Relaxation dynamics in molecular alloys. II. Supercooled (C2F6)1−x (CClF3)x plastic crystals

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Relaxation dynamics in molecular alloys. II. Supercooled $(C_2F_6)_{1-x}(CClF_3)_x$ plastic crystals

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Dielectric measurements on quenched $(C_2F_6)_{1-x}(CClF_3)_x$ fluorocarbon alloys are reported. In a wide concentration range, rapid cooling prevents these samples from unmixing and the plastic phase, characterized by translational order and orientational disorder, can be supercooled. The relaxation dynamics of crystals with $x = 0.32$ is examined in detail. For temperatures below 50 K it exhibits a dominant primary and indications of secondary relaxation, i.e., typical features of glasses. The α-relaxation process is parametrized in terms of a modified Vogel–Fulcher law. Using this representation, $(C_2F_6)_{0.68}(CClF_3)_{0.32}$ can be characterized as fragile glass according to Angell's classification scheme.

I. INTRODUCTION

A large number of molecular crystals exhibit an orientationally disordered phase[1] in which the high symmetry of the translational (center-of-mass) lattice is achieved via a fast reorientational motion of the aspherical molecules. With decreasing temperatures, most of these compounds undergo structural phase transitions and reveal long-range orientational order at low T.

During the last decade, an increasing number of mixed molecular compounds has been detected in which the formation of long-range orientational order becomes suppressed in a wide range of concentrations.[2] In these, so-called, orientational glasses (OG) the molecular reorientations undergo a cooperative freezing transition devoid of long-range orientational order. In OG, the interplay of site disorder and anisotropic (elastic or electric) interactions are thought to be responsible for the frustrated ground state.[2]

A glassy low-temperature state can also be achieved by rapid cooling (supercooling) of the plastic phase. Well-known examples in this category of metastable low-temperature phases are cyclo-hexanol[3,4] and cyano-adamantane.[5,6] In particular for the latter compound the ageing kinetics leading to orientational order of quenched samples has been studied in detail.[7] It seems plausible that the cooling rate and the steric hindrance of the molecules with respect to reorientations are important parameters to reach the glassy state in these undiluted molecular crystals.

In this paper, we examine the dielectric properties of the fluorocarbons in continuation of our earlier studies of this class of chemicals.[8-11] In particular, it was shown previously[11] that the eutectic mixture $(CF_4)_{0.46}(CClF_3)_{0.54}$ when supercooled from its liquid state, shows a glassy low-temperature behavior, similar to the observations in numerous other quenched organic solutions.[12] Here, it will be demonstrated that $(C_2F_6)_{1-x}(CClF_3)_x$ crystals can be supercooled from their plastic states that extend up to dipole concentrations of more than 50%.

The investigations of the phase diagram of slowly cooled $(C_2F_6)_{1-x}(CClF_3)_x$ fluorocarbon mixtures have already revealed the difficulties to maintain thermal equilibrium (part I of this investigation; Ref. 10). However, the diffusive nature of unmixing transitions offers the chance to prevent segregation by rapid passage through the transformation regime. As a representative example, samples with $x \approx 0.3$ will be discussed in some detail. Then, it is demonstrated that segregation can be suppressed by quenching up to dipole concentrations of 60%. Finally, we provide experimental evidence that the relaxation dynamics of supercooled $(C_2F_6)_{1-x}(CClF_3)_x$ alloys is typical for glassy crystals.

II. EXPERIMENTAL DETAILS

Measurements of dielectric constant ϵ' and loss ϵ'' were performed on highly pure chemicals using the same equipment as reported in Part I.[10] However, the thermal treatment of the $(C_2F_6)_{1-x}(CClF_3)_x$ fluorocarbon mixtures with $x = 0.23$, 0.32, 0.46, 0.61, 0.78, and 0.92 was different. For the present investigation, samples were rapidly cooled down to 4 K. The quenches were started from $T \approx 130$ K for $x \leqslant 0.32$. From the phase diagram (part I; Ref. 10) it is readily seen that here plastic crystals were supercooled. A $(C_2F_6)_{0.68}(CClF_3)_{0.32}$ sample was also quenched starting at 180 K and exhibited identical results. Obviously, for this dipole concentration, the temperature range in which the plastic phase is stable is wide enough that homogeneous solid solutions can be formed, despite a rapid quench. The solidification process has enough time to complete. For convenience, samples with larger dipole concentrations were quenched starting from 180 K. Cooling was performed with typical rates of 30 K/min for 70 K $< T < 120$ K and with even higher cooling rates below these temperatures. This was achieved by pumping cold helium through the sample chamber in a home built variable flow cryostat. With this setup, a definite variation of the cooling rates was difficult. However, a sample accidently cooled with only ≈ 15 K/min showed the same features as the more rapidly cooled ones. On subsequent warming, the dielectric constants were recorded. Heating rates of typically 0.3 K/min were applied.

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In experiments using rates from 0.1–1 K/min, it was checked that the results did not depend on the choice of a certain ramping velocity. In some cases temperatures were stabilized over a period of 1 h. These measurements explicitly showed that for $T < 60$ K, the relaxation spectrum $\epsilon''(\omega)$ was constant with time (the angular frequency $\omega = 2\pi\nu$).

III. RESULTS AND DISCUSSION

A. Relaxation and diffusion in supercooled $(C_2F_6)_{0.68}(CClF_3)_{0.32}$

For a demonstration of the cooling rate effect, in Fig. 1, comparison is made between data taken on slowly cooled $(C_2F_6)_{0.71}(CClF_3)_{0.29}$ and on a supercooled sample with $x = 0.32$. It shows that the temperature dependent dielectric constant of the latter specimen is strongly enhanced between 30 and 80 K. Heating above 85 K, the rapidly cooled sample approaches the behavior of the annealed one.

To establish that the observed enhancement of the dielectric constant and its frequency dependence are caused by rotating dipoles and not simply as the consequence of an unmixing process, time dependent dielectric measurements were performed. After the quench of a $(C_2F_6)_{1-x}(CClF_3)_x$ crystal to 4 K, the temperatures of the sample were stabilized for at least 1 h at 35, 50, 60, and 65 K and the temporal evolution of ϵ' was monitored. At these temperatures, the dielectric constants of the rapidly cooled samples exceed those of the annealed ones. Therefore, the permittivity is expected to decrease with time if unmixing is effective. However, at 35 K this quantity was constant within experimental errors. Also at 50 K, ϵ' was time independent after a decrease of 0.16% in the first 9 min. Only at 60 K, a significant temporal decrease of the dielectric constant was observed. It was possible to describe this behavior with

an exponential decay. It was however not possible to extrapolate unambiguously to the long time limit of the capacitance $C_L = C(t \to \infty)$. The best fit to the data taken at 60 K yielded at C_L that was 20% larger than the capacitance of the annealed sample at that temperature. This indicates that even at 60 K, the supercooled crystal is far from being macroscopically segregated. The time constant of the decay, yielded by the best fit was 6 h (the time constant was considerably enhanced when the long time capacitance was constrained to the value of the annealed sample). Finally, at 65 K the best fit with an exponential form yielded a time constant of ≈ 45 min with C_L being down to the value of the annealed sample.

The picture that emerges from these experiments is the following: the quench freezes the $CClF_3$ dipoles into orientationally disordered configurations. Possibly also the displacements of the molecules from their center of mass lattice are partially conserved. Already at 50 K, some of these energetically rather unfavorable topological configurations are relaxing and lead to probably short range ordered arrangements with a somewhat lower polarizability. The relaxation dynamics, on the other hand, is rather unaffected by these topological rearrangements, since the dielectric loss spectrum $\epsilon''(\omega)$ was constant during the observation time t of 1 h. $\epsilon(\omega, t)$ behaves totally different at 65 K. Here, diffusion is effective enough to allow unmixing of the binary alloy on laboratory time scales.

B. Suppression of unmixing

After having demonstrated that below 50 K diffusion on mesoscopic length scales is negligible, the effects of the variation of composition will be examined in the following. In particular, it will become clear that unmixing can be suppressed at least up to $CClF_3$ concentrations $x \approx 0.6$.
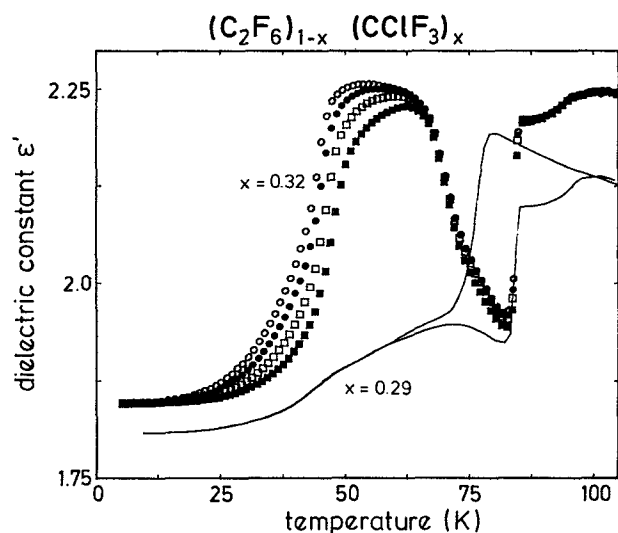
Figure 2 depicts the temperature dependence of the di-

FIG. 1. Comparison of the dielectric constants $\epsilon'(T)$ of quenched and annealed $(C_2F_6)_{1-x}(CClF_3)_x$ crystals with $x \approx 0.3$. The data for slowly cooled $(C_2F_6)_{0.71}(CClF_3)_{0.29}$ sample, ramped up and down with rates of 0.3 K/min, are represented as lines. Results from a supercooled crystal with $x = 0.32$ are presented for various frequencies ($\bigcirc$ 0.12 kHz, $\bullet$ 1 kHz, $\square$ 10 kHz, $\blacksquare$ 100 kHz).
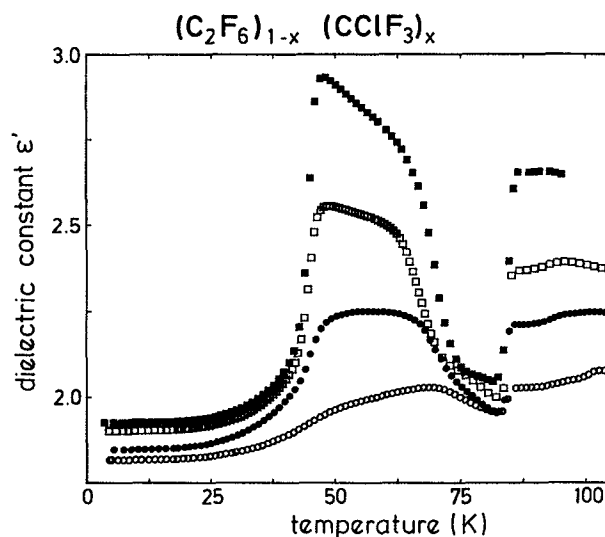

FIG. 2. Real part of the dielectric constant of $(C_2F_6)_{1-x}(CClF_3)_x$ as a function of temperature. The measuring frequency was 1 kHz. Different symbols refer to different concentrations x ($\bigcirc$ 0.23, $\bullet$ 0.32, $\square$ 0.46, $\blacksquare$ 0.61).

electric constant of $(C_2F_6)_{1-x}(CClF_3)_x$ samples with various concentrations $0.23 \leqslant x \leqslant 0.61$. All $\epsilon'(T)$ curves exhibit the features already described for the 32% crystal (cf. Fig. 1). Near 40 K, the dielectric constant starts to increase. The effect is the more pronounced the higher the dipole concentration is. Above 60 K, the dielectric constants $\epsilon'(T)$ drop off again. The decrease in ϵ' at these temperatures is due to the solid–solid phase separation into components with low permittivities. For example, in the $CClF_3$-rich phase, segregation is accompanied by dipole ordering. Finally, near 80 K a distinct anomaly occurs for all samples. As is clear from the phase diagram, this indicates the transformation of the specimens into their plastic states. Near 50 K, dielectric dispersion shows up in all samples (cf. Fig. 1 for $x = 0.32$), which is accompanied by appreciable dielectric loss. The loss curves are frequency dependent and thus indicate the presence of dipole reorientation processes. The peak values of the losses increase with the dipole concentration.

For an estimate of the number of dipoles that are involved in the relaxation processes, the dielectric losses were plotted on a logarithmic frequency scale. Almost symmetrical spectra were obtained for all concentrations (cf. inset of Fig. 4 for $x = 0.32$). The data for temperatures between approximately 40 and 50 K were fitted using the Cole–Cole relaxator function in order to evaluate the area under the loss curves and hence the static susceptibility χ_s.[13] The thermal scatter in this quantity was relatively large. This reflects the uncertainties of this procedure which is always encountered when describing relatively broad dielectric loss peaks.[13] Therefore in Fig. 3 only the mean values of χ_s are shown for various concentrations together with bars indicating scatter. The mean static susceptibilities rise linearly with the dipole

content up to $x \approx 0.6$ and then linearly decrease and extrapolate to zero at $x \approx 0.97$.

The static susceptibilities of the slowly cooled $(C_2F_6)_{1-x}(CClF_3)_x$ samples with $x \leqslant 0.23$ could be described using a Curie law $\chi_s = xC/T$ with $C = 6$ K.[10] In the preceding paper,[10] it was shown that this quantity which is determined by the dipole density and dipole moment of $CClF_3$, is in reasonable agreement with theoretical expectations. The solid line in Fig. 3 is calculated using the same Curie constant, i.e., $\chi_s = x\,6\,K/T_0$. Here, $T_0 = 45$ K is the midpoint of the temperature interval in which the susceptibilities were averaged. The agreement with the experimental results is good, indicating that at least up to $x \approx 0.6$ segregation does not occur. The rapid decrease of the susceptibility for samples with a larger dipole concentration is not necessarily due to unmixing. It is also possible that in these $CClF_3$ rich samples, the dipoles tend to order electrically, since it is known that pure trifluoromethane crystallizes in a structure with an antiferroelectric symmetry.[14] On the other hand, this result indicates that samples with dipole concentrations $x \leqslant 0.6$ are electrically disordered at least for temperatures above 40 K.

C. $(C_2F_6)_{0.68}(CClF_3)_{0.32}$ glassy crystals

In the following section evidence is provided that at lowest temperatures the quenched fluorocarbon mixtures exhibit a glassy state. We focus on discussing samples with $x = 0.32$ which have been studied most thoroughly. Figure 4 depicts the dielectric loss of $(C_2F_6)_{0.68}(CClF_3)_{0.32}$ as a function of temperature and frequency. At high frequencies, only one maximum is clearly resolved in the $\epsilon''(T)$ plot. For lower frequencies, a shoulder becomes visible on the low-
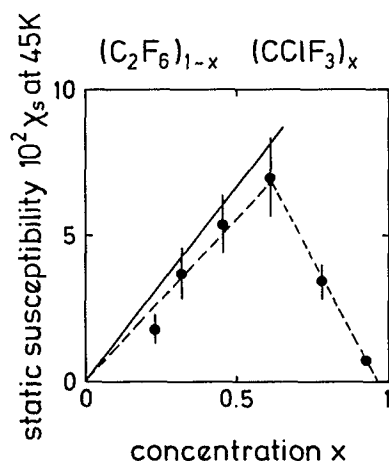

FIG. 3. Static susceptibility χ_s of quenched $(C_2F_6)_{1-x}(CClF_3)_x$ mixtures plotted vs the dipole concentration. The bars indicate the scatter of χ_s for 40 K $< T <$ 50 K. The solid line is calculated with the same Curie law used to describe the annealed mixtures. This extrapolation (to concentrations $x > 0.23$ and temperatures $T = 45$ K) fits the present data reasonably well. Only for $x = 0.23$ significant deviations show up. Like before[20] these indicate the presence of additional contributions outside the range where the susceptibility was averaged. The dashed line is drawn to guide the eye. It extrapolates to zero near $x = 0.97$. This possibly marks the concentration down to which $CClF_3$ rich annealed mixed crystals exist.
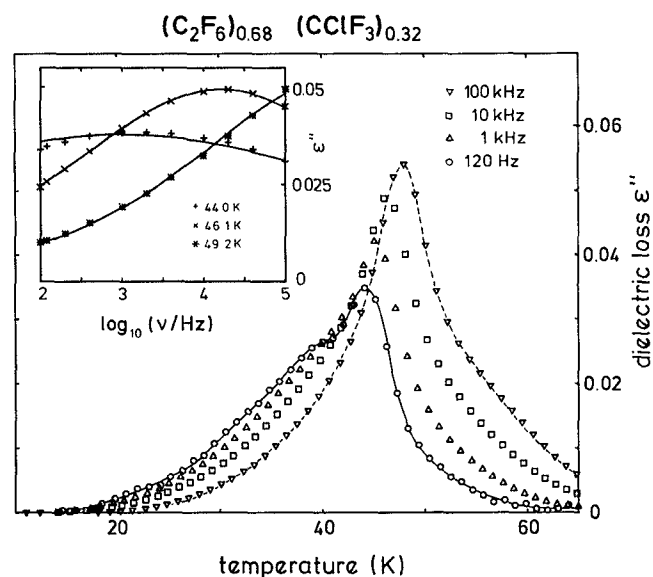

FIG. 4. Dielectric loss ϵ'' of $(C_2F_6)_{0.68}(CClF_3)_{0.32}$ as a functions of temperature for various frequencies. Lines for $\nu = 120$ Hz and for $\nu = 100$ kHz are drawn to guide the eye. The inset depicts the frequency dependence explicitly. The lines served to estimate the static susceptibilities. Here they are drawn to guide the eye.

temperature wings of the main peaks. However, the lowest measuring frequency used in the present investigation is not low enough to resolve two maxima even in tan $\delta = \epsilon''/\epsilon'$ where the shoulders are more pronounced. Also in the frequency dependent representation (inset of Fig. 4) only single peak structures were observed. While in cyano-adamantane[6] and cyclo-hexanol,[4] the high-temperature (α-) peak is more than a hundred times larger as compared to the excitations seen at lower T (β process), the two contributions are roughly of the same magnitude in the fluorocarbon crystal. A separation of the two processes is therefore not advisable as long as the frequency range of measurements is not extended considerably. On the other hand for the estimate of the total number of dipoles contributing to both processes, an explicit separation of the relaxation spectrum is not required.

The determination of the mean relaxation times is hampered more seriously by the lack of separability of the primary and the secondary relaxations. In particular, the time constants characterizing the low-temperature process are not accessible from the dielectric loss spectra. Temperature dependent relaxation times τ can be deduced from the high-temperature peaks only if the following assumptions hold: (i) that the secondary (β-) contributions impose a negligible shift on the peak temperatures and (ii) that the α-relaxation spectra are symmetric vs $\log(\nu)$. Under these assumptions, the $\epsilon''(T)$ curves of $(C_2F_6)_{0.68}(CClF_3)_{0.32}$ yield a mean relaxation times $\tau = 1/(2\pi\nu_m)$ as depicted in Fig. 5. Also the authors who reported the relaxation rates ν_m of cyclo-hexanol[4] and cyano-adamantane[6] (their results are included in Fig. 5) followed this procedure, although the Cole–Cole plots of the latter compound are known to exhibit an asymmetric shape.[6]

The representation of Fig. 5 is a modified Arrhenius plot

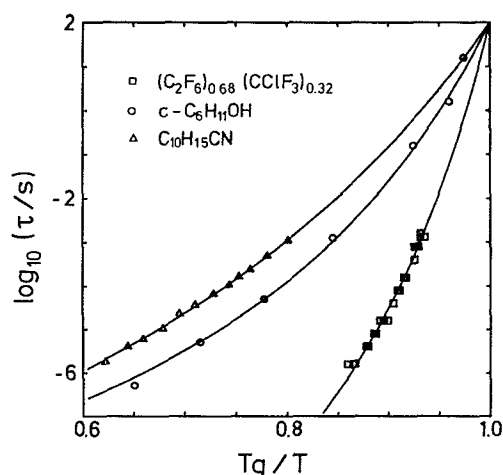
FIG. 5. Relaxation times τ of several glassy crystals plotted vs the normalized inverse temperature T_g/T. The glass transition temperatures T_g are 174 K for cyano-adamantane ($\triangle$, $C_{10}H_{15}CN$, data taken from Ref. 8), 148 K for cyclo-hexanol ($\bigcirc$, c-$C_6H_{11}OH$, data taken from Ref. 6) and 41.3 K for $(C_2F_6)_{0.68}(CClF_3)_{0.32}$ ($\square$, present data from three different crystals). The solid lines were calculated using the parameters D, T_0, and τ_0 for $C_{10}H_{15}CN$ (17.8, 107.5 K, 3.0×10^{-11} s) c-$C_6H_{11}OH$ (9.7, 109.3 K, 9.7×10^{-11} s), and $(C_2F_6)_{0.68}(CClF_3)_{0.32}$ (8.5, 33.9 K, 1.0×10^{-15} s).

and emphasizes the deviations from purely activated behavior. This is achieved by displaying the relaxation rates versus a normalized inverse temperature scale. The scaling variable $T_g = T(\tau = 100 \text{ s})$ is identified with the calorimetric glass temperature that corresponds to relaxation times of roughly 100 s. Although this time constant is dictated by experimental convenience and therefore to some extent arbitrary, it provides a suitable means of rationalizing the relaxation behavior of glassforming compounds. This has been demonstrated for a large number of supercooled liquids by Angell (who invented this type of representation) and others.[15] This lead Angell to classify glassforming liquids into strong and fragile ones.[16] The latter show the strongest deviations from thermally activated behavior. Strong glasses, on the other extreme, reveal pure Arrhenius relaxation characterized by a straight line in Fig. 5.

Although the appropriate parametrization of deviations from thermally activation is sometimes discussed controversely[17] we have chosen the familiar Vogel–Fulcher law[18] $\tau = \tau_0 \exp[DT_0/(T - T_0)]$. The solid lines in Fig. 5 are calculated with this equation and the parameters τ_0, T_0, and D given in the caption of this figure. In $(C_2F_6)_{0.68}(CClF_3)_{0.32}$ the glass transition temperature $T_g = 41.3$ K, the Vogel–Fulcher temperature $T_0 = 33.9$ K and the fragility parameter $D = 8.5$. From Fig. 5, it is clear that the fragility increases from cyano-adamantane ($D = 17.8$), to cyclo-hexanol ($D = 9.7$) and finally to the fluorocarbon alloys ($D = 8.5$ for $x = 0.32$). In particular, the latter compounds are rather fragile glassformers. With the limitations concerning the determination of the relaxation times in mind we will not overemphasize this point. Moreover, it is noted that Fig. 5 only contains results from compounds that are characterized reasonably well by dielectric methods. A more complete list covering also other experimental techniques was not attempted, since this subject has been reviewed several times.[19]

Finally, we comment on the shape of the dielectric loss peaks. As shown in the inset of Fig. 4, ϵ'' vs $\log(\nu)$ is very broad. The width is much broader than the 1.14 decades as expected for a monodispersive Debye relaxator and increases with decreasing temperatures. Apparently, part of the remarkable breadth of the loss curves is the proximity of the primary and secondary relaxations on the frequency scale, as well as local concentration fluctuations in these solid solutions. However, it is interesting to note that magnetic and dielectric loss curves with similar widths and temperature dependencies have been reported for spin glasses[20] and for orientational glasses,[21] respectively. By contrast, the breadth of the α relaxation in supercooled viscous liquids, which in many cases is also temperature dependent, is typically considerably smaller.[22] The precise reason for this dissimilarity is unclear. Random fields due to the substitutional disorder could be one reason for this appearance.

Owing to their translational order, plastic crystals may adapt themselves better to mathematical modeling than structural glasses. It is therefore hoped that the present investigations will help to stimulate theoretical efforts aimed at a deeper understanding of the freezing in supercooled mixed crystals.

IV. SUMMARY AND CONCLUSIONS

In part II of this contribution to the relaxation dynamics in molecular alloys, we have provided experimental evidence that solid solutions of C_2F_6 and $CClF_3$ can be supercooled from the plastic phase in a wide concentration range ($0.2 < x < 0.6$). Supercooling prevents the mixed crystals from unmixing and freezes in the center-of-mass lattice and the orientational disorder of the high-temperature plastic phase.

The dipolar relaxation dynamics of $CClF_3$ in the host matrix has been studied in detail in the supercooled state. It is dominated by the appearance of primary (α-) relaxation processes. Indications of fast secondary relaxations were detected at low temperatures. We parametrized the α relaxation in terms of a modified Arrhenius plot that allows a classification of glasses into strong and fragile.[16] We found that the fluorocarbon alloys investigated belong to the class of fragile glasses and thus are characterized by a high density of configurational states in the topology of the potential energy surface.[16] Accordingly, they should reveal a high heat capacity anomaly at the glass transition.[16]

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