Peculiarities of crystallization of aged and as-quenched glassy selenium

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Glassy selenium is a fertile object for the study even nowadays. Selenium is a member of the chalcogen's family. The chalcogen's are VIa group elements of the periodic table. The principal commercial source of selenium is as by product of copper refining, its major uses are in the manufacture of electronic equipment, in pigments, and in making glass.

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1. Introduction

Selenium is a nutritiously essential element. People used selenium for healthy joints, heart and eyes. It plays a crucial role in DNA system, the immune system and the reproductive system. It also helps fights cancer and other diseases. Over than internal human uses selenium it also used in manufacturing. It is used to color and decolorized glasses [1].

Physical aging is known an important but still one of the most controversial problem in modern glass science, remaining highly disputable even for such canonical glass-former as floppy selenium [2].

Chalcogenide glassy semiconductors belong to the non-crystalline materials with sophisticated structure which is not structurally in equilibrium state. The processes of structural relaxation lead to a change (sometimes significant) in physical properties, including mechanical and dielectric [2-4].

Selenium, the simplest representative of amorphous chalcogenides is known to consist of a chain and ring fragments. In this study we report changes in some physical properties caused by relaxation.

2. Samples and measurements technique

Glassy selenium was obtained by conventional melt-quenching technology with maximal temperature of melt T=1173 K held 3 h, and then spontaneously cooked at air to room temperature. We studied "aged" (for several tens of years) specimens for "rapid" relaxation processes to be excluded.

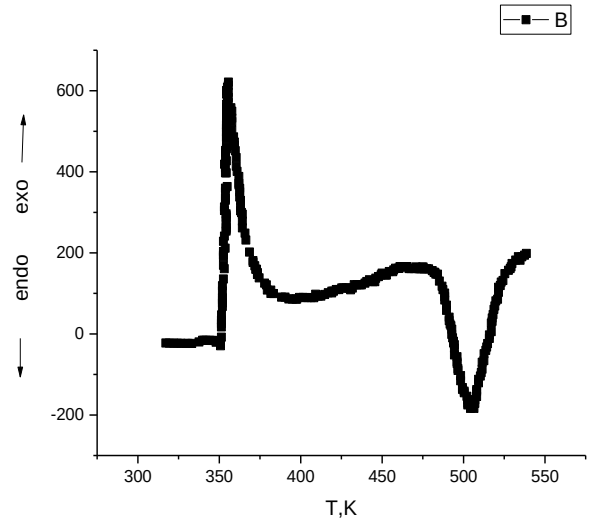
Techniques exploited are differential thermal analysis (DTA), X-ray powder diffraction (XRD), dielectric and mechanical spectroscopy.

3. Results and discussion

Result of structural relaxation is revealed by differential thermal analysis (DTA) methods on "aged" at room temperature for more than ten years and "as-quenched" samples of glassy selenium. We can observe a significant difference in temperature of crystallization peaks, which is shown in Fig. 1. The glass formation, crystallization, and melting phenomena are clearly visible as endothermic, exothermic, and endothermic peaks, in the diagrams respectively. As shown, effect of glass formation (T_g = 326 K), clear peaks of crystallization (T_c = 347 K), and melting (T_m=491 K) seen on DTA curves on "aged" samples of glassy selenium, while on 'as-quenched" samples – T_g = 322 K, T_c= 395 K, T_m= 490K. In both cases heating velocities were nearly 5 K/min.

Difference observed in T_c values probably is caused by transition from homogeneous nucleation in as-quenched selenium to heterogeneous in "aged" samples.

As seen the crystallization of "aged" selenium begins at 348 K and held with less energy consumption than the "as-quenched", which begins in the vicinity of the crystallization temperature of 393 K and the peak broadens and becomes wider.



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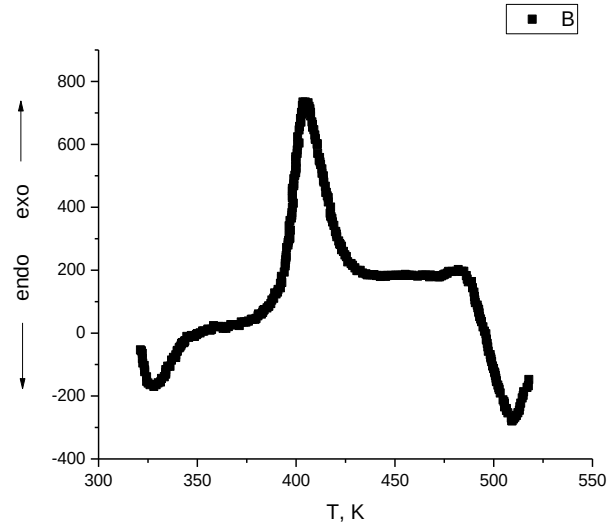

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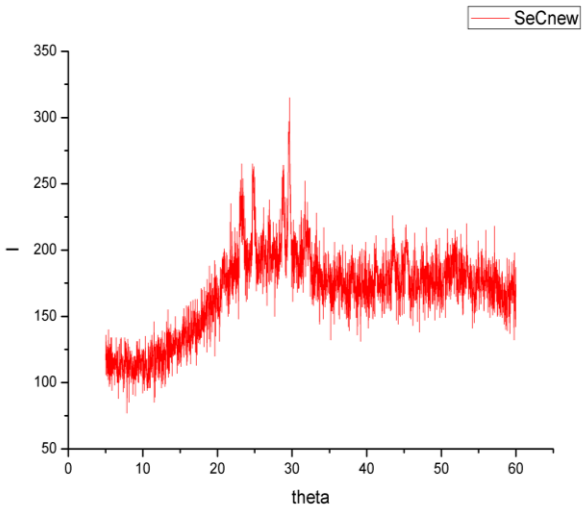
Fig. 1. DTA curves for "aged" (a) and "as-quenched" (b) glassy selenium

XRD data confirm amorphous origin of "aged" and as-quenched samples (Fig. 2). About glassy state of investigated samples testify images of micro fracture pattern and surface, obtained by electron microscope at different zooming, which are shown on Fig. 3.



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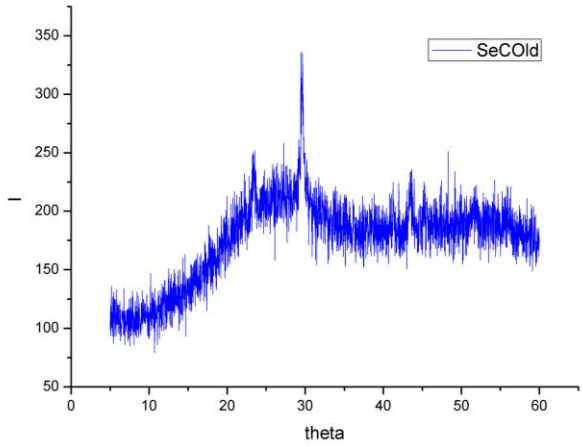

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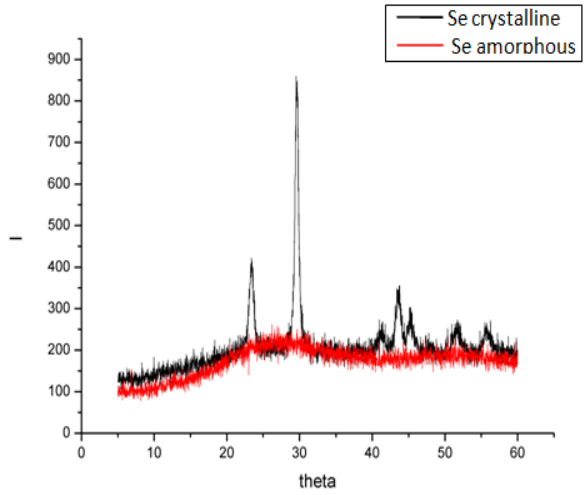

c

Fig. 2. X-ray diffraction patterns of "aged" (a), as-quenched (b) and crystallized in comparison with amorphous (c) selenium samples

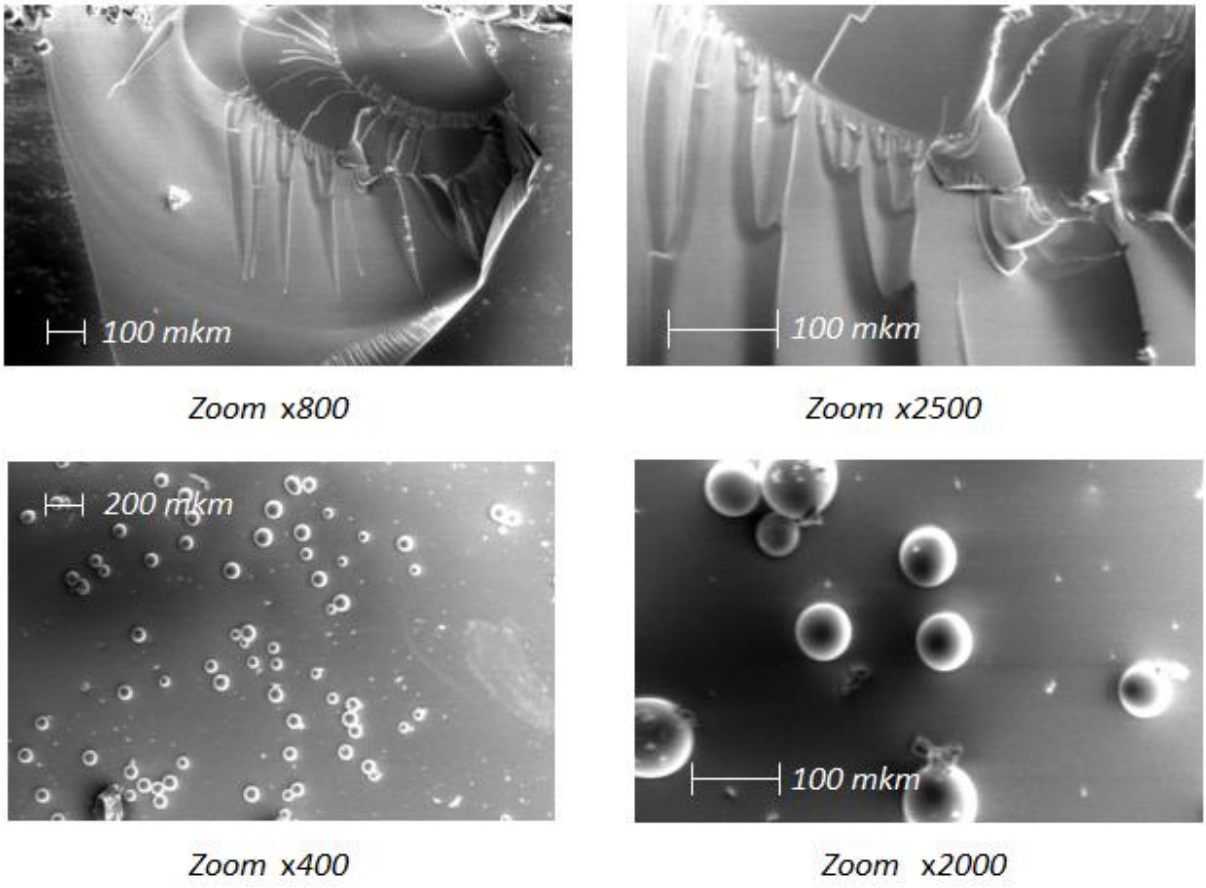

Fig. 3. Microfracture pattern and surface images of glassy selenium, obtained by electron microscope

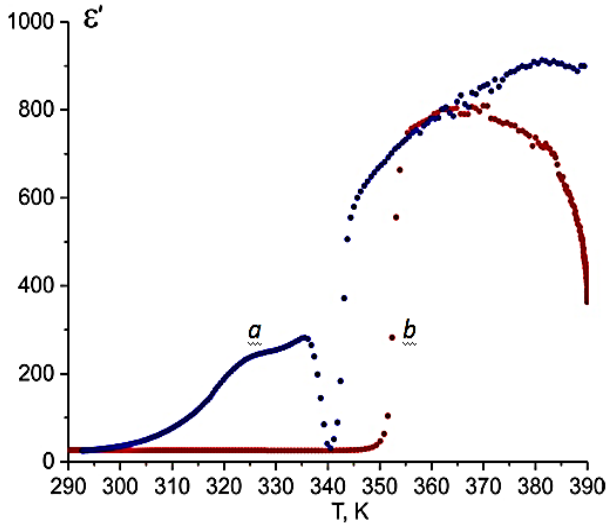

Fig. 4. Temperature change of dielectric permittivity for "aged" (a) and "as-quenched" (b) selenium samples

In parallel with the DTA, crystallization processes was studied by dielectric spectroscopy. As example, the results of dielectric investigation at kilohertz frequency range shown in Fig. 4. Temperature change of sample dielectric permittivity ε' show the anomaly at beginning of crystallization of "aged" selenium at 338 K, and for "as-quenched" at 358 K. High value of ε' is due to high conductivity and dielectric losses of sample.

Investigation of internal friction temperature dependences at ultralow frequencies (0,01 –1 Hz) by inverse torsion pendulum of as-quenched selenium samples show the presence of several peaks (Fig. 5), which in the high-temperature region are associated with the softening (323 K) and crystallization (near 373 K) of the glassy selenium. Unfortunately, analogous investigations on aged samples of selenium were not carried out because of the sample destruction at the crystallization even with minimal deformations.

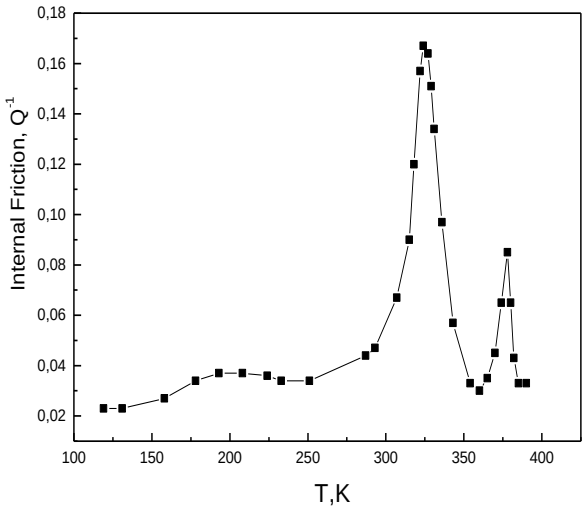

Fig. 5. Temperature dependence of internal friction at frequency 1 Hz in glassy selenium

The difference between temperature anomalies received by DTA, dielectric and mechanical spectroscopy can be caused by different heating rates of samples in each research methods. It can be supposed that the different behavior of glassy selenium properties due to the presence of crystalline phase nuclei (nanocrystals) in aged samples.

Nearly all physical properties of amorphous selenium evince an aging behavior, which is just a form of structural relaxation whereby the proper changes with time as the material is left to anneal isothermally. At room temperature, the whole relaxation normally occurs over a time scale of approximately 1000 hours (42 days). The aging behavior has been reported for various properties and is a fundamental property of all glasses.

Pure glassy selenium is sensitive to crystallization and invariable crystallizes at a rate determined by the nucleation process, the morphology of growth, and the temperature.

4. Conclusion

Thus, even after decades of aging at room temperature, glassy selenium remains amorphous, but in it forms nanocrystals, which lead to a significant difference in the kinetics of crystallization of "aged" and "as-quenched" glasses. Physical properties of amorphous selenium also experience aging processes, which probable is caused by a structural relaxation. Preliminary Raman scattering results strongly support this mechanism of structural relaxation.

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References

[1] M. Micouleut, Rep. Progr. Phys. **79**, N6 (2016).
[2] S. Dash, P. Chen, P. Boolchand, J. Chem. Phys. 146224506 (2017).
[3] R. Golovchak, A. Kozdrast, O. Shpotyk, S. Kozukhin, J. M. Saiterm, J. Mater. Sci. **44**, 3962 (2000).
[4] V. S. Minaev, N. M. Parfenov, S. P. Timoshenkov, V. P. Vassiliev, V. V. Kalugin, L. P. Batynya, J. Non-Cryst. Sol. **404**, 174 (2014).

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