

# Dielectric spectroscopy of aged glassy and revitrified selenium

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The temperature-frequency dependences of the complex dielectric constant ( $\epsilon^*$ ) real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) components are studied in aged under normal laboratory conditions for several decades glassy and revitrified selenium at frequencies 10 Hz - 50 kHz and in the temperature range from 293 K to 420 K. The most significant difference in the behavior of dielectric constant in aged and revitrified samples is observed at the crystallization of glassy samples. In aged samples a significant dielectric dispersion was detected, which is probably due to the micro-heterogeneity of the glass structure. This latter can be associated with the presence of transition regions between the vitreous matrix and nuclei of crystalline clusters.

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## 1. Introduction

Chalcogenide glassy semiconductors (ChGS) have attracted increasing interest for a long time. This is due to their electrical and optical properties and the possibility of application in many solid-state devices. In particular, vitreous selenium, as the brightest representative of ChGS, and films based on its alloys have successfully been used in xerography, as photosensitive elements, in switching devices, and for information storage [1]. It is necessary to note that in single-crystalline Se microtubes even ferromagnetic or ferroelectric (multi-ferroic) behavior was found [2]. These unique materials remain the subject of intensive study even nowadays [3, 4].

Selenium is almost the only elemental substance that is easily obtained in the form of bulk glass, i.e. which has a high ability to glass forming. At the same time, it is known that the vitreous state is metastable and has excess internal energy relative to the corresponding crystal. On the one hand, metastability imposes technological limitations on the processing and application of glass. On the other hand, the metastable state creates unique opportunities for the fabrication and optimization of microstructures due to both structural relaxation (SR) and crystallization. These are technologically easy methods of modifying properties, including electrical and dielectric. For example, stability and aging at low temperatures were investigated by additives of selenium-based glasses [5, 6]. Also, SR and modification of dielectric properties by the introduction of impurities have been studied in detail in vitreous selenium, but such studies have been conducted in a limited temperature range [6, 7] and time [5, 8]. In this regard, this paper compares the dielectric properties of aged and freshly synthesized samples of glassy selenium, including the crystallization temperature range.

## 2. Experimental details

### 2.1. Preparation of glassy alloys

Initially, bulk samples of vitreous selenium were obtained several tens (30-35) years ago by the usual quenching technique by using high purity Se (99.999%). The starting material in the form of flattened drops with a diameter of 3 - 5 mm was sealed in ampoules of fused quartz, which were thoroughly cleaned and kept at 150°C for 24 hours. Ampoules with an inner diameter of 18 - 20 mm with selenium were evacuated to a vacuum of  $4 \times 10^{-3}$  Pa and sealed off with an oxygen-gas burner. Subsequently, selenium was melted in a horizontal furnace (250 °C), heated to 500 – 550°C (770 - 820K), and kept at this temperature for at least 24 h with periodic mixing by rocking. Sharp cooling of the melt was carried out by immersing the ampoules with the melt in a mixture of water and ice. Thus, obtained glassy selenium ingots were stored at room temperature in the dark and on the air for decades. For revitrification the aged glassy selenium obtained by the procedure described above was re-subjected to similar technological treatment and before investigation kept only for several days to avoid high-speed relaxation processes. The amorphous nature of both aged and revitrified selenium alloys is confirmed by the results of X-ray phase analysis shown in Fig.1 (curves 1, 2). The glassy state of the studied samples is evidenced by a characteristic conchoidal fracture of the sample's microstructure images obtained by an electron microscope (Fig. 2 at different magnification).

### 2.2. Dielectric measurements

Rectangular plates with a thickness of ~ 1 mm and an area of ~ (20 - 25) mm<sup>2</sup> were cut from the glass-like ingots. The surface was ground with fine powder (M10).

Conducting silver paste L100 produced by Kemo-electronic with a resistance of  $0.01 - 0.1 \Omega/\square$  was used as electrodes.

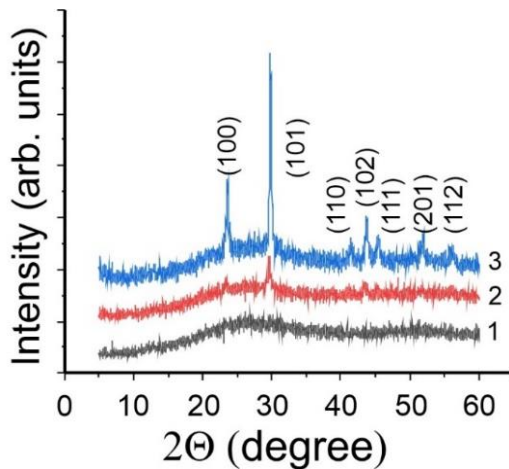


Fig. 1. X-ray diffraction pattern on revitrified (1), aged glassy (2), and crystallized (3) samples of selenium (color online)

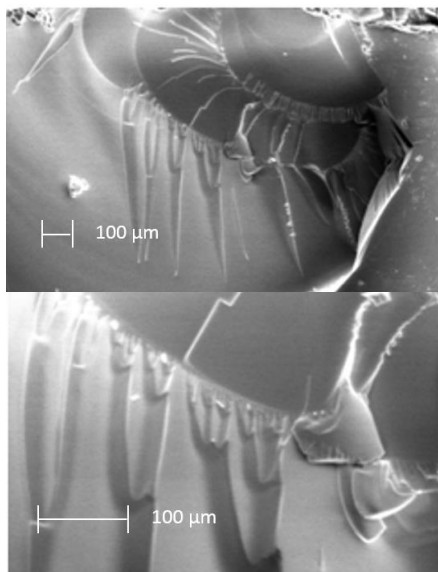


Fig. 2. Glass fracture photographs of selenium glass obtained using an electron microscope

The sample with the supplied electrodes was placed in a cryostat holder of the immersed type. In such systems, a sealed container with a sample holder is immersed directly into a Dewar vessel with liquid nitrogen. This makes it possible to perform long-term measurements and vary the rate of temperature change. In our studies, it was  $0.1\text{K}/\text{min}$ . The most significant changes in the properties of selenium samples occur at above room temperature, so the study of dielectric properties was carried out in the temperature range  $300\text{K} - 420\text{K}$ . Measurement of dielectric response in the frequency range  $10\text{ Hz} - 50\text{ kHz}$  was carried out using our automated measuring system based on impedance meters LCR-819 from GoodWill company (GW Instek). The sample is placed in the cryostat holder and connected to the LCR-meter in a four-

wire circuit. This allows to taking into account the resistance and parasitic inductance of the connecting conductors. The LCR-819's built-in software has a calibration function that memorizes the correction factors at different frequencies, which allows compensating the frequency dependence of connecting coaxial cable parameters. The values of the real  $\epsilon'$  and imaginary  $\epsilon''$  components of the complex dielectric constant  $\epsilon^* = \epsilon' + i\epsilon''$  were calculated using a parallel dielectric substitution scheme.

X-ray and thermal analysis, as well as electron microscopic studies, were carried out using standard techniques.

### 3. Results and discussion

Dielectric constants temperature and frequency dependences of the revitrified sample of selenium during the first heating are shown in Fig. 3 and Fig. 4. As seen below room temperature,  $\epsilon'$  is almost constant, and  $\epsilon''$  is negligibly small. Therefore, measurements are given only for temperatures above  $290\text{K}$ . At a certain temperature close to the glass transition temperature  $T_g$ , the values of  $\epsilon'$  and  $\epsilon''$  begin to increase. The dependence of  $\epsilon'(T)$  in the region of  $T_g$  at several frequencies is shown in the insert to Fig. 3a. In the same temperature range, the dielectric dispersion becomes quite noticeable. In the temperature range of glass crystallization ( $365\text{K} - 375\text{K}$ ) maxima of  $\epsilon'$  and  $\epsilon''$  are observed which are superimposed on the monotonic growth of these parameters with temperature increasing.

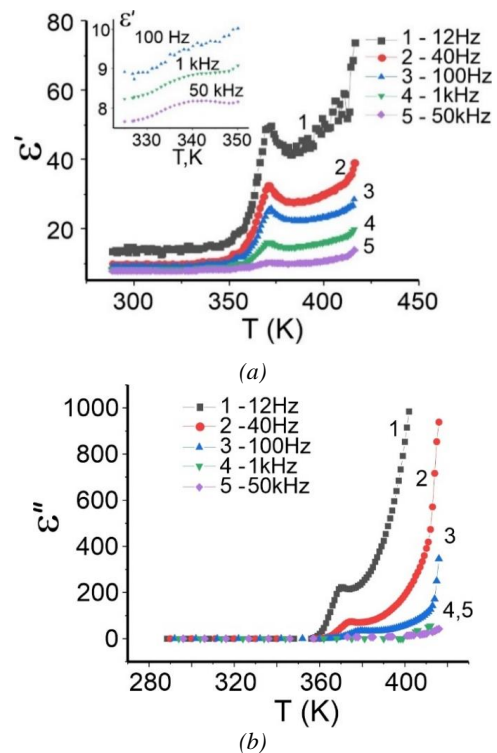


Fig. 3. The real  $\epsilon'$  (a) and imaginary  $\epsilon''$  (b) parts of the complex dielectric constant  $\epsilon^*$  temperature dependences obtained in revitrified selenium samples (color online)

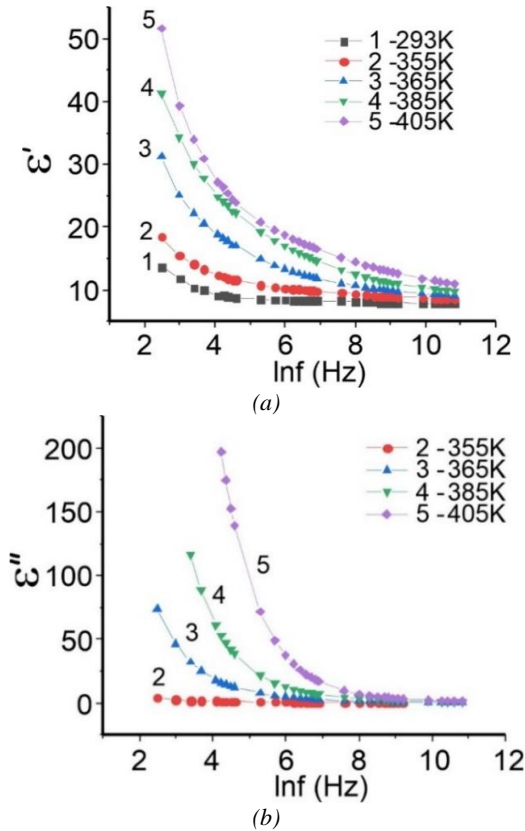


Fig. 4. Frequency dependences of the complex dielectric constant  $\epsilon^*$ : real  $\epsilon'$  (a) and imaginary  $\epsilon''$  (b) parts obtained in revitrified selenium samples (color online)

Similar dependencies for aged selenium glasses are shown in Fig. 5 and Fig. 6. For a clearer presentation of the obtained results, only on Fig. 5 temperature dependences  $\epsilon'$  and  $\epsilon''$  are shown on a logarithmic scale. It should be noted that in the temperature range  $T < T_g$  the values of  $\epsilon'$  and  $\epsilon''$  for aged samples of glassy selenium are much higher (even ten times depending on the frequency of the measuring field) than in revitrified samples. But the most significant difference in the behavior of dielectric constants observed in the crystallization region, namely anomalies associated with crystallization in aged glasses are observed at much (by about 35K) lower temperatures and have a very sharp form in comparison with revitrified samples.

The authors of some articles in particular [7, 9], explained the frequency behavior of the dielectric constant of chalcogenide glasses below  $T_g$  mainly by the induced dipoles and processes of charge carrier jump through the potential barrier between localized charged  $D^+$  and  $D^-$  centers ( $D^+$  and  $D^-$  are the dangling chemical bonds), which form a dipole.

According to [9, 10],  $\epsilon'' = A\omega^m \sim f^m$ , where  $A$  is some constant,  $\omega = 2\pi f$  is the cyclic frequency of the measuring field, the frequency exponent  $m$  has negative values and is expressed as follows:  $m = -4kT/W_m$  i.e. is the temperature-dependent and the value of which is determined by the potential barrier  $W_m$  between localized states. The values of  $m$  and  $W_m$  for selenium-based glasses (probably not aged for a long time at room temperature)

were estimated earlier in [8, 11, 12] and are of the order of  $-(0.2 - 0.5)$  and  $(0.2 - 0.4)$  eV, respectively.

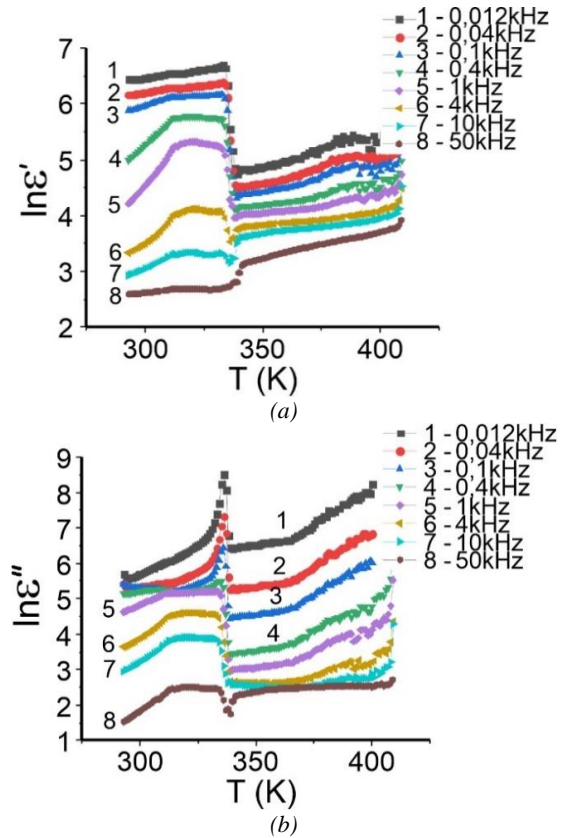


Fig. 5. The real  $\epsilon'$  (a) and imaginary  $\epsilon''$  (b) parts of the complex dielectric constant  $\epsilon^*$ : temperature dependences obtained in aged samples of glassy selenium (color online)

For aged selenium glasses, the double logarithmic dependences of  $\ln \epsilon''$  vs  $\ln f$  below the glass transition temperature  $T_g \approx (320 - 325)$  K are presented in Fig. 7. In contrast to the results described in the above articles, this dependence is not straight lines, indicating more complex behavior. At frequencies less than 50 Hz, the parameter  $m$  is in the range  $-(0.3 \dots 0.6)$  as in [8, 11, 12], and in the frequency range greater than 500 Hz, the value of  $m$  is becoming to value about  $-0.85$ .

Obtained results indicate the presence of an additional mechanism of polarization due to the processes of long-term structural relaxation in the glassy state, which makes a significant contribution to the dielectric constant. This is confirmed by the constructed Cole-Cole diagrams the evolution of which with the temperature change in aged glassy selenium is shown in Fig. 8. As can be seen, Cole-Cole diagrams can be observed only before the crystallization of the aged glass and with temperature, increasing are masked, especially at low frequencies, due to the increase of electrical conductivity and, accordingly, dielectric losses. The parameters of relaxation polarization at 320 K estimated from the Cole-Cole diagrams are as follows: relaxation depth  $\Delta \epsilon \sim 500$ , average relaxation time  $\tau \sim 1.3 \cdot 10^{-3}$  s, distribution parameter  $\alpha \sim 0.3$ . Of course, the values of these parameters are temperature dependent, but the correct selection of the contribution to



the total complex dielectric constant of observed relaxers is problematic.

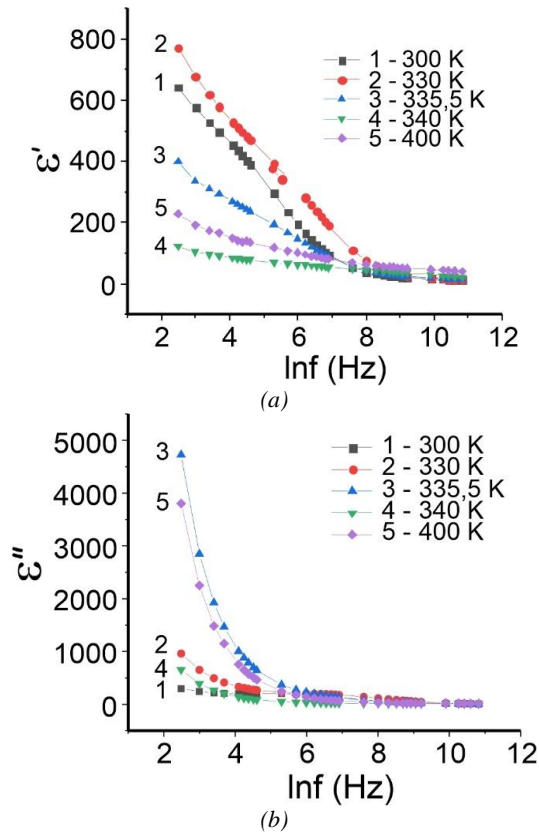


Fig. 6. Frequency dependences of the complex dielectric constant  $\epsilon^*$  real  $\epsilon'$  (a) and imaginary  $\epsilon''$  (b) parts obtained in aged samples of glassy selenium at different temperatures (color online)

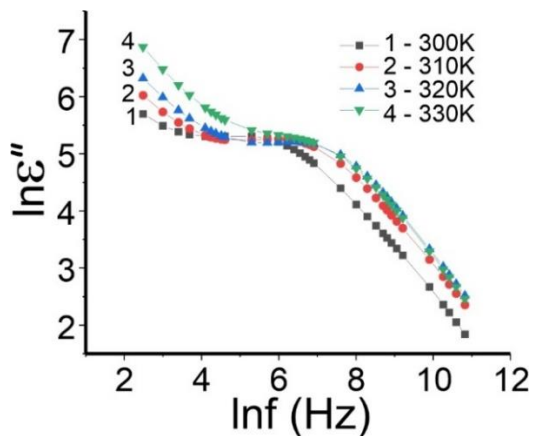


Fig. 7. Dependences of  $\ln \epsilon''$  vs  $\ln f$  for determination the parameter  $m$  in aged glassy selenium: 1 – 300K, 2 – 310K, 3 – 320K, 4 – 330K (color online)

Nevertheless, we can assume that the observed effects are associated with Maxwell-Wagner relaxation, i.e. the formation of space charges. In microheterogeneous systems, charge carriers can accumulate at the boundaries between clusters, which leads to polarization at the "interface". This occurs only when the clusters differ in the values of dielectric constant or conductivity. The main

cause of polarization at the "interface" is usually the difference in conductivity because the dielectric constant varies from cluster to cluster much less than the conductivity. At the same time the crystallization of aged glasses is accompanied by a rapid almost abrupt change of  $\epsilon'$  and  $\epsilon''$  (Figs. 5, 6) in a narrow temperature range (336K – 337K), which is nearly 30K lower than in revitrified samples, where, as indicated above, the dielectric constants anomalies associated with crystallization are observed at (365–375) K. Moreover, from frequencies, up to  $\approx 5$  kHz with increasing temperature in the narrow range  $\epsilon'$  decreases sharply, but at frequencies higher than 10 kHz, as can be seen from Fig. 5a, – increases. Similar anomalies are observed in the behavior of dielectric losses ( $\epsilon''$ ). This complex behavior of the dielectric response in aged selenium glasses indicates the disappearance of some and the emergence of other polarization mechanisms during their crystallization.

The connection of the observed dielectric anomalies with the crystallization processes is the results of differential thermal analysis (DTA) [13], which are shown in Fig. 9 for revitrified (curve 1) and aged glassy (curve 2) selenium, respectively. The thermograms clearly show the effects of softening ( $T_g$ ), crystallization ( $T_c$ ), and melting ( $T_m$ ). Crystallization in aged glass begins at a temperature near 350K and is very sharp, while in revitrified selenium crystallization begins at a temperature of 390K and the corresponding exothermic DTA peak is wider. Also, the glass transition temperature of aged glassy selenium as shown earlier [14] shifts to higher temperatures and is almost masked by the crystallization effect. The disagreement in the obtained crystallization temperatures between DTA and dielectric spectroscopy may be due to the different heating rates of the tested samples in several research methods.

It is known that the crystallization process of glass is determined by two factors: the formation of crystallization centers (nucleus) and the growth of crystals on them. These processes are interrelated and only the presence of these two factors leads to a noticeable crystallization of the glass. The process of nucleation is associated with a local change in structure, i.e. structural relaxation, which requires a long time at room temperature; it can be described as a process of restructuring of short-range order.

At the same time, due to the relatively high viscosity of glass at room temperature, the growth rate of crystals is low, as it requires significant atomic displacements. If the crystals growth rate in the glass is low, then such glass does not crystallize, as the nucleus of crystals (which do not appear on X-ray diffraction) are not prone to growth. However, an increase in temperature above  $T_g$  leads to a significant decrease of viscosity and increase in self-diffusion and, as a consequence, the crystals rate growth. The sharp diffraction peaks (Fig. 1, curve 3) indicate the significant crystallization of both aged glassy and revitrified selenium during heating up to 400K. The locations of clearly observed peaks (100), (101), (110), (102), (111), (201), and (112) are in good agreement with the values for the trigonal phase of Se crystals [15]. It can

be assumed that in aged samples there is high crystal nuclei density and happens a rapid (explosive)

crystallization, which is manifested in the DTA curves and sharp changes in dielectric properties.

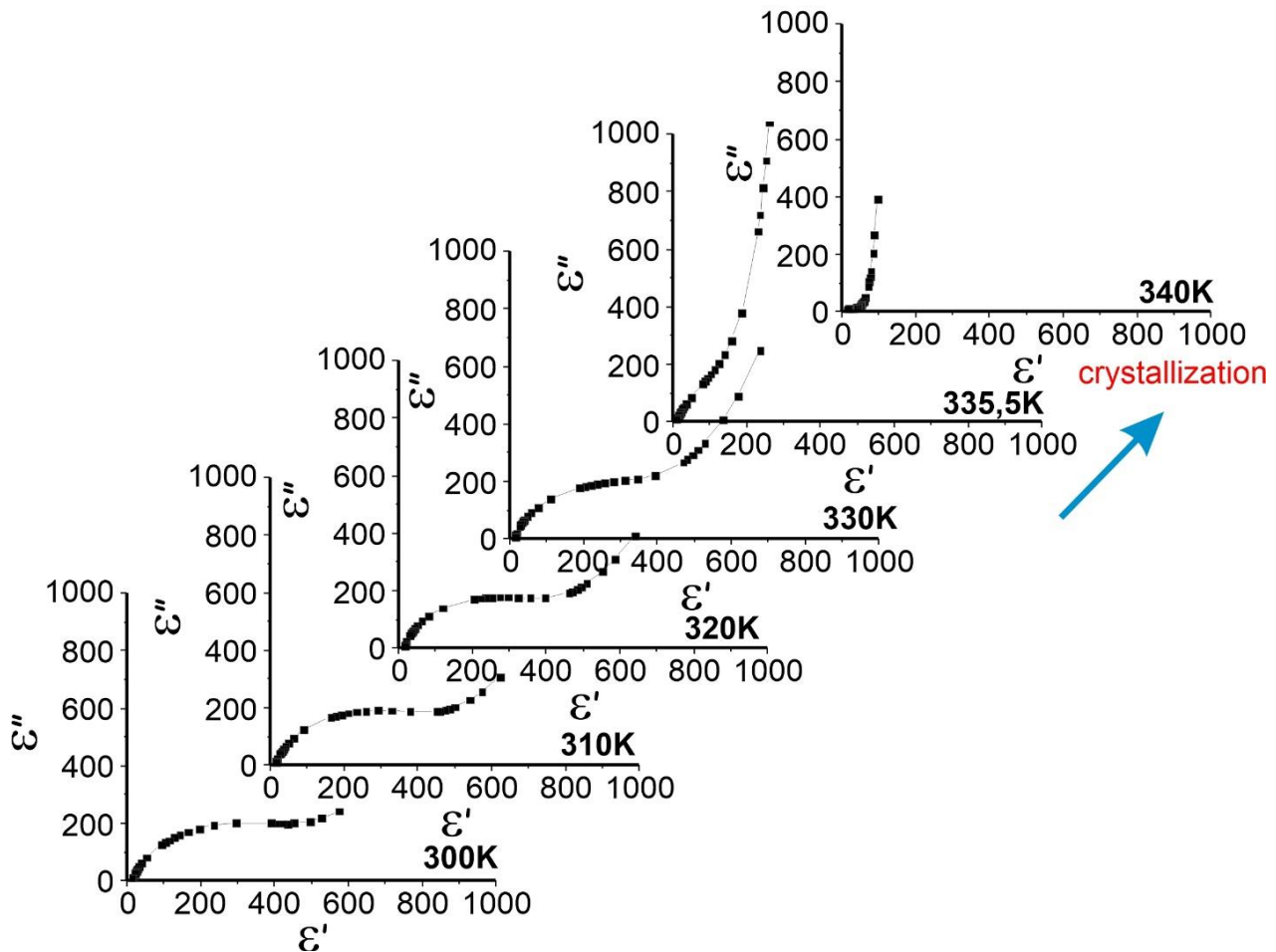


Fig. 8. Cole–Cole plots:  $\epsilon''$  versus  $\epsilon'$  at various temperatures for aged selenium glass (color online)

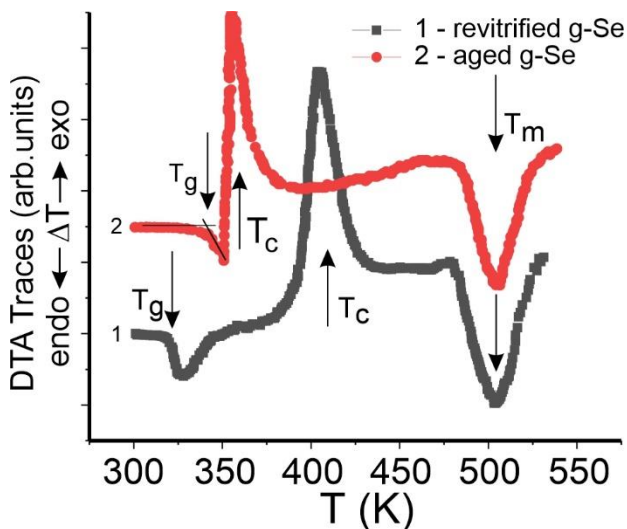


Fig. 9. The DTA curves of revitrified (a) and aged (b) glassy selenium (color online)

#### 4. Conclusions

The temperature-frequency dependences of the complex dielectric constant components in aged glassy selenium under normal conditions for tens of years and its revitrified samples obtained by re-melting were investigated in the frequency range from 10 Hz to 50 kHz and at temperatures from 293 K to 420 K. In aged glassy versus revitrified selenium as a result of structural relaxation there is an additional mechanism of polarization and the corresponding dielectric dispersion, which is probably due to the micro-heterogeneity of the structure and associated with the transition regions between the amorphous matrix and clusters of crystalline phase nuclei. Their presence causes a significant difference in the behavior of dielectric parameters during crystallization of aged and just quenched glassy selenium.

#### References

- [1] Kasap P. Capper, (Eds.), Springer Handbook of Electronic and Photonic Materials, Springer International Publishing, 1536 (2017).

- [2] A. Pal, S. Shirodkar, S. Gohil, S. Ghosh, U. Waghmare, P. Ayyub, *Sci. Rep.* **3**, 2051 (2013).
- [3] R. I. Alekberov, A. I. Isaev, S. I. Mekhtiyeva *J. Optoelectron. Adv. M.* **22**(11-12), 596 (2020).
- [4] S. Saraswat, V. K. Tomar, N. Chandel, N. Mehta, *Optoelectron. Adv. Mat.* **14**(5-6), 274 (2020).
- [5] S. Dash, P. Chen, P. Boolchand, *J. Chem. Phys.* **146**(22), 224506 (2017).
- [6] A. Sharma, N. Mehta, *Eur. Phys. J. Appl. Phys.* **59**(1), 10101 (2012).
- [7] M. Abkowitz, D.F. Pochan, *J. Appl. Phys.* **51**(3), 1539 (1980).
- [8] A. Dwivedi, R. Arora, N. Mehta, N. Choudhary, A. Kumar, *Semiconductor Physics, Quantum Electronics & Optoelectronics* **8**(3), 45 (2005).
- [9] J. C. Giuntini, J. V. Zanchetta, D. Jullien, R. Eholie, P. Houenou, *J. of Non-Crystalline Solids* **45**(1), 57 (1981).
- [10] F. Kremer, S. A. Rozanski, *The Dielectric Properties of Semiconducting Disordered Materials*, in book: F. Kremer, A. Schönhalz (Eds.), *Broadband Dielectric Spectroscopy*, Springer, Berlin; New York, 475 (2003).
- [11] N. Choudhary, A. Kumar, *Turkish Journal of Physics* **29**(3), 119 (2005).
- [12] R. Arora, A. Kumar, *Phys. Stat. Sol. A* **115**(1), 307 (1989).
- [13] V. I. Mikla, A. A. Horvat, N. Mehta, V. V. Minkovich, A. A. Molnar, *Optoelectron. Adv. Mat.* **13**(5-6), 364 (2019).
- [14] O. Shpotyuk, R. Golovchak, A. Kozdras, *Physical ageing of chalcogenide glasses*, in book: J.-L. Adam, X. Zhang (Eds.), *Chalcogenide Glasses. Preparation, Properties and Applications*, Woodhead Publishing, 209 (2014).
- [15] K. Lu, Haoyue Zhang, Y. Zhong, H.-J. Fecht, *J. Materials Research* **12**(4), 923 (1997).

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