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Dielectric relaxation in compressed glassy and orientationally disordered mixed crystals

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Results of isobaric and isothermal studies of dielectric relaxation in a vitrifying orientationally disordered crystal $[(CH_3)_3C(CH_2OH)]_{0.70}[(CH_3)_2C(CH_2OH)_2]_{0.30}$ under pressures reaching $P=1.8$ GPa are discussed. The application of the linearized derivative-based analysis made it possible to detect validity domains of the Vogel-Fulcher-Tammann $\tau=\tau_0^{VFT}\exp(D_T T_0/T-T_0)$ relation, the critical-like $\tau(T)\propto(T-T_X)^{-g}$ dependence as well as their pressure counterparts. The agreement with predictions of the dynamical scaling model (DSM) is worth stressing. This suggests that the decoupling of translational and orientational degrees of freedom may be the key mechanism responsible for the validity of the DSM description for glassy systems. The application of high pressures led to the emergence of a phase transition, absent in studies under atmospheric pressure. The parametrization of the pressure evolution of the phase transition temperature $[T_{tr}(P)]$ via the extended Simon-Glatzel-type relation suggests the possible maximum of $T_{tr}(P)$ at extreme pressures. It is concluded that the nontypical increase of the fragility strength coefficient (D_T) noted on cooling in studies under atmospheric pressure [A. Drozd-Rzoska *et al.*, Phys. Rev. B **73**, 224205 (2006)] may be due to approaching the phase transition hidden under compression.

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I. INTRODUCTION

The vitreous, silicate glass artifacts were mass produced as early as in the fourth millennium B.C. in ancient Egypt and Mesopotamia.[1,2] Surprisingly, the glass transition phenomena are the areas of great interest and challenging studies also at the beginning of the 21st century.[3–6] Many theoretical models have been proposed to explain the unusual dynamics of glassy materials but none of them seem to account for the myriad of properties found for glass transition.[3–6] Hence, experimental results based on novel or infrequently used experimental methods may be an important milestone. Studies of experimental model systems such as colloidal liquids[5,7] or an isotropic phase of nematic crystals,[8–10] reducing the complexity present in structural glass formers,[5,6] may also be a promising strategy. Results described in this paper incorporate both these approaches.

Orientationally disordered crystals (ODIC), known also as plastic crystals, can be considered as one of the most important experimental model systems for the glass transition studies.[11,12] In such materials, centers of the mass of globular molecules are translationally ordered as in a solid crystal; however, the molecular orientation of permanent dipoles is disordered as in a liquid. Despite the fact that in ODIC the dynamics on approaching the glass temperature (T_g) is governed solely by orientational degrees of freedom, in many aspects it resembles the "canonical pattern" of supercooled liquids and polymers.[13–19] Worth recalling here are the broadband dielectric spectroscopy (BDS) studies, the research method commonly recognized as fundamental for testing the dynamics of vitrifying systems.[19] For temperature evolution of the main α-relaxation process an impressive slowing down, well portrayed by the Vogel-Fulcher-Tamamnn (VFT) relation, was noted, namely[14–19]

$$\tau(T)=\tau_0^{VFT}\exp\left[\frac{D_T T_0}{T-T_0}\right], \tag{1}$$

where the temperature T_0 is associated with the estimation of the ideal glass transition and the fragility strength coefficient D_T can be considered as the measure of fragility for the given temperature domain.[5,6,19]

In plastic crystals the main α-relaxation process can be accompanied by the secondary, β relaxation as in structural glasses.[13,17] Based on molecular dynamics simulation Affouard and Descamps stated in the conclusions of Ref. 11 "…systems whose dynamics are almost completely controlled by orientational degrees of freedom (ODOF) share some common dynamical features with liquid glass formers, relatively well described by the idealized version of the mode coupling theory (MCT)…." The further theoretical evidence given by the same authors in Ref. 12 strongly supported the compatibility of plastic crystals and the MCT. These results are in fair agreement with the recently obtained critical-like MCT behavior of relaxation times,[18] with the singularity linked to the "magic" time scale of $\tau\approx 0.1$ μs.[20] BDS studies also revealed some artifacts specific to plastic crystals. As pointed out in Ref. 16 plastic crystals exhibit a stronger broadening of the distribution of relaxation times on cooling than in structural glasses, particularly in the low-frequency part. Recently, in the glassy plastic crystal $[(CH_3)_3C(CH_2OH)]_{0.70}[(CH_3)_2C(CH_2OH)_2]_{0.30}$ (abbreviated as $NPA_{0.7}NPG_{0.3}$) the increase of the D_T coefficient on cooling in subsequent dynamical domains was noted.[18] Such behavior is contrary to the one usually noted in supercooled liquids and glasses.[21] To the best of the authors' knowledge a similar increase of D_T on cooling was observed only in isotropic *n*-pentylcyanobiphenyl (5CB), a rodlike liquid nematic liquid crystalline compound.[10] This was related to the influence of prenematic heterogeneities whose size and lifetime increase on cooling towards the isotropic-nematic transition. For the $\mathrm{NPA}_{0.7}\mathrm{NPG}_{0.3}$ plastic crystal also the possibility of the alternative, critical-like description of the evolution relaxation time was indicated, namely,[18]

$$\tau(T) = \tau_0 (T - T_X)^{-g}. \tag{2}$$

For the high temperature region this behavior was linked to the MCT[5] predictions for approaching the ergodic-nonergodic crossover, yielding $T_X^{MCT} \approx 248$ K, $g \approx 3.7$,[18] as mentioned above. For the time scale slower than $\tau(T_X^{MCT}) \approx 10^{-7}$ s, i.e., for $T_g = 160\ \mathrm{K} < T < 248$ K, the superior parameterization with $T_X \approx 150$ K and $\mathbf{g} \approx 9$ was obtained.[18] Regarding this result the coincidence with predictions of the dynamic scaling model[22,23] (DSM) was recalled in Ref. 18. For the DSM below the caging temperature, which may coincide with T_X^{MCT}, the appearance of cooperative domains associated with a hidden dynamic phase transition associated with the critical temperature T_C located below the glass temperature (T_g) is assumed.[22,23] Based on this, the universal cooperative length scale described by relation (2) with $T_C = T_X$ and the exponent $\mathbf{g} \approx z\nu = 6 \times 3/2 = 9$, where z is the dynamic exponent and ν is the exponent describing the evolution of the correlation length on approaching the hypothetical phase transition,[22,23] was derived.[18] In structural glasses such behavior can only be obtained if the Arrhenius-type multiplicator is additionally taken into account in relation (2),[22,23] but this additional term has to reduce significantly the reliability of the fitting. Moreover, the validity of the Arrhenius description above the caging temperature, suggested in Refs. 22 and 23, may be not a general feature in the opinion of the authors.

In the last decade studies linking both temperature and pressure appeared to be one of the most prominent strategies applied for resolving the glass transition puzzle (Refs. 5, 6, 21, and 24–26 and references therein). Worth recalling is the fact that the temperature shift is related both to the activation energy and the density changes whereas pressure changes are related solely to densification. Consequently, experimental studies involving both pressure (P) and temperature (T) may be considered as the fundamental reference for theoretical models or for resolving certain puzzling conclusions emerging from studies under atmospheric pressure. Unfortunately, the number of pressure studies on plastic crystals is limited[27–34] and only a few of them are related to preliminary BDS measurements at moderate pressures $P < 300$ MPa.[28–31]

This paper presents broadband dielectric spectroscopy studies on $\mathrm{NPA}_{0.7}\mathrm{NPG}_{0.3}$ mixed glassy crystal pressurized up to extreme $P = 1.8$ GPa. To analyze the obtained results the derivative-based transformation of data[21] was applied, making the distortion-sensitive insight into the evolution of dielectric relaxation times possible. The pressurization revealed the existence of a different phase transition, whose vicinity seems to be also important for the dynamics at atmospheric pressure. Finally, the analysis focuses on the pressure evolution of the phase-transition temperature.

II. EXPERIMENTAL

Dielectric measurements were made using the Alpha Novocontrol BDS analyzer and the piston-based pressure setup for which a detailed description is given in Refs. 24 and 26. The sample was placed in a flat parallel capacitor with a $d = 100\ \mu$m gap. It is worth recalling that pressure was transmitted to the sample via the deformation of a Teflon film and no possibility of contamination from the pressurized liquid, silicone oil, was possible.

Experiments were conducted on a mixed crystal formed by neopentylalcohol [NPA, i.e., $(\mathrm{CH}_3)_3\mathrm{C}(\mathrm{CH}_2\mathrm{OH})$] and neopentylglycol [NPG, i.e., $(\mathrm{CH}_3)_2\mathrm{C}(\mathrm{CH}_2\mathrm{OH})_2$]. Both pure compounds have been the focus of many works.[35–37] Mixed crystals $[(\mathrm{CH}_3)_3\mathrm{C}(\mathrm{CH}_2\mathrm{OH})]_{1-\mathrm{X}}[(\mathrm{CH}_3)_2\mathrm{C}(\mathrm{CH}_2\mathrm{OH})_2]_{\mathrm{X}}$, are known to give rise to continuous orientationally disordered face-centered-cubic solid solutions for the whole concentration range and, in addition, for molar compositions lower than approximately 0.5 an orientational glass state appears.[35] In this work results are reported for $[(\mathrm{CH}_3)_3\mathrm{C}(\mathrm{CH}_2\mathrm{OH})]_{0.70}[(\mathrm{CH}_3)_2\mathrm{C}(\mathrm{CH}_2\mathrm{OH})_2]_{0.30}$ ODIC mixed crystal (abbreviated as $\mathrm{NPA}_{0.7}\mathrm{NPG}_{0.3}$). The details for the sample preparation are given in Ref. 37. The referenced BDS results under atmospheric pressure are given in Ref. 18. Within the limit of the experimental error we did not note any difference on compression and decompression of the tested sample. On decompression we tested both the position of the phase transition and values of relaxation times for selected pressures. We would like to stress that the comparison of experimental data on compression and decompression is always a very difficult task for studies involving extreme pressures. This is associated with parasitic related effects within the pressure chamber and the hydraulic press.

III. RESULTS AND DISCUSSIONS

The multiplot of dielectric loss curves for pressurized $\mathrm{NPA}_{0.7}\mathrm{NPG}_{0.3}$ is presented in Fig. 1. Noteworthy is the clear manifestation of the phase transition at $P_{tr} \approx 0.5$ GPa. Below and above this transition, loss curves can be well portrayed by a single Havriliak-Negami distribution function, namely,[15,19]

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1 + (i\omega\tau)^a]^b}, \tag{3}$$

where $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ is the dielectric strength, ε_∞ represents the asymptotic value of permittivity at high frequencies, and ε_s is the value of the opposite limit. The power exponents are responsible for the shape of the loss curve. They are related to the shape coefficients describing $\varepsilon''(f)$ curve introduced by Jonscher:[19,38] $m = a$ for the low-frequency wing and $n = ab$ for the high-frequency wing.

It can be seen that on passing P_{tr}, the low-pressure relaxation process disappears and a high-pressure phase α process shifted towards lower frequencies emerges.

This shift is clearly visible in the pressure evolution of relaxation times presented in Fig. 2. The application of the derivative-based analysis, shown in insets in Fig. 2, made it possible to detect dynamical domains emerging on compres-

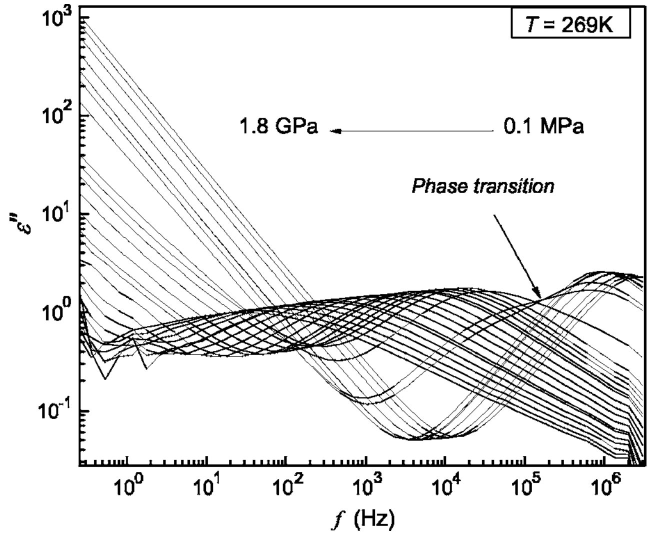

FIG. 1. The multiplot of dielectric relaxation data for isothermal-pressure studies in the tested $NPA_{0.7}NPG_{0.3}$ mixed glassy plastic crystal.

sion. The upper inset presents the analysis focused on the validity of the pressure counterpart of the VFT relation, namely,[21,39]

$$\tau(P) = \tau_0^{PVFT} \exp\left[\frac{D_P P}{P_0 - P}\right], \quad T = \text{const}, \tag{4a}$$

$$(d \ln \tau/dP)^{-1/2} = (V'_a)^{-1/2} = (D_P P_0)^{-1/2} P_0 - (D_P P_0)^{-1/2} P = A - BP, \tag{4b}$$

where D_P is the pressure-related fragility strength coefficient and P_0 is the extrapolated pressure for the ideal glass transition at given temperature T=const. $V'_a(P)$ is the measure of the apparent activation volume. The derivative-based plot via relation (4b) yields $P_0 = A/B$ and $D_P = 1/AB$.[21] The lower inset is aimed at testing the validity of the pressure counterpart of the critical-like relation (2), namely,[21]

$$\tau(P) = \tau_0^P (P_X - P)^{-\mathbf{g}'}, \tag{5a}$$

$$(d \ln \tau/dP)^{-1} = (V'_a)^{-1} = \mathbf{g}'^{-1} P_X - \mathbf{g}'^{-1} P = A - BP, \tag{5b}$$

where the derivative plot based on relation (5b) yields the singular pressure $P_X = A/B$ and the power exponent $\mathbf{g} = 1/B$.

Plots via relations (4b) or (5b) indicate domains of validity of relations (4a) and (5a) and give the ultimate values of basic parameters. These can be next used to the final fit of $\tau(P)$ data via relations (4a) and (5a), reduced solely to the τ_0^{PVFT} and τ_0^P prefactors. The comparison of the upper and the lower inset in Fig. 2 shows that relations (4a) and (5a) are equally reliable for portraying the pressure evolution of relaxation times. The insets also show that domains below and above the phase-transition pressure (P_{tr}) only differ in their prefactors in relations (4a) and (5a). On compressing above $P_X \approx 1$ GPa the slowing down of relaxation times continues but it is anomalous, namely, even not as slow as anticipated from the Arrhenius dependence.

Figure 3 presents the related pressure evolution of dielectric strength. It is noteworthy that also in this case there is a clear correlation between the behavior below and above P_{tr}. Both domains can be described by parabolic functions which differ only in their constant terms, as shown in the inset in Fig. 3. Hence, dependences describing the behavior of $\Delta\varepsilon(P)$ both above and below P_{tr} have the maximum at $P_X \approx 1$ GPa.

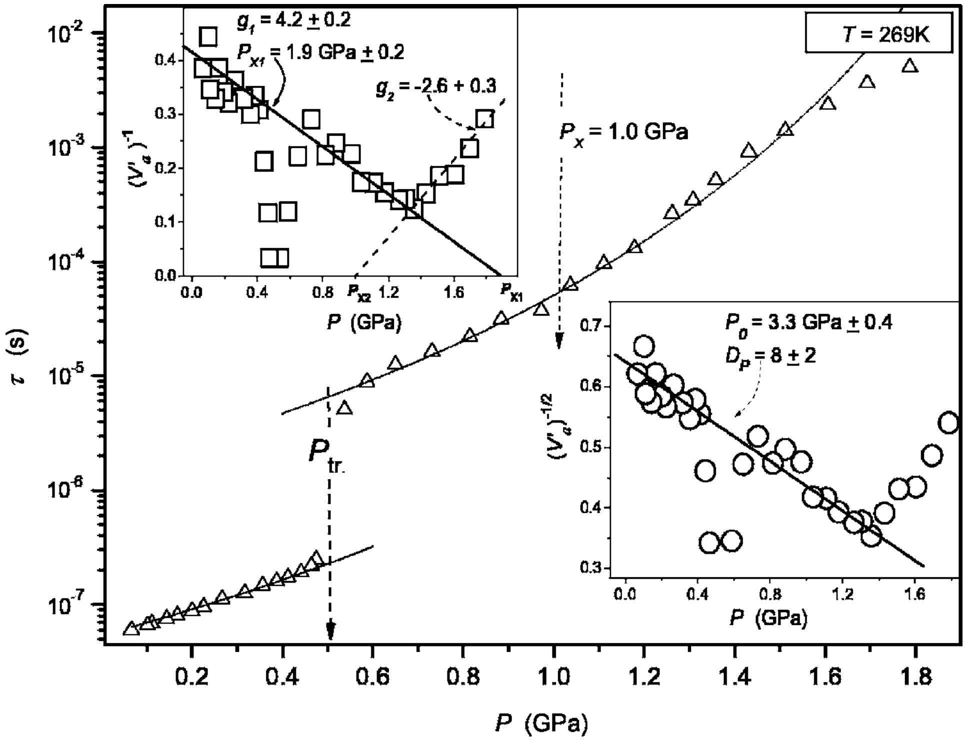

FIG. 2. The evolution of dielectric relaxation time for the pressurized $NPA_{0.7}NPG_{0.3}$ mixed plastic crystal at T=269 K. The insets show results of the derivative analysis focused on testing the pressure counterpart of the VFT relation [lower inset, Eq. (4b)] and the critical-like dependence [upper inset, Eq. (5b)]. The solid curve in the main part of the plot is based on relation (4a) with D_P and P_0 obtained from the linear regression analysis in the lower inset and τ_0^{PVFT} =0.54 ns for $P < P_{tr}$ and τ_0^{PVFT} =1.7 μs for $P > P_{tr}$.

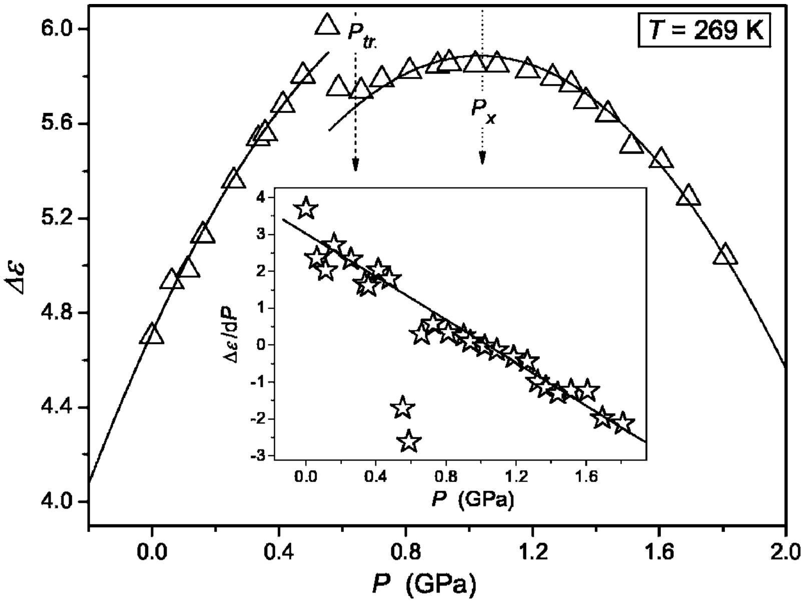

FIG. 3. The evolution of dielectric strength in the pressurized $NPA_{0.7}NPG_{0.3}$ mixed plastic crystal at constant temperature. The inset shows the derivative analysis of data from the main plot; the analysis of data from the main plot $\Delta\varepsilon/dP=A+2BP$, with $A=2.92$ and $B=1.42$. The data in the main plot are portrayed by the second-order polynomial $\Delta\varepsilon(P)=C+AP+BP^2$ with $C=4.38$ for $P>P_{tr}$ and $C=4.76$ for $P<P_{tr}$.

The temperature evolution of relaxation times in strongly compressed ($P=1.8$ GPa) tested ODIC is shown in Fig. 4. There is no manifestation of the aforementioned phase transition here. This is due to the fact that $T_{tr}(P=1.8\text{ GPa})\approx 396$ K (see below) whereas our measurements, because of technical reasons, started at $T\approx 350$ K. The lower inset in Fig. 4 is related to testing the validity of the VFT relation (1), namely,[21]

$$\left[\frac{d\ln\tau}{d(1/T)}\right]^{-1/2} = [H'_a(1/T)]^{-1/2} = [(D_T T_o)^{-1/2}] - \frac{[T_0(D_T T_0)^{-1/2}]}{T} = A - \frac{B}{T}, \qquad (6)$$

where $H'_a(T)=H_a(T)/R$, $H'_a(T)$ is the apparent activation enthalpy, $T_0=B/A$, and $D_T=1/AB$.

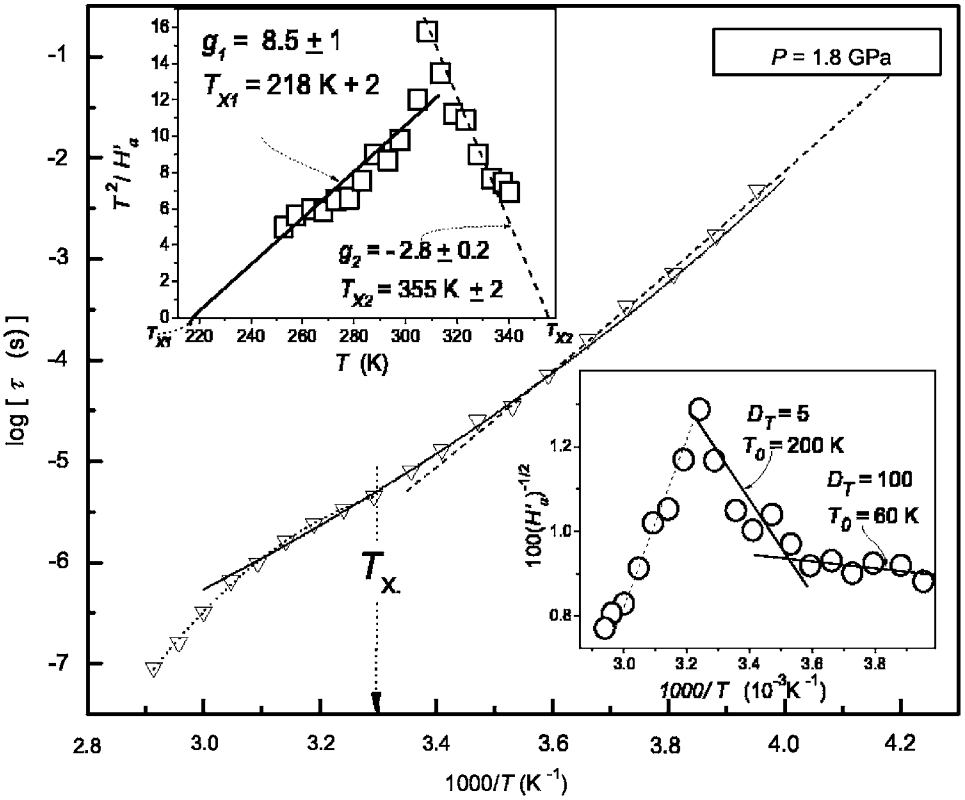

FIG. 4. The temperature evolution of dielectric relaxation in the compressed $NPA_{0.7}NPG_{0.3}$ mixed plastic crystal. The insets show results of the derivative analysis focused on the validity of the VFT [Eq. (6), lower inset] and the critical-like dependence [Eq. (7), upper inset]. The solid and the dashed curve in the main part of the plot is parametrized by the VFT relation (1) with D_T and T_0 taken from the lower inset for the following dynamical domains. The fit yielded prefactors $\tau_0^{VFT}=1.2\times10^{-9}$ s (solid curve) and $\tau_0^{VFT}=2.1\times10^{-18}$ s (dashed curve, low temperature domain).

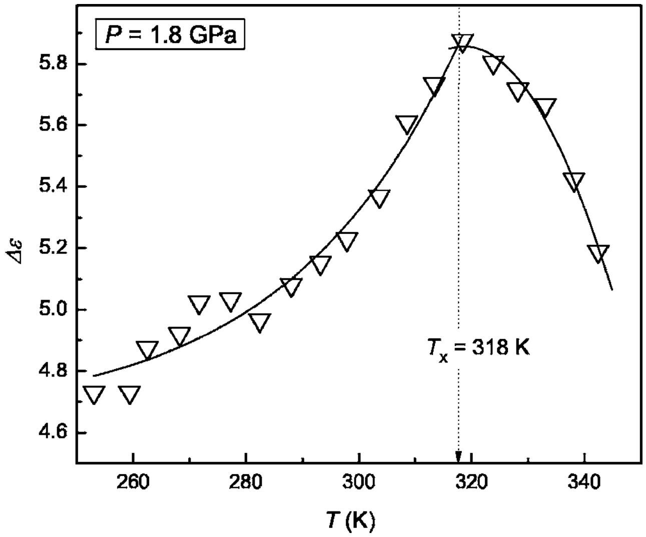

FIG. 5. The temperature evolution of dielectric strength in the compressed $NPA_{0.7}NPG_{0.3}$ mixed plastic crystal at constant pressure. The decrease for $T<T_X$ is portrayed by the first-order exponential decay.

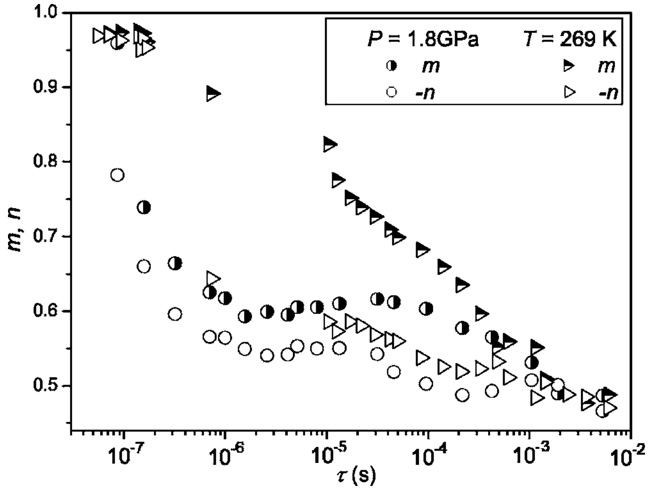

FIG. 6. The evolution of coefficient describing the low frequency (m) and the high frequency (n) wings of dielectric loss curves in the $NPA_{0.7}NPG_{0.3}$ mixed plastic crystal on slowing down when cooling and pressuring for the isobar and isotherm given in the figure.

The upper inset is focused on the distortion-sensitive test of validity of the critical-like dependence (2), namely,[21]

$$T^2/H'_a(T) = T^2/\{d[\ln \tau(T)]/d(1/T)\}$$
$$= T^2/H'_a(T) = g^{-1}(T - T_X) = A - BT, \qquad (7)$$

where $\mathbf{g}=1/B$ and $T_X=A/B$.

Derivative plots via relations (6) or (7) indicate domains of validity of relations (1) and (2) and yield ultimate values of basic parameters. The final analysis of $\tau(T)$ data via relations (1) and (2) is then reduced solely to fitting the τ_0^{VFT} and τ_0^T prefactors.[21] It is noteworthy that above $T_X \approx 318$ K the slowing down is anomalous, i.e., it is even not so slow as expected from the simple Arrhenius behavior. For $T<T_X$ the dynamics is similar to the one noted for structural glass formers, namely, the value of the fragility strength coefficient D_T increases on cooling in the subsequent dynamical domains.[21] However, the value of the relaxation time at the crossover between dynamical domains associated with the different set of parameters in the VFT relation (1) is equal to $\tau \approx 63$ μs, hence, it is different from the magic universal time $\tau \approx 0.1$ μs.[20,21,25] The upper inset in Fig. 4 shows that an alternative critical-like description via relation (2) also gives a reliable portrayal of data for $T<T_X$, with $g=8.5\pm 1$ and $T_X=218$ K, which seems to coincide with predictions of DSM,[21,22] also noted in temperature tests under atmospheric pressure.[18]

The temperature evolution of dielectric strength in compressed $NPA_{0.7}NPG_{0.3}$ is presented in Fig. 5. It shows that on cooling towards T_X first an anomalous increase of $\Delta\varepsilon(T)$ occurs. Below T_X it decreases on cooling, similar to the behavior in canonical glass formers.[15,16] The change $\Delta\varepsilon(T)$ in this region can be well portrayed by the first-order exponential decay. Figure 6 presents the evolution of parameters describing the distribution of relaxation times when slowing down the time scale on cooling of the compressed tested ODIC or on pressuring. It seems that for time scales $\tau < 10^{-7}$ s the distribution may approach the Debye pattern.[15] There is a very distinct change in the form of the loss curves on slowing down between 10^{-7} s and 10^{-6} s, i.e., near the magic time scale.[20] For $\tau=10^{-2}$ s the loss curves become symmetric and "very stretched," i.e., $m \approx n \approx 1/2$ for both tested paths. It seems that the broadening may continue on further cooling or pressuring. A very distinct broadening and symmetrization of loss curves was already pointed out as a possible characteristic feature of glassy ODICs in temperature measurements under atmospheric pressure.[16,18]

Results presented above showed that the compressed $NPA_{0.7}NPG_{0.3}$ sample exhibits a thermodynamic phase transition, absent in tests under atmospheric pressure. Figure 7 shows pressure evolution of $T_{tr}(P)$. It can be well parametrized by the extended Simon-Glatzel type relation recently proposed for the evolution of the glass temperature,[40] which can be rewritten in the form

$$T_{tr}(P) = F(P)D(P) = T_{tr}^0\left(1 + \frac{\Delta P}{\Pi}\right)^{1/b} \exp\left(-\frac{\Delta P}{c}\right), \qquad (8)$$

where $\Delta P = P - P_{tr}^0$, values of T_{tr}^0 and P_{tr}^0 are correlated reference pressure and temperature. $F(P)$ and $D(P)$ are for the rising and the damping term, respectively.

Following Refs. 40 and 41 we would like to point out the possibility of the extension of the above relation down to asymptotic pressure π at $T \rightarrow 0$. It can be easily shown that, neglecting the damping term $c^{-1}=0$, the transformation of experimental data via $(d \ln T_{tr}/dP)^{-1} = A + bP = [b(\Pi - P_{tr}^0)] + bP$ should yield a linear dependence.[40] The lack of such behavior may suggest that the damping term cannot be neglected. In such a case one may expect that for the optimal selection of the damping coefficient the plot $[d \ln T_{tr}/dP + c^{-1}]^{-1}$ vs P should result in a linear dependence. Consequently, relation (8) can be written in the invariant form

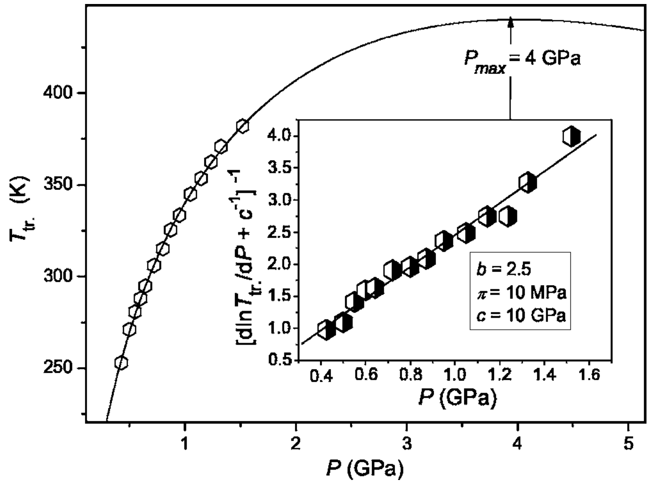

FIG. 7. The pressure evolution of the pressure-induced phase transition in $NPA_{0.7}NPG_{0.3}$ plastic crystals. The inset shows the linearized, derivative-based analysis focused on testing the validity of relations (8) and (9). The parameters given in the inset have been obtained via the linear regression and serve for plotting the curve portraying $T_{tr}(P)$ data in the main plot. The extension of the curve exhibits an inflection (maximum) indicated by the arrow.

$$T_{tr}(P) = T_0^{tr}\left(1 + b\frac{\Delta P}{A + bP_0^{tr}}\right)^{1/b}\exp\left(\frac{\Delta P}{c}\right) = T_0^{tr}\left(1 + \frac{P - P_0^{tr}}{\pi + P_0^{tr}}\right)^{1/b}\exp\left(\frac{P - P_0^{tr}}{c}\right), \qquad (9)$$

where the asymptotic pressure for $T_0^{tr} \to 0$ is equal to $\pi = A/b$.

The possibility of the application of relation (9) for portraying $T_{tr}(P)$ data with parameters obtained due to the aforementioned derivative transformation is shown in Fig. 7. Originally, it was proposed for portraying the evolution of melting curves with inflection at extreme pressures and for showing the possibility of the inflection and reentrant plasticization in vitrifying pressurized liquids.[41] For the tested ODIC the extrapolation of the obtained $T_{tr}(P)$ curve exhibits an inflection near $P_{\max} \approx 4$ GPa, as shown in Fig. 7. We would like to stress that this extrapolation is based on data for $P < 1.8$ GPa, hence the appearance of $P_{\max}$ has to be considered as a speculative possibility. The complex pattern of dynamics in the tested materials caused the estimation of the glass temperature evolution $T_g(P)$ from the condition $\tau(T_g) = 100$ s (Refs. 5, 6, 24, and 26) impossible. Hence, we could only estimate $dT_g/dP = (28 \pm 3)$ K/GPa for $P < 0.5$ GPa. This value is a decade smaller than the one observed for glass-forming liquids and polymers.[6,19,24,26]

Concluding, the results presented above for strongly compressed $NPA_{0.7}NPG_{0.3}$ glassy orientationally disordered mixed crystals revealed the existence of several features, absent in tests under ambient pressure.[18] First, pressurization induces a phase transition for which the analysis via relation (9) suggests the occurrence of an inflection under strong compression. It seems that the anomalous increase of the fragility strength coefficient noted in the subsequent dynamical domains on cooling under atmospheric pressure[18] may be linked to the vicinity of the phase transition, similarly as in the isotropic phase of liquid crystalline *n*-pentylcyanobiphenyl.[10] However, for the tested mixed ODIC the transition remains hidden in the compressed state for studies under atmospheric pressure. Noteworthy is the anomalous behavior at higher temperatures presented in Fig. 4. The slowing down on cooling takes place but it is anomalous in respect to the Arrhenius dependence and to the "glassy" pattern [relation (1)]. However, such behavior can be found in some liquids on approaching the phase transition, i.e., in the region of the strong influence of pretransitional fluctuations.[42,43] Similar anomalous behavior appears for the pressure evolution of relaxation times in Fig. 2 but at very high compression. In the opinion of the authors both these anomalous domains may be due to the vicinity of the phase transition curve $T_{tr}(P)$ and consequently such behavior supports the speculative parametrization presented in Fig. 7. For the isothermal pressure behavior this can be associated with the approaching inflected $T_{tr}(P)$ curve of phase transitions. The derivative analysis of experimental data presented in the upper insets in Figs. 2 and 4 indicates the possibility of portraying this anomalous, hypothetically pretransitional, behavior by the following relations:

$$\tau(T) = C_T + A_T(T^* - T)^{\phi} \quad \text{for } T < T^* \approx 355 \text{ K and } \phi \approx 2.8, \qquad (10)$$

$$\tau(P) = C_P + A_P(P - P^*)^{\phi} \qquad (11)$$

$$\text{for } P > P^* \approx 1 \text{ GPa and } \phi \approx 2.6, \qquad (11)$$

where C_T, A_T, C_P, and A_P are constant amplitudes, $T^* = T_{X2}$ in Fig. 3 and $P^* = P_{X2}$. It is noteworthy that the singular temperature and pressure in the above relations are remote from the phase transition curve $T^* \approx T_{tr}(1.8\text{ GPa}) - 37$ K and $P^* \approx P_{tr}(269\text{ K}) - 5$ GPa, and probably they can be linked to the onset of pretransitional fluctuations[10] or the frustration[44] caused by them. Two facts resulting from relations (10) and (11) are worth noting. First, power exponents related to the pressure and temperature paths are almost the same. This seems to coincide with the postulate of the isomorphism of critical phenomena.[45] Second, the value of P^* coincides with the P_X pressure in Fig. 2. We would like to stress that the analysis of these anomalous domains in a way typical for critical phenomena[42,43,45] is not possible because a reliable estimation of the nonpretransitional background seems to be impossible. For lower temperatures in Fig. 4 and pressures for $P < 1.3$ GPa experimental data are fairly well portrayed by the critical-like relations (2) and (5a). The time scale of this domain and the value of the $\mathbf{g} \approx 8.3$ exponent obtained in temperature studies indicate a relationship with the dynamical scaling model.[22,23] It is noteworthy that such a description seems to be valid in the tested ODIC, both under atmospheric pressure[18] and under $P = 1.8$ GPa (this paper). For isothermal-pressure behavior we obtained the evidence for $\mathbf{g}' \approx 4.2$. However, there are no DSM predictions related to pressure behavior so far, to the best of the authors' knowledge. These results and the ones presented in Ref. 18 may suggest that the interplay between translational and orientational degrees of freedom may be one of the most important factors for the DSM, also in compressed systems. In the opinion of the authors, results presented above also indicate that for plastic crystals, heterogeneities or cooperative regions in disordered surroundings may be an important artifact for the dynamics.

Summarizing, glass transition studies under pressure may be helpful in understanding many properties under ambient pressure, but extreme pressures may reveal a still undiscovered plethora of phenomena.

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