

Opalescence during low-temperature structural transitions in inorganic glasses

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A “critical” opalescence and a change in the density of vibrational states have been observed during a low-temperature ($T \ll T_g$) structural transition in inorganic glasses. This is the first report of such observations.

According to the present theory,¹ the structure of glassy solids and the density of vibrational states in them are shaped during vitrification near T_g and then do not change at temperatures $T < T_g$. In the course of a study of the low-frequency Raman spectra of nitrate glasses (Ca, K)(NO₃)₃ ($T_g = 334$ K) and borate glasses (Li₂O)_{0.3}(B₂O₃)_{0.7} ($T_g = 750$ K), we have found that this conceptual understanding is not always correct.

The experiments used a triple multichannel spectrometer,² a 90° scattering geometry, and laser excitation. Spectra were recorded for 15 min at temperature points 20 K apart. The temperature was varied at a rate of 0.02–0.03 K/c between points. Before measurements were taken, the sample was held 10 min at the given point.

Repeated measurements of the spectra of the nitrate and borate glasses carried out over the temperature range 80–300 K revealed no deviations from the standard behavior. However, the very first cooling of the samples to 10 K, followed by heating, resulted in the onset of a turbidity, a decrease in transparency, and an increase in elastic scattering: by four orders of magnitude in the nitrate glasses and by three orders of magnitude in the borate glasses. During heating, the turbidity set in at a temperature of 50–70 K, and it disappeared at 200 K in the borate glasses and 300 K in the nitrate glasses. An unannealed sample of a nitrate glass turned out to be an exceptional case: In this sample, these effects in fact began during the cooling, at temperatures below 50 K. The optical quality of the samples underwent no visible changes after the first and subsequent cooling-heating cycles. No cracks, striations, or residual turbidity were observed.

Let us look at some experimental results. Figure 1a shows the behavior of the 1050-cm⁻¹ line, corresponding to a valence vibration of the NO₃⁺ group, in a nitrate glass over a cycle of cooling and heating (we will say simply “cycle”). The shape and the position of the line remain the same over the entire temperature range. The decrease in the line intensity which is measured results from the onset of turbidity in the

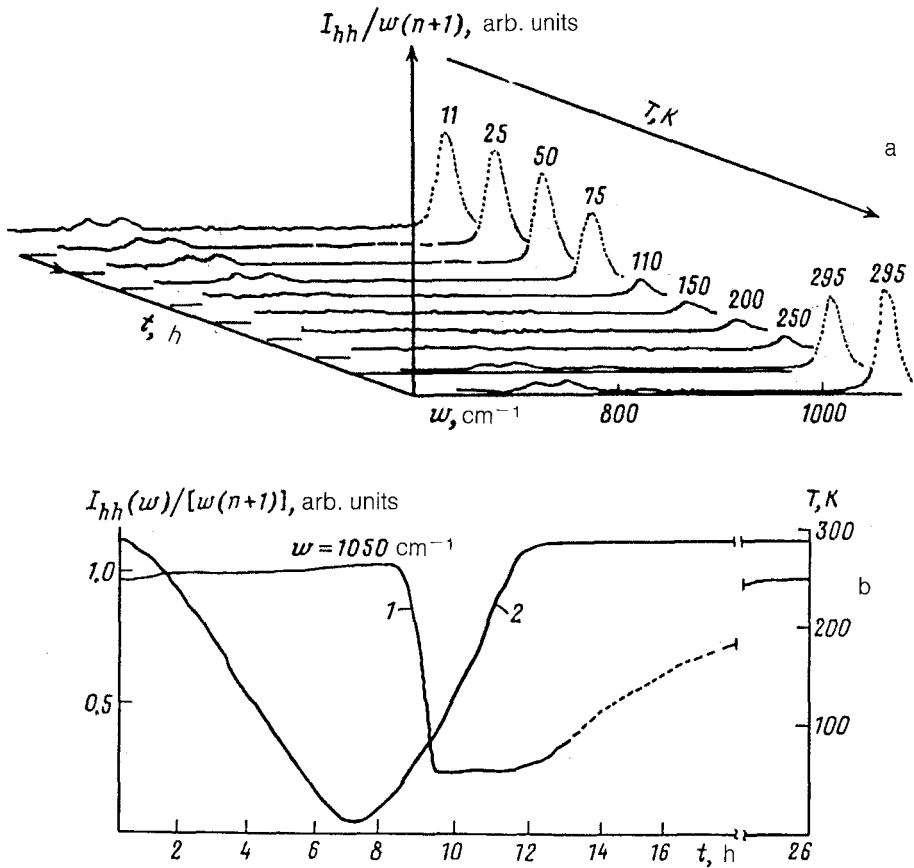


FIG. 1. a: Time and temperature dependence of the changes observed in the 1050-cm⁻¹ line. b: Time evolution of the reduced intensity of the polarized 1050-cm⁻¹ line, i.e., $I_{hh}/\omega[n, \omega, T] + 1$ (1), and of the temperature (2) during the experiment.

sample. It characterizes the loss of transparency by the sample. Figure 1b shows the variations in the temperature and the measured intensity of the 1050-cm⁻¹ line during the experiment. We can work from these results to estimate the time over which the samples lose their transparency ($\sim 10^3$ s) and the time over which the transparency is restored ($\sim 10^4$ s). During subsequent cycles, these effects did not occur; i.e., these were one-time effects. Figure 2a shows the changes in the shape of the low-frequency Raman spectrum during the cooling of a nitrate glass during the first cycle. These changes are caused by (first) a change in the Bose-Einstein factor $n(\omega, T)$, (second) the temperature dependence of the intensity and width of the quasielastic-scattering spectrum, and (third) (according to a calculation from the experimental data) a change in the density of vibrational states. It can be seen from Fig. 2b that after a cycle the density of vibrational states decreases in the frequency interval 50–200 cm⁻¹. This decrease varies from sample to sample. On the average, it amounts to 15% of the

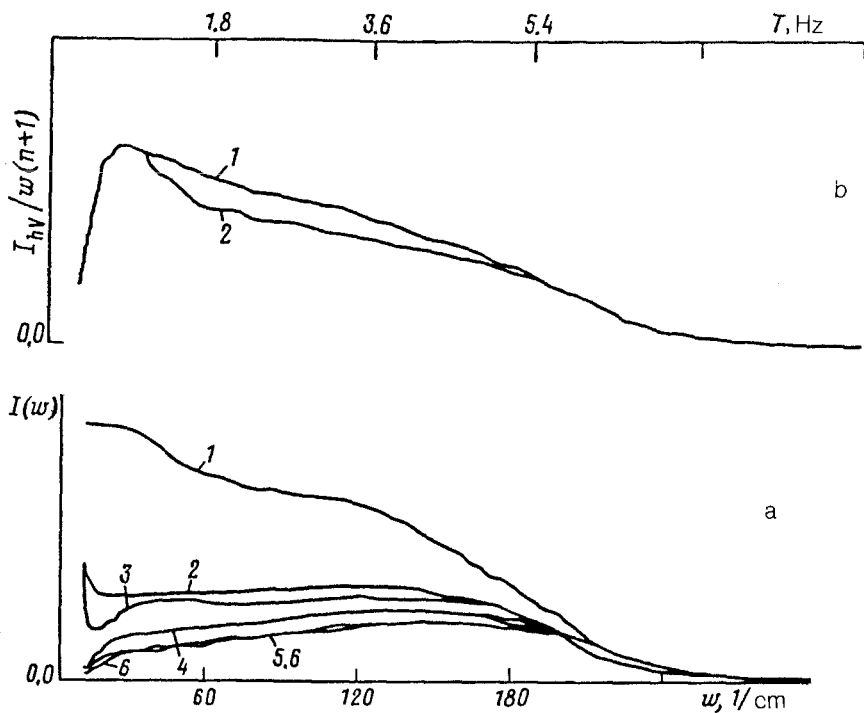


FIG. 2. a: Low-frequency Raman scattering spectra of a nitrate glass at frequency shifts $10\text{--}300\text{ cm}^{-1}$ at several temperatures. 1—300 K; 2—100; 3—70; 5—50; 4—25; 6—14 K. b: Density of vibrational states $g(\omega) \sim I_m/\omega[n(\omega, T) + 1]$ in a nitrate glass (1) before and (2) after the first cooling-heating cycle.

integral density of vibrational states. During subsequent cycles, the density of vibrational states does not change.

A study of the low-frequency Raman scattering spectra and a calculation of the density of vibrational states from them for the borate glasses revealed that, despite the increase in the elastic scattering and the loss of transparency by all three samples during heating, the density of vibrational states remains constant during the first cycle and also during subsequent cycles. This density is described by a log normal distribution with $\omega_c = 65\text{ cm}^{-1}$ (Ref. 3).

The observed increase in the elastic scattering is analogous to the critical opalescence which appears in crystals⁴ during phase transitions. It is a strong elastic scattering of light near the point of a phase transition in regions in which different crystalline phases touch each other. The "critical" opalescence in a glass is distinguished from that in a crystal by the following circumstances. In a glass, it is observed over broader temperature and time intervals. Second, it is of a one-time nature in a glass. The first of these distinctions stems from the large scatter in the parameters of the bonds in the structure of a glass. The second stems from the metastability of the glassy state.

These results can be described in the following way. During the cooling of the

melt, stressed bonds arise in the disordered system of bonds which forms in the glass. Later, some of these stressed bonds relax, while some remain in a stressed state. If a glass is cooled to low temperatures, the thermal contraction may lead to a rupture or a switching in the vicinity of stressed bonds. A region of localized deformation stress arises; we call this region a "switched-bond defect." The dimensions of a switched-bond defect are a few angstroms, according to the changes in the density of vibrational states. The concentration of these switched-bond defects is determined by the history of the glass (on whether it was annealed or quenched during its preparation), on the bond rupture energy, and on the processes which tend to delocalize the stress. As the temperature is lowered, the total number of defects increases, as a result of the creation and conservation of defects. If the sample is then heated, the interatomic distances increase, and the atoms become able to execute larger displacements. The mobility of the atoms increases, and the stress near switched-bond defects begins to relax. The structural network of the glass converts to a state with a minimal deformation stress. The defect relaxation regions can be tens of angstroms in size. The relaxation times found from the time scales for the onset and disappearance of the turbidity are 10^3 – 10^4 s. This result agrees with the structural relaxation times determined from the damping of mechanical agents.⁵ When the concentration of switched-bond defects becomes sufficiently high, we would expect these defects to interact with each other. The relaxation in one such defect would initiate a relaxation in another, and the instabilities in the structure of the glass associated with this restructuring of bonds would extend over a large volume. The result of this process would be a dynamic nonuniformity of the structure and thus a nonuniformity of the refractive index. The latter causes a pronounced elastic scattering of light, i.e., a critical opalescence. The appearance of this opalescence means that the irregularities have a size on the order of the light wavelength, i.e., several thousand angstroms.

The fact that the critical-opalescence effect is of a one-time nature and is governed by the duration of the experiment, which is comparable to the time scale of structural relaxation, shows that the internal stress in the structure of the glass is relieved to a large extent after the first cooling–heating cycle, and the structure becomes stabler. The formation of switched-bond defects during subsequent cycles cannot be ruled out. However, the concentration of these defects will be too low to trigger a structural relaxation over the entire volume of the glass.

The effects observed here are consistent with the conclusion that in the temperature interval 50–70 K, which is in the region of low-temperature anomalies,¹ the structure of a glass which is formed near the vitrification temperature undergoes significant changes as the result of processes which are analogous to the structural changes that occur in crystals at the point of a phase transition.

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