

## **Multiple glass transitions in vapor-deposited orientational glasses of the most fragile plastic crystal Freon 113**

A. Vila-Costa<sup>1</sup>, J. Ràfols-Ribé<sup>1,§</sup>, M. Gonzalez-Silveira<sup>1</sup>, A. Lopeandía<sup>1</sup>, J. Ll. Tamarit<sup>2</sup>,  
J. Rodríguez-Viejo<sup>1,\*</sup>

<sup>1</sup> Grup de Nanomaterials i Microsistemes. Departament de Física. Universitat Autònoma de Barcelona. 08193 Bellaterra, Spain

<sup>2</sup> Grup de Caracterització de Materials, Departament de Física and Barcelona Research Center in Multiscale Science and Engineering, Universitat Politècnica de Catalunya, EEBE, Campus Diagonal-Besòs, Av. Eduard Maristany 10-14, 08019 Barcelona, Catalonia, Spain.

§ present address: Department of Physics, Umeå University, SE-901 87 Umeå, Sweden.

\* corresponding author: javier.rodiguez@uab.es

### Abstract

We investigate by fast-scanning nanocalorimetry the formation of Freon 113 films from the vapor phase at deposition temperatures ranging from 50-to-120 K, that is spanning above and below the transition temperature of the glassy crystal to the plastic crystal, ( $T_{gc}=72$  K). Analysis of the heat capacity curves indicates that vapor deposition at  $T < T_g$  of the highly fragile Freon 113 yields structural and orientational glasses in the as-deposited state depending on the temperature range of deposition. Interestingly, growing above  $T_{gc}$  produces plastic crystals with a conformational  $C_1/C_s$  ratio that changes with  $T_{dep}$  above and below 110-120 K, the temperature at which previous works have identified the arrest of the transformations between the  $C_1$  and  $C_s$  conformers.

## Introduction

Plastic crystals (PCs) are considered as model systems to study the glass transition phenomena both theoretically and experimentally because, in spite of their translational symmetry, they exhibit an orientational disorder. PCs are commonly found for molecules displaying pseudo-globular molecular shape with van der Waals molecular interactions but displaying short range order. While structural (conventional) glasses (SGs) are amorphous solids lacking both translational and orientational long range order, commonly obtained by quenching the supercooled liquid, orientational glasses (OGs) display translational order and orientational disorder and, in addition, they exhibit similar glassy properties that SGs. In molecular systems forming PCs it is difficult to access the SG since a transition from the liquid to the PC state and, later on, to a glassy crystalline state, typically occurs during cooling. In this case, the center of mass of the molecules remains unchanged at the lattice sites but the rotational degrees of freedom at the molecular level are frozen in non-equilibrium positions and the glassy crystal (GC) is in a non-ergodic state.<sup>1-7</sup> Only two cases, ethanol and cyclohexene,<sup>2,5,8</sup> have been shown to exhibit multiple glass transitions, i.e. glassy crystal to PC and SG to liquid. Indeed, for sufficiently high cooling rates (above 30 K/min) the SG can be accessed in these organic molecules. It is interesting to note that for both molecular systems the glass transition temperature from the GC to the supercooled PC and the SG to the supercooled liquid (SCL) occurs at similar temperatures in spite of the differences of the starting glass state.

Freon 113 (1,1,2-trichlorotrifluoroethane,  $\text{Cl}_2\text{FC-CF}_2\text{Cl}$ ) exhibits a PC phase with cubic symmetry (bcc) which gives rise to a GC below the temperature of 72 K and an ordered

crystal with monoclinic symmetry.<sup>9-11</sup> It represents one of the rare examples of fragile PC, being in addition the one with the highest kinetic fragility with  $m=136$ .<sup>11</sup> The stable crystalline phase of Freon 113 is extremely difficult to form, a general experimental fact for many halo-ethane derivatives due to the existence of internal molecular degrees of freedom which promote the appearance of distinct conformers (trans and gauche).<sup>12-17</sup> To obtain it, Kolesov et al.<sup>9</sup> cooled the plastic phase of Freon 113 to the liquid-nitrogen temperature, and then annealed it for 10-14 h at a temperature of 79 K, that is 3-4 K below the transition temperature ( $T=82.5$  K) at which the stable crystalline phase transforms into the PC phase on heating. On the contrary, Vispa et al.<sup>11</sup> were unable to form the stable crystal phase of F113. Previous works on Freon 113 have failed to access the SG,<sup>10,11</sup> being the unique low-temperature phase the GC that forms upon cooling the PC. On heating at 1 K/min Vdovichenko et al.<sup>10</sup> found the glass-like transition between GC and PC phases at  $T_{gc}=72$  K and, in addition to this transition, they measured a heat capacity anomaly at around 120 K which was attributed to the arrest of the degrees of freedom due to the internal molecular rotation from the  $C_1$  to the  $C_s$  molecular symmetry conformation that differs in a  $120^\circ$  rotation around the C-C single bond, similar to the anomaly found for Freon112.<sup>10,17,18</sup> The trans  $C_1$  conformer is energetically more stable by approximately 1.6 kJ/mol than the gauche  $C_s$  conformer.<sup>19</sup>

The high fragility of Freon 113 was attributed to the high configurational entropy of this system due to the existence of the aforementioned intramolecular modes which increase the number of energy minima in the energy landscape.<sup>11</sup> Owing to the van der Waals intermolecular interactions, halo-ethane derivatives are known to exhibit strong orientational correlations related to the small difference between conformers although

separated by a large energy barrier strongly temperature dependent. These special properties make Freon 113 an interesting system to build up stable glasses by means of vapor deposition.<sup>20-22</sup> Moreover, the van der Waals intermolecular interactions suggest high surface mobility that can support efficient packing during the vapor deposition process. Interestingly, the strong temperature dependence of the potential energy should provide the possibility to scan the different minima in the energy landscape. As far as we know, only ethanol, tetrachlormethane and Freon 134a, all of them exhibiting PC phases, have been studied by vapor deposition.<sup>23-26</sup> In all these works, only the SG was formed at deposition temperatures below  $T_g$ . On the contrary, we show that vapor deposition at  $T < T_g$  of the highly fragile Freon 113 yields structural and orientational glasses in the as-deposited state depending on the temperature range of deposition. Growing above  $T_g$  produces PCs with a  $C_1/C_s$  ratio that changes with  $T_{dep}$  above and below 110-120 K.

### **Experimental Section**

Both the growth of the Freon 113 films by vapor deposition and the  $C_p$  measurements, were carried out within a Helium cryostat with a base vacuum better than  $5 \times 10^{-7}$  mbar in a temperature interval ranging from 50 to 200 K. The cryostat was adapted to hold a prechamber linked to an injection system with a tube inserted perpendicular to the sample holder. The flow of Freon 113 into the vacuum chamber was controlled by a high-precision leak valve. Two nearly identical calorimetric chips were thermally linked to the substrate and connected to the instrumentation as described in previous publications.<sup>27,28</sup> The reference chip was completely isolated from the Freon 113 flow while the sample chip had a mask that ensures deposition only onto the active area of

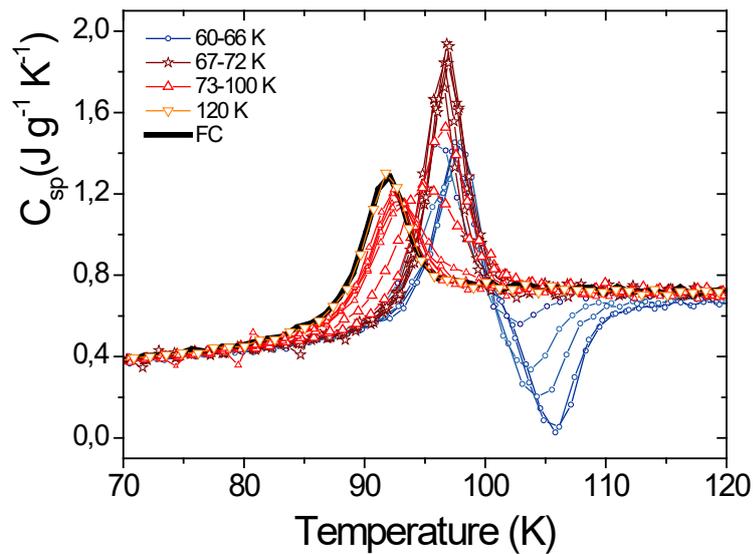
the chip that contains a 200 nm thick Al layer to improve the temperature homogeneity. The experiments were conducted as follows: once the temperature of the chips was set to the desired deposition temperature ( $T_{\text{dep}}=50\text{-}120$  K, corresponding to  $T_{\text{dep}}/T_g=0.60\text{-}1.67$ ) the leak valve was opened and Freon 113 condensed at rates around 1nm/s onto the sample chip. After the  $\approx 75$  nm thick films were formed the chip was passively cooled at  $-500$  K/s to 35 K and the calorimetric scan started right away with a typical heating rate of  $3 \times 10^4$  K/s up to  $\approx 150$  K. The second up scan corresponded then to a sample that was quenched from the final temperature of the previous scan, typically around 150 K. Samples prepared this way are termed glassy crystal fast cooled, GCFC. For the other samples the nomenclature used throughout the text is: Glassy crystal vapor deposited (GCVD) refers to Freon 113 films prepared directly from the vapor into the glassy crystal phase below 72 K, while GC1 are glassy crystals prepared in the plastic crystal phase above 72 K but below 110-120 K and quenched to the base temperature of 35 K.

## Results and Discussion

Due to the complex phase pattern of Freon 113, vapor deposition at different temperatures may yield a number of slightly dissimilar structures such as structural glasses, glassy crystals when the films are deposited at temperatures below the glass transition temperatures or supercooled liquid or plastic crystal if  $T_{\text{dep}}$  is higher than any of the  $T_g$ 's or even the stable monoclinic crystal. In addition the subsequent heating scan to measure the heat capacity will produce transformations between them. The richness of the specific heat,  $C_{\text{sp}}$ , curves associated with samples vapor-deposited within the range 60-120 K is illustrated in Figure 1. This graph permits a fast visualization of the influence of the deposition temperature on the progression of the heat capacity. The

curves correspond to the first heating scan after the sample has been vapor-deposited at  $T_{\text{dep}}$  and immediately after quenched at  $-500 \text{ K/s}$  to  $35 \text{ K}$ . A second up scan that turns out to be identical for all samples irrespective of their deposition temperature is shown as a black solid line for comparison. As described in the experimental section these samples are obtained by cooling the vapor-deposited films that in the first scan have been taken to  $150 \text{ K}$ , well above the GC to PC transition. Since the only possible phase upon cooling the PC is the GC<sup>11</sup> we identify the endotherm of the black solid curve ( $T_{\text{on}}=88 \text{ K}$ ,  $T_{\text{peak}}=92 \text{ K}$ ) with the transition from a GC to the PC phase. Samples prepared in this way are called glassy crystal fast cooled, GCFC. The temperature shift of  $16 \text{ K}$  between the standard calorimetric  $T_{\text{gc}}$  ( $72 \text{ K}$ ) and  $T_{\text{on,GCFC}}$  ( $88 \text{ K}$ ) is mostly related to the high heating rates inherent to our nanocalorimetric technique, i.e.  $3.5 \times 10^4 \text{ K/s}$ .

To allow for easier identification of changes in the calorimetric traces we subdivide the data into 4 regions: blue open circle curves that show an endothermic overshoot with  $T_{\text{peak}}=97-98 \text{ K}$  followed by an exothermic event of varying enthalpy are deposited in the temperature range below  $66 \text{ K}$ ; brown-colored, star symbols, samples with a large endothermic transition ( $T_{\text{peak}}=97 \text{ K}$ ) are vapor-deposited between  $67$  and  $72 \text{ K}$ ; red up triangle curves are grown in a wide  $T$  range from  $73-100 \text{ K}$  and the peak maximum downshifts from  $97$  to  $92.5 \text{ K}$  with increasing  $T_{\text{dep}}$ ; samples deposited at or above  $120 \text{ K}$  (down triangle orange solid line) are calorimetrically identical to GCFC glasses.



**Figure 1** Complete dataset of specific heat curves deposited at temperatures ranging from 60 to 120 K. Colors and symbols correspond to: blue open circles to samples grown below 66K; brown stars to  $T_{\text{dep}}=67-72$  K; red up-triangles to those vapor deposited in the interval from 73 to 100 K. The orange down triangles correspond to a sample vapor deposited at  $T_{\text{dep}}=120$  K. The continuous black line corresponds to a sample quenched from 150 K to 35 K (glassy crystal fast cooled, GCFC).

Figure 2 shows representative specific heat curves associated with the different deposition temperature regions of Figure 1. We also include a reference curve for a sample that is fast quenched from the plastic crystal phase (GCFC, Figure 2a). Next, we describe the main features in each of these regions:

- Vapor-deposition at  $T_{\text{dep}} \leq 60$  K ( $0.83T_g$ ) enables direct access to a structural glass (SG) that upon fast heating experiences a glass transition (onset of devitrification at  $T_{\text{on,SG}}=94$  K) into the liquid state (endothermic peak) and immediately crystallizes (exothermic signal) into the PC state at  $T_{\text{xt}}=102$  K, as shown in Figure 2b. We do observe a slight variation of the onset temperature and enthalpy overshoot of the SG with deposition temperature (Fig. 2b) that we tentatively ascribe to the formation of SGs with varying stability in resemblance to the behavior observed in other molecular glass formers such as toluene, ethylbenzene or larger pharmaceutical or semiconductor

organic molecules that form highly stable glasses when vapor deposited at around  $0.85-0.9 T_g$ .<sup>29-32</sup> This is to our knowledge the first evidence of a SG in Freon 113.

- Interestingly increasing the deposition temperature up to 67 K ( $0.93T_g$ ) yields glasses with lower amounts of SG (Figure 2c), as noted by the smaller crystallization peak and by the smaller contribution of the peak to the endothermic signal (illustrated by the dashed black arrows pointing downwards in Figure 2c). In parallel with the decrease of the SG phase, another peak clearly develops at a slightly lower temperature (1 K below) increasing its intensity with increasing deposition temperature (arrow pointing upwards in Figure 2c). We interpret this region as the coexistence of two phases: a structural glass (SG) and a glassy crystal (GCVD) with relative amounts that depend on  $T_{dep}$ .

- Samples grown in the narrow temperature range 68-72 K ( $0.94-1.03 T_g$ ) (Figure 2d) grow in a pure glassy crystalline phase (GCVD from Glassy Crystal Vapor Deposited) with an onset temperature,  $T_{on,GCVD}=93$  K. This temperature is only 1 K below the devitrification temperature of the structural glass while differs by  $\approx 5$  K from  $T_{on,GCFC}$ . That is, samples vapor deposited directly as a GC, GCVD, are kinetically more stable than samples quenched from the PC, GCFC. Several indirect evidences do support the adscription of this peak to a GC to PC transition and not to the ordered crystal towards the PC (OC to PC transition) that according to Kolesov et al.<sup>9</sup> occurs at 82.5 K. i) Films grown within this temperature interval at different growth rates (between 0.5-2.5 nm/s) show different onset temperatures similarly to what is observed in vapor-deposited glasses,<sup>33</sup> as shown in figure S1. On the contrary, the OC should exhibit a well-defined onset temperature nearly independent of the growth rate in this small range variation. ii) Due to our fast heating rates during the up scans, the onset temperatures appear shifted to higher temperatures. We have analyzed the dependence of this peak with the

heating rate in the range 100-to- $3.5 \times 10^4$  K/s. The onset at 100 K/s is already below 82 K and the extrapolation to lower heating rates ( $10^{-2}$  K/min) (see supplementary information and Figure S2) yields onset temperatures in the domain 70-72 K far from the 82.5 K measured for the OC to PC transition by Kolesov et al.<sup>9</sup> In addition, we recall that the OCl in Freon 113 is a sluggish phase that requires extensive annealing protocols to be produced. Since  $T_{gc}=72$  K, depositing a film above this temperature should yield a PC that upon quenching transforms into a GC.

- If the deposition temperature is raised above  $T_{gc}=72$  K ( $1.00T_g$ ) the as-deposited phase should be a PC that upon fast cooling ( $q=-500$  K/s) transforms into a GC. However, we observe significant differences depending on the deposition temperature as clearly shown in figure 2e. Between 73 ( $1.01T_g$ ) and 78 K ( $1.08T_g$ ), there is a transition region in which the endothermic signal continuously shifts to lower temperatures as deposition temperature is increased. Above 78 K and up to 100-110 K the endothermic signal of the first scan remains constant with an onset temperature around 89 K, slightly above the onset temperature of GCFC and below the  $T_{on}$  of the SG. We name samples deposited in this temperature region as GC1. If the deposition temperature is raised above 110-120 K, after quenching we obtain a GC that is calorimetrically equivalent to the GCFC described previously.

The schematics in Figure 3 show the assignment of phases grown within the various temperature regions, the corresponding phases upon quenching to low temperature ( $T=35$  K) and the transformations occurring during the temperature up scans up to 150 K. Based on the above description it is clear that the heat capacity of Freon 113 shows multiple glass transitions similarly to ethanol and cyclohexane.

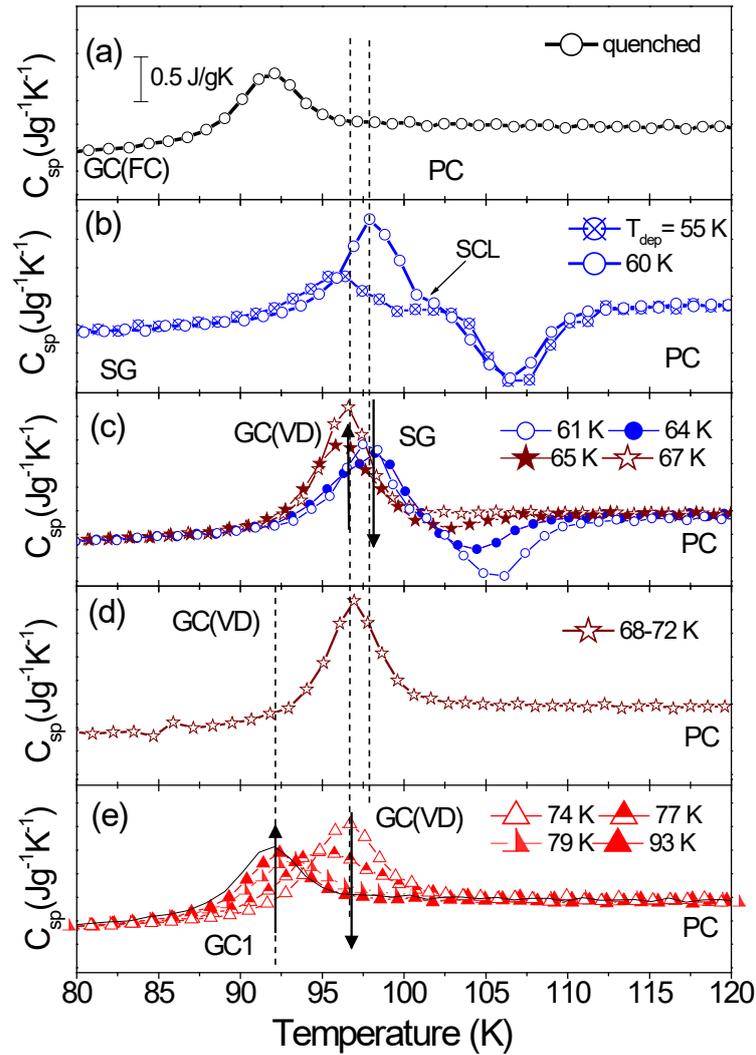


Figure 2. Representative specific heat curves as a function of temperature for samples: (a) GCFC: 2<sup>nd</sup> scan after quenching the sample from  $T=150$  K, the temperature attained in the first scan and 1<sup>st</sup> scans of (b) sample vapor-deposited at  $T_{\text{dep}}=60$  K and cooled to low-temperature, (c)  $T_{\text{dep}}=61-67$  K ( $0.85-0.93T_g$ ); (d)  $T_{\text{dep}}=68-72$  K ( $0.94-1.00T_g$ ); and (e)  $T_{\text{dep}}>74$  K ( $>1.03T_g$ ). The black line corresponds to a sample vapor deposited at 120 K. This curve is equivalent to curve GCFC in (a). The up/down vertical arrows refer to increase/decrease of the different phases.

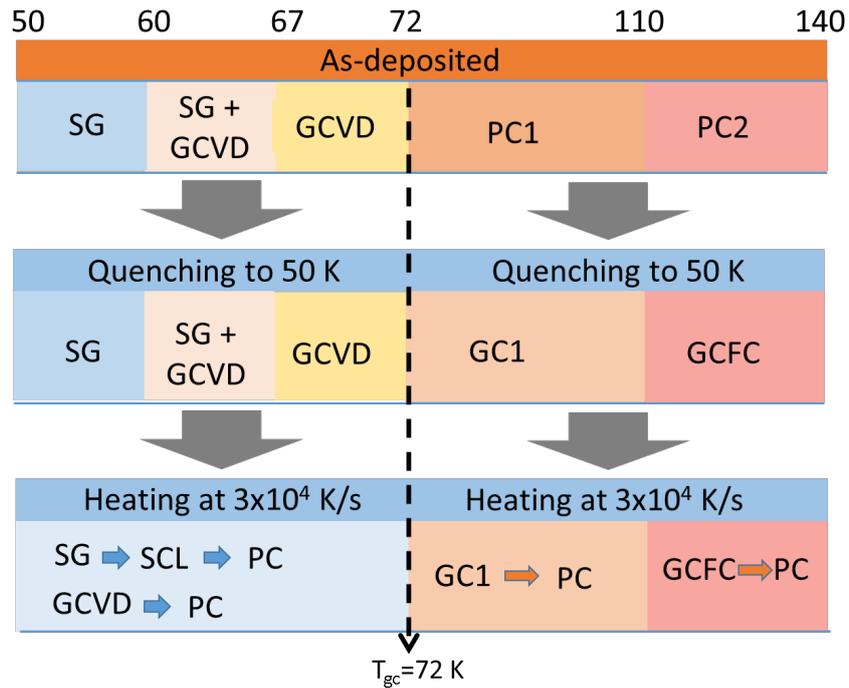
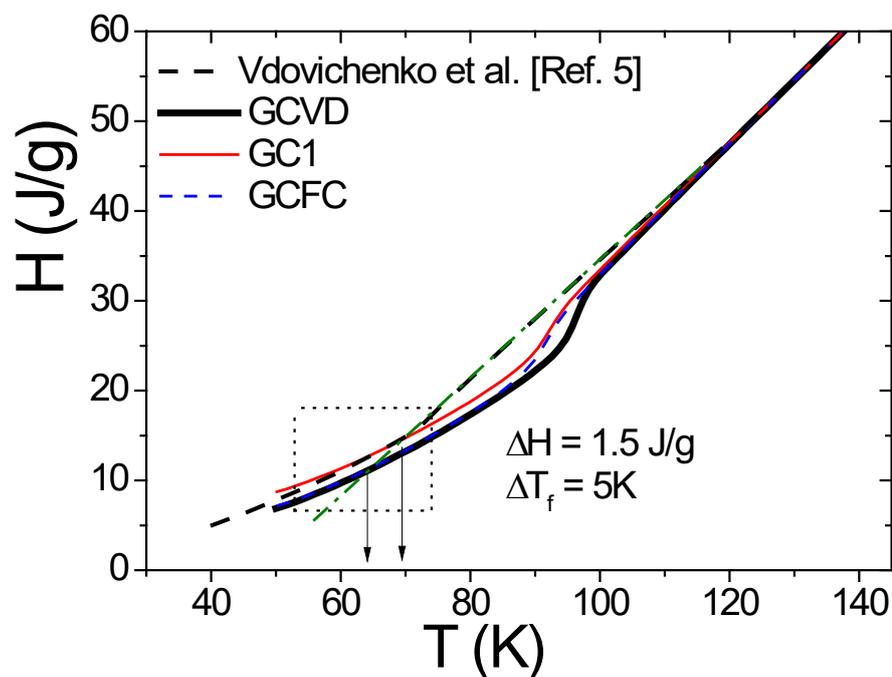


Figure 3. Schematic illustration of the phases formed at different deposition temperatures (upper panel), the corresponding low-temperature phases after quenching (middle panel) and the observed transitions during the heating scan (lower panel).

The complex scenario of Figure 2e with a progressive variation of the endothermic peak associated with the glass transition as the deposition temperature increases up to 110-120 K and the fact that deposition above 120 K yields a GC calorimetrically equivalent to the GCFC merits further discussion. What could be the reason for having different GC phases (GC1-like or GCFC) depending on the value of  $T_{\text{dep}}$  above  $T_{\text{gc}}$ ? To answer this question we first plot the enthalpy (Figure 4a) and entropy (Figure 4b) for the PC and GC phases for samples GC1, GCVD and GCFC (red, black solid and blue dashed lines, respectively, Figure 4a) in the temperature range up to 140 K. The data is obtained after numerical integration of the corresponding specific heat curves of Figures 2a, c and d. The enthalpy graph shows that the GC grown from the vapor at 67 K has a lower enthalpy by 1.5 J/g and a lower limiting fictive temperature ( $T_f'$ ) by roughly 5 K with respect to

GC1 deposited at 93 K. The limiting fictive temperature obtained by the intersection of the plastic line with the glass line in the enthalpy plot is a good indicator of the stability of the film, the lower the value of  $T_f'$  the higher the stability of the glass. On the contrary, in spite of the higher kinetic stability of GCVD compared to GCFC, both glasses show relatively similar enthalpy traces with differences of around 0.1 J/g and 1 K for the enthalpy and  $T_f'$ , respectively that are within our experimental uncertainty. Figure 4a also shows the enthalpy curve obtained from the heat capacity data of Vdovichenko et al.<sup>10</sup> We do observe a small disagreement with our enthalpy data right above  $T_g$ . Figure 4b shows the entropy of the three samples together with data from Kolesov et al.<sup>9</sup> for the reference OC and from Vispa et al. for the GC and PC phases.<sup>11</sup> Since our measurements do start at around 50 K we vertically shift the entropy of the PC to match in the temperature interval from 120-140 K the entropy measured in ref.<sup>11</sup> It is worth mentioning that the crystalline phase measured by Kolesov et al.<sup>9</sup> still has a significant amount of residual entropy probably linked to some conformational disorder and therefore the excess entropies of the GCVD ( $T_{dep}=67$  K) and GCFC with respect to the OC are vanishingly small, approaching our limit of resolution. On the contrary, the GC1 obtained by quenching the sample vapor-deposited at 93 K has a large amount of excess entropy with respect to the OC and to GCFC and GCVD. To understand this behavior we turn to previous heat capacity measurements that showed the change of molecular conformations between  $C_1$  and  $C_5$  is frozen in F113 at around 120 K. In fact, a heat capacity change of 1 kJ/mol is apparent in the  $c_p$  curve of Vdovichenko et al.<sup>10</sup> at around 120 K. Our current heat capacity data is not able to discriminate such transition due to the low signal-to-noise ratio in the high temperature region. Despite this, we interpret the existence of different GC phases as due to the variation of cis/trans conformations

giving rise to glasses of different stability. Samples grown at 120 K or above maximize the amount of  $C_1$  molecular conformations that are the most stable producing a more stable PC. On the contrary, growing roughly below 110-120 K produces PCs that have not reached the most stable configuration. It is worth to note that the difference in enthalpy in the vapor phase between both molecular conformations is around 6 J/g.<sup>19</sup> The enthalpy difference between GC1 and GCVD (or GCFC) of  $\approx 1.5$  J/g may reflect that growing in the T range from 72 to 110 K results in a PC crystal in which the distribution of  $C_1$  molecules is not optimized with respect to the most stable configuration.



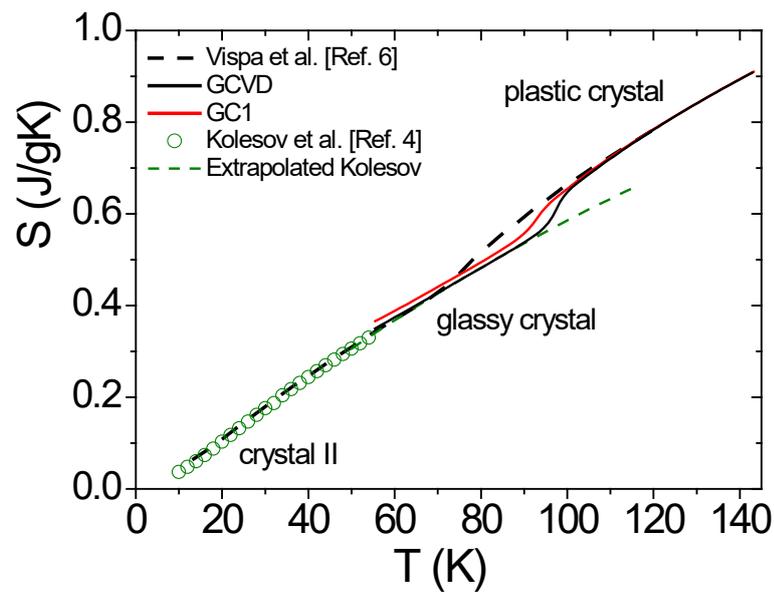


Figure 4. (a) Enthalpy vs temperature for samples GCFC, GC1 and GCVD ( $T_{\text{dep}}=67$  K). The black dashed line is the enthalpy calculated from the specific heat of Vdovichenko et al.<sup>10</sup> The green dashed line is the extrapolation of the PC line to determine the limiting fictive temperature as the intersection with the glassy crystal line, marked by the arrows. (b) Entropy as a function of temperature for GCVD and GC1 and curves from Kolesov et al.<sup>9</sup> for the ordered crystal phase (open circles) and its extrapolation (green dashed line) and from Vispa et al.<sup>11</sup> for the PC and GC phases (dashed black line).

## Conclusions

Vapor-deposition of Freon 113 in the range 50-130 K ( $0.89-1.80 T_g$ ) produces films with different glass transitions depending on the deposition temperature. Deposition at 10 K below  $T_{gc}$  produces a SG that upon fast heating undergoes a glass transition followed by rapid crystallization into the plastic phase. As we increase temperature the amount of SG decreases with a parallel increase of a glassy crystal phase. The SG shows features that mimic those of highly stable vapor-deposited glasses such as the variations of the onset temperature and the enthalpy overshoot with  $T_{\text{dep}}$ . Deposition at temperatures close to  $T_{gc}$  results in a glassy crystal with enthalpy and excess configurational entropy similar to the glass quenched from the PC but with a higher kinetic stability indicated by the higher onset temperature of devitrification. However, when  $T_{\text{dep}}$  is just above  $T_{gc}$  the

heat capacity curves are compatible with a PC that has not reached full equilibration, i.e. the number of  $C_1/C_s$  molecular conformations does not correspond to the lower energy phase. When  $T_{\text{dep}}$  is much higher than  $T_{\text{gc}}$  the films grow in an energetically favored plastic phase and transform to a glassy crystal during quenching.

### Acknowledgments

This work has been partially supported by the Spanish MINECO through Projects No. MAT2016-79579-R, FIS2017-82625-P and MAT2014-57866-REDT. JLT also acknowledges the Generalitat de Catalunya under Project No. 2017SGR-0042. We would like to thank C.A. Angell for inspiring and motivating us to study this problem.

**Supporting Information.** Influence of the deposition rate on the onset temperature of the glassy crystal phase and comparison of the transformation times of the GC with respect to the alpha relaxation of the PC.

### References

- 1 R. Brand, P. Lunkenheimer and A. Loidl, *J. Chem. Phys.*, 2002, **116**, 10386–10401.
- 2 M. A. Ramos, S. Vieira, F. J. Bermejo, J. Dawidowski, H. E. Fischer, H. Schober, M. A. González, C. K. Loong and D. L. Price, *Phys. Rev. Lett.*, 1997, **78**, 82–85.
- 3 K. Adachi, H. Suga and S. Seki, *Bull. Chem. Soc. Jpn.*, 2006, **41**, 1073–1087.
- 4 D. L. Leslie-Pelecky and N. O. Birge, *Phys. Rev. Lett.*, 1994, **72**, 1232–1235.
- 5 S. Benkhof, A. Kudlik, T. Blochowicz and E. Rössler, *J. Phys. Condens. Matter*, 1998, **10**, 8155–8171.
- 6 M. Jiménez-Ruiz, A. Criado, F. J. Bermejo, G. J. Cuello, F. R. Trouw, R. Fernández-Perea, H. Löwen, C. Cabrillo and H. E. Fischer, *Phys. Rev. Lett.*, 1999, **83**, 2757–2760.
- 7 R. Brand, P. Lunkenheimer, U. Schneider and A. Loidl, *Phys. Rev. Lett.*, 1999, **82**, 1951–1954.
- 8 O. Haida, H. Suga and S. Seki, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 802–809.
- 9 V. P. Kolesov, E. A. Kosarukina, D. Y. Zhogin, M. E. Poloznikova and Y. A. Pentin, *J.*

- Chem. Thermodyn.*, 1981, **13**, 115–129.
- 10 G. A. Vdovichenko, A. I. Krivchikov, O. A. Korolyuk, J. L. Tamarit, L. C. Pardo, M. Rovira-Esteva, F. J. Bermejo, M. Hassaine and M. A. Ramos, *J. Chem. Phys.*, 2015, **143**, 84510.
  - 11 A. Vispa, M. Romanini, M. A. Ramos, L. C. Pardo, F. J. Bermejo, M. Hassaine, A. I. Krivchikov, J. W. Taylor and J. L. Tamarit, *Phys. Rev. Lett.*, 2017, **118**, 105701.
  - 12 M. Rovira-Esteva, N. A. Murugan, L. C. Pardo, S. Busch, J. L. Tamarit, S. Pothoczki, G. J. Cuello and F. J. Bermejo, *Phys. Rev. B*, 2011, **84**, 64202.
  - 13 P. Negrier, M. Barrio, J. L. Tamarit, L. C. Pardo and D. Mondieig, *Cryst. Growth Des.*, 2012, **12**, 1513–1519.
  - 14 I. V Sharapova, A. I. Krivchikov, O. A. Korolyuk, A. Jezowski, M. Rovira-Esteva, J. L. Tamarit, L. C. Pardo, M. D. Ruiz-Martin and F. J. Bermejo, *Phys. Rev. B*, 2010, **81**, 94205.
  - 15 P. Negrier, J. L. Tamarit, M. Barrio and D. Mondieig, *Cryst. Growth Des.*, 2013, **13**, 782–791.
  - 16 P. Negrier, M. Barrio, J. L. Tamarit, D. Mondieig, M. J. Zuriaga and S. C. Perez, *Cryst. Growth Des.*, 2013, **13**, 2143–2148.
  - 17 S. S. K. Kishimoto, H. Suga, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1691.
  - 18 L. C. Pardo, F. J. Bermejo, J. L. Tamarit, G. J. Cuello, P. Lunkenheimer and A. Loidl, *J. Non. Cryst. Solids*, 2007, **353**, 999–1001.
  - 19 K. Le Bris, K. Strong, S. M. L. Melo and J. C. Ng, *J. Mol. Spectrosc.*, 2007, **243**, 142–147.
  - 20 S. F. Swallen, K. L. Kearns, M. K. Mapes, Y. S. Kim, R. J. McMahan, M. D. Ediger, T. Wu, L. Yu and S. Satija, *Science*, 2007, **315**, 353–6.
  - 21 E. León-Gutierrez, G. Garcia, A. F. Lopeandía, J. Fraxedas, M. T. Clavaguera-Mora and J. Rodríguez-Viejo, *J. Chem. Phys.*, , DOI:10.1063/1.3009766.
  - 22 E. Leon-Gutierrez, A. Sepúlveda, G. Garcia, M. T. Clavaguera-Mora and J. Rodríguez-Viejo, *Phys. Chem. Chem. Phys.*, 2010, **12**, 14693–8.
  - 23 M. Tylinski, Y. Z. Chua, M. S. Beasley, C. Schick and M. D. Ediger, *J. Chem. Phys.*, 2016, **145**, 174506.
  - 24 Y. Z. Chua, M. Tylinski, S. Tatsumi, M. D. Ediger and C. Schick, *J. Chem. Phys.*, 2016, **144**, 244503.
  - 25 A. Drobyshev, A. Aldiyarov, K. Katpaeva, E. Korshikov, V. Kurnosov and D. Sokolov, *Low Temp. Phys.*, 2013, **39**, 714–718.
  - 26 A. Drobyshev, A. Aldiyarov, A. Nurmukan, D. Sokolov and A. Shinbayeva, *Low Temp. Phys.*, 2018, **44**, 831–839.
  - 27 A. F. Lopeandía, E. León-Gutierrez, J. Rodríguez-Viejo and F. J. Muñoz,

- Microelectron. Eng.*, , DOI:10.1016/j.mee.2007.01.054.
- 28 A. F. Lopeandía, J. Rodríguez-Viejo, M. Chacón, M. T. Clavaguera-Mora and F. J. M. Noz, *J. Micromech. Microeng*, 2006, **16**, 965–971.
  - 29 K. L. Kearns, S. F. Swallen, M. D. Ediger, T. Wu and L. Yu, *J. Chem. Phys.*, 2007, **127**, 154702.
  - 30 C. Rodríguez-Tinoco, J. Ràfols-Ribé, M. González-Silveira and J. Rodríguez-Viejo, *Sci. Rep.*, 2016, **6**, 35607.
  - 31 C. Rodríguez-Tinoco, M. Gonzalez-Silveira, J. Ràfols-Ribé, G. Garcia and J. Rodríguez-Viejo, *J. Non. Cryst. Solids*, 2015, **407**, 256–261.
  - 32 K. Ishii, H. Nakayama, S. Hirabayashi and R. Moriyama, *Chem. Phys. Lett.*, 2008, **459**, 109–112.
  - 33 K. L. Kearns, P. Krzyskowski and Z. Devereaux, *J. Chem. Phys.*, 2017, **146**, 203328.