

## INFLUENCE OF HIGH PRESSURES ON ELECTRICAL AND THERMOELECTRIC PROPERTIES OF Cu-Ge-As-Se GLASSES

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We report the results on the high pressure effect (up to 50 GPa) upon the electrical resistivity, thermoelectric power, the tangent of dielectric loss angle and impedance of glassy chalcogenides  $(\text{GeSe})_{1-x}(\text{CuAsSe}_2)_x$ .

**Keywords:** electrical resistivity, thermoelectric power, tangent of dielectric loss angle, chalcogenides

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### INTRODUCTION

Multicomponent crystalline and amorphous materials of Cu-, Ag-, Ge-, In-, As-, Sb-based chalcogenides reveal interesting combination of electrical, optical, magnetic, mechanical, and other physical properties [1-10].

In particular, some of them as well the materials of Cu-Ge-As-Se system exhibit thermistor properties, some glasses display a memory switching, transit from a high impedance to low impedance state at high current densities and temperature increasing. Despite of variety of models proposed for a switching effect in chalcogenide glass semiconductors, a nature of these transitions is imperfectly understood [11, 12].

The aim of present work is the study of high pressure influence on electrical and thermoelectrical properties of  $(\text{GeSe})_{1-x}(\text{CuAsSe}_2)_x$  materials and the evaluation the ability to control a transition from high impedance to low impedance state under high pressures. The ability of transition from high impedance to low impedance state and the changes in a structure under pressures up to 50 GPa are studied using the electrical resistance, the tangent of dielectric loss angle, complex impedance, thermoelectric force.

The work reports the experimental results obtained for two glassy materials:  $\text{CuAsSe}_2$  ( $x=1$ ) and  $(\text{GeSe})_{0.05}(\text{CuAsSe}_2)_{0.95}$  ( $x=0.95$ ).

### 1. Materials: synthesis, structure, and properties at atmospheric pressure

Glass materials were synthesized by the melt-quench from  $T=800\text{K}$ . Original components (at least of ACS quality) were alloyed in silica containers evacuated up to  $10^{-4}$  Pa and filled with ultrapure argon to  $0.5 \times 10^5$  Pa. The synthesized compounds were tested on Shimadzu XRD 6000 and Shimadzu XRD 7000 diffractometers and scanning electron microscopes. The materials were studied using the confocal Raman spectroscopy and atomic force microscopy Alpha300R (Witec). The diode-pumped solid-state laser of wavelength 488 nm and He-Ne laser of wavelength 633 nm served as the coherent light source. The density of samples was measured using helium pycnometer AccuPyc II 1340 (Micromeritics) providing high-accuracy estimation of a true solid density. Vickers microhardness tests was carried out with HVS-1000A Micro Hardness Tester which is equipped with automatic turret and digital display. It has been established that atomic structure of glasses is specified by a short-range order peculiar to crystalline compound  $\text{CuAsSe}_2$ . The powder diffraction patterns of studied materials (with  $\text{CuK}\alpha$  monochromatic radiation) exhibit a few halos (Fig.1) typical to glassy materials of Cu-Ag-Ge-As-Se and Ag-Ge-As-S [13, 14]. The experimental atom radial distribution function of glasses (RDF) was constructed by using the data on X-ray scattering in a wide angular range (Shimadzu XRD 7000,  $\text{Cu-K}\alpha$ ,  $8-140^\circ$  on  $2\theta$ ).

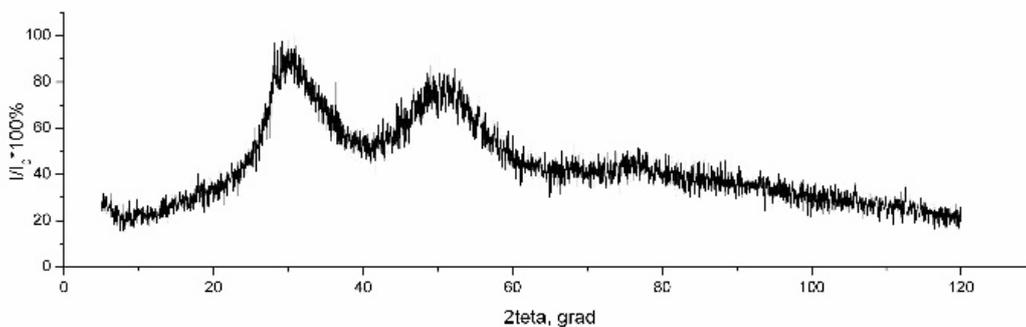


Fig. 1. Diffraction pattern of  $(\text{GeSe})_{1-x}(\text{CuAsSe}_2)_x$ ,  $x=0.95$ .

Fig. 2 presents the RDFA for  $(\text{GeSe})_{1-x}(\text{CuAsSe}_2)_x$ ,  $x=0.95$  plotted on experimental data and the RDFA for crystalline and glassy on the data derived from [15]. The radius of first coordination sphere estimated from the RDFA curve for glassy  $(\text{GeSe})_{1-x}(\text{CuAsSe}_2)_x$ ,  $x=0.95$  is  $\sim 2.4 \text{ \AA}$ . Interatomic bond distances of Cu and Se as well Cu and As contribute to the first coordination shell. Radius  $2.4 \text{ \AA}$  corresponds to Poling sum radii of Cu and Se. The radius of a second shell  $3.8 \text{ \AA}$  conforms to distances between Se-Cu-Se atoms in the bases of tetrahedrons. Since the crystalline  $(\text{GeSe})_{1-x}(\text{CuAsSe}_2)_x$ ,  $x=0.95$ , as well as  $\text{CuAsSe}_2$  has a cubic structure, based on the proximity of RDFA for both glasses we may suggest that glassy  $(\text{GeSe})_{1-x}(\text{CuAsSe}_2)_x$ ,  $x=0.95$ , reveals the same structural 3-dimensional units conforming to crystalline  $\text{CuAsSe}_2$  with sphalerite structure. These 3-dimensional units form the base of glassy  $\text{CuAsSe}_2$ . Statistically Ge atoms may occupy the positions of As and Cu atoms in sphalerite-type structure. These data agree with data of work [15]. Thus, 3-dimensional units of  $\text{CuAsSe}_2$  the short-range ordering preserving within 1 nm make the lattice base of studied glasses. The short-range ordering is a distance in a coordination polyhedron (a local coordination of atoms). The packing of coordination polyhedral in various structures characterizes a medium-range order (4, 5, 6 coordination spheres). The Cu atoms in glassy  $\text{CuAsSe}_2$  are ionized and an ionic formula  $\text{Cu}^{1+}\text{As}^{3+}\text{Se}_2^{2-}$  is valid.

The analysis of Raman spectra (the confocal microscope Alpha300R, He-Ne laser of wavelength  $\lambda = 633 \text{ nm}$  and power 30 mW) confirms that 3-dimensional units  $\text{CuAsSe}_2$  make the atomic structure base of glassy  $(\text{GeSe})_{1-x}(\text{CuAsSe}_2)_x$ ,  $x=0.95$ . Fig. 3 depicts the Raman spectrum of glassy  $(\text{GeSe})_{1-x}(\text{CuAsSe}_2)_x$ ,  $x=0.95$ . The most intense band of the spectrum is in the range of  $200 \text{ cm}^{-1} - 250 \text{ cm}^{-1}$ . In this range, a maximum becomes well-marked at  $230 \text{ cm}^{-1}$ . Also the spectrum involves wide bands with a maximum at  $140 \text{ cm}^{-1}$ . Principal bands of chalcogenide spectra are broad under the influence of a phonon state density. Such a broadening is characteristic for amorphous materials and associated with a lack of a long-range order, the deformation of glass structural units in a disordered amorphous lattice.

In this case the short-range order is of importance in explaining the optical activity of modes. A Raman spectrum curve is failed to be clearly drawn in the sum of Gaussian curves, which conform to vibrations in potential interatomic bonds, because of a large number of potential vibrational modes contributing to the general spectrum and due to near values of atomic radii and atomic weights of Cu-Ge-As-Se system components. Nevertheless, we can point out some features of Raman spectrum for glassy system Cu-Ge-As-Se.

First, the mostly expressed peak in the Raman spectrum (that as well is observed for glassy materials As-Se and Cu-As-Se with slight Ge content) on a frequency of  $230 \text{ cm}^{-1}$  is associated with vibrations of As- and Se-atoms in tetrahedral unites  $[\text{AsSe}_3]$  that characterizes the 3-dimensional structure of the glass. An As-atom is on a top of the tetrahedron; on other three tops are Se-atoms. The presence of this peak indicates to the predominance of As-Se bonds over others such as Cu-Se, Ge-As, and Ge-Se.

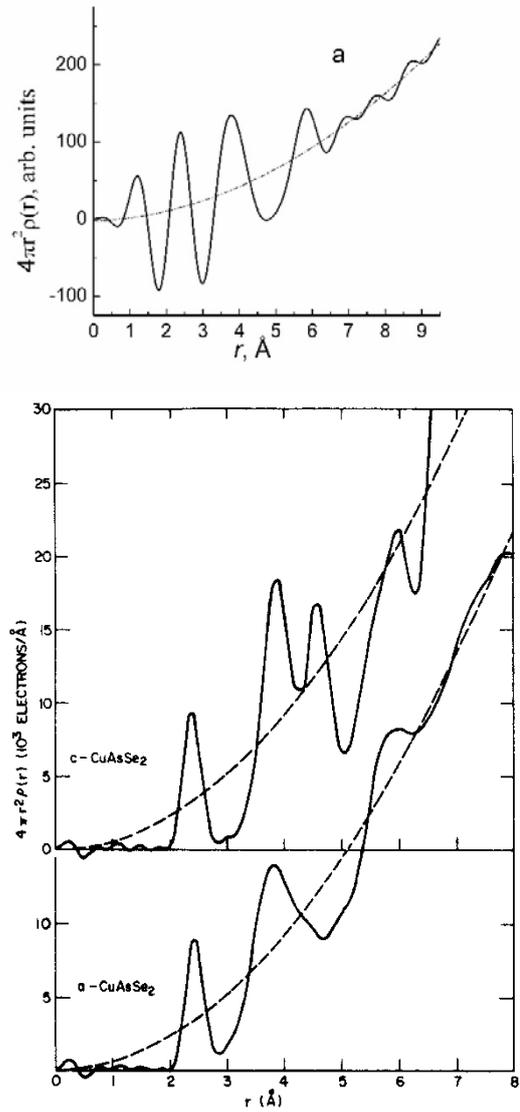


Fig. 2. Radial distribution function of atoms: a – for  $(\text{GeSe})_{1-x}(\text{CuAsSe}_2)_x$ ,  $x=0.95$  (derived in the present work); b – for crystalline  $\text{CuAsSe}_2$  (up) and glassy  $\text{CuAsSe}_2$  (down) (derived in work [15]).

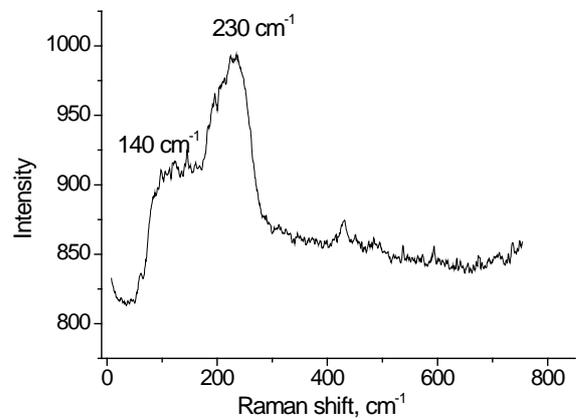


Fig. 3. Raman spectrum of glass material.

The wide band on frequencies 120-140  $\text{cm}^{-1}$  is associated with the vibrations of Cu-Se and probably with Ge-As. All abovementioned is in agreement with our modeling of atomic structure of studied glasses. So, the analysis of data on X-ray diffraction, the radial distribution function, and the Raman spectra allows for the conclusion that 3-dimensional units of  $\text{CuAsSe}_2$  form the base of the atomic structure for glassy  $\text{CuAsSe}_2$  and  $(\text{GeSe})_{1-x}(\text{CuAsSe}_2)_x$ ,  $x=0.95$ . Microhardness of  $(\text{GeSe})_{1-x}(\text{CuAsSe}_2)_x$ ,  $x=0.95$  sample is 185 HV at load of 0.1 kg and delay time corresponds to 1 second. The comparison of this value with the microhardness of glassy  $\text{Cu-AsSe}_{1.5}$  [16] reveals that the existence of structural 3-dimensional units in such materials with more than 10-15 atomic percentage of Cu provides like values of the microhardness.

All materials researched under atmospheric pressure demonstrate semiconducting electrical properties at  $T = (10-460)$  K. In  $\text{CuAsSe}_2$ , a sharp increase in the conductivity and a transition from high impedance state (0.2 Ohm·m) to low-impedance state ( $3 \cdot 10^{-5}$  Ohm·m) with change of semiconducting conductivity to metallic occur when increasing the temperature above 460 K and rising the stress,  $(\text{GeSe})_{0.05}(\text{CuAsSe}_2)_{0.95}$  attains thermistor properties. Still, a nature of transition switching effect in chalcogenides remains unexplored. One of reason for this effect is suggested to be the formation of a crystalline channel with low electrical resistivity by virtue of undergoing the reaction  $3\text{CuAsSe}_2 \rightarrow \text{Cu}_3\text{AsSe}_4 + 2\text{AsSe}$  and the occurrence of low impedance crystalline phase  $\text{Cu}_3\text{AsSe}_4$ . In glassy  $(\text{GeSe})_{0.05}(\text{CuAsSe}_2)_{0.95}$ , in which the base of glass network is of  $\text{CuAsSe}_2$  3-dimensional units as well and Ge-atoms occupy the positions of Cu and As statistically, germanium prevents crystallization. And the effect of transition from low impedance to high impedance state, which was observed in  $\text{CuAsSe}_2$ , changes to the thermistor behavior in material with Ge content, i.e. the glassy  $(\text{GeSe})_{0.05}(\text{CuAsSe}_2)_{0.95}$  is heating without crystallization while passing the current through the sample, and the conductivity increases.

## 2. EXPERIMENTAL METHOD

### Methods of research of material properties under high pressures

The direct-current measurements of the electrical resistivity of the samples was carried out in the toroid high-pressure apparatus in the range of 0-7 GPa at pressure rise and release. A detail description of the method was reported in works [17, 18]. The contacts to the surfaces of samples were indium-deposited. In order to achieve high pressures from 10 to 50 GPa, we used a high-pressure chamber (HPC) with rounded cone-plane diamond anvils. Artificial carbonado diamonds are good electrical conductors what allows the estimation of electrical properties of samples placed into the HPC [19-20]. To create the temperature gradient one of anvils was heated, the temperature of anvils at the points of contacts were measured by two copper thermocouples. Seebeck coefficient or absolute thermoelectric power  $S$  were calculated by measuring the potential difference (thermoelectric power) induced in the sample through copper branches

$$S = S_C + \frac{U_{12}}{T_1 - T_2}$$

where  $S_{Cu}$  is the copper absolute thermoelectric power (1.8  $\mu\text{V/K}$ ),  $U_{12}$  is the measured thermoelectric power,  $T_1$  and  $T_2$  are the temperatures of heated and cooled ends of the sample. The electrical properties in the range of pressures from 10 to 50 GPa were measured by the impedance spectroscopy technique using Solartron and RCL-2000 impedance meter-analyzer in the range of frequencies from 10 Hz to 1 MHz.

## 3. RESULTS AND DISCUSSION

The measurements of the electrical resistivity in  $(\text{GeSe})_{0.05}(\text{CuAsSe}_2)_{0.95}$  in the dc field reveals a hysteresis (Fig.4). An increase in pressure from atmospheric to 6.4 GPa reduces the electrical resistivity by two orders and pressure drop recovers that to initial value.

In studied samples, the thermoelectric power is positive in a whole range of pressures and the conductivity is of p-type (Fig. 5). Thermoelectric power values are large which are typical for semiconductors (30 mV/K and 6 mV/K for  $(\text{GeSe})_{0.05}(\text{CuAsSe}_2)_{0.95}$  and  $\text{CuAsSe}_2$ , respectively). When pressure increasing from 12 to 50 GPa the thermoelectric power value reduces three-fold in  $\text{CuAsSe}_2$  and twenty-folds in  $(\text{GeSe})_{0.05}(\text{CuAsSe}_2)_{0.95}$ , and respectively ten-folds and fifty times when pressure increasing from normal to 50 GPa. By reducing pressure from maximum (50 GPa) to atmospheric the thermoemf of studied chalcogenides varies slightly, and at normal pressure the thermoemf was of the order the same as at the maximum pressure. So the pressure processing of studied compounds can be considered as a technique to obtain the materials of high thermoelectric power value unalterable in a wide baric range from 10 to 50 GPa. The thermoelectric power in studied materials depends on the time during that the applied pressure operates. In the vicinity of some pressures, a character of the thermoelectric power-time dependence is different at pressure increase and decrease: the thermoelectric power rises with time under a pressure at a sample loading and increases under the same pressure after unloading.

The baric dependences for the thermoelectric power, real impedance, and the tangent of dielectric loss angle of  $(\text{GeSe})_{0.05}(\text{CuAsSe}_2)_{0.95}$  (Fig.6) exhibit peculiarities of a behavior (a change in a decreasing or increasing rate of parameters and a local minimum on the thermoelectric power baric dependences for studied compounds) in one and the same pressure areas. Thermoelectric power values sharply decrease with an increase in pressure up to 27 GPa in glassy compound of  $(\text{GeSe})_{0.05}(\text{CuAsSe}_2)_{0.95}$ . A behavior of the tangent of dielectric loss angle and the electrical resistivity - the former slightly grows, the latter weakly reduces with a rise in pressure up to 27 GPa - testifies to glassy state to be preserved. With further increase in pressure the thermoelectric power dependence on pressure changes in the range of 27-30 GPa accompanied with a fast fall of the resistivity and rise of the dielectric dissipation factor.

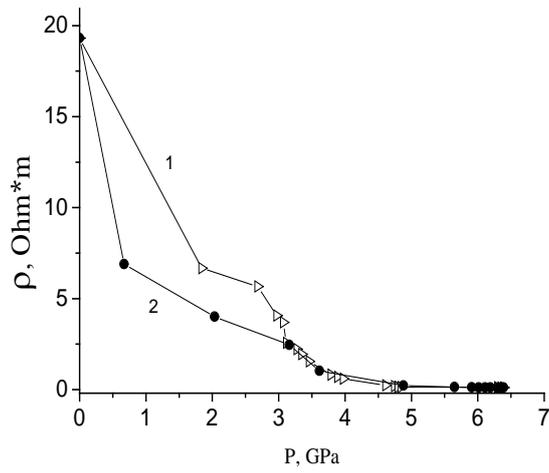


Fig. 4. Baric dependences of resistivity for glassy  $(\text{GeSe})_{0.05}(\text{CuAsSe}_2)_{0.95}$  at pressure rise (curve 1) and drop (curve 2).

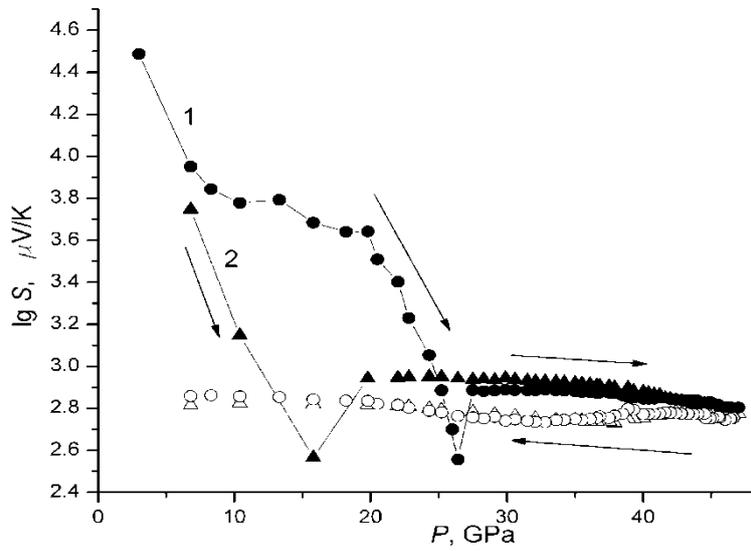


Fig. 5. Baric dependences of decimal logarithm of thermoelectric power in glassy  $(\text{GeSe})_{0.05}(\text{CuAsSe}_2)_{0.95}$  (curve 1) and  $\text{CuAsSe}_2$  (curve 2) at pressure increase (painted signs) and decrease (counter signs). Arrows indicate the direction of pressure variation.

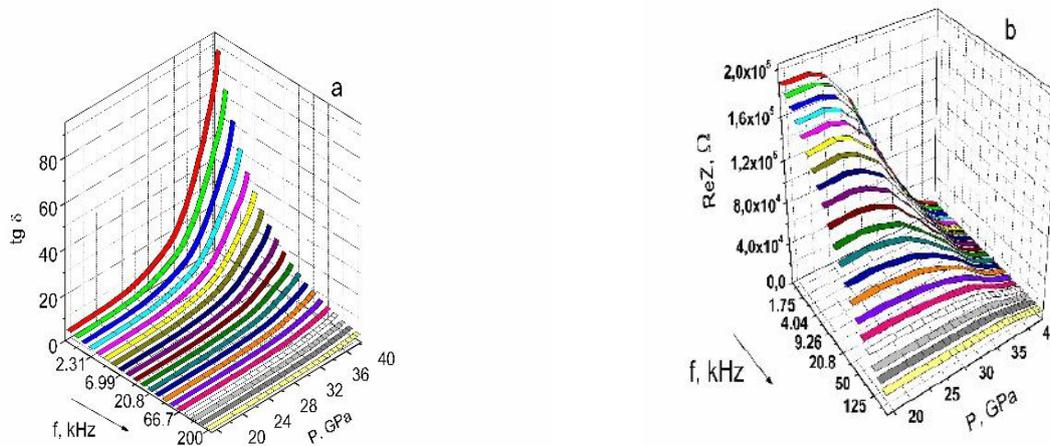


Fig. 6. Frequency-baric dependences of the tangent of dielectric loss angle (a) and real part of impedance (b) of glassy  $(\text{GeSe})_{0.05}(\text{CuAsSe}_2)_{0.95}$ .

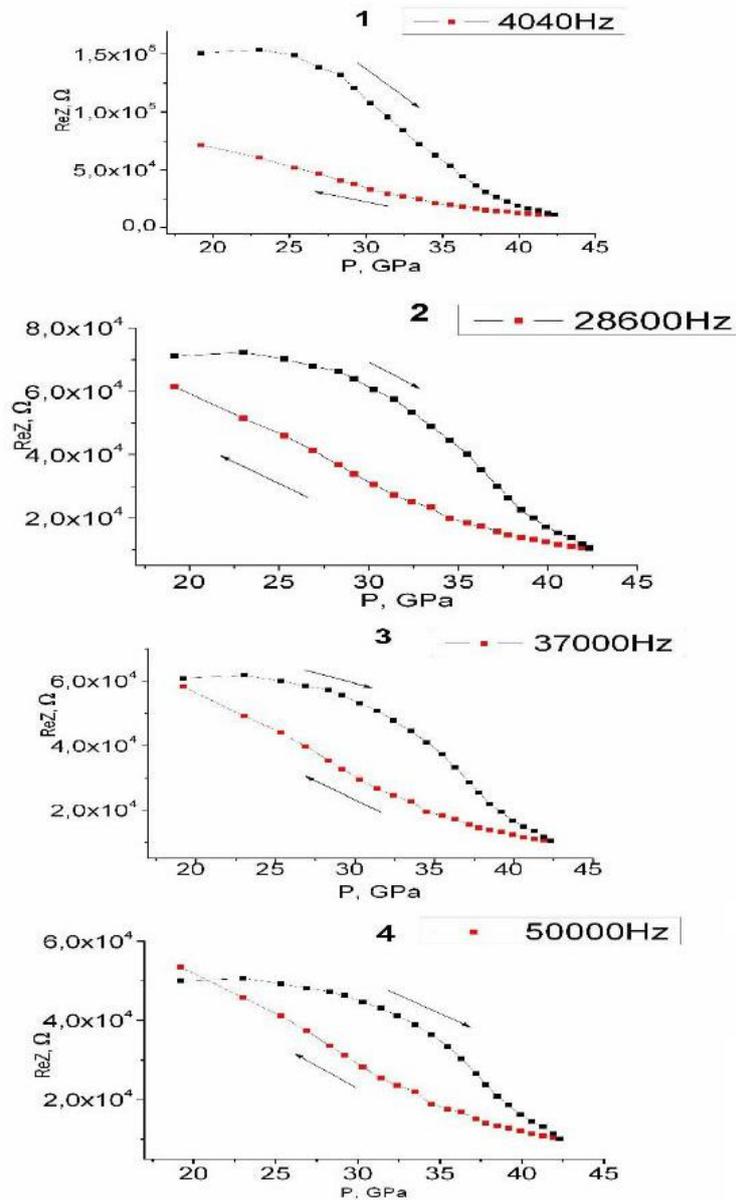


Fig.7. Baric dependencies of the real part of the impedance  $(\text{GeSe})_{0.05}(\text{CuAsSe}_2)_{0.95}$  when pressure increases and decreases on different frequencies. Arrows indicate the direction of pressure variation.

The lower a frequency, the faster increase in the dielectric dissipation factor at lower pressures and the more influence of the active conductance and lesser of the reactive conductance. All curves corresponded to the measurements on constant frequencies are practically merge in the field of 38-47 GPa after decrease in the resistivity several-fold. Such a behavior of the resistivity with a rise in pressure on different frequencies can be explained by a change in parameters of glass units at packing, further increase in a number of carriers, and drop of activation energy.

The behavior of thermoelectric power with a pressure drop can be stemmed from the excess carriers of defects and impurities.

If the increase of pressure triggered the crystallization of explored glassy materials then, first of all,  $\text{Cu}_3\text{AsSe}_4$  phase would stand out the resistivity of

which is several orders less than the resistivity observed in a whole range of pressures studied. In favor of crystallization failure speaks the fact that the alternating current measurements of electrical properties in a baric interval from 10 to 50 GPa reveal the hysteresis of electrical parameters with return to values measured before pressure increasing (Fig. 7).

#### 4. CONCLUSION

In our investigation, we establish the pressure regions of strong changes in a behavior of the thermoelectric power and electrical properties of  $(\text{GeSe})_{1-x}(\text{CuAsSe}_2)_x$  chalcogenides: about 19 GPa, about 36 GPa, and 43-44 GPa – in glassy  $\text{CuAsSe}_2$ , about 27 GPa, and 38-43 GPa – in glassy  $(\text{GeSe})_{0.05}(\text{CuAsSe}_2)_{0.95}$ .

A decrease in the electrical resistivity by several orders with an increase in pressure up to 50 GPa and the return to an initial value indicate the changes in the electronic structure, increase of a number of carriers, variations of parameters of structural units of glass materials.

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