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The Search for Ferroelectric domain structures in carbohydrate glasses using atomic force microscopy

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Determination of Ferroelectric Properties in Carbohydrate Glasses Using Atomic Force Microscopy

D-glucose was studied as a possible candidate for ferroelectric domain imaging using an Atomic Force Microscope (AFM). The large dipole moment of carbohydrates is such that they may show localized ferroelectric domain formation in liquid phase. Samples were heated at their melting point on glass slides and then left to cool to room temperature in a desiccator. Differential Thermal Analysis (DTA) was used to test the effectiveness of this method, and it was found that the oven preparation created samples with 41% crystallinity, where both a glass transition and sharp melting peak were observed. DTA was again used to find a way to create a better amorphous sample. An assessment of the effect of cooling rate on glass formation was conducted using a Differential Scanning Calorimeter (DSC). Surface images of a ferroelectric ceramic and the surface of an amorphous glucose sample were taken using AFM Constant Force Topography

The Search for Ferroelectric Domain Structures in Carbohydrate Glasses Using Atomic Force Microscopy



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Abstract

D-glucose was studied as a possible candidate for ferroelectric domain imaging using an Atomic Force Microscope (AFM). The large dipole moment of carbohydrates is such that they may show localized ferroelectric domain formation in liquid phase. Samples were heated at their melting point on glass slides and then left to cool to room temperature in a desiccator. Differential Thermal Analysis (DTA) was used to test the effectiveness of this method, and it was found that the oven preparation created samples with 41% crystallinity, where both a glass transition and sharp melting peak were observed. DTA was again used to find a way to create a better amorphous sample. An assessment of the effect of cooling rate on glass formation was conducted using a Differential Scanning Calorimeter (DSC). Surface images of a ferroelectric ceramic and the surface of an amorphous glucose sample were taken using AFM Constant Force Topography Mode.

Background

Hyper-Rayleigh Scattering experiments have indicated evidence of localized ferroelectric domain formation in polar liquids. Several systems, such as nitromethane/nitrobenzene and acetonitrile have been studied and exhibit this effect. Domain formation is thought to occur when $\mu^2 p / (k_B T) > 1$ where μ is the dipole moment of the liquid and p is the dipole moment of the molecules. Above this point, regions of localized dipole alignment are favorable over thermal fluctuations, which would normally disrupt their formation. In liquids, the threshold dipole density is $\mu^2 p = 49 \text{ D}^3 \text{M}$ at $T = 300 \text{ K}$. [1] The goal was to find an organic molecule with a dipole density above the threshold, which can form an amorphous phase without crystallizing. If the material were allowed to crystallize, any domain ordering in the liquid would be replaced by that of the crystal. AFM techniques where a voltage is applied to the scanning probe tip have been used to image domains in known ferroelectric materials. Carbohydrates are known glass formers, so crystalline D-glucose was used in our study. It exhibits a large dipole moment ($\mu = 3.8 \text{ D}$) [2], which sets the dipole density well above the threshold (123 $\text{D}^3 \text{M}$). The high glass temperature of glucose, measured at $T_g = 318 \pm 0.3 \text{ K}$, allows the AFM setup to be used at room temperature.

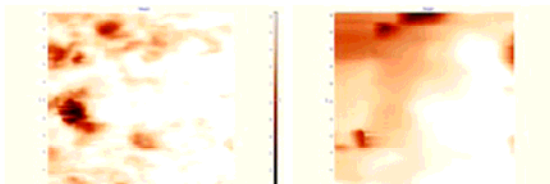
DSC Data

(Table 1a) DSC data from samples prepared in oven

	Melting Temp (K)	Glass Temp (K)	Melting Enthalpy (J/g)	% Crystallinity
Crystalline	435 ± 0.2 K	--	189 ± 6.8 J/g	95 ± 3.5%
Oven Prep	430 ± 2.6 K	318 ± 0.3 K	80.2 ± 2.1 J/g	41 ± 2.1%
Second Run in DSC	430 ± 2.6 K	320 ± 0.2 K	0.014 ± 0.002 J/g	≤0.6%

(Table 1b) DSC data from variable cooling rate experiment.

Sample Cooling Rate	Glass Temp (K)	% Crystallinity	Enthalpy in Glass Transition (J/g)
1 K/min	43.3 ± 5.1 K	≤0.6%	34.7 J/g
5 K/min	43.3 ± 5.1 K	≤0.6%	1.62 J/g
10 K/min	45.6 ± 2 K	≤0.6%	24.2 J/g

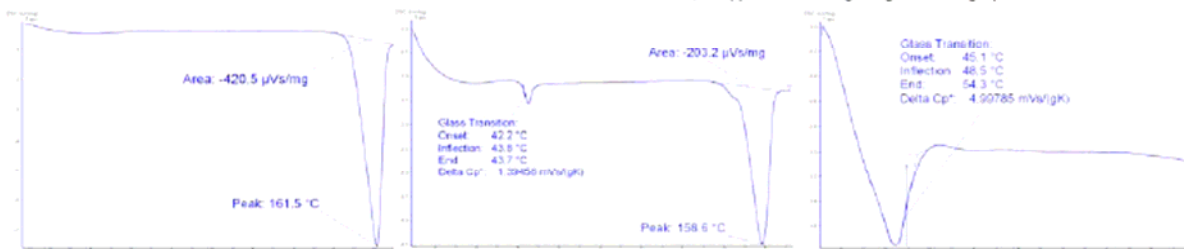


(Fig. 2) Constant Force (Topography) Mode scan of BST capacitor dielectric ceramic before (left) and after (right) grinding and polishing.

Thermal Analysis

Anhydrous, crystalline D-glucose was obtained from J.T. Baker Chemical Co. and used without further preparation. Enthalpy of fusion for crystalline glucose is $185.1 \pm 1.9 \text{ J/g}$. [3] and glucose samples used in this study were found to be 95% crystalline, as shown in Table 1a. A Netzsch Instruments STA 449 C Jupiter Simultaneous Thermal Analyzer, calibrated to indium ($\Delta H_{\text{fus}} = 28.6 \pm 0.02 \text{ J/g}$), was employed to test how effectively oven heating at ~443 K prepared glasses. A DSC curve of crystalline sample is shown in Fig. 3a, and the large melting peak shows that the sample was 95% crystalline. Samples were heated at their melting point in an oven for 5 minutes, then let cool to room temperature (cooling rate ≥50 K/min). When scanned in the calorimeter (Fig 3b), both a glass transition and crystal melting are shown, and crystallinity decreased to $41 \pm 2.1\%$.

When oven heating failed to create an amorphous sample, glucose glass was prepared and evaluated in the DSC. The sample was heated, starting at room temperature, at a rate of 10 K/min to 180 K, then cooled at a variable rate, and reheated to assess how cooling rate affects glass-formation. The three cooling rates tested were 1, 5 and 10 K/min. From this point, the enthalpy of the amorphous melting was calculated from the indium calibration standard. Table 1b shows that a faster cooling rate doesn't produce more glass, although all samples were amorphous. The largest enthalpy was from the 1 K/min cooling rate, the 10 K/min was smaller and the 5 K/min was much smaller than either. Fig. 1c shows the curve of the second heating, in which only a glass peak is evident. An upper bound for percent crystallinity of these samples is ≤0.6%.



(Fig. 1a) DSC curve of crystalline glucose.

(Fig. 1b) DSC curve of glucose heated for 5 minutes in glass shop oven (41% crystalline)

(Fig. 1c) DSC curve of second heating of glucose program with a cooling rate of 10 K/min

References

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- [3] M. Hurta, I. Pitkanen, J. Knuutinen, Carb. Res. 339, 2267 (2004)

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AFM Imaging

An NT-MDT SMENA Scanning Probe Microscope was used for surface imaging. Barium Strontium Titanate (BST) capacitor dielectric, a ceramic with known ferroelectric and piezoelectric properties, was first ground using silicon carbide sandpaper and a variable speed grinder, then finished with diamond lapping solution and Cerium Oxide Final Polishing Compound. Constant Force Topography mode with a scanning speed of 0.74 Hz was selected to assess surface roughness of the sample. After the surface was polished several times using the CeO₂ polish, the largest variations left on the surface were pits, which fell into the ~1-2 μm depth range (near the vertical range of the instrument), bordered by larger flat regions, where the surface variation was well within the range of the tip. Fig. 2 shows both before and after grinding and polishing images. When it was determined that the surface was smooth enough to attempt a domain search, a voltage was applied to the tip and the sample surface was scanned for domains, but it was discovered that a faulty component generated a spurious signal and the error was not corrected to run in time. It was also found that the hygroscopic nature of glucose causes problems for the AFM. A sample of glucose glass was prepared using the method previously detailed. When the tip made contact with the sample surface, it became stuck, as evident from a sharp turn in the photodiode signal, as well as a general lag in responsiveness when approaching or receding from the sample. Furthermore, a scan returned a blank image. Even when contact to atmospheric moisture was reduced by placing the sample in a desiccator for several hours immediately after heating, the AFM exhibited this behavior. Due to these difficulties and a lack of time, no further AFM scans of glucose were run.

Conclusion

Glucose was determined to be a bad choice of molecular system for this study. It meets the criteria for dipolar density, and it also excels as a glass-former. DSC scans verified that several samples were amorphous and nearly 0% crystalline, but the formation of amorphous samples has its pitfalls. The tendency to caramelize when heated to the melting point makes the process require careful attention, and even when the sample appears to have changed phase completely, there may still be some lingering crystals. Furthermore, once the AFM was used to attempt to scan the surface for topography, the tip became stuck and no useful data could be acquired. These techniques for forming and scanning amorphous samples might, however, be applied to other organic glass-forming liquids in future studies.