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THE MAIN FEATURES OF CHANGES OF SOUND VELOCITY IN GLASSES AT THE VICINITY OF GLASS TRANSITION TEMPERATURES

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Ultrasonic waves velocity v measurements are used for monitoring the processes of structural relaxation in glasses near glass transition temperature T_g . Different thermal histories of glasses are employed. Using relaxation of "mildly quenched" and "overstabilized" glasses enabled reliable tracing of the temperature dependence of v in metastable liquid states below T_g ; the curve is a smooth continuation of high-frequency limiting values estimated from measurements above T_g . Time dependence of v in isothermal experiments is non-exponential due to both nonlinearity and to the existence of several relaxation processes: the latter fact is confirmed by "cross-over" experiments.

The main purpose of the paper is the attempt to move in the direction of studying the states of glassforming systems which are difficult to reach — namely, those of metastable liquid (non-equilibrium with respect to crystallisation but truly stable with respect to structural rearrangements within the totality of disordered states; later we shall call them "equilibrium states") for brevity (ignoring the possibility of crystallisation) at temperatures T below the temperature of normal glass transition T_g . The latter is conventionally defined as corresponding to the value of viscosity $\eta = 10^{13}$ P, that is to the values of the structural relaxation times τ on the order of minutes. Since the dependence $\tau(T)$ in the vicinity of T_g is extremely sharp, reaching the states in question requires very long stabilisation times, and even verifying that equilibrium is really attained is very difficult. On the other hand there are many problems demanding information on the properties of glassformers in such states, both thermodynamic (it is sufficient to mention the Kauzmann's paradox of the entropy $S(T)$ curve extrapolated from labile states intersecting curve $S(T)$ for crystal at a finite temperature $T_K \rightarrow 0K$), and kinetic. The latter are important, beside questions of more academic interest, for technological problems of manufacturing articles (such as high-precision scales for automatic machining) not liable to ageing as well as for TV and video sets. Experimental studies of the processes of stabilisation imply monitoring of a property permitting sufficiently quick measurement. It is important that various properties may be sensitive to different features of the structure. Therefore it seems advisable not to limit ourselves to the one, even most preferable property but develop various methods with a perspective of the parallel monitoring of many different properties. Among them ultrasonic velocities can have a sufficiently good perspective, though their ability to compete with such properties as refractive index n or dielectric permittivity κ is an open question; the drawback being rather large size of samples for measurements and hence not quite sufficiently quick establishing of the thermal equilibrium. The important task for future development would be parallel monitoring of many differing properties and comparing the results.

Two facts can be considered as basic for the approach to above stated problem. (Here we shall investigate the possibilities of using ultrasonic velocity v measurements as measurable quantity defining the state of the material, and imply a "normal behavior" v : increasing with lowering T , and — abruptly diminishing dv/dT at the transition into the non-equilibrium glassy state: transition takes place at $T=T_g' \approx T_g$ depending on the rate of cooling) First, it is always possible to obtain reproducible states by heating the sample well above T_g and after that strictly repeating the time regime $T(t)$ of changing temperature. The following isothermal ($T=\text{const}$, say T_1) exposure in the glassy state always leads to increasing v . This process we shall call "stabilizing from below" (meaning from a mildly quenched state). The second fact is that in the process of manufacturing it more often than not attains some "overstabilized" state (not easy to reproduce unless the whole thermal history of the sample is known) which after heating to the vicinity of T_g appears to be highly nonequilibrium and such as leads to decreasing v in the isothermal exposure at the same T_1 ; this we shall call "stabilizing from above". If

two processes $v(t)$ "from above" state and "from below" value $v = v_0$, then one can assume that the equilibrium state is attained, and $v_0 = v(T_1)$, sound velocity in this state. This method can be used for reliable prolonging the curve $v(T)$ below the range which is usually considered as that of metastable supercooled liquid.

In addition to these results, themselves sufficiently important, one can obtain in the course of described experiments a valuable information about relaxation behavior of the glasses under study. Here again, it is important, that the curves $v(t)$ represent the underlying fundamental process of structure relaxation, and such curves for different measurables (v, n, κ, \dots) are needed for sufficiently full understanding of the process.

The following examples of using ultrasonic velocity measurements for the purposes described have been early partly published in not accessible editions [1-3].

Fig.1 shows results of tracing the equilibrium curve $v(T)$ according to the described programme for boron trioxide. Two main features can be seen: the curve splices well with the literature data [4] for the melt above T_g , and there is a definite curvature — $-dv/dT$ diminishes at lowering T ; the latter bears on the acoustical analogue of the Kauzmann's paradox: without this curvature extrapolated v would become larger than in the crystalline state. (One can expect a similar behavior of $S(T)$ curve with smooth diminishing toward a value somewhat higher than in the crystal at 0 K; such assumption seems preferable to conclusions by some modern theories predicting a true thermodynamic second order transition at equilibrium somewhere near T_K .)

In more details we shall present results obtained on industrial optical glasses. Alkali-boro-silicate glasses BK-8 ($T_g=530^\circ\text{C}$) and K-8 ($T_g=540^\circ\text{C}$) have been studied. The following figures illustrate the time dependencies of sound velocities in isothermal exposures at various temperatures and after varying different thermal histories, and the equilibrium curve $v(T)$ obtained as described above for one of them.

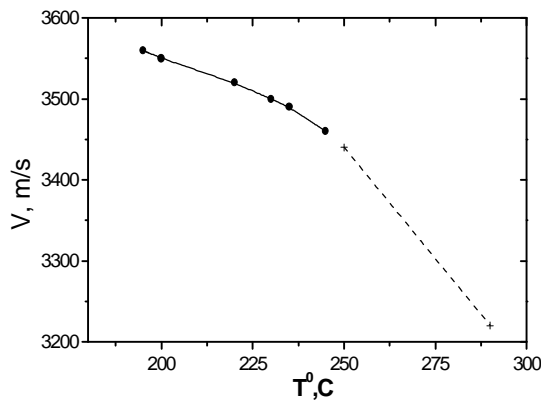


Fig.1 Temperature dependence of sound velocity in B_2O_3 in the equilibrium states. Crosses - data from [4].

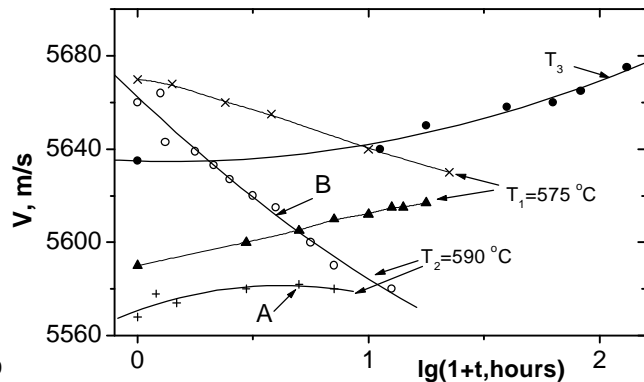


Fig.2 Sound velocity relaxation in the BK-8 glass during isothermal exposures

Fig. 2 illustrates relaxation behavior of sound velocity in BK-8 in some of the experiments performed for the latter purpose. The initial state has been obtained by heating the sample manufactured industrially. The starting point of each exposure was reached by a quick temperature change from the previous exposure followed by 15-minute lag for equilibrating the temperature inhomogeneity. Two pairs of curves are shown, were obtained at some temperatures (575 and 590 stabilising processes from "above" and from "below". First of all, one can see non-linearity: relaxation times τ_A and τ_B , for instance, differ by the factor of 3 (the curves in this picture were approximated by a single relaxation law). It is also clear that the two curves in each pair converge to a common limiting value (not quite reached in the case 575 C).

In Fig 3 the limiting values obtained in this way. are shown as a function of temperature. Even at lower T , where the common limiting value has not been reached, its value is sufficiently well given by the fork of actually reached values. Three points at higher temperatures are found from fitting the

frequency dependent velocities by a proper model of viscoelastic relaxation [1]. Here a smooth common curve joining low- and high-temperature points also can be drawn in the error limits though independent fitting procedure for high-temperature data suggested somewhat deviating values. Similar results have been obtained for glass K-8.

Figs. 4 illustrates relaxation of sound velocity in glass K-8. The time dependence of velocity in isothermal exposures at 482 °C ($T_g = 540^\circ\text{C}$) is shown. Two runs correspond to different

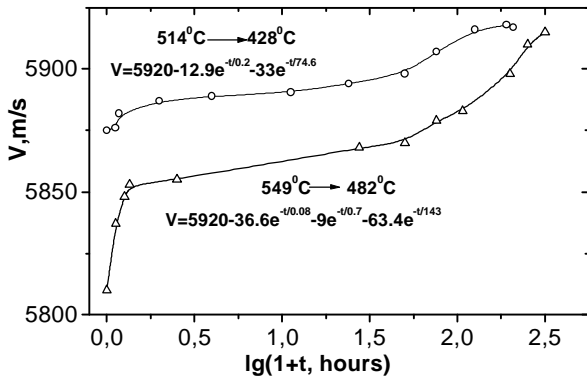


Fig.3. Equilibrium values of sound velocity in the optical glass BÊ-8, as a result of stabilisation near T_g .

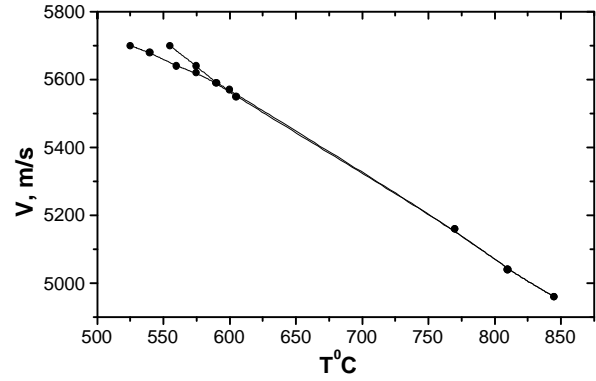


Fig.4. Relaxation of sound velocity in the glass optical glass Ê-8 at 482 °C after preliminary stabilisations at 514 and 549 °C.

temperatures of previous stabilisation (514 and 549 °C). The curves cannot be described by a single relaxation time. The fit by 3 exponentials is shown in the figure but there is no definite reason to assume a discrete relaxation spectrum. Only the width of the spectrum and its loosely defined shape can be unequivocally suggested by the experiment. One should bear in mind that were spectrum really discrete, the values of relaxation times found from independent fittings should not depend on initial conditions.

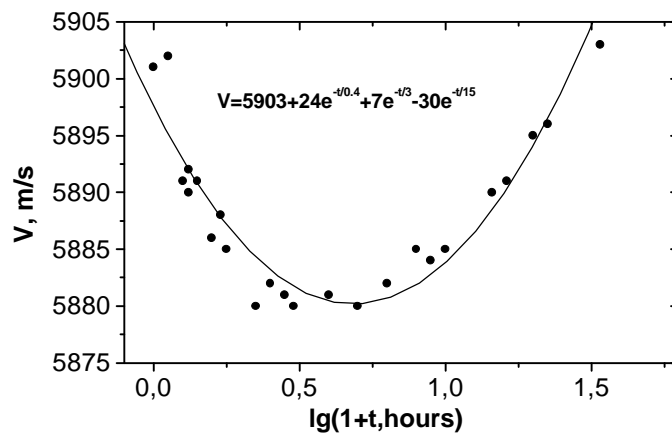


Fig.5. "Cross-over" experiment in the glass Ê-8. Preliminary treatment is described in the text.

Fitting equations shown in the figure are purely conditional and no objective physical meaning should be attached to the values of separate parameters.

Fig. 5 shows the result of so-called cross-over experiment in glass K-8. Its purpose is to underline the width of relaxation spectrum. Here the glass, after the complete stabilising at a high temperature (540 °C) was held at constant $T = 465$ °C for 300 hours (first isothermal exposure) after

which it was quickly brought to 492 °C (second exposure monitored in Fig. 5). The simplest model implied by this kind of behavior possesses two widely differing relaxation times (or a continuous spectrum that can be divided into groups or ranges of such widely differing relaxation times). The first exposure at lower temperature brings to equilibrium the quicker mechanism while the slower one remains in somewhat non-equilibrated state. In the second exposure this mechanism continues equilibration “from below” while the quicker one starts equilibration anew “from above”.

REFERENCES

1. Smerdin S.N. Acoustical properties of optical glasses and their melts: Diss. Cand. Phys.-math.sci. Leningrad State University, L., 1986. 516 p. (in Russian).
2. Smerdin S.N., Nikonov A.M., Nemilov S.V., Solovyev V.A., Bogdanov V.N. Sound velocity changes during annealing processes // *Vestnik LGU*. 1986, iss. 3, p. 101-103. (in Russian).
3. Bogdanov V.N., Pakhnin A.Ya., Solovyev V.A., Nemilov S.V. Ultrasonic investigations of the structural relaxation in a glassy boron trioxide // Abstracts of reports of the XVI All-Russian Conf. On acoustoelectronics and solid state physics. Syktyvkar, 1994, p. 28-31. (in Russian).
4. Goldblatt N., Figgins R., Montrose C.J., Macedo P.B. The temperature dependence of the high frequency longitudinal modulus in B₂O₃ // *Phys.Chem.Glasses*. 1971, v.12, N 1, p.15-18.