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SUPPLEMENTARY INFORMATION

Secondary relaxation in ultrastable etoricoxib: evidence of correlation with structural relaxation

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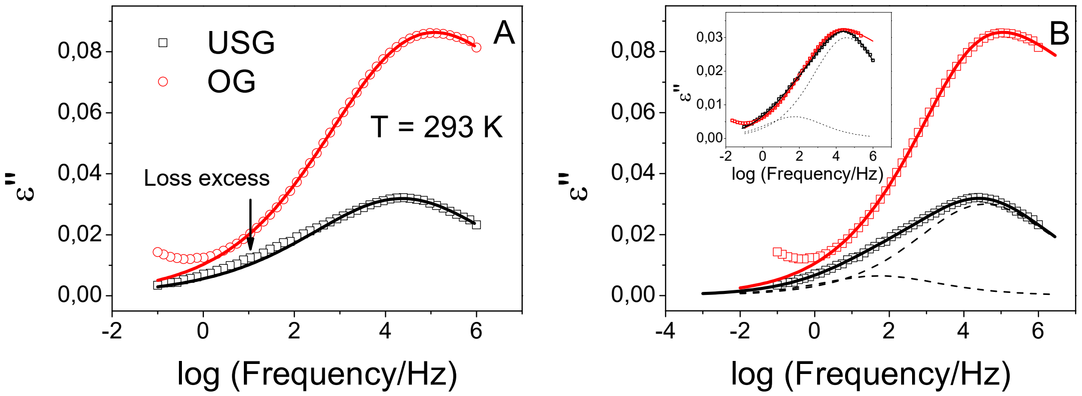
Fitting analysis of dielectric loss

While the dielectric loss of the OG can be perfectly fitted with one HN function, in the case of the USG, the same fitting of the dielectric loss yields a more inaccurate result. In fact, if the peak maximum is forced to be well fitted, the low frequency side of the spectra shows some loss excess. We argue that this excess is originated by some hidden process. Indeed, the fitting of the spectra with two HN functions, one of which at lower frequencies and with lower strength, yield a much more accurate result, as we see in the Supplementary figure 1.



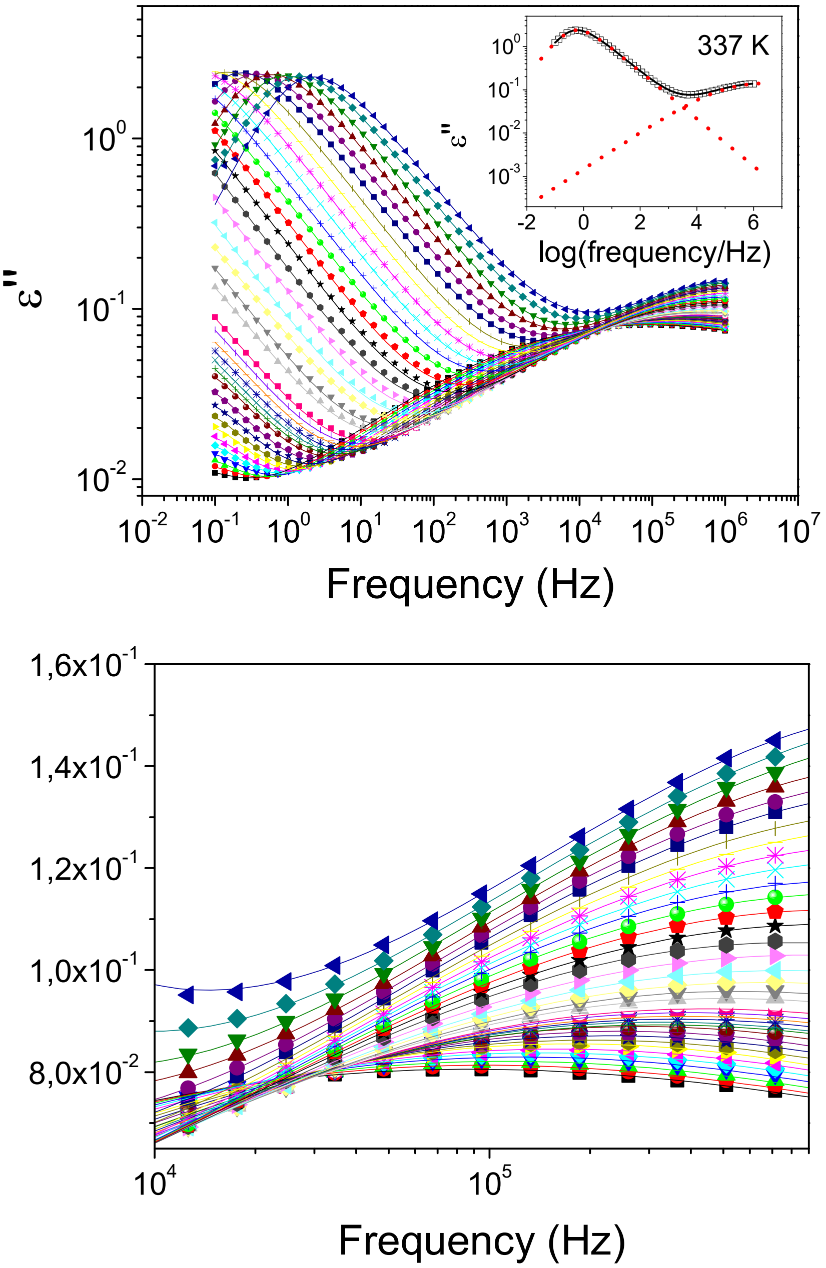
Supplementary figure 1. Dielectric loss of the secondary relaxation process of ordinary (red) and ultrastable (black) glass of etoricoxib measured at 293. In Panel A, the loss is fitted with only one HN function. While the OG is satisfactorily fitted, in the case of the USG the loss at frequencies far from the maximum is not well fitted, suggesting the presence of a hidden process in the low frequency side, which could be related to a JG relaxation. In Panel B, the same dielectric loss is fitted with two HN functions, showing a higher agreement between fitted and experimental data. In the inset, the red curve (OG) has been normalized by the peak intensity and shifted towards lower frequency values to match the maximum of the USG loss.

Analysis of secondary relaxation close to T_g

As mentioned in the main text of the article, close to T_g and into the supercooled liquid state we observe a change to a stronger temperature dependence of the secondary relaxation time of the OG. Due to the fast nature of the secondary process, and close to T_g, part of the relaxation process remains out from the measurable frequency range. Also, in this temperature range, the secondary process is closer to the structural one, being the latter much more intense and particularly obscuring the dielectric signal of the former. Therefore, the data analysis in the mentioned temperature range must be carefully performed.

To analyse these data, we have first, fitted the structural relaxation process with a HN function focussing in the frequency range where there is no contribution from the secondary relaxation. We have first fitted the spectra corresponding to higher temperatures in order for the structural process to be completely visible in the experimental frequency window. Taking that spectra as a reference, we have fitted the spectra corresponding to lower temperatures by slightly changing the parameters, and the process is repeated. In that way, we can successfully fit the structural relaxation process even when the process is not completely visible in the available frequency range.

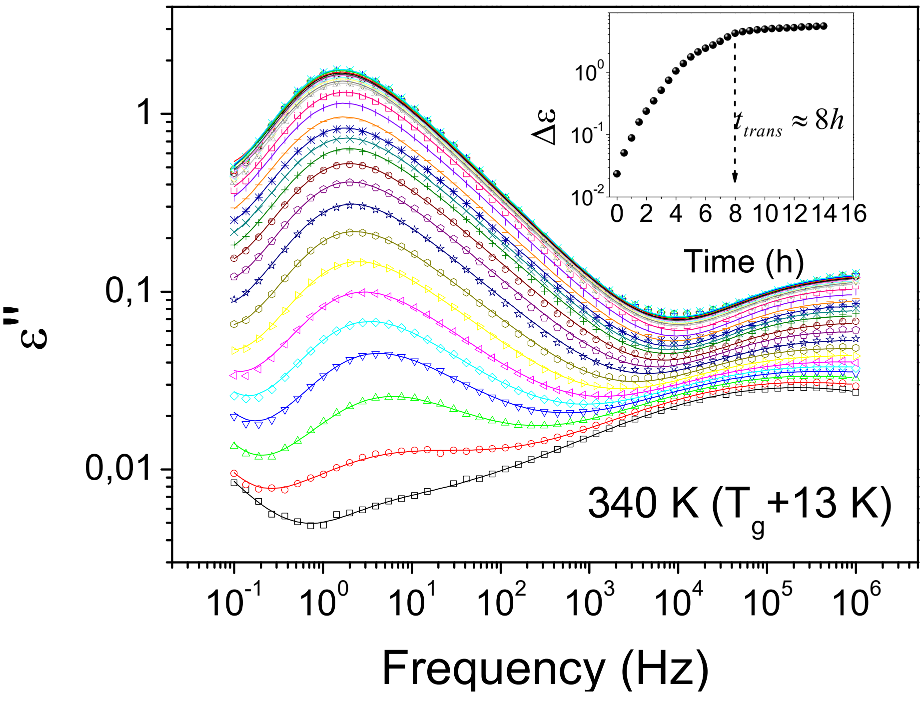
After that, and for each spectrum from lower to higher temperatures, we have focused on the frequency range where the main dielectric contribution comes from the secondary relaxation process. In that frequency range, we have added a second HN function to fit the experimental data. The resulting fits are shown in the Supplementary figure 2.



Supplementary figure 2 Loss spectra of etoricoxib OG around T_g. From left to right, the curves correspond to the temperature range 293 K < T < 337 K, where ΔT = 1 K from 293 K to 313 K and ΔT = 2 K from 313 K to 337 K. A) Whole frequency range, showing the two relaxation processes fitted with two HN functions. In the inset, we show the two HN individual functions used for fitting for a particular temperature. B) Detail of the frequency range where the secondary process is predominant, showing the good quality of the fitting.

Transformation above T_g

In the Supplementary figure 3 we show the evolution of the dielectric spectra of ultrastable etoricoxib during annealing at 340 K (T_g + 13 K). As already reported for other ultrastable glass formers, the alpha relaxation peak, corresponding to the supercooled liquid phase, emerges throughout time. In parallel, we can also see the increase in intensity (shown in the inset) and relaxation time of the secondary relaxation process, which is recovering equilibrium properties. After 8 hours of annealing, the transformation process is completed and the sample has completely transformed into the supercooled liquid state. The characteristics of the secondary relaxation of glass obtained after cooling of the sample after annealing exhibits the same characteristics as the OG obtained by cooling from the melting temperature.

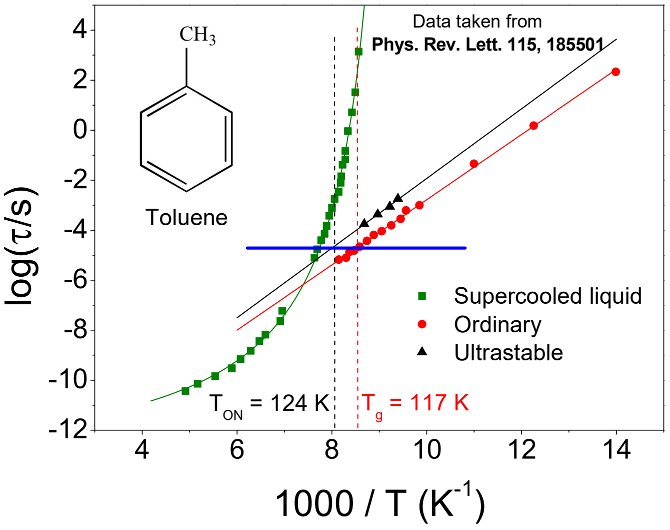


Supplementary figure 3. Evolution of the dielectric spectra of an ultrastable glass of Etoricoxib during annealing at 340 K, 13 K above its glass transition temperature. The emergence of the structural relaxation time is observed, together with a shift towards larger frequencies and intensification of the secondary relaxation process. In the inset, we plot the intensity of the structural relaxation as a function of time. After approximately 8 hours, the process is completed and the sample is completely transformed.

The measured transformation time corresponds to approximately 5 orders of magnitudes longer than the structural relaxation time of the liquid at that temperature, which is an indication of the enormous kinetic stability of the prepared USG.

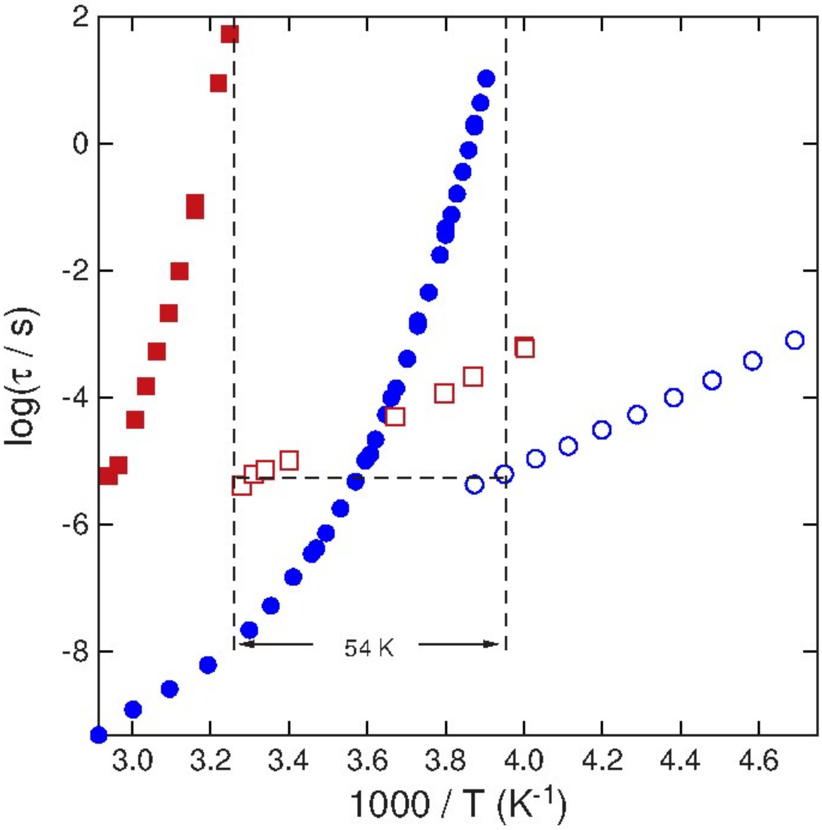
Secondary relaxation in toluene USG

In the main text of this paper, we show a correspondence between the enhancement in onset temperature of devitrification, related to the structural relaxation (at T_{on}, τ_α=100 s), and the enhancement of the secondary relaxation. In particular, extrapolation of the secondary relaxation time of both OG and USG at the corresponding devitrification temperature (T_g or T_{on}, respectively) exhibits the same value. The same observation can be done from the reported data of USG of toluene [Yu, H. B.; Tylinski, M.; Guiseppi-Elie, A.; Ediger, M. D.; Richert, R. Suppression of β Relaxation in Vapor-Deposited Ultrastable Glasses. *Phys. Rev. Lett.* **2015**, *115* (18), 185501.] (Supplementary figure 4). In that case, the increase of the isochronal JG β-relaxation temperature, $\Delta T_\beta = 6\ K$, is coincident with the enhancement of T_{on} in the USG. As a result, extrapolation of the secondary relaxation time of both OG and USG at the corresponding devitrification temperature exhibits the same value.



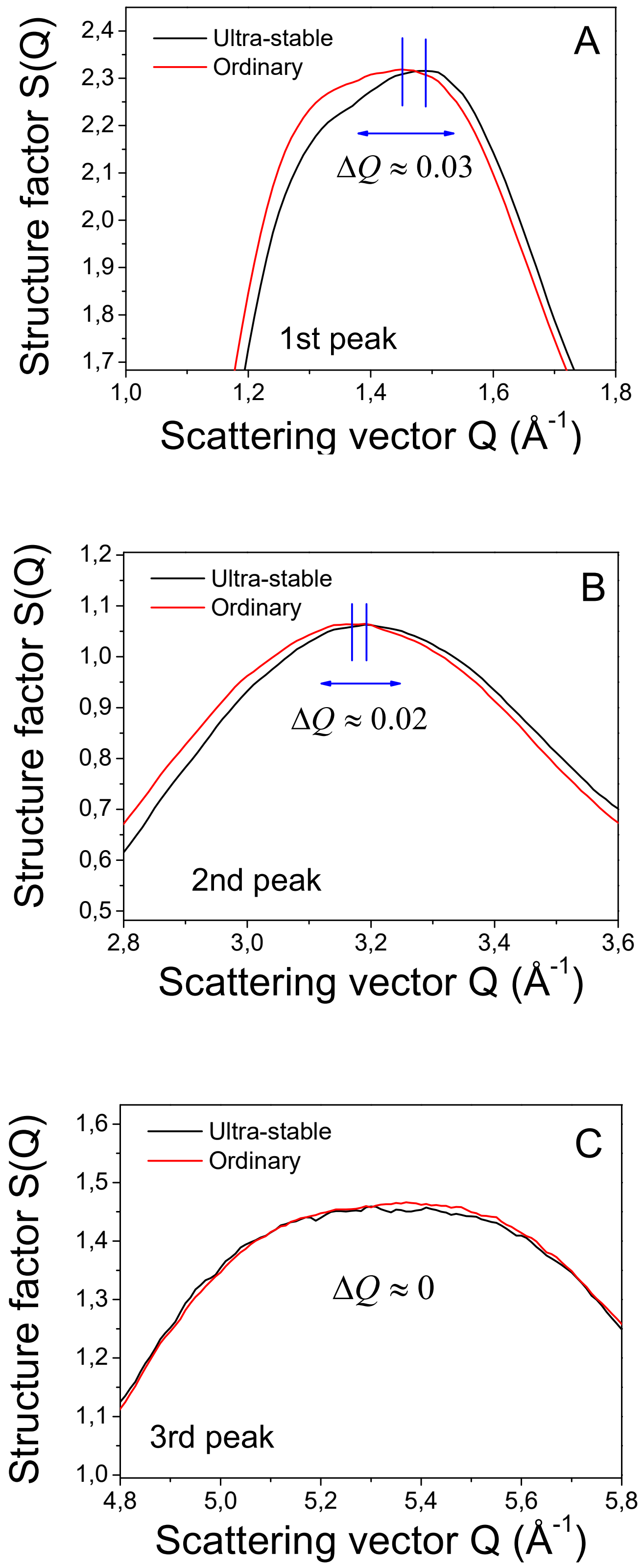
Supplementary figure 4. Relaxation map of toluene obtained from Phys. Rev. Lett. 115, 185501. The blue line indicates the invariant value of τ_β *for the OG or the USG at the corresponding devitrification temperature.*

Scaling of secondary relaxation at variable pressure



Supplementary figure 5. Logarithm of characteristic time of dielectric loss maximum of DGEBA (diglycidyl ether of bisphenol-A, M_w*=380 g/mol, also known as EPON 828) for α-relaxation and JG-relaxation in isobaric condition versus reciprocal temperature. Red symbols (P=400 MPa), blue symbols (P=0.1 MPa). The difference in* T_g *is 54 K, which is matched by the separation of the JG β-relaxation time as indicated by the dashed line.*

Detail of structure factor of USG and OG glasses (Figure 1B).



Supplementary figure 6. Zoom of the 3 first peaks of the diffraction pattern shown in Figure 1B of the main text. The curves have been vertically shifted for better comparison.