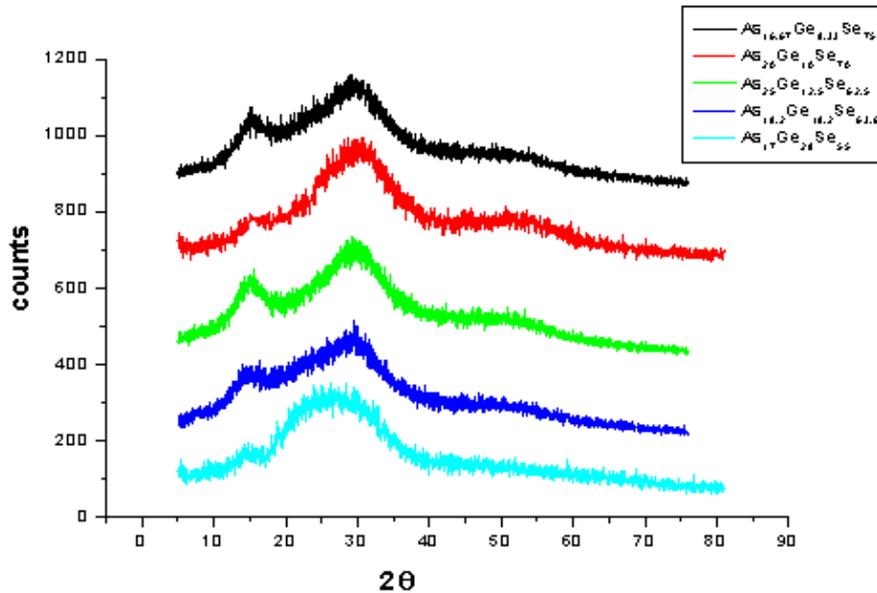


Fig.1. X-ray diffraction patterns of ChGS of As – Ge – Se system.

Table 1.

№	compositions	2θ, grad	Q ₁ , Å ⁻¹	d=2π/Q ₁ , Å	D, Å	ΔQ, Å ⁻¹	L=2π/ ΔQ, Å
1	As _{16.67} Ge _{8.33} Se ₇₅	15.27	1.084	5.796	4,72	0.257	24.455
2	As ₂₀ Ge ₁₀ Se ₇₀	15.05	1.092	5.751	4,67	0.242	25.95
3	As ₂₅ Ge _{12.5} Se _{62.5}	15.02	1.066	5.89	4,79	0.324	19.41
4	As _{18.2} Ge _{18.2} Se _{63.6}	14.78	1.049	5.99	4,87	0.238	26.44
5	As ₁₇ Ge ₂₈ Se ₅₅	14.85	1.078	5.826	4,74	0.234	26.838

FSDP origin is usually connected with cluster void model supposed by Elliot [20] according to which the structure regions divided from each other by voids (pores) or region with decreased atomic density are clusters. The contrast in atomic density between correlated-packed clusters and voids causes the FSDP revealing in diffraction picture. According to [7,20] FSDP is caused by correlation between cation structural units, for example of $\text{Ge}(\text{S},\text{Se})_4$ tetrahedron type in $\text{a-Ge}(\text{S},\text{Se})_2$ or AsS_3 (AsSe_3) pyramid one in $\text{a-As}_2\text{S}_3$ ($\text{a-As}_2\text{Se}_3$). Moreover, the analytic formula connecting FSDP position (Q_1) with nanovoid diameter (D)

$$Q_1 = \kappa\pi/D \quad (3)$$

in the case of correlation between tetrahedral structural elements $\kappa = 1.5$ [37]. «ab initio» estimation of Q_1 for different tetrahedral in ordered materials is carried out by application of cluster void model and it is shown that $\kappa = 1.5$ for them. Author of [36] using Eliot model on FSDP nature and experiments by positron annihilation lifetime spectroscopy (PALS) shows that $\kappa = 1,75$ in glass with pyramidal structural elements. Accepting the fact that both types of structural units (As_2Se_3 , GeSe_2) and selenium chain molecule taking under consideration the both coefficients take place in ChGS materials under consideration the nanovoid diameter average values are estimated by formula (3) and results are presented in table 1.

From table it is seen that D value increases with decrease of selenium part in ChGS of As-Ge-Se system. If take under consideration the fact that nanovoids form as a result of atom absence in them then it would be reasonable to connect the increase of their diameter with increase of average atomic radius of the given compositions. Indeed, the concentration increase of arsenic and germanium atoms with big atomic radius causes the increase of material average atomic radius.

Knowing the chemical composition and using the experimental data on density of obtained chemical compositions the numerical values of local structure parameters are calculated.

The average value of coordination number (Z), packing density (κ), atomic volume average value (V_a) are calculated by formulae 4-6 and the obtained results are presented in table 2.

$$Z = 4X_{\text{Ge}} + 3X_{\text{As}} + 2X_{\text{Se}} \quad (4)$$

$$\kappa = \frac{\rho N_A}{\sum_i X_i A_i} \quad (5)$$

$$V_a = \frac{1}{\rho} \sum_i x_i A_i \quad (6)$$

The relative part of free volumes is often characterized by parameter of so-called compactness (δ) and is defined by formula [35]:

$$\delta = \frac{\sum_i (x_i A_i) / \rho_i - \sum_i (x_i A_i) / \rho}{\sum_i (x_i A_i) / \rho} \quad (7),$$

where X_{Ge} , X_{As} and X_{Se} are molar parts in ChGS composition, x_i , A_i and ρ_i are molar parts, atomic masses and densities of elements including into ChGS composition, ρ are experimentally obtained density values of the investigated substances.

The heteropolar bond energy between atoms including in investigated compositions and their degree of covalency are defined by formulae (8) and (9) [38-39]. The obtained results are presented in table 2. The obtained results are presented in table 2.

$$E_{A-B} = (E_{A-A} E_{B-B})^{1/2} + 30 (\chi_A - \chi_B)^2 \quad (8)$$

$$C = 100 \exp \left[- (\chi_A - \chi_B)^2 / 4 \right] \quad (9),$$

where E_{A-A} and E_{B-B} are energies of homeopolar bonds of A and B atoms, χ_A and χ_B are their electronegativity. From table 2 it is seen that degree of covalency of all chemical bonds including into investigated ChGS materials is enough high one. That's why the obtained results can be interpreted by the theory developed for materials with covalent bond.

Table 2.

communications	E, kC/mol	DC %
As-As	146	
As-Ge	170.77	99,28
As-Se	147.37	96,64
Ge-Ge	188	
Ge-Se	163.6	92,97
Se-Se	172	

The knowing of such structure parameters as bond energy, cohesion energy (energy required for breakage of all bonds) is necessary for understanding of composition dependence of physical properties. The calculation of given parameters requires the knowing of existing chemical bonds and their quantity in the investigated composition. Chemical bond approaches model (CBA) is used with this goal [40-43]. According to CBA the probability of heteropolar bond formation exceeds the homeopolar bond one, moreover, the most strong bonds (bonds with high energies) forms at the beginning and consistency of given bond formation corresponds to consistency of energy decrease up to the moment whereas the accessible atom valency would satisfied and finally the bonds energy is additive one. The supposed chemical formulae of the investigated compositions taking under consideration the given principles are presented in table 3. In third composition the glass structure consists of totally stitched tetrahedral ($\text{Ge}[\text{Se}_{1/2}]_4$) and pyramidal ($\text{AsSe}_{3/2}$) structural units which consist of energy-advantageous heteropolar bonds. In 1st, 2nd and 4th compositions along with the given element the homeopolar bonds with chalcogens atoms also take part, i.e. the excess selenium atoms take part in binding of the given elements and also

they connect between each other in chain and ring formations. The chemical formulae of last composition differ by excess of non-chalcogen element atoms. The accessible germanium atom valency is satisfied because of high bond energy Ge-Se (bond energy is 49,42 kcal/mol), excess part of arsenic atoms form the homeopolar bonds As-As. Taking under consideration the expected chemical bonds and their percent part in the investigated materials presented in table 2 the cohesion energy is estimated by following formula [38-39].

$$CE = \sum_i c_i E_i \quad (10)$$

where c_i and E_i are quantity and energy of expected bonds.

According to theory of topological limitation formed by Philips and Torp the material glassy-forming ability is defined by ratio between the number of limitations of interatomic force fields and atom degree of freedom [44-46]. For system in 3D space the atoms have three degrees of freedom which partly or totally are eliminated by the presence of hard bond limitations. There is critical composition at which the number of limitations (N_{co}) is balanced by quantity of degrees of freedom (N_d) accessible in network, i.e. $N_{co} = N_d$. Moreover, glass formation tendency is maximum one and it is known as threshold of hardness percolation. There are two types for mechanical limitations: $N\alpha = Z/2$ is known as limiting the extension of bond per atom and $N\beta = 2Z - 3$ is known as the limitation of bond of bends per atom in network $N\beta$. The general quantity of limitations is $N_{co} = 5/2 Z - 3$. The glass state is considered as floppy state when limit number is less than the value of degree of freedom ($N_{co} < 3$). In conditions when limit number is bigger than accessible value of degree of freedom the glass state becomes stressed rigid state.

According to [44-46] the glassy semiconductors with polymer structure consisting of weakly-stitched chains become hard ones when the chain stitching takes threshold meaning. In covalent systems the stitching degree is also expressed in terms of average coordination number Z . The transition of glass from floppy state into stressed rigid one will take place near $Z = 2,40$ ($N_{co} = 3$).

However, the continuing investigations in this direction show that indeed there are two transitions of rigidity but not one predicted by theory of topological

limitations on chalcogenide glasses [47-50]. Indeed, two types of transitions of rigidity are observed in binary chalcogenide glasses at Z different values [47-49]. Based on results of these investigations, authors of [51-53] works report about existence of the intermediate phase between floppy and stressed rigid states in disordered chains.

Parameter R defined by ratio of number of possible chalcogens atom covalent bonds of to the number of possible covalent bonds of non-chalcogenide atoms plays the important role in result analysis of structure percolation threshold investigation of disordered materials [54]. Thus, $R=1$ presents itself the case of stoichiometric composition consisting of only energy profitable heteropolar bonds which explicitly evidence on chemical threshold existence. $R > 1$ values correspond to chemical compositions rich by selenium (samples 1,2, table 3) in which there are homeopolar bonds Se-Se along with existence of heteropolar bonds As-Se, Ge-Se. And in $R < 1$ values the chemical compositions differ by lack of chalcogens atoms for total satisfaction of non-chalcogen atom valent requirements (samples 5, table 2).

This composition differs by the existence of homeopolar bonds As-As (the valent requirements are totally satisfied because of high bond energy value Ge-Se for germanium atoms).

The topological and chemical ordering of amorphous matrixes of disordered materials are characterized by such values as average coordination number Z and parameter R . That's why it is reasonable to consider the dependence of physical parameters characterizing the structure of these values.

The dependences of structural parameters of ChGS investigated materials such as density (ρ_a) (fig. 2), average value of atomic volume (V_a) (fig. 3), packing coefficient (χ_a) (fig.4), compactness (δ_a) (fig.5) and cohesion energy (CE) (fig. 6) on Z and R are shown in figures.

As it is seen from the figures all graphs of physical parameter dependences on Z and R (at $Z=2,5$; $R = 1$) have the extreme points which are either maximum (ρ_a, χ_a, δ_a) or minimum (V_a) or (CE) dependence changes that is considered as the existence of percolation chemical threshold corresponding to stoichiometric chemical composition of As-Ge-Se system $[0,625(As_{0,4}Se_{0,6})][0,379(Ge_{0,333}Se_{0,666})]$.

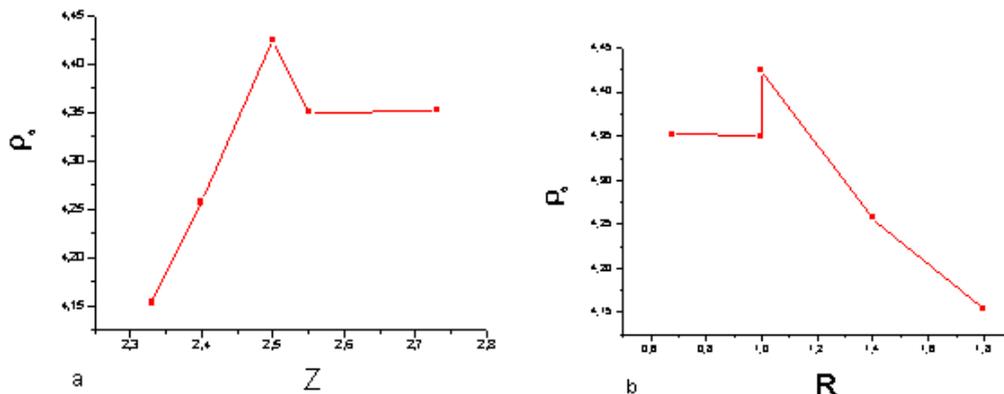


Fig.2. The density dependence (ρ_a) on Z (a) and R (b).

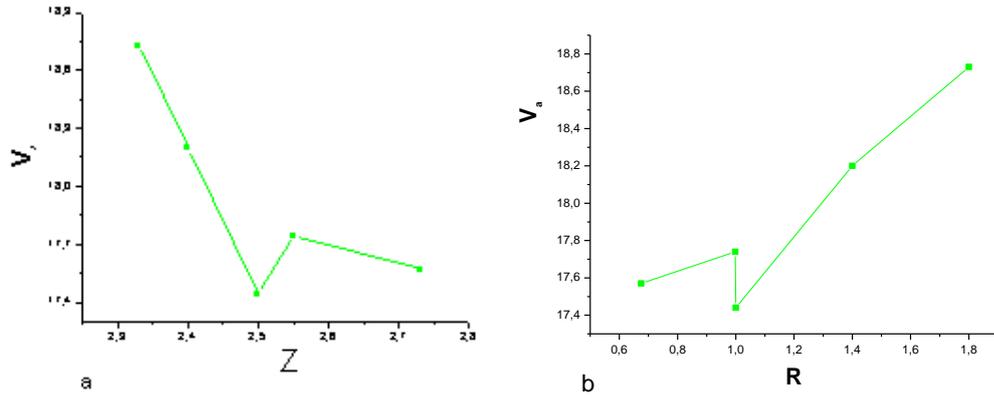


Fig.3. The dependence of atomic volume average value (V_a) on Z (a) and R (b).

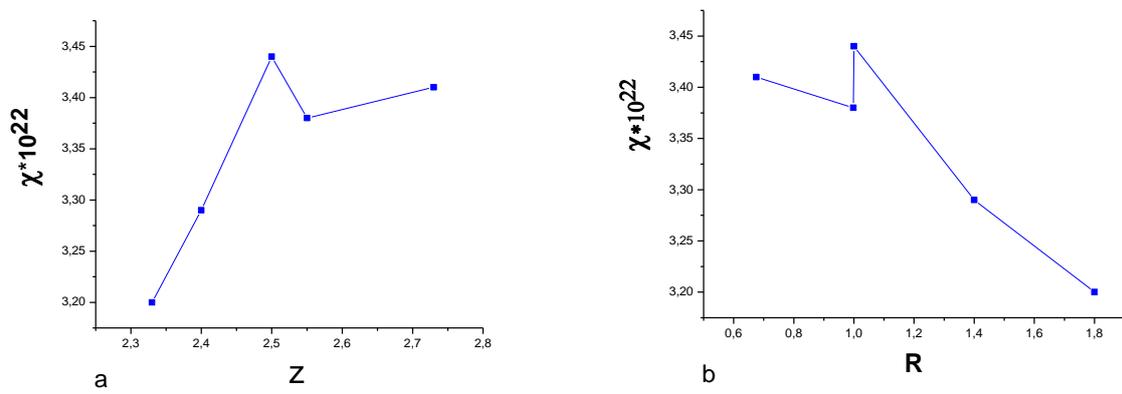


Fig.4. The dependence of packing index on Z (a) and R (b).

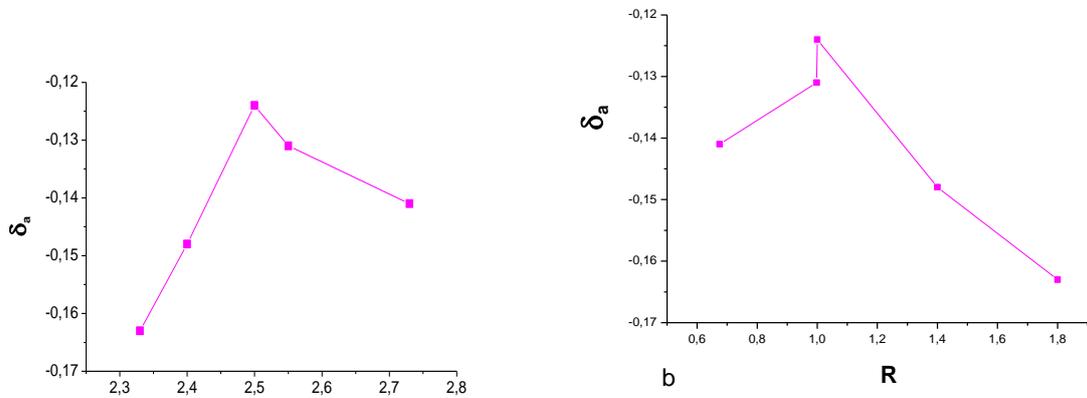


Fig.5. The dependence of compactness (δ_a) on Z (a) and R (b).

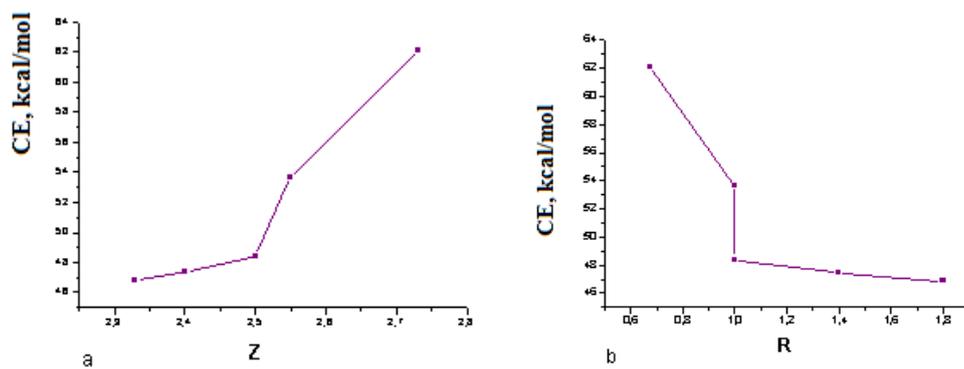


Fig.6. The dependence of cohesive energy (CE) on Z (a) and R (b).

At $Z=2,5 \div 2,55$ and $R=1 \div 0,998$ the dependences in figures 2-6 differ from other regions that evidences the existence of intermediate state corresponding to chemical composition of samples with serial numbers 3,4.

Finally, note that glassy-forming ability of noncrystalline materials is characterized by number of LP

electrons which are defined by formula $N_l = V - Z$ (V is average valency value) (table 3) for investigated compositions. $R > 1$ and $Z < 2,55$ values correspond to compositions with large number of LP electrons contributing to high glassy-forming ability of the given compositions.

Table 3.

№	compositions	Z	R	N_l	N_{co}
1	$As_{16,67} Ge_{8,33} Se_{75}$ [0,417($As_{0,4}Se_{0,6}$)]·[0,252($Ge_{0,333}Se_{0,666}$)]·[$Se_{0,332}$]	2,33	1,8	3,34	2,83
2	$As_{20} Ge_{10} Se_{70}$ [0,5($As_{0,4}Se_{0,6}$)]·[0,303($Ge_{0,333}Se_{0,666}$)]·[$Se_{0,198}$]	2,4	1,4	3,2	3
3	$As_{25} Ge_{12,5} Se_{62,5}$ [0,625($As_{0,4}Se_{0,6}$)]·[0,379($Ge_{0,333}Se_{0,666}$)]	2,5	1	3,0	3,25
4	$As_{18,2} Ge_{18,2} Se_{63,6}$ [0,455($As_{0,4}Se_{0,6}$)]·[0,552($Ge_{0,333}Se_{0,666}$)]·[$Se_{0,016}$]	2,55	0,998	2,904	3,375
5	$As_{17} Ge_{28} Se_{55}$ [0,425($As_{0,4}Se_{0,6}$)]·[0,85($Ge_{0,333}Se_{0,666}$)]·[$-Se_{0,275}$]	2,73	0,675	2,54	3,825

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