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Cold Sintering Diisopropylamonium Bromide to Form Organic Ceramic Pellets

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Abstract

Diisopropylamonium bromide is an organic ferroelectric compound. Standard sample preparation methods either require a powder or a single crystal. Certain measurements cannot be done on powders due to equipment limitations, and single crystals are difficult and time consuming to produce and handle. Cold sintering is a relatively new process that allows the creation of ceramics. The original cold sintering process was adapted to work for diisopropylamonium bromide. This allows the creation of ceramics with a large surface area. These pellets can achieve up to 95% of the theoretical maximum density. While the pellets are currently unsuitable for electric testing at this time it appears promising that they will be viable in the near future. Currently, the pellets are much quicker to produce than the crystals, and are more compact than powder. This means that once further research is complete, they will be viable alternative samples.

Key Words: Diisopropylamonium Bromide, Cold Sinter, Ceramic, Ferroelectric

Introduction

Ferroelectric materials are defined as materials that are spontaneously polarized and the polarization can be switched through the application of an external electric field. Diisopropylamine bromide (DIPAB) is an organic ferroelectric salt. In order to fully explore the properties of DIPAB it is essential to create electrically stable samples in a variety of sizes. The most common method of doing this is to grow crystals of DIPAB from solution. This process is extremely complex and can be time consuming as it can take up to a month for a single solution to produce harvest worthy crystals, although it is just as likely to not produce any usable samples [4].

The next challenge is making sure the crystals are in the monoclinic phase. The literature on the subject states that the shape of the crystal indicates the phase it is in, and the thinnest, and hardest to work with crystals are the monoclinic crystals [1]. While recent x-ray diffraction studies seem to indicate that DIPAB is orthorhombic regardless of shape when it forms at room temperature, the thin crystals previously thought to be monoclinic ferroelectric are still difficult to work with as the ferroelectric axis is the long axis with the least amount of surface area [3]. This results in extreme difficulty creating samples and attaching electrodes as often the tip of a brush that would be used to apply a typical electrode such as colloidal silver is larger than the face of the crystal containing the polarization axis. This fact makes it difficult to conduct pyroelectric, piezoelectric, and photovoltaic measurements on these crystals.

Creating ceramics has been around for thousands of years [2]. It is a process that involves sintering powders at very high temperatures to achieve densities greater than 95% that of the

theoretical maximum for the substance [2]. The large temperature needed to achieve this generally makes this process unavailable to organic compounds such as DIPAB as they break down at these temperatures. This had been constant since humankind began making ceramics. Then the authors of *Cold Sintering: A Paradigm Shift for Processing and Integration of Ceramics* published a method in which they were able to achieve up to 97% the theoretical maximum density of cold sintered metals. The authors used the term cold sintered to describe the temperature they were creating their ceramics at (27°C-200°C) compared to the previous temperatures (>1000°C). This was achieved by using a solvent to dissolve the crystal boundaries and then applying pressure so that when the solvent left the metal the boundaries would reform and connect to one another [2].

At the time this project was undertaken the process had still yet to be done in organic compounds. Adapting the cold sintering method to work with DIPAB would allow the creation of large surface area, ferroelectric, samples. This would have to be done at lower temperatures as DIPAB decomposes/sublimates at temperatures above 273°C.

Methods

Creation of Organic Ceramic Pellets

The pellet pressing method was adapted from the *Cold Sintering: A Paradigm Shift for Processing and Integration of Ceramics* paper published in Angewandte Chemie. There were various hydraulic presses used throughout the creating of the samples without variance in the sample quality. The diisopropylammonium bromide was synthesized in a one to one diisopropylamine to hydrobromic acid molar ratio. The salt was then dried and recrystallized no less than three times. More recrystallizations were done as needed to reduce any visual

impurities in the salt. The DIPAB was then powdered in a mortar and pestle. The dye is stainless steel with a cylindrical pressing rod. The pressing area of the dye is 2π cm^2. Before each pellet was created the dye was cleaned with methanol and purified water then dried. After each pellet was formed the dye was cleaned with methanol, purified water, and all moving parts were oiled using silicon oil.

The pellets were created by using 0.35g-0.65g DIPAB. This was stirred into water measured to have 12%-15% of the mass of the DIPAB salt. Using the solubility data provided in Ben Sukup's thesis this results in 15%-20% of the salt being dissolved by mass [6]. This was thoroughly mixed and then placed into the pressing dye. At this point the pressing dye contained mylar that is 2.5 µm thick. A second piece of mylar was used to cover the DIPAB to reduce the reactive area during the pressing. The DIPAB was then subjected to $3.4 * 10^8$ Pa over the course of 45 minutes. After the removal the sample was placed in an oven to be annealed at 414 K over the course of 16 hours [1]. The slow heating and cooling rate reduced the thermal strain on the pellet in order to preserve the integrity of the pellet. There was also an 8-hour period where the temperature remained at 414 K to ensure the pellet reached thermal equilibrium in all parts.

Pellets could then be polished to meet a desired thickness. This would occur though the use of a solvent and cloth designed to not leave behind fabric contamination. The cloth would be saturated with methanol and placed on a smooth surface. The pellet would then be moved across the surface of the cloth for no more than 15 seconds. The pellet would then be allowed to dry, before repeated polishing. This is done so that any solvent which has made its way into cracks on the surface of the pellet can evaporate and allow the DIPAB to recrystallize. This helps to maintain the integrity of the pellet. This method can also remove surface oxidation from the pellet. Density was calculated after the polishing.

Capacitance Measurement

Data was recorded from an HP 4192A Impedance analyzer using a premade LabView 2016 program. A capacitor was made of the pellet using a homemade apparatus. This device consisted of a copper plate attached to a beryllium-copper spring. The spring was attached to a copper disk with a diameter of 2 cm. The disk was freshly coated in a carbon conducting paste for every measurement. This whole system was attached to another carbon paste covered copper plate acting as the second parallel plate electrode to the capacitor, though the use of nylon screws. This device was able to accurately measure the thickness as well as the dielectric constant when using glass as a standard. During these tests the dissipation factor (D-Value) was recorded to be as low as 0.012.

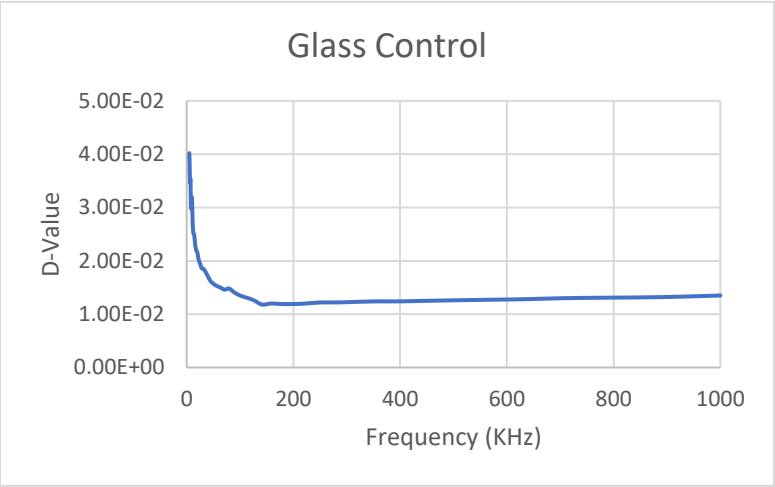

Figure 1: The graph of the dissipation factor vs frequency for a glass standard

X-Ray Diffraction

The pellets were subject to x-ray diffraction powder studies by an XRSCF-Empyrean machine. The spectra were gathered as typical powder data would be gathered. Then to determine the phase the data was compared against the CIF file that was used as a standard for DIPAB. Using Mercury to model the crystal faces as well as produce a powder spectrum the crystal unit cell was determined.

Results

The pellets have up to 95% of the theoretical maximum density for DIPAB. The theoretical maximum was obtained from CIF files found on an online library. The pellets seem to come in two visual forms. One form has larger single crystals within the pellet. This leads to a less dense pellet. The other is a white pellet and these tend to be more dense. This is likely due to the increased ability of the smaller crystals to pack together, whereas the larger crystals must have more space along the crystal boundaries. The pellets often develop a yellow-brown color on the surface. This is thought to be due to an oxidative effect, though the exact mechanism of the oxidation was never determined. The pellets seem to make poor dielectrics as they have large D-values when placed in capacitors. This made it impossible to run a Sawyer Tower test to obtain polarization vs electric field loops as any measurements made would have been wildly inaccurate. As a result, it was never definitively determined that these pellets maintain their ferroelectric properties.

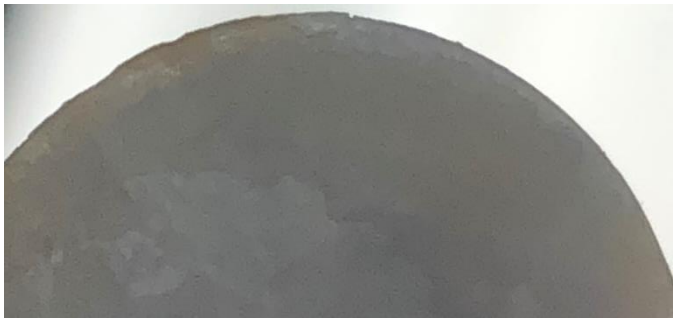

Figure 2: Pellet with small grains that does not allow the as much of the light from the back-side illumination through. Density is 94% of the theoretical maximum.

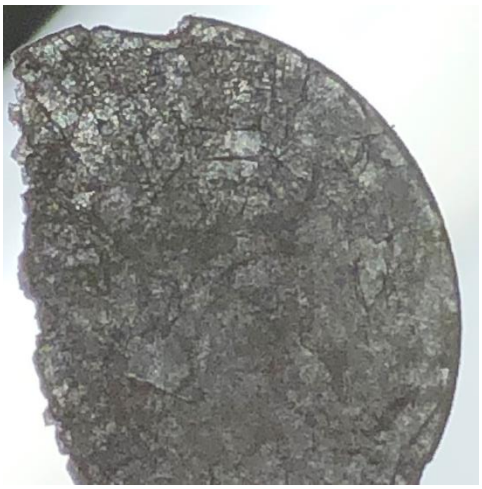

Figure 3: Pellet shown with illumination on the back side contains larger crystal grains that allow more light to be transmitted by the pellet. 85% of the theoretical maximum density.

Figure 4: This pellet has excessive oxidation. It appears as though it is possible it contains liquid bromine in the red spot on the lower right edge of the pellet.

Figure 5: This is an example of a pellet which only has surface oxidation around the edges of the pellet. Often times this is the best case for a pellet.

To be sure the measurements made on the ceramic pellets was producing accurate data one was ran with the pellet in series with a piece of glass. The glass should have a much smaller capacitance and therefore dominate when in series as series capacitances add inversely.

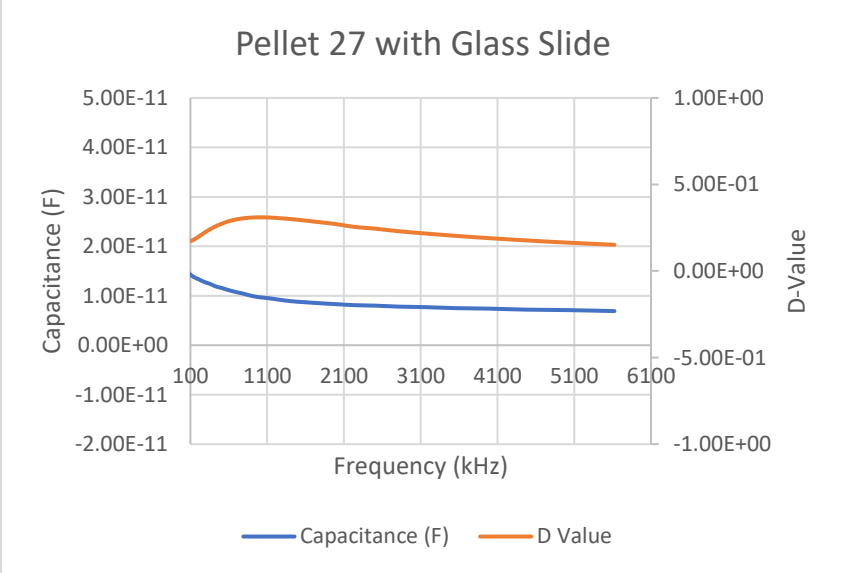

Figure 6: This is the capacitance and D-Value data for both the ceramic pellet and a glass slide. It shows that the measurements read are accurate as it is within 7 pF of the expected 18pF capacitance for the system, while the D-value is relatively low.

This was done as a method to double check and make sure there was no large source of error in the experimental measurement setup. The measure capacitance was on the same order of magnitude of the expected value for the pellet in series with the glass slide. Any error between the two values can be attributed to uncertainty in the dielectric constant as glass has a range from

5-10 and DIPAB has a value that can vary widely depending on the temperature. For these calculations DIPAB has a dielectric constant of 85 [1]. These results indicate that the measurement method is accurate.

Figure 7 and Figure 8 both come from data measured during the same test. These show how the capacitance measurements on the DIPAB pellets can vary extremely. The large D-value of 5 paired with it being inconsistant with D-values being inversly porportional to frequency should that this measurement is not valid. Unfortunately values like these were all that were obtained with attempting to measure the capacitance of the DIPAB pellet. The capacitance measured in figure 8 has a lowest value of 19.6 nF. The theoretical capacitance for the pellet in the measuring apparatus is 200 pF. The difference in the values between the theoretical and measured values can only be explained by error in the value being measured due to the high D-Value. As this type of error occurred during every attempt to measure the capacitance of a pellet it was impossible to do a Sayer Tower measurement as an appropriate reference capicitor could not be chosen. Along the

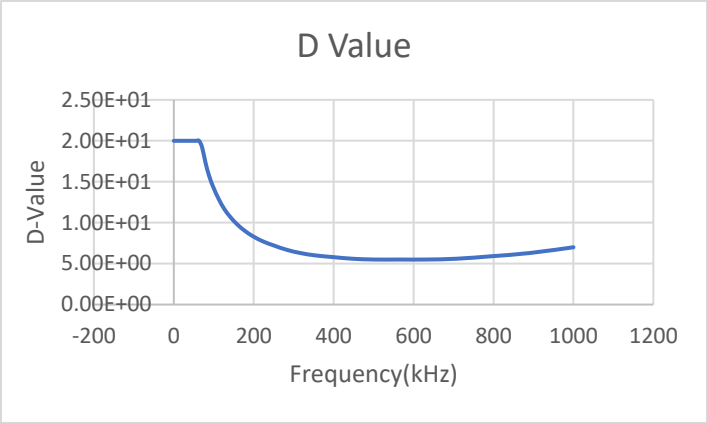

Figure 7: Here shows a measured D-value not being inversely proportional to frequency. The value is also large and indicates that the measured capacitance is not accurate.

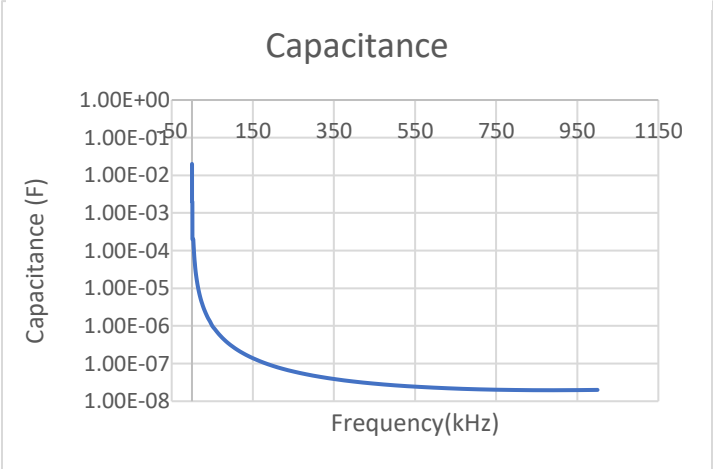

Figure 8: Note the log scale on the capacitance. While capacitance is inversely proportional to frequency it would not have such an extreme effect. This data was collected in the same experiment as figure 7.

same lines, due to the inherant leakage of the DIPAB pellet any measurements made involve capacitance are likely inaccurate.

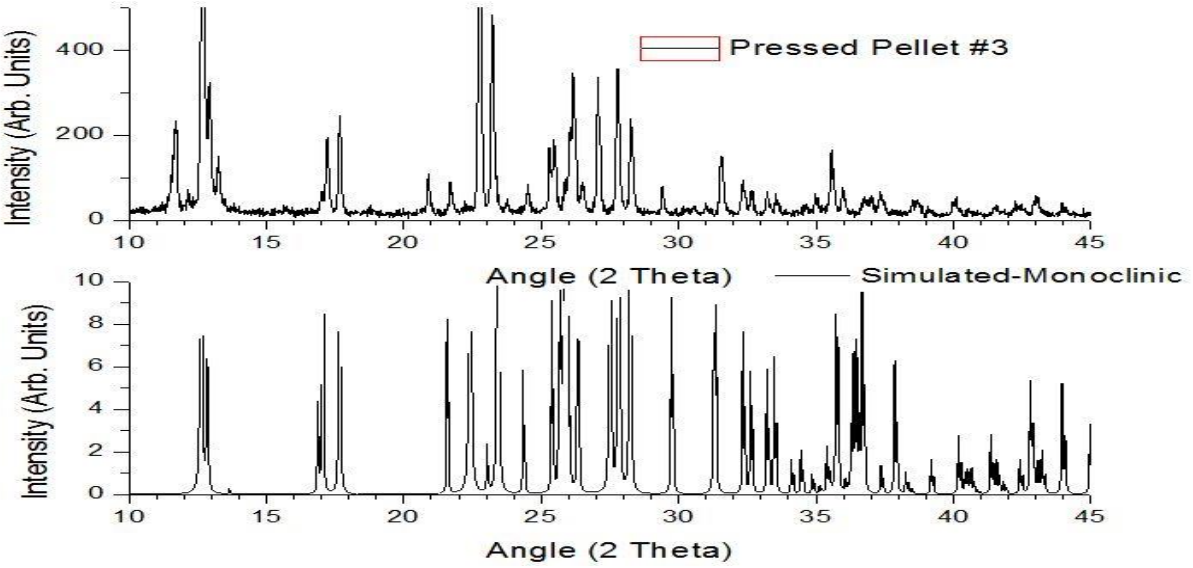

Figure 9: This image shows the spectrum from a pressed pellet that had been annealed. It is lacking the peak at 16 used for the identification of the orthorhombic phase. This combined with the fit of the other peaks indicates that this pellet is monoclinic.

Through the use of x-ray diffraction it is possible to determine the phase of the crystals. Before the pellet is heated for the annealing they present with a powder spectrum of the orthorhombic DIPAB powder. After annealing they present with the monoclinic spectrum of DIPAB powder. It is worth noting that the monoclinic unit cell at room temperature is ferroelectric for single crystal samples of DIPAB [1]. In figure 9 there is a peak at 11.5 that does not occur in the simulated spectra for monoclinic DIPAB. This peak also does not appear in the simulated spectra for orthorhombic DIPAB. This indicates that it was

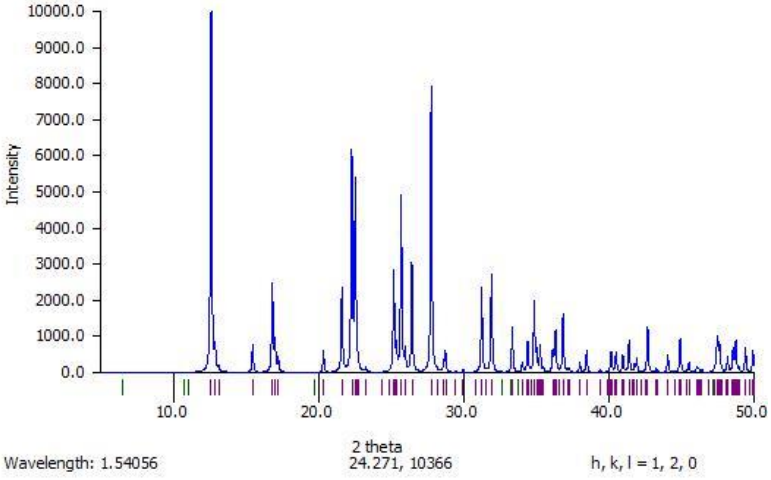

Figure 10: This is the simulated spectra for orthorhombic DIPAB

contamination. Overall, after annealing and before polishing the crystals provide a strictly monoclinic spectra. It is possible that after polishing some of the pellet recrystalizes back into the monoclinic form. This needs more investigating.

Future Work

The next step is to prove that these pellets are ferroelectric, and measure the polarization of the pellet out of plane. This will allow them to be used in place of single DIPAB crystals in future experiments. There is no indication that the pellets reach or stay in the triclinic non-ferroelectric phase that has been reported [5]. These pellets have a large surface area, and if they provide the ability to access the axis of polarization then the bulk photovoltaic conversion efficiency should be able to be measured. Then this process can likely be adapted to any powder system that is at least partially soluble. Cold sintering of organic ceramics can significantly reduce the need for crystal growth during material characterization research.

Conclusion

This project has shown that it is reliable to cold sinter diisopropylamonium bromide into pellets that have at least 90% the theoretical density of a single crystal of the same size. The method is faster than traditional evaporative growth as this takes no more than an hour and evaporation can take weeks. The project did not exhaust all possibilities in refining the sample making process such that the pellets would have lower dissipation factors and make electrical measurements possible. The pellets can be converted to the monoclinic phase though the same annealing process as a typical powder. This indicates that the pellet is likely ferroelectric. Future

refinement of the process will likely provide a method of creating DIPAB pellets that are capable of being accurately measured in regards to their electrical properties.

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