

# Crystallization of Se-Te glasses in ultrasonic field

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The Se<sub>100-x</sub>Te<sub>x</sub> (x = 0-10 at.%) glasses were crystallized in several ways: (1) by a long-term aging at room temperature, (2) by heating at about the glass transition temperature, and (3) by simultaneous heating and treatment in ultrasonic field. Measuring of optical transmission in the range of 400-1000 cm<sup>-1</sup> was used as a non-destructive method sensitive to initial stages of crystallization. By means of removing of the surface layer with the following re-measurement of transparency one can evaluate the nucleation heterogeneity; it is shown that the most homogeneous ceramics is formed in the low-Te region (1%Te and 2%Te) while pure Se and high-Te glasses (0%, 5%, 10%Te) tend to the surface nucleation. Ultrasonic treatment reveals new effects of optical anisotropy and enlightenment. The results are discussed from synergetic point of view using the notions about alternative hypervalence bonds and their self-organization in the form of bond wave.

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## 1. Introduction

Crystallization is a key process/property in glass science and technology. A fundamental question of why some substances are so resistant to crystallization that their melt can be easily undercooled giving a massive non-crystalline solid, i.e. glass, is discussed intensively for at least last century. As to the practice, the general problems of glass-forming ability of a melt (a property that evaluates by critical cooling rate for a liquid of given chemical composition) and of stability of resulting glass (which correlates with glass resistance against low-temperature crystallization during storage and/or employment) also concern with crystallization. In addition, a new class of chalcogenide glass-ceramics as materials for optical application from visible to far-IR [1-4] are of an increasing interest.

Glass-ceramic materials are obtained by partial crystallization of glassy matrix. This process is actually investigated here, using selenium glass as the simplest matrix. Besides, the matrix is modified by Te (from 1% to 10 %) in order to investigate the composition-dependent effects since glass-ceramics represents usually a many-component system with special additions in order to provide homogeneous nucleation.

Crystallization of glass is a rather complex process, which can be considered at least on three levels. First level deals with classical crystallization *kinetics*, i.e. crystalline fraction as a function of time; the temperature being either constant (isothermal crystallization) or variable (non-isothermal case). On the second level the *heterogeneity* of crystallization in terms of distribution of crystalline fraction between surface and volume is considered. The third *morphological* level concentrates on the form, dimension and mutual orientation of the growing crystals. In our work we touch on all three aspects: (1) we use the

IR optical transmission for observation of crystallization development in non-isothermal case; (2) the extent of heterogeneity was evaluated by means of removing of surface layer with the following measuring of transmission; and (3) by measuring of transmission in two perpendicular directions we obtain information about the crystallization morphology.

A general feature of this work is application of ultrasonic (US) field in the process of glass crystallization. Known technological applications of ultrasonic treatments concern mainly with the destruction of materials in strong US fields, e.g., crushing of catalyst in order to increase its surface and thus catalytic ability. Since our goal is non-destructive modification of material, we use the low intensity US fields in a "soft" cavitation regime, when US waves are transmitted into a liquid medium in which the sample under treatment is placed. The data of ultrasonic treatments of glassy materials are actually absent now, with a possible exception of the so called "metallic glasses" (namely, the Pd-based compositions), for which US field was shown to accelerate crystallization and change crystallization morphology [5,6]. It is unclear, however, in what extent these results are true for classic bulk glasses such as oxide and chalcogenide ones. This is the first investigation of this type made on bulk chalcogenide glasses.

## 2. Experimental

The Se-Te samples were initially in the form of "tablets" of 15 mm thick and 20 mm diameter with the polished parallel planes A-A ( $d_{A-A}=15$  mm). They were synthesized in the Institute of Pure Materials (Nizhniy Novgorod; laboratory of Prof. M.F. Churbanov) by the known technology that provides impurity-free optical grade glasses. The samples history during the 7-years

period of their treatment is shown in **Table 1**. Note that beginning from treatment S2 the second pair of planes B-B appears (see No.4 and  $d_{B-B}$  in Table 1), and the samples look like bricks with rounded ends.

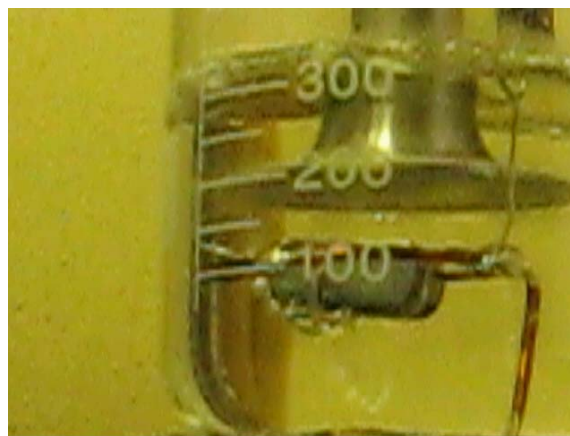
*Table 1. Experimental steps and corresponding sample dimensions.*

No treat	$\tau$ , months	Treatment		Mean dimensions	
		Notation	Character	$d_{A-A}$ , mm	$d_{B-B}$ , mm
1	0	-	As prepared	14,8	-
2	60	A	Ageing	14,8	-
3	62	S1	Removal of surface layer from the A-A pair of planes	13,8	-
4	70	S2	Removal of surface layer from A-A planes and forming of B-B planes	11,9	12,0
5	72	U1(40°C)	US treatment in cell	12,2	11,9
6	81	R	Relaxation	12,2	11,9
7	82	U2(50°C)	US treatment in cell	12,2	12,0
8	83	S3	Removal of surface layer	10,8	10,6
9	83	U3(40°C)	US treatment in cylindrical glass (Fig.1)	10,8	10,6
10	83	U4(50°C)	US treatment in glass with subsequent quenching	10,8	10,6

Optical transmission experiments were made in the Institute of General Physics (Laboratory of Prof. B.G. Plotnichenko) using Bruker IFS-113V spectrometer in the range of 400-4000  $\text{cm}^{-1}$ . The low-frequency limit of 400  $\text{cm}^{-1}$  is stipulated by a relatively large thickness of our samples. The data above 1000  $\text{cm}^{-1}$ , in the so called "window of transparency" in which the impurities bands (Se-O,  $\text{CO}_2$ , etc.) are usually detected, does not interesting in our study. Thus, we consider only interval of 400-1000  $\text{cm}^{-1}$ , which corresponds to the so called "phonon resonances" region, in which two resonances 490  $\text{cm}^{-1}$  and 740  $\text{cm}^{-1}$  representing 2<sup>nd</sup> and 3<sup>rd</sup> overtones of 245  $\text{cm}^{-1}$  main band for Se together with a relatively weak band 630  $\text{cm}^{-1}$  of unknown nature, are observed.

Ultrasonic treatments were carried out using standard equipment consisting of US-generator, magnetic transducer, and US waveguide-emitter. The own frequency of the system is  $22.4 \pm 0.1$  kHz. The emitter was placed into a cooled glassy cell or in a cylindrical glass (Fig.1), both filled with water which plays a role of exited

medium. The frequency of cavitation field distributes in a very wide range from few Hz to 1GHz with a relative maximum at about few MHz. Cavitation is accompanied by dissipation of energy with the following heating of a liquid. Owing to this effect, there is no need in additional equipment for heating of a sample since  $T_g$  for Se is as low as about 35°C; moreover, in the first two experiments (U1 and U2 in Table 1) the cooling cell was employed in order to diminish the heating effect of cavitation. Temperature in the cell or in the glass was regulated by previously calibrated input power of US-generator. In every 5-minutes run the temperature increases continuously from the room temperature (about 20°C) to the end temperatures of 40°C or 50°C indicated in Table 1. The sample under treatment is placed on a metallic plate at the top of the cooling cell, or in a special holder in cylindrical glass shown in Fig.1.



*Fig.1. Ultrasonic treatment of Se-Te sample in cylindrical glass (U3 and U4 in Table 1); the cavitation babbles are also seen.*

The US-treatment scheme is follows: (1) the sample and emitter insert into container filled with water, the distance between the upper side "A" of the sample and the emitter end/plane being 1 cm; (2) US-generator switches on with the previously defined input power; (3) treatment for 5 minutes, which is accompanied by heating due to cavitation; (4) generator switches off; (4) the sample either cools in container (for U1, U2, U3 in Table 1) or being placed into another glass filled with water of room temperature (for U4 in Table 1). All the glasses of Se-Te series are treated subsequently in one and the same day. The optical transmission of the series was measured at the same day or 1-2 days later.

### 3. Results and discussion

#### 3.1. Change of transparency

Chalcogenide glasses are transparent in IR-region. For selenium the "window of transparency" begins from 1000  $\text{cm}^{-1}$ , so we have chosen the value of optical transmission

at  $\omega_0=1000\text{ cm}^{-1}$  as a measure of transparency ( $T$ ) in our Se-Te series. The transparency is very sensitive to both the treatment and the composition of glass, as it is seen in Fig.2, where pure Se (0%Te) and low-Te glass (1%Te) are compared.

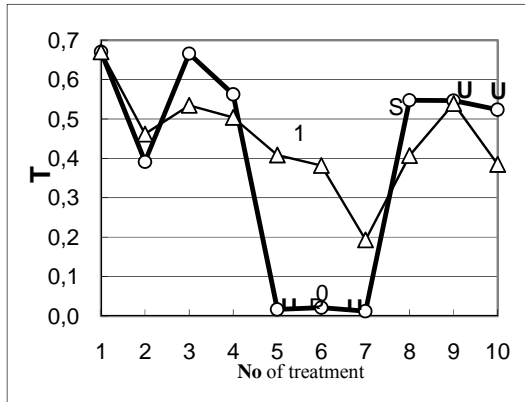


Fig.2. Transparency of pure Se (0%) and  $\text{Se}_{99}\text{Te}_1$  (1%) glasses as a function of the sample treatment (see Table 1 for decoding). The data correspond to the A-A direction.

When considering Fig.1 from phenomenological point of view, one can emphasize, first, a strong influence of small addition (1%Te) on the transparency change during treatments and, second, a strong influence of treatment No.5 (US-treatment in cell) on both the fall of transparency (Se becomes actually opaque) and a strong effect of doping in resisting of this fall (1%Te inhibits darkening from  $T=0,01$  for Se to  $T=0,4$  for  $\text{Se}_{99}\text{Te}_1$ ).

In order to interpret changes in transparency we assume that an observed darkening of glass is connected with the development of internal phase boundaries due to crystallization of glassy matrix. It seems likely that only the first stages of crystallization, nucleation and initial growth, can be detected in this way as far as glass becomes opaque long before a considerable crystalline fraction (say, 10% and higher) appears. To prove these assumptions we have investigated the final sample  $\text{Se}_{99}\text{Te}_1$  of  $T=39\%$  (see No.10 for 1%Te in Fig.2) by means of X-ray diffraction. The diffraction picture represents an ordinary diffuse "glassy" Se peak disposed at about  $2\text{ \AA}^{-1}$  with two narrow crystalline peaks [100] and [101] on it. The crystalline peaks intensity, being of the order of the "glassy" peak intensity, indicates that crystalline fraction in glassy matrix is not more than few percents.

### 3.2. Heterogeneity of crystallization

Glass-ceramic materials are usually homogeneous as respect to crystal distribution within the sample. This is achieved by special composition of glassy matrix, in which special impurities providing homogeneous nucleation are also added. In our case of simple Se-Te system homogeneous crystallization hardly realizes. In

order to investigate this numerically we propose the following method.

From Fig.2 it is seen that ageing of initial glass (No.2) leads to an expected decrease of transparency due to spontaneous crystallization. After removal of the surface layer (No.3) transparency increases, up to the initial value in the case of Se (0%), a fact that leads to the conclusion about the entirely surface character of spontaneous crystallization in pure Se. In other samples, however, recovery is incomplete, as it is shown in Fig.3, so nucleation is "less heterogeneous".

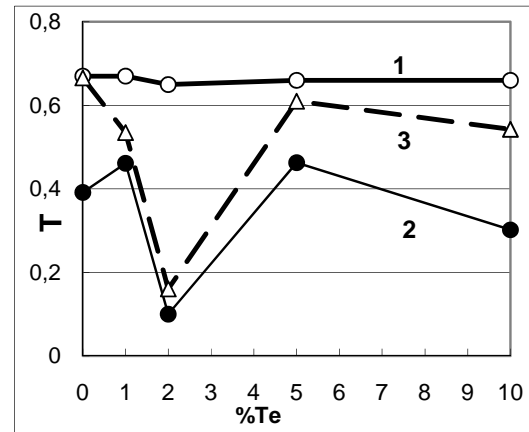


Fig. 3. Compositional dependence of transparency for fresh samples (1), aged ones (2), and the aged samples after removal of surface layer (3).

One can evaluate the extent of crystallization heterogeneity by means of the ratio

$$G_2 = (T_3 - T_2) / (T_1 - T_2) \quad (1)$$

where index (1,2,3) at  $T$  corresponds to the stage of treatment indicated as No in Table 1. Index "2" here corresponds to crystallization due to 60-month ageing (No.2 in Table 1) of initial samples.

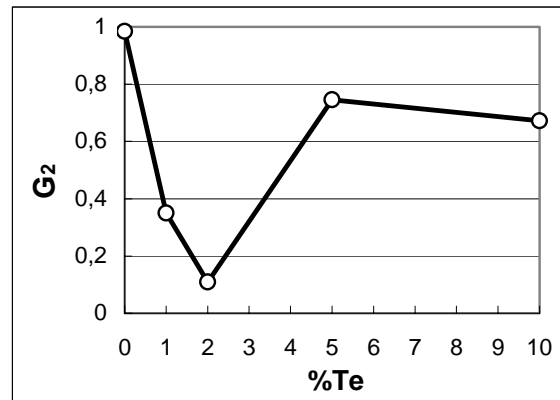


Fig.4. Extent of crystallization heterogeneity in Se-Te glasses.

In Fig.4 one can see a strong non-linear effect of small additions of Te on distribution of crystalline nuclei in selenium glass: while Se and common Se-Te glasses ( $\geq 5$  at%Te) crystallize mostly from the surface, the low-Te glasses (1%Te and, especially, 2%Te) tend to crystallize homogeneously.

It should be noted that this method does not take in mind a change in optical path due to removal of the surface layer: it is clear that such a procedure should increase transparency of a sample when other conditions being equal. In order to evaluate maximum error due to thinning, let us consider the 2%Te sample in which the  $(T_3-T_2)$  value is minimal. If one attributes this difference entirely to the sample thinning, then the revised values are  $(T_3-T_2)^*=0$  and  $G_2^*=0$  (an ideal homogeneous case) instead of initial values  $(T_3-T_2)=0.06$  and  $G_2=0.11$ . This is not a considerable correction, thus, the thinning effect on  $G_2$  can be neglected as compared with the compositional effect shown in Fig.4.

### 3.3. Ultrasonic treatments

Ultrasonic experiments start beginning from No.4 in Table 1. There are four treatments (U1, U2, U3, U4 and Nos.5,7,9,10, respectively); each one differs from other in one or two respects: 40°C in U1 and U3 *versus* 50°C in U2 and U4, cooling cell in U1 and U2 *versus* chemical glass (Fig.2) in U3 and U4, free cooling in the same container in U1, U2, U3 *versus* soft quenching in the room temperature water in U4. Using such a wide region of treatment conditions in this pioneering work we searched *new effects* due to ultrasonic action but not their detailed investigation.

#### 3.3.1. Temperature contribution

Ultrasound treatment in the cavitation regime always means simultaneous heating of glass, the temperature being passing through the glass transition temperature of selenium ( $T_g \approx 35^\circ\text{C}$ ) up to the end temperature of 40°C or 50°C, which are indicated in Table 1. Since temperature itself can contribute into crystallization, the temperature effect in change of transparency due to cavitation should be evaluated. Thus, a special experiment on Se glass (0%Te) having the same prehistory as No.4 in Table 1 (ageing with following removing of surface layer) was made. This sample was subjected to temperature treatment in US-cell, however, without switching on the US-generator. The time-temperature regime, from room temperature to 40°C, was the same that for the U1 treatment (No.5 in Table 1). Optical spectra of this sample are compared in Fig.5 with the spectrum of Se sample having the same time-temperature prehistory plus an additional US treatment. It is seen a reasonable variations of intensity, however, without changing of form of spectra in the considered region of 400-1000  $\text{cm}^{-1}$ . Apropos, the form does not change after US-treatments, being depending only on chemical composition of a sample.

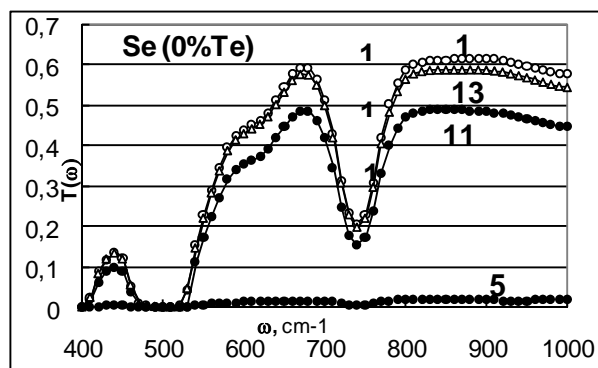


Fig. 5. IR-spectra of Se glasses subjected to thermal treatment (13) and ultrasonic/thermal treatment (5). The sample 13 was previously aged (11) and then grinding and polishing (12) in the same manner that the sample 5 was pre-treated.

In Fig.5 it is seen that the temperature subjected Se sample has a slightly decreased transparency (i.e. transmission at 1000  $\text{cm}^{-1}$ ), from  $T(12)=0.58$  to  $T(13)=0.55$ . Contrary, ultrasonic treatment of the serial Se sample having  $T_4=0.57$  (see No.4 for 0%Te in Fig.2) made the resultant sample 5 almost dark (see spectrum 5 with  $T_5=0.01$  in Fig.5, and also No.5 for 0%Te in Fig.2). Based on this result one can state that the temperature contribution in change of transparency is negligible as compared with ultrasonic contribution.

On the other hand, the ultrasonic contribution cannot be separated from the temperature one, since US energy strongly dissipates in both the medium and the sample. Thus, we can consider either temperature effect on transparency and underlying crystallization (e.g., 12→13) or ultrasonic/temperature effect (e.g., 4→5). Therefore in Table 1 we fix the end temperature of the medium as the parameter of ultrasonic treatment, the other parameters being container (cooling cell or “chemical” glass) and quenching (free cooling in the container or water quenching). They are also given in the Table.

#### 3.3.2. Ultrasonic induced anisotropy

The glass is known to possess an intrinsic isotropy. In practice, however, some anisotropy, which is induced both accidentally and advisedly, can exist. In order to evaluate anisotropic effects we have created the second B-B pair of planes perpendicular to initial A-A planes (see treatment No.4 in Table 1) and having actually the same optical path or thickness (compare columns  $d_{A-A}$  and  $d_{B-B}$  in Table 1). The relation of transparencies in perpendicular directions  $T_B/T_A=A$  is considered as a measure of optical anisotropy,  $A=1$  being the case of ideal isotropy. Note that A-A planes are parallel to the US-transmitter (see Fig.1).

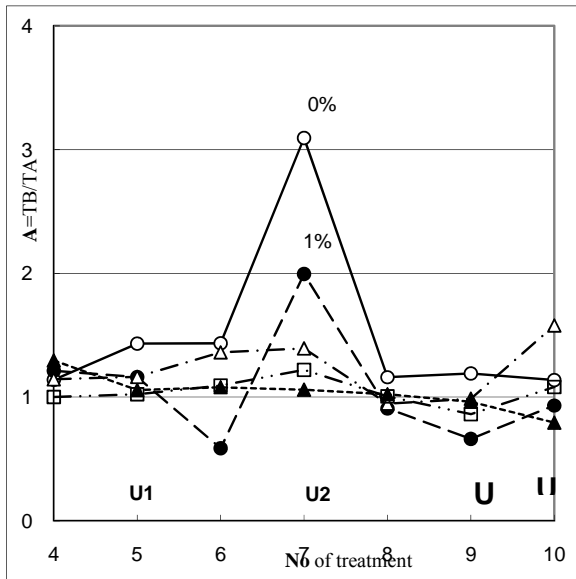


Fig. 6. Optical anisotropy of Se-Te glasses depending on treatment (see Table 1 for the treatment details). Each broken line and related points correspond to a definite composition: open circles for 0%, close circles for 1%, open triangles for 2%, closed triangles for 5%, and open squares for 10%Te.

From Fig. 6 it is seen that high-Te samples of 5%Te (closed triangles) and 10%Te (open squares) are most isotropic, while Se and 1%Te can generate a considerable anisotropic response, up to 3 times for Se (0%) after second ultrasonic treatment (U2).

As to the treatments, U2 and U4, both having the highest final temperature of 50°C, are most effective in developing anisotropy. Thus, lifting of temperature together with temperature gradients (U2) may be the factors that increase anisotropy as a result of US treatment.

The anisotropy development *after* US treatment, as it is seen for No. 6 (relaxation) in Fig. 6, is of a special interest. From synergetic point of view this means that the patterns that were formed in the process of ultrasonic treatment U1 continued their evolution when ageing of sample below  $T_g$ . The source of optical anisotropy is unclear (it may be, for example, a collective reorientation of crystallites in glassy matrix), and special experiments and/or methods need in order to understand the nature of this phenomenon.

### 3.3.3. Ultrasonic induced enlightenment

Once another way to evaluate optical anisotropy is to compare the change of transparency in the A-A and B-B directions separately, as it is shown in Fig. 7 and Fig. 8. The  $\Delta T$  value there is a difference between the treated state (e.g., No. 7 for U2 treatment) and the previous state (the relaxed No. 6 state for U2).

From Fig. 7 it is seen that the first US treatment U1 leads to strong darkening for Se, but ineffective for all other compositions, except slight almost isotropic darkening ( $\Delta T < 0$ ) for 1%Te and a more pronounced darkening in the B-B direction for 5%Te.

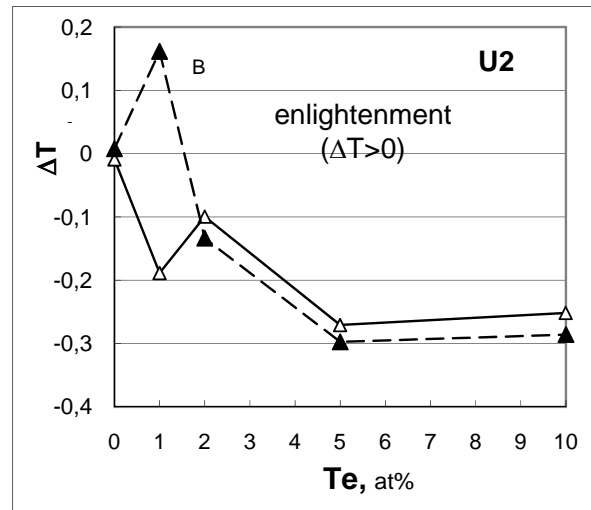
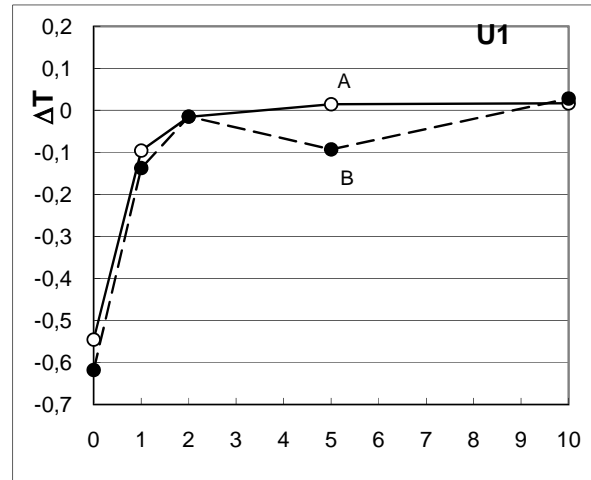


Fig. 7. Change in transparency of Se-Te glasses in different directions as a result of US-treatment in the cooled cell.

The next U2 treatment reveals an unusual effect of *enlightenment* ( $\Delta T > 0$ ), which is observed at 1%Te. It is interesting that enlightenment in the B-B direction is compensated by the darkening in the A-A direction, a fact that may mean that there is no crystallization during the U2 treatment of the 1%Te sample, but the just existing crystallites does reorient in the exited anisotropic medium (see Fig. 1; side A is parallel to the emitter end).

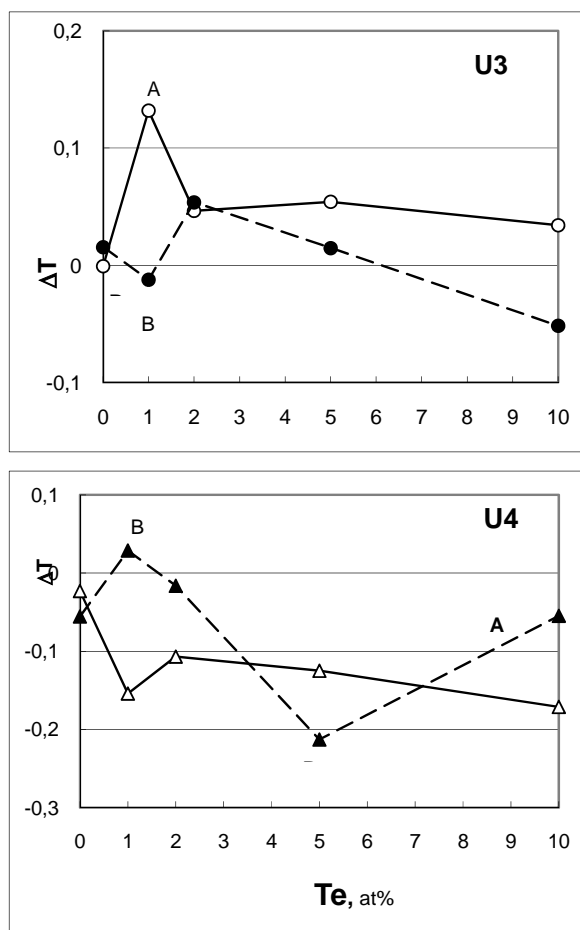


Fig.8. Change in transparency of Se-Te glasses in different directions as a result of US-treatment in glass (Fig.1).

During U3 treatment side A is enlightened for all the samples, while perpendicular side B may both darkened and lightened depending on the glass composition. Development of anisotropy  $\Delta A = |\Delta T_A - \Delta T_B|$  is seen for 1%, 5%, and 10% samples. Finally, the U4 treatment clearly demonstrates development of anisotropy for all the compositions except pure Se, in which anisotropic effect  $\Delta A$  is actually absent for all the US treatments. This conclusion on the first glance is inconsistent with Fig.6, in which just Se at U2 reveals the largest anisotropy  $A=3$ . However, it is an apparent contradiction since  $A = T_B/T_A$  evaluates just existing anisotropy, while  $\Delta A = |\Delta T_A - \Delta T_B|$  evaluates misbalance in transparency change in perpendicular directions, which arises as a result of the treatment under consideration.

#### 4. Conclusions

In this pilot study of ultrasonic influence on bulk chalcogenide glasses we reveal both fruitfulness and complexity of US treatments. On the one hand, it is shown a possibility of large change in glass transparency and specific effects such as development of anisotropy and/or

enlightenment, on the other hand, the effects vary in a wide limits and in a rather chaotic way, when the dependencies (of glass composition/prehistory and of the treating regime) can be collected but not understood in usual terms. Analysis of the obtained data leads to the conclusion that we deal with the self-organizing structures that develops in glass, and ultrasonic field can participate actively at their formation. Such an approach, however, is rather unusual in glass science and never was directly used for preparing of materials with desired properties, e.g. chalcogenide ceramics with definite optical and mechanical properties. At the same time, there exist a basis for realization of synergetic approach in glasses, because they are *open systems* (especially at the temperature-related treatments), which consists of *bistable elements* (ordinary bonds in reverse transformation into alternative hypervalent bonds after Dembovsky [7-8]), that act *cooperatively* (in the form of bond wave, i.e. spatio-temporal correlation of the bond exchange acts, after Chechetkina [9-11]). It seems likely that further experiments, which take into account the self-organizing nature of chemical bonding in glass, permit to understand the observed effects with following using them in practice.

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