Triple junctions enhance thermally-driven plasma generation using pyroelectric crystals

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Abstract

Traditional methods of generating non-equilibrium gas discharges have involved using electrodes at hundreds to thousands of volts, but by taking advantage of the material properties of non-centrosymmetric crystals, a plasma can be generated with alternative sources of energy such as vibration or heat. In this study, a lithium tantalate pyroelectric crystal was thermally cycled with a resistance heater to produce an atmospheric pressure gas discharge. Due to the intrinsic properties of the crystal, a change in temperature with respect to time creates a significant electric potential at the crystal surface, leading to the breakdown of the nearby air molecules and the formation of plasma. A copper plate parallel to the crystal and a picoammeter were used to determine the current of the plasma. By coating the pyroelectric crystal with a variety of patterns of silver paint, "triple points" or "triple junctions" were created that significantly enhanced the resultant current of the discharge, which was found to be on the order of 10 nA for an unmodified crystal, and on the order of up to 80 nA for the painted pyroelectric. Time-integrated visualization showed the formation of surface discharges on both crystals during the thermal cycling. While the results are still preliminary, it seems that the angle of the triple junction created on the surface of the crystal influences the resultant current. As the angle becomes more acute, the measured current increased. This was corroborated by modeling the experimental setup computationally in COMSOL. Under steady state conditions, the voltage and electric field were determined for the various surface modifications, and it was found that the local electric field at the triple junction was significantly enhanced as a function of the angle. With further study, substantial discharges could be generated without the need for a power supply, and potentially lead to the development of portable plasma devices, air and water purification via waste heat capture, or surface treatment.

1. Introduction

Atmospheric pressure gas discharges occur when there is a significant electrical discharge in a gas; the constituent particles are broken down and a small percentage of the medium, most commonly air or argon, is ionized [1]. This composition of ions and free electrons in gas or vacuum is referred to as *plasma*, and has unique properties that are taken advantage of in a variety of industrial, medical, and scientific contexts, from surface sterilization to welding. Standard methods of producing these discharges require sustaining a potential difference of hundreds to thousands of volts across a gap to breakdown the gaseous medium and generate a plasma. While laboratory or industrial settings readily have access to the infrastructure this would require, this study explores unconventional methods of generating plasma discharges that could be used without extensive equipment. More specifically, by using the unique properties of non-centrosymmetric crystals, gas discharges could be generated at atmospheric pressure with only pressure or heat as the input source [2].

Non-centrosymmetric crystals are a subset of crystal classes that exhibit unique properties when its internal structure is deformed. The misalignment (non-symmetry) of the crystal about a certain axis causes the crystal to generate large electric fields on the order of thousands of volts on its surface when its atoms are displaced slightly [3]. While piezoelectric crystals (and the piezoelectric effect) respond electrically to applied stresses, pyroelectric crystals are a subclass of these crystals, and respond electrically to both applied stresses and changes in temperature. Thermoelectric materials function differently from pyroelectric crystals in that an electric potential difference is induced when there is a temperature gradient spatially, whereas pyroelectric materials respond to temperature gradients across time. By cycling the heating and cooling of a pyroelectric crystal such as lithium tantalate, large potential differences exceeding the breakdown voltage of air can be induced to generate atmospheric gas discharges [2].

As was demonstrated by Johnson et al., atmospheric plasma was successfully generated and sustained from thermally cycling pyroelectric crystals [2]. The order of the captured current was only on the order of nanoamps however. In this work, the plasma generation testing rig was recreated and methods to enhance the plasma current of the pyroelectric were explored. Specifically, the phenomena of “triple junctions” or “triple points” (distinct from the point at which multiple phases of matter exist in thermodynamic equilibrium) was taken advantage of to substantially enhance the local electric field and current of the generated plasma. A number of prior studies have shown both computational and experimental results that suggest that triple junctions, the intersection of a gas, metal, and dielectric, substantially enhance the electric field at the point when subjected to a potential difference [4,5]. While the exact principles behind this phenomena is not well known, the sharp difference in the permittivity of the materials at the intersection seems to be the main factor.

In this study, these triple junctions were created artificially on the surface of pyroelectric crystals with coats of silver paint to enhance the resultant plasma current. The experimental setup was also modeled in COMSOL to determine the relative enhancement of the local electric field compared to that of an unmodified crystal surface and the obtained experimental results. By studying the strategies available to enhance the plasma current from thermally-driven plasmas, the same techniques could potentially be applied to larger scale applications that are more controllable, from enhancing the output of piezoelectric transformers to spacecraft propulsion [6].

2. Materials and Methods

The experimental setup stage was constructed from optical components (ThorLabs Inc.) installed on a mechanical micropositioner (MFA-CC motorized linear stage, Newport). A 2.5 cm x 2.5 cm resistance heater (polymide insulated flexible heater, Omega Engineering) was attached to a 1 mm x 2.5 cm x 2.5 cm $LiTiO_3$ crystal (Precision Micro-optics) and connected to a power supply (Agilent E3631A triple output dc power supply). A counter-electrode (needle or copper plate) was positioned 1 mm away from the crystal and connected to a picoammeter (Keithley 6487) to measure the resultant current at a sampling rate of 3 Hz. The data was recorded with a program written in LabView. For the needle counter-electrode setup, the temperature of the resistance heater was taken with a thermocouple (Omega Engineering) and a Canon EOS Rebel T3i digital camera was used to take time-integrated photos of the discharge over 15 s and 30 s exposures. The input voltage was set at 25 V with a duty cycle of 20% for a period of roughly 300 s to compare peak currents for a number of differing crystal types and surface modifications. The copper plate setup was used as surface modifications were introduced because it was difficult to identify the exact location of a triple junction and position the needle counter electrode accordingly. A schematic and photo of the experimental setups can be seen in Figure 1 below.

All collected data was analyzed and plotted in MATLAB. Because the scale of the measured currents was on the order of nA, it was difficult to obtain consistent data that could be appropriately analyzed with error bars. The picoammeter experienced significant delays in sampling as it was required to switch between measured orders of current from picoamps to nano amps. Experimental results were confirmed by running the tests multiple times to ensure consistency and current values were averaged over time for the purpose of comparison as necessary.

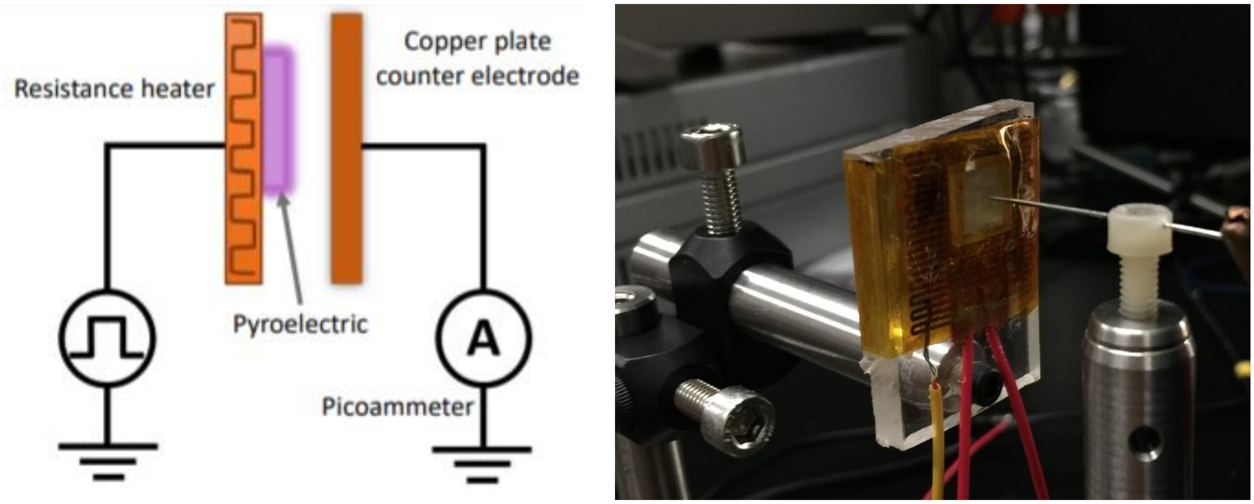

Figure 1. Schematic of plasma-generation testing rig setup with plate counter electrode (left). Photo of experimental setup with needle counter electrode (right).

COMSOL Multiphysics 4.4 software was used to model the electrostatic behavior of triple junctions. General values for permittivity for each material were assigned to each domain (ε = 100 for the crystal, ε = 10000 for the metal, and ε = 1 for air) and Poisson's equation was solved within the domain for the experimental setup in 2D and 3D, shown below as

$$\nabla^2 V = -\frac{\rho_v}{\epsilon}$$

where V is the potential, ρ_v is the volume charge density, and ε is the permittivity.

It was assumed that there was no volume charge density in the domain being analyzed, and the magnitude of the electric field was determined at each point in the domain. The simulations were tested for both mesh and domain independence by varying the region of computation as well as mesh size. In 3D, the magnitude of the triple point of interested was plotted along the z-axis at the center of the crystal as shown in Figure 3, and scaled to a "baseline" configuration without any metallic surface modification on the surface of the crystal. The data was exported and analyzed in MATLAB to generate all subsequent plots.

3. Results and Discussion

3.1. Thermally-driven plasma generation

To confirm the viability of the plasma generation testing rig, the experiments from Johnson et al. were repeated. Using a grounded needle counter-electrode, the input voltage of the resistance heater was varied and the resultant current and crystal temperature were compared to the obtained values. Long exposure photos were also taken to confirm the formation of plasma on the surface of the crystal, as can be seen in Figure 4 below.

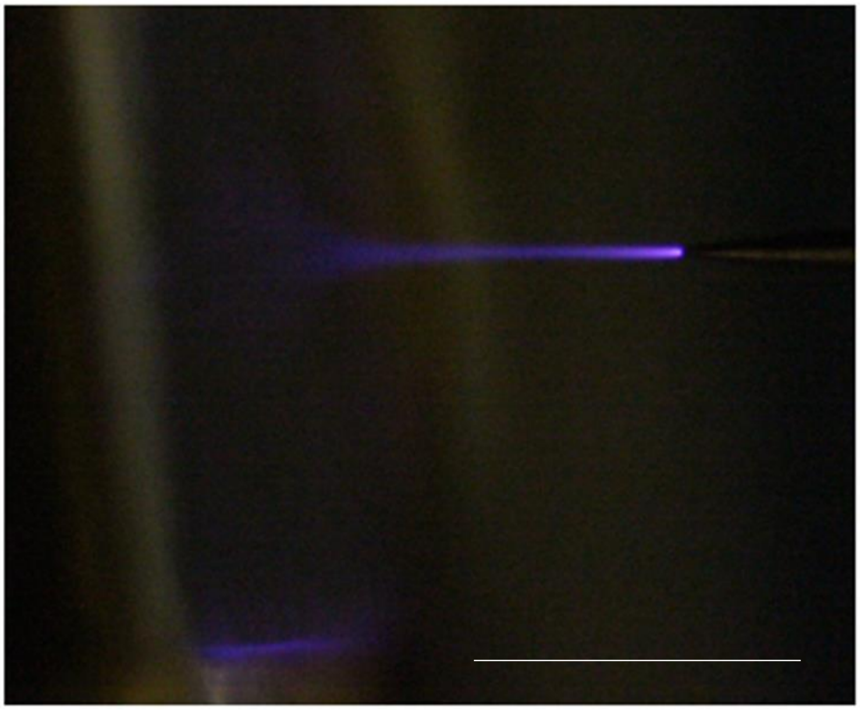

Figure 4. Long exposure image of plasma generated from needle electrode. Scale bar is 1 cm.

The results were strongly corroborated with the findings from previous work. As can be seen in Figure 5, the obtained current measurements from the picoammeter and temperature readings from the thermocouple were plotted against time. While the prior study used an infrared camera (FLIR T420) to determine the temperature of the crystal, for the purposes of verifying the functionality of the testing rig, it was assumed that the temperature of the resistance heater was similar to that of the crystal for the relatively short heating cycles. This study also used lithium tantalate instead of the lithium niobate $LiNbO_3$ from the previous study, as they were both more plentiful and exhibited similar pyroelectric properties, with pyroelectric coefficients of -83 and -176 μC m^{-2} K^{-1} for the lithium niobate and lithium tantalate respectively [7]. It was found that under constant heat input conditions, the temperature change of the crystal correlated with an increase in the measured current, reaching orders of 20-30 nA at 1.25 W cm^{-2}. This confirmed the results obtained by Johnson et al., and validated that the experimental testing rig could both generate and measure thermally-driven gas discharges from pyroelectric crystals. Despite thermal cycling, it was difficult to maintain the current and magnitude of polarity for the pyroelectric crystal. This is most likely due to both the decreasing temperature gradient as the crystal was heated as well as the attraction of ambient free charges in air to the surface of the crystal surface.

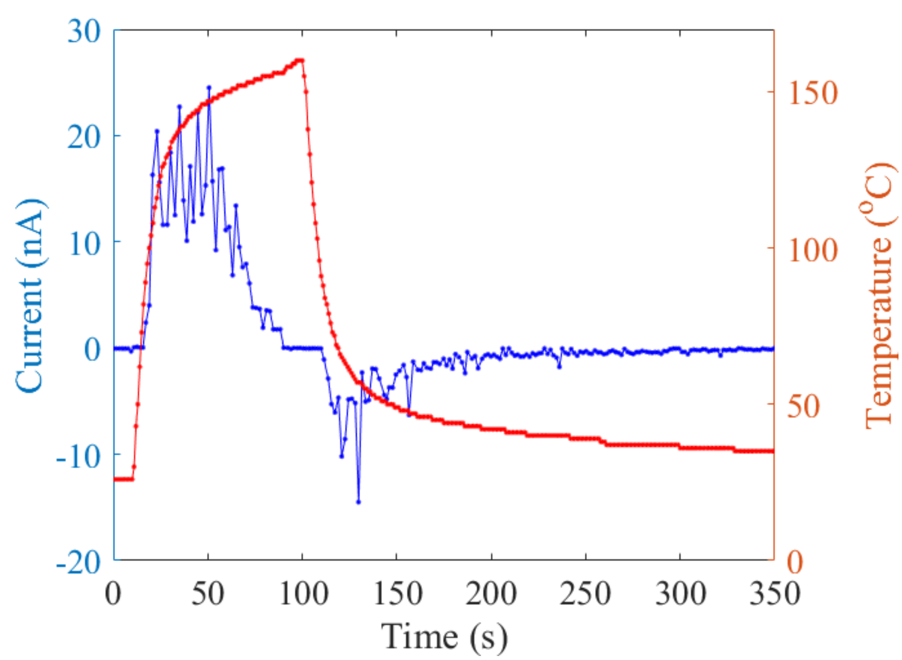

Figure 5. Plot of temperature and current vs. time for needle counter electrode setup

3.2. Current enhancement

Having established the functionality of the testing rig, a number of strategies were considered to enhance the plasma current from the pyroelectric crystal. Changing the crystal type, modifying the angle of the crystal plane relative to the counter-electrode, and a variety of surface modifications were tested in the experimental setup. The latter proved most effective at significantly affecting the measured current, most likely due to the occurrence of triple junctions at the surface of the crystal. The needle counter-electrode was replaced with a plate counter-electrode so that it would cover the entirety of the exposed areas of interest. With a needle, it was difficult to position the tip of the counter-electrode precisely over the location of the triple junction. Wire mesh, copper electrodes, and a number of patterns of silver paint were applied to the lithium tantalate crystal, as can be seen in Figure 6.

Figure 6. Variety of crystal surface modifications applied to induce triple fields on crystal.

It was found that coating the crystal surfaces with silver had the greatest affect on the plasma current, so a variety of patterns were applied to the crystals to determine the affect of the surface modification geometry. A schematic of the configurations can be seen below in Figure 7.

From the work of Jordan et al., it was found that, in 2D, the local electric field enhancement increased as the angle of the triple point became sharper. Of the setups pictured in Figure 7, the “concave” patterns exhibited higher measured currents than the other cases, which were largely similar to the currents obtained from an unmodified lithium tantalate crystal.

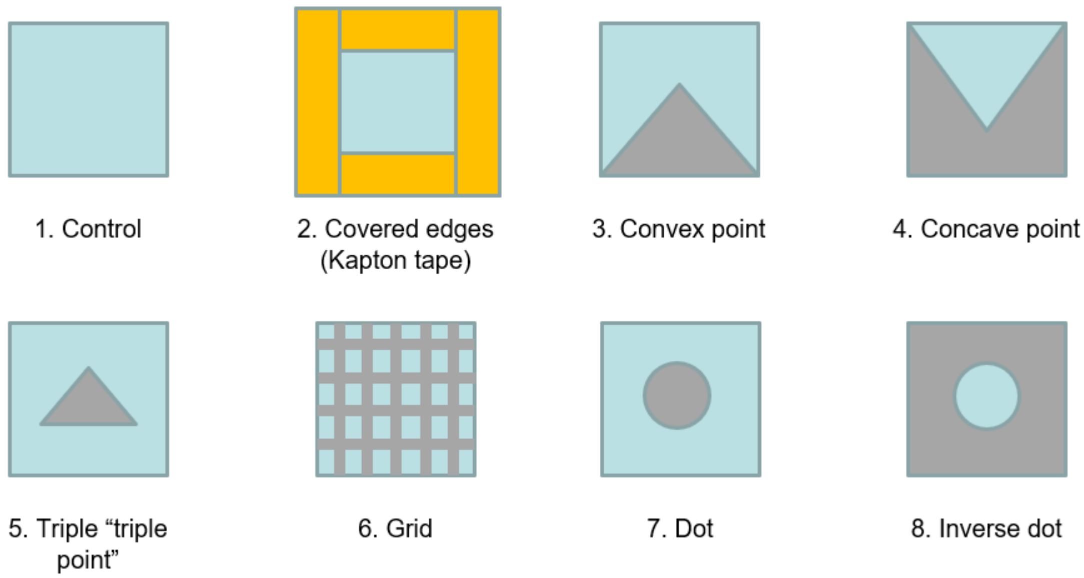

Figure 7. Planned surface modification setups with silver paint on lithium tantalum crystal

A new set of crystals were masked with tape and then coated with silver paint, each at an decreasing angle from 180^{o} to 30^{o}. The crystals can be seen below in Figure 8.

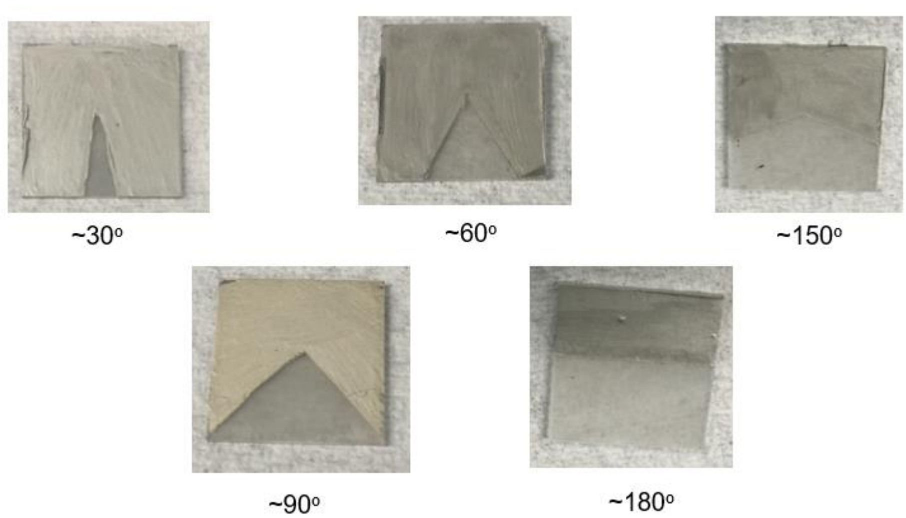

Figure 8. Photos of silver paint coated crystals at decreasing angles

These crystals were then each positioned 1 mm away from the copper plate counter-electrode and subjected to a 10% duty cycle over a period of 300 s at 2.5 W cm^{-2}. The plot of current vs. time for each of the crystal setups can be seen below in Figure 9.

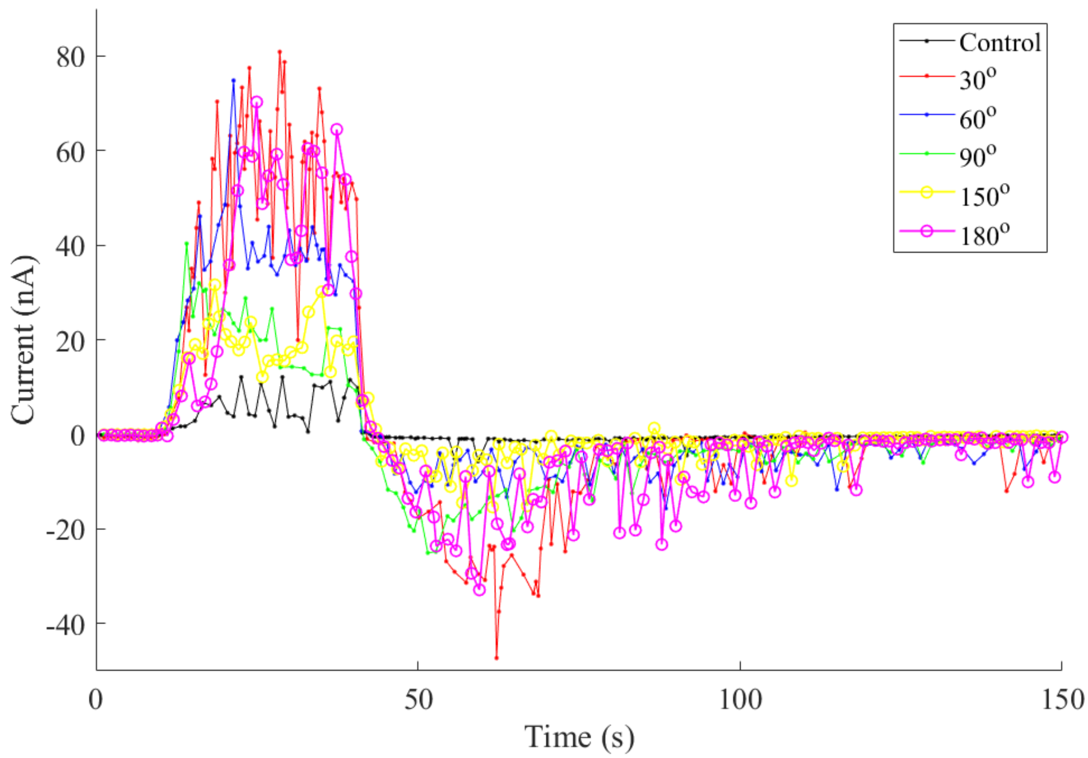

Figure 9. Plot of current vs. time for the pyroelectric crystals pictured in Figure 8. Note that the peak current seems to increase inversely with angle.

Not only was the current significantly enhanced from the baseline case (nearly a seven-fold increase), there was a clear trend of an increase in current as the angle was decreased, which supports the computational work done by [TRIPLE POINT ANGLE PAPERS]. Peak currents of 80 nA were observed for the 30° crystal, compared to the 12 nA obtained by the unmodified crystal.

3.3.COMSOL Modeling

To corroborate the experimental results, the same crystal configurations were modeled in COMSOL Multiphysics to determine the effect of induced triple junctions on the potential and local electric field of the crystal. The simulation was computed at the same scale of the experiment with boundary conditions enforced at the surfaces of the pyroelectric and the counter-electrode. The schematic for the geometry and boundary conditions can be seen below in Figure 10 and 11 for the 2D and 3D cases respectively.

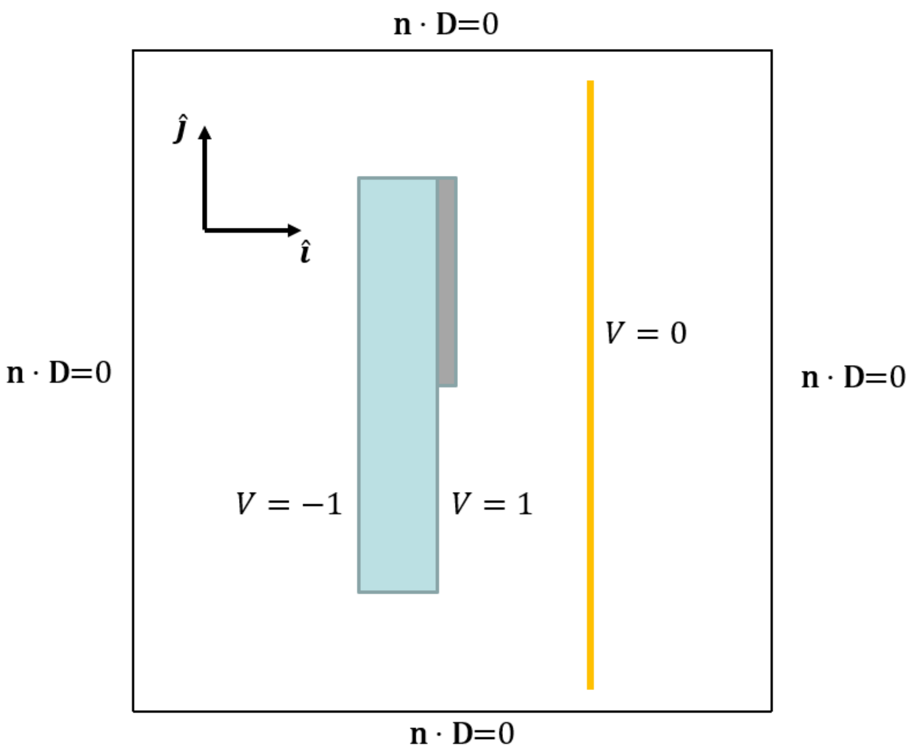

Figure 10. Schematic of 2D COMSOL setup with boundary conditions.

For the 2D setup, a clear locally enhanced electric field can be seen. Figure 12 shows the magnitude of the electric field for the simulation in space. Because arbitrary values were used for the voltages of the crystal and the permittivities of the materials, the values for the

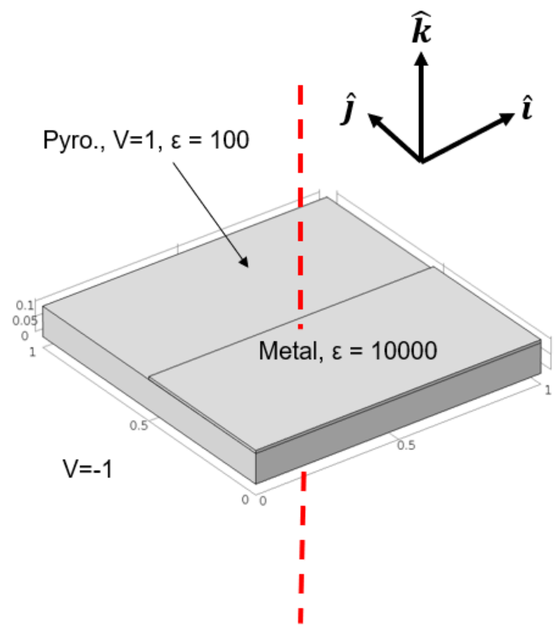

Figure 11. Schematic of 3D COMSOL 180° setup. The dotted red line represents the values of interest at the triple junction of the crystal.

potential and electric field are only significant in that they are far greater at the triple junction than anywhere else in the domain. Extending the model to 3D, plots were generated for the magnitude

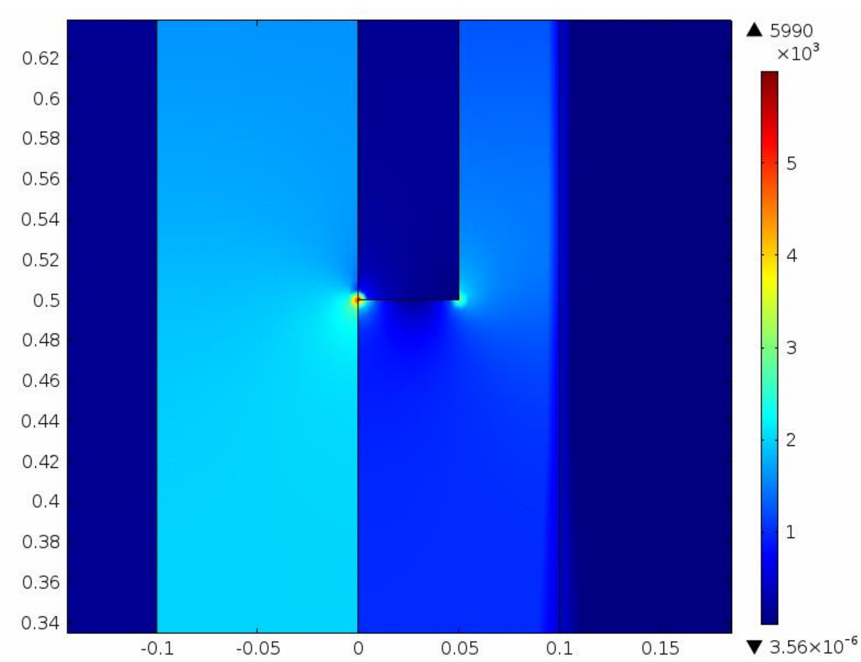

Figure 12. Plot of electric field magnitude in space.

of the electric field along the center axis of the crystal and normalized with respect to the maximum value of the baseline case, as shown in Figure 13. For each of the 3D models, a metal “coating” was modeled at the same angles as the experimental setups.

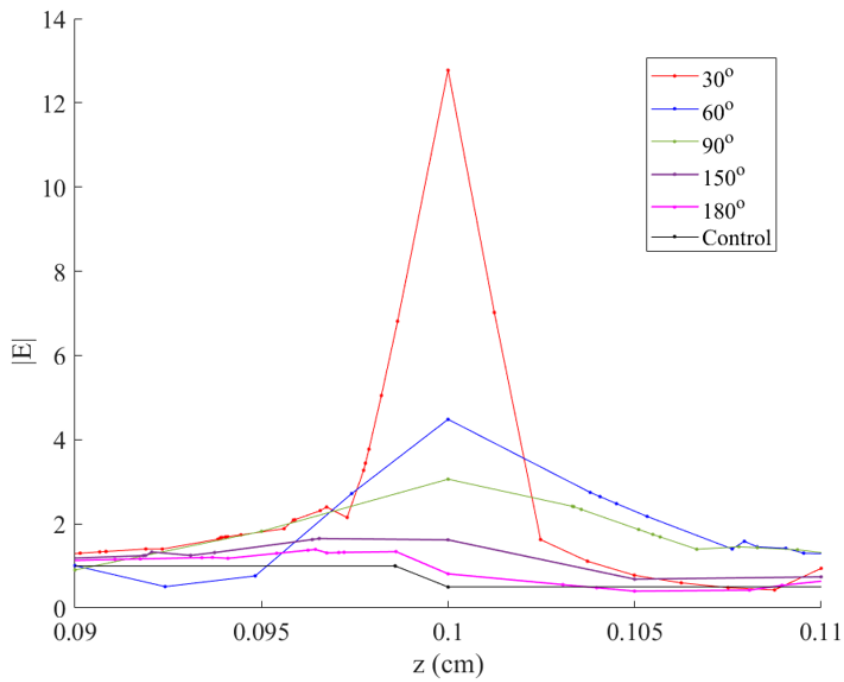

Figure 13. Normalized plot of electric field magnitude along thickness of the modeled crystal.

From the simulation, a 13-14-fold increase can be seen in the smallest angle triple junction modification compared to the unmodified crystal. This supports the results found experimentally as well as similar findings from previous work. While an increase in the local electric field does not necessarily imply a linear increase in current, the simulation supports the hypothesis that the electric field, and resultant current, is enhanced significantly more with triple junctions present.

Currently, the experimental setup described previously is being moved into a vacuum chamber to determine the nature of the discharge being observed. At the scale of the measured currents, it is unlikely the plasma is due to space discharges, and may be due to pyroelectric electron emission, a phenomenon studied in detail by Geuther et al. [8].

4. References

1. A. Schutze, J. Y. Jeong, S. E. Babayan, Jaeyoung Park, G. S. Selwyn and R. F. Hicks, "The atmospheric-pressure plasma jet: a review and comparison to other plasma sources," in IEEE Transactions on Plasma Science, vol. 26, no. 6, pp. 1685-1694, Dec. 1998. doi: 10.1109/27.747887
2. Johnson, Michael J, et al. “Thermally Induced Atmospheric Pressure Gas Discharges Using Pyroelectric Crystals.” Plasma Sources Science and Technology, vol. 23, no. 6, 2014, p. 065018., doi:10.1088/0963-0252/23/6/065018.
3. Neidholdt, Evan L., and J. L. Beauchamp. “Compact Ambient Pressure Pyroelectric Ion Source for Mass Spectrometry.” Analytical Chemistry, vol. 79, no. 10, 2007, pp. 3945–3948., doi:10.1021/ac070261s.
4. Jordan, Nicholas M., et al. “Electric Field and Electron Orbits near a Triple Point.” Journal of Applied Physics, vol. 102, no. 3, 2007, p. 033301., doi:10.1063/1.2764211.
5. Dunaevsky, A., et al. “Lifetime of Ferroelectric Cathodes.” Journal of Applied Physics, vol. 89, no. 8, 2001, pp. 4480–4485., doi:10.1063/1.1355285.
6. Kemp, Mark A., and Scott D. Kovaleski. “Optimization of the Ferroelectric Plasma Thruster for Microspacecraft Propulsion.” 2007 IEEE Pulsed Power Plasma Science Conference, 2007, doi:10.1109/ppps.2007.4345776.
7. Bowen, Chris R., et al. “Pyroelectric Energy Harvesting: Materials and Applications.” Ferroelectric Materials for Energy Applications, 2018, pp. 203–229., doi:10.1002/9783527807505.ch7.
8. Geuther, Jeffrey A., and Yaron Danon. “Electron and Positive Ion Acceleration with Pyroelectric Crystals.” Journal of Applied Physics, vol. 97, no. 7, 2005, p. 074109., doi:10.1063/1.1884252.