

On the Possibility of the Existence of Inorganic Glasses with Plasticity at Temperatures Below the Softening Point

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Many studies note the importance of the plasticity of glass for improving their mechanical properties [1–3]. The plasticity of glasses is the subject of research and is included in the titles of articles on both oxide [4, 5] and chalcogenide [6, 7] glasses. However, all these works use the concept of plasticity, which does not imply the possibility of numerical measurement of this property. The methodology of numerical measurement of plasticity was developed in the works of Y.V. Milman (see, for example, [8]). This article analyzes the prospects for obtaining chalcogenide glasses with a high degree of plasticity by introducing silver chalcogenides in their composition. In this case, numerical values of plasticity according to Milman are used.

It has been shown previously that the introduction of silver chalcogenides in the composition of chalcogenide glasses leads, on the one hand, to a significant increase in their plasticity (δ_v) [9], and on the other hand, to a slower decrease in the softening temperature (T_g) compared to the introduction of chalcogenides of other monovalent and even divalent metals [10]. This is explained by the formation of Ag–Ag metallophilic bonds, whose existence in silver chalcogenides was confirmed by the quantum chemical calculations [11]. Unlike the covalent bonds that form chalcogenide glasses, metallophilic ones are non-directional. As for chalcogenide glasses containing silver, earlier works that studied the structure of glasses by direct structural methods repeatedly pointed out the high mutual coordination of silver atoms and the small distance between them [12–14].

Taking into account the points mentioned above, in this paper a comparison of correlation dependencies $\delta_v - T_g$ is carried out for classical chalcogenide glasses (Sb–Ge–Se)–A, glasses containing up to 40 mol % of monovalent metal chalcogenide (As₂S₃–Tl₂S)–B, and glasses containing up to 40 mol % silver chalcogenide (0.73GeSe₂ · 0.27Sb₂Se₃)–Ag₂Se–C.

The magnitude of δ_v for all glasses was calculated using the Milman equation [8]:

$$\delta_v = 1 - 14.3(1 - \nu - 2\nu^2) \frac{H_V}{E},$$

where E is Young's modulus, H_V is the Vickers microhardness, and ν is Poisson's ratio. It should be noted that although the concept of plasticity is often used when discussing the mechanical properties of glasses, its numerical values are not given in the literature. Therefore, to illustrate the application of the Milman equation, the plasticity values calculated using it and using the experimental values E , H_V , and ν are given below [1]: 13Na₂O–6MgO–10CaO–71SiO₂ (window glass) $\delta_v = 0.23$; 12Na₂O–6MgO–18Al₂O₃–6B₂O₃–58SiO₂ $\delta_v = 0.18$; and 25Cs₂O–20Al₂O₃–55B₂O₃ $\delta_v = 0.32$.

We now return to building dependencies $\delta_v - T_g$ for chalcogenide glasses. The values required for this are E , H_V , and ν , as well as T_g , for glasses *A* and *B* taken from [15], and for glasses *C* from [9]. The reduced temperature (is used as the temperature axis) T^* , equal to the temperature at which the measurements are taken (in this case, room temperature), expressed in fractions T_g on the Kelvin scale. The obtained dependencies are shown in Fig. 1.

As T_g approaches the temperature of the measurements, the plasticity of the glass increases naturally, tending to a value comparable to 1. The material begins to exhibit real plasticity when $\delta_v > 1$. The introduction of a monovalent metal compound in the glass composition (Tl_2S), which destroys the developed three-dimensional network of bonds in the As₂S₃ glass, reinforces this trend. An even more pronounced increase in this tendency is observed when introducing Ag in the glass composition. On the one hand, silver also destroys the three-dimensional developed network of directed covalent bonds that effectively prevent the mechanical deformation of glass. On the other

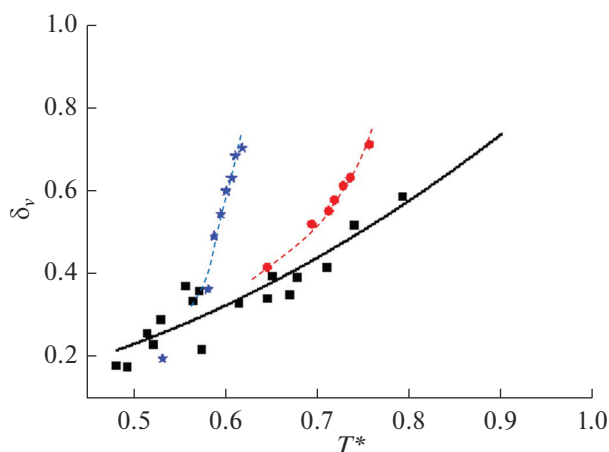


Fig. 1. Dependencies of glass plasticity according to Milman on the temperature of measurements, expressed in fractions of T_g of the corresponding to glass. Circles denote glasses of the $\text{As}_2\text{S}_3\text{--Tl}_2\text{S}$ system (calculation using experimental data [15]); squares denote glasses of the Sb--Ge--Se system (calculation using experimental data [15]); asterisks denote experimental data for glasses of the $(0.73\text{GeSe}_2 \cdot 0.27\text{Sb}_2\text{Se}_3)\text{--Ag}_2\text{Se}$ [9] system.

hand, silver forms metallophilic bonds. These nondirectional bonds do not create a significant obstacle to the mechanical deformation of glass, but, by maintaining a developed network of interatomic interactions, they effectively slow down the decrease in T_g .

Extrapolation of dependence $\delta_v(T^*)$ for glasses with silver to high values of T^* allows us to assume the possibility of the existence of glasses that are subject to plastic deformation under external influence at temperatures below T_g . This possibility does not fit well into the classical theory of the glassy state. The softening temperature implies that there is sufficient energy from thermal fluctuations to initiate an atomic rearrangement. Plasticity implies the possibility of the deformation of a solid body when a directed mechanical stress is applied. For each silver atom in its chalcogenides, there are 2–4 metallophilic bonds [16]. Apparently, they are sufficient to prevent the transition of the silver atom from one local minimum of potential energy to another. However, due to their nondirectionality, they are not able to prevent, for example, shearing mechanical stress. An example of such a material is glassy Ag_2Se film, which does not crystallize when heated to at least 420 K [17] and has, according to the results of measurements using the load-unload method, a ductility equal to 0.9 [9]. In the work [18], glasses of the Ag--Ge--Se system containing glassy, liquation regions of the Ag_2Se composition were studied. The authors concluded that for these glassy inclusions $T_g = 560$ K, and the average coordination number of the glassy network is 2.26.

The conducted analysis of the experimental data convincingly demonstrates the specificity of the influ-

ence of silver chalcogenide on the properties of chalcogenide glasses, which can be explained by the formation of metallophilic bonds. It can be expected that in the case of the synthesis of chalcogenide glasses containing 50–60 mol % silver chalcogenide, they will have a plasticity approaching 0.9, which is a value characteristic of elemental metals.

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CONFLICT OF INTEREST

The author of this work declares that he has no conflicts of interest.

REFERENCES

- Januchta, K., Stepniewska, M., Jensen, L.R., Zhang, Y., Somers, M.A.J., Bauchy, M., Yue, Y., and Smedskjaer, M.M., Breaking the limit of micro-ductility in oxide glasses, *Adv. Sci.*, 2019, vol. 6, no. 18, article no. 1901281. <https://doi.org/10.1002/advs.201901281>
- Redmond, K., Oxide glass exhibits plasticity without fracture at room temperature, *MRS Bull.*, 2020, vol. 45, no. 2, pp. 78–79. <https://doi.org/10.1557/mrs.2020.48>
- Frankberg, E.J., Kalikka, J., García Ferré, F., Joly-Pottuz, L., Salminen, T., Hintikka, J., Hokka, M., Koneti, S., Douillard, T., Le Saint, B., Kreiml, P., Cordill, M.J., Epicier, T., Stauffer, D., Vanazzi, M., Roiban, L., Akola, J., Di Fonzo, F., Levänen, E., and Masenelli-Varlot, K., Highly ductile amorphous oxide at room temperature and high strain rate, *Science*, 2019, vol. 366, no. 6467, pp. 864–869. <https://doi.org/10.1126/science.aav125>
- Vandembroucq, D., Deschamps, T., Coussa, C., Perriot, A., Barthel, E., Champagnon, B., and Martinet, C., Density hardening plasticity and mechanical ageing of silica glass under pressure: A Raman spectroscopic study, *J. Phys.: Condens. Matter*, 2008, vol. 20, no. 48, article no. 485221. <https://doi.org/10.1088/0953-8984/20/48/485221>
- Lee, K.-H., Yang, Y., Ding, L., Ziebarth, B., Davis, M.J., and Mauro, J.C., Plasticity of borosilicate glasses under uniaxial tension, *J. Am. Ceram. Soc.*, 2020, vol. 103, no. 8, pp. 4295–4303. <https://doi.org/10.1111/jace.17163>
- Varshneya, A.K. and Mauro, D.J., Microhardness, indentation toughness, elasticity, plasticity, and brittleness of Ge--Sb--Se chalcogenide glasses, *J. Non-Cryst. Solids*, 2007, vol. 353, nos. 13–15, pp. 1291–1297. <https://doi.org/10.1016/j.jnoncrsol.2006.10.072>
- Yannopoulos, S.N., Intramolecular structural model for photoinduced plasticity in chalcogenide glasses, *Phys. Rev. B: Condens. Matter Phys.*, 2003, vol. 68, no. 6, article no. 064206. <https://doi.org/10.1103/PhysRevB.68.064206>

8. Milman, Y.V., Chugunova, S.I., Goncharova, I.V., and Golubenko, A.A., Plasticity of materials determined by the indentation method, *Usp. Fiz. Met.*, 2018, vol. 19, pp. 271–308.
<https://doi.org/10.15407/ufm.19.03.271>
9. Tveryanovich, Yu.S., Fazletdinov, T.R., Tverjanovich, A.S., Pankin, D.V., Smirnov, E.V., Tolochko, O.V., Panov, M.S., Churbanov, M.F., Skripachev, I.V., and Shevelko, M.M., Increasing the plasticity of chalcogenide glasses in the system $\text{Ag}_2\text{Se}-\text{Sb}_2\text{Se}_3-\text{GeSe}_2$, *Chem. Mater.*, 2022, vol. 34, no. 6, pp. 2743–2751.
<https://doi.org/10.1021/acs.chemmater.1c04312>
10. Tver'yanovich, Yu.S., Fazletdinov, T.R., and TomaeV, V.V., Peculiarities of the effect of silver chalcogenides on the glass-formation temperature of chalcogenide glasses with Ionic conduction, *Russ. J. Electrochem.*, 2023, vol. 59, no. 8, pp. 567–572.
<https://doi.org/10.1134/S1023193523080086>
11. Evarestov, R.A., Panin, A.I., and Tverjanovich, Yu.S., Argentophilic interactions in argentum chalcogenides: First principles calculations and topological analysis of electron density, *J. Comput. Chem.*, 2021, vol. 42, no. 4, pp. 242–247.
<https://doi.org/10.1002/jcc.26451>
12. Bychkov, E., Price, D.L., Benmore, C.J., and Hannon, A.C., Ion transport regimes in chalcogenide and chalcogen halide glasses: From the host to the cation-related network connectivity, *Solid State Ionics*, 2002, vols. 154–155, pp. 349–359.
[https://doi.org/10.1016/S0167-2738\(02\)00572-6](https://doi.org/10.1016/S0167-2738(02)00572-6)
13. Salmon, P.S., Xin, S., and Fischer, H.E., Structure of the glassy fashion conductor AgPS_3 by neutron diffraction, *Phys. Rev. B*, 1998, vol. 58, no. 10, pp. 6115–6123.
<https://doi.org/10.1103/PhysRevB.58.6115>
14. Akola, J., Jovári, P., Kaban, I., Voleská, I., Kolář, J., Wagner, T., and Jones, R.O., Structure, electronic, and vibrational properties of amorphous AsS_2 and AgAsS_2 : Experimentally constrained density functional study, *Phys. Rev. B*, 2014, vol. 89, article no. 064202.
<https://doi.org/10.1103/PhysRevB.89.064202>
15. Borisova, Z.U., *Glassy Semiconductors*, New York: Springer, 1981.
16. Tveryanovich, Yu.S., Fazletdinov, T.R., Tverjanovich, A.S., Fadin, Yu.A., and Nikolskii, A.B., Features of chemical interactions in silver chalcogenides responsible for their high plasticity, *Russ. J. Gen. Chem.*, 2020, vol. 90, no. 11, pp. 2203–2204.
<https://doi.org/10.1134/S1070363220110304>
17. Tveryanovich, Yu.S., Razumtcev, A.A., Fazletdinov, T.R., Krzhizhanovskaya, M.G., and Borisov, E.N. Stabilization of high-temperature Ag_2Se phase at room temperature during the crystallization of an amorphous film, *Thin Solid Films*, 2020, vol. 709, no. 1, article no. 138187.
<https://doi.org/10.1016/j.tsf.2020.138187>
18. Wang, Y., Mitkova, M., Georgiev, D.G., Mamedov, S., and Boolchand, P., Macroscopic phase separation of Se-rich ($x < 1/3$) ternary $\text{Ag}_y(\text{Ge}_x\text{Se}_{1-x})_{1-y}$ glasses, *J. Phys.: Condens. Matter*, 2003, vol. 15, no. 16, article no. S1573.
<https://doi.org/10.1088/0953-8984/15/16/307>

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