

Towards A Single Crystal Triboelectric Series

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Abstract— Triboelectrification is one of the oldest concepts observed in physics, yet consistent measurement and theory of the phenomenon has been notoriously elusive. To effectively model a material's ability to exchange charge with another, one must clearly define the structures of the materials being charged (both surface and bulk states), reduce environmental effects during contact (e.g. surface water), and keep track of any discharge on the way to the measured charged state. Prior studies have typically failed at accounting for at least one of these considerations. In this paper, we present experimental data on the contact charging of magnesium (MgF_2), calcium (CaF_2), lithium (LiF), and barium (BaF_2) fluoride single crystals (10 mm x 10 mm) under vacuum conditions (< 1 mTorr). Our apparatus provides a more complete picture of the charge movement by measuring the electrostatic force between the crystals in addition to the traditional measurement of residual charge, as well as any transient triboluminescence (RF and X-ray) that results from charge movement to the final charged state. By using single crystal fluorides, the material structure is well-defined and with surfaces that are less susceptible to contamination, so we provide contact electrification data to challenge theoretical models of triboelectrification.

I. INTRODUCTION

Triboelectrification, or contact charging, is the observed phenomenon that when two materials are brought into contact with each other they may exchange charge. Although this type of charge transfer has been known for thousands of years, the underlying mechanism is still not understood for insulators [1, 2]. Generally if two different materials exchange charge when brought into contact they will exchange charge in the same direction every time. Such consistent charge polarity led to the concept of a triboelectric series [3, 4] allowing the prediction of surface charge polarity following contact with any other material in the series. However, the list is mostly qualitative and quantitative data is needed to form a well-defined theory with predictive power. To reliably generate independently repeatable quantitative data the characteristics of the two surfaces being brought into contact must be known, as well as monitoring for any discharge processes that occur during charging and measurement of the charged surfaces. Building a quantitative model of contact charging is impossible if the interacting surfaces are not known.

Two hurdles to understanding the nature of the surfaces to be studied are: contamination from the various environments the materials are exposed to both before and during the experiment; and common materials not having well-defined molecular geometry at the interface. [5] The experiment reported here attempts to overcome these hurdles by using macroscopic single crystals composed of fluoride materials, allowing the molecular geometry at the interface to be better understood and potential contaminants to be removed more easily than experiments involving other materials.

The other information needed to create a model with strong predictive power is data on the charging characteristics of these now well-defined materials. In previous experiments it has been shown that materials will not charge to arbitrarily high values, but reach a plateau at some point. It is important to identify whether the plateau is due to a fundamental property of the charging mechanism, such as for conductors in contact charging where the charge transfer reportedly results from the equalization of the fermi levels [6, 7], or if it is due to a property of the experiment itself, such as a geometry that allows for discharging of the materials. If the latter is the case then a plateau could simply indicate that the material is charging and discharging at the same rate and is at an equilibrium, where the former suggests that the charging mechanism has reached a point where it can no longer drive charge transfer. The experiment discussed here is designed to monitor any discharge characteristics that might determine the plateau. Changes in charging behavior that correlate with changes in discharge would indicate that extra steps are needed to identify how strong the charging truly is for a quantitative model, and the traditionally measured plateau is not a pure indication of the strength of the charging.

Many previous experiments have assumed that materials charge with only one polarity, so that measuring the total charge on a material is assumed to provide all the information necessary to understand the charging behavior of the system. However, Baytekin *et al.* (for example) have shown that there is the possibility for materials to exhibit bipolar charging [1]. By incorporating the measurement of electrostatic force between charged crystals in our experiment we are able to obtain additional information to help to identify charging traits that a net charge measurement alone could not provide. For example, the net charge cannot identify a charge distribution on a surface, or if any bipolar charging is taking place. In the case of bipolar charging with equal amounts of positive and negative charge transfer, the total charge measurement would read zero, but the electrostatic force between the charged surfaces would be present and measureable, and hence able indicate that charge transfer had taken place.

The experiment presented here is designed to combine the goals of having well-defined surfaces, monitoring discharge, and tracking charge through its force signature. Two different fluoride crystals are brought into contact with each other and then separated under vacuum conditions (< 1 mTorr). During the contact and separation process radio frequency (RF) and X-ray emissions are monitored for to detect discharge and a load cell records the electrostatic force as a function of distance between the crystals. After each contact one of the crystals is placed into a Faraday cup to measure its charge. The contact/separation cycle is repeated a number of times before the run is completed. After the experiment is completed, the chamber is opened, and the crystals are realigned then cleaned with dry acetone before the next repeat. The mechanics of the experiment are summarized in [8].

II. MATERIALS

Materials are desired that have well-defined surface geometry at the atomic scale and that are likely to be resistant to contamination in the environments the material is exposed to. To satisfy the geometric requirements, macroscopic single crystals were chosen (10 mm x 10 mm, either 0.5 mm or 1 mm thick), obtained from MTI Corporation (Richmond, CA). Crystals were polished by the manufacturer to a reported roughness of $R_a < 25 \text{ \AA}$, and shipped in vacuum-sealed 1000 clean class plastic bags. The crystals are stored in a desiccator until ready for use. To satisfy the contamination requirements fluoride crystals were chosen as any sorption undergone while exposed to atmosphere is reported to be reversible upon placement in a vacuum [9,10]. The fluorides used in this experiment are those of magnesium (MgF_2), calcium (CaF_2), lithium (LiF), and Barium (BaF_2). All the crystals used have the (100) face polished within 1.5° , providing the surface to be charged. Dry acetone (>99.9% purity, Sigma Aldrich) on a lint-free cloth is used to clean the crystals.

III. METHODS

A. Mounting Crystals

The two crystals to be contacted in the experiment are mounted in a vacuum chamber (~40 cm diameter, 20 cm high) capable of reaching pressures less than 1 mTorr (0.13 Pa) (Pa). One crystal is mounted to a Teflon anvil on an actuated stage, used to bring the crystals into contact with one another. The second crystal is mounted on an aluminum silicate anvil supported by a set of parallel leaf springs designed to reduce rotation during contact and allow control over the contact force. Both crystals are mounted using double-sided Teflon adhesive tape (3M 9495LE). After the crystals are mounted, they are aligned to each other by rotation of the Teflon anvil and viewing the surfaces by camera in two perpendicular directions. The crystals are then cleaned *in situ* with acetone to remove surface contaminants.

B. Crystal Contact

The crystals are brought into contact in order to allow them to exchange charge. The crystal mounted on the Teflon anvil approaches the other crystal at 1 mm/s. When the crystals make contact they move with each other for 3 seconds as the load increases between them to ~5 N. The crystals are held together at maximum load for 5 s, then returned to their starting positions at 1 mm/s. When the crystals reach their home positions, the crystal mounted on the double spring system is inserted into a Faraday cup to measure the total residual charge on the surface. This process is repeated fifty times to generate a charging curve. After fifty contacts the chamber is opened to atmosphere and the crystals are realigned and wiped with dry acetone before another run begins. Every crystal type was tapped against every other type, with fresh crystals being used each time the pair was changed.

To verify that the fluorides were showing some reversibility in sorption, experiments were performed where the crystals were wiped with deionized water instead of acetone before the run. Experiments were also completed where the crystals were baked at $\sim 100^\circ\text{C}$ for 20 minutes in vacuum before the contact/release procedure was started.

C. Measurements

During the contact and release procedure various measurements are taken to characterize the charging. A load cell is mounted behind the teflon anvil to record the force between the crystals on approach, during contact, and while they return to their starting positions. By taking force measurements in addition to charge measurements, one can infer information on the charge distribution, including the possibility of bipolar charging, which the charge measurement alone cannot provide. Figure 1 shows an example of the force data. As can be seen, previously charged crystals exhibit an attractive force (negative on figure 1) as they approach, and as they are released. The maximum attractive force upon approach (“pull-in force”) can be different than the maximum attractive force when the crystals release and return to their start position (“pull-off force”). The larger pull-off force could be indicative of a non-electrostatic adhesive mechanism that occurs during contact when the crystals are in contact; bipolar charging that is only strong when the crystals are essentially in contact; or that the crystals undergo some discharge between the end of one contact and the beginning of another.

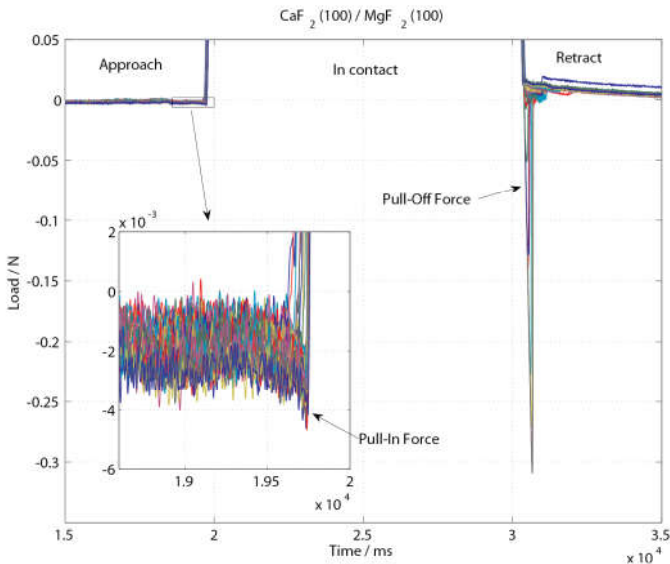


Fig. 1. Load cell output as calcium fluoride contacts and releases from magnesium fluoride. Positive is compression / repulsion, negative is tension / attraction. The tensile force as the crystals release is substantially larger than the electrostatic attraction force just prior to contact of previously charged crystals (shown in the inset).

An RF antenna, photodiode, and an X-ray detector measure any electromagnetic radiation that may occur in order to help monitor for discharging during the experiment.

After the crystals have been tapped together the crystal on the double spring system is inserted into a Faraday cup attached to an electrometer (Keithley 6514) that provides a

charge measurement with 10 pC resolution. The apparatus and its measuring capabilities are described in detail in [8].

IV. RESULTS

A typical charging curve is shown in figure 2. The charging curves give clear indication that MgF_2 will charge negatively against all three of the other fluorides explored in this experiment. However, while the sign of charging was consistent from one run to another, and from one set of crystals to a duplicate set, there was enough variation in the charging behavior to prevent any quantitative conclusions. Further, all combinations of the remaining three crystals (CaF_2 , LiF , and BaF_2) showed polarity flips in their charging curves from one run to another, which prevents even a simple triboelectric series from being created for the crystals in this experiment.

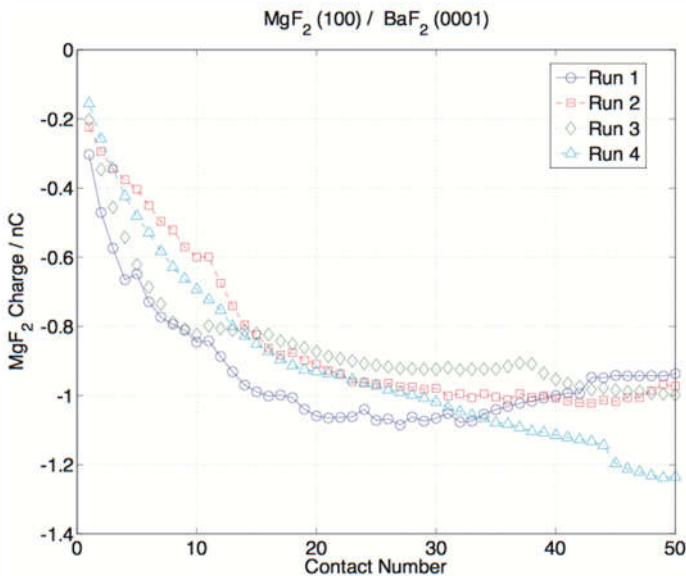


Fig. 2. Typical charging curve for fluorides. In this example magnesium fluoride is being tapped against barium fluoride in vacuum (< 1 mTorr). The crystals are cleaned with acetone before the run. Displayed is the magnesium fluoride charge measured as a function of the number of times the crystals have been tapped together. Between each run the crystals are realigned and cleaned with acetone.

The polarity flips between CaF_2 , LiF , and BaF_2 prevented a triboelectric series for fluorides from being established, however the experiment did provide some enlightening observations. The first has to do with the polarity flip seen in experiments with BaF_2 and CaF_2 . The charging curve is shown in figure 3, where it can be seen that the shape of the charging curve changes when the polarity flips. Such a change in the charging curve could be an indication of multiple competing charging mechanisms. For example, the initial charging that plateaus could be driven by a chemical process, where the linear charging that then takes over in the opposite direction could be due to material transfer from one

crystal to another. Further experiments are needed to characterize the crystal surfaces before and after the tapping experiment to help understand the possible mechanisms at play.

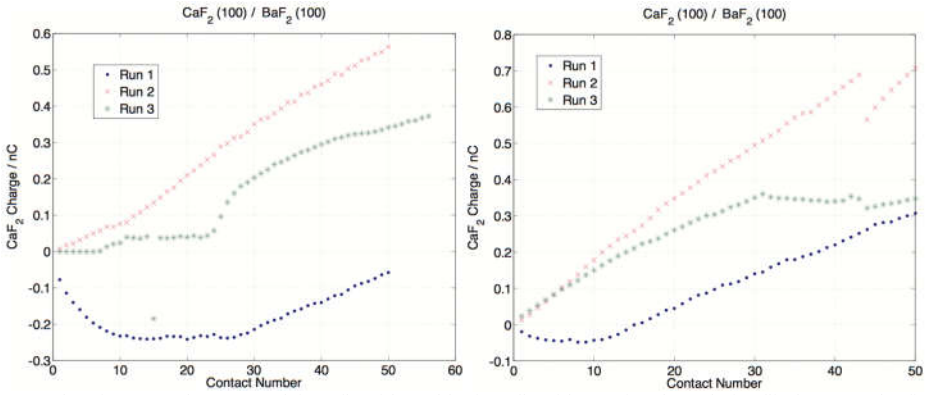


Fig. 3. Charging curve between calcium fluoride and barium fluoride. Notice the polarity flip between the first run and the second run which appears in both the first $\text{BaF}_2 / \text{CaF}_2$ crystal pair, and the second replacement set. This type of polarity flip prevents creation of a triboelectric series from our current data. However, careful examination shows that during the first run where the polarity flips, the shape of the curve changes as well, from the typical plateau to a highly linear pattern. This could indicate competing mechanisms of charge transfer

When wiped with deionized water, rather than acetone, the fluorides showed an order of magnitude increase in total charging. When baked before the tapping portion of the experiment began, the fluorides showed an order of magnitude decrease in total charging. That water being added or removed at the beginning of the experiment made a substantial difference to the charging of the fluorides indicates that atmospheric water adsorption may not be completely reversed by simply placing the crystals in vacuum, and so the fluorides may not be resistant to other contaminants either. The fluorides are reportedly less likely to retain surface water than other crystalline materials, so it is instructive to compare how intentional wetting and baking affects crystals that strongly retain surface water to see if the changes in charging are even more dramatic. Accordingly, additional experiments were run with R-plane oriented sapphire (Al_2O_3 (1-102)) against z-cut quartz (SiO_2 (0001)) and Zirconia (ZrO_2 (100)). The results were comparable to those of the fluorides in terms of the magnitude of changes resulting from water and baking treatments. In the non-fluoride experiments there was a polarity flip between the acetone-treated and the water-treated experiments. With the fluorides the polarity flips present even without water, which makes it difficult to tell whether the water is itself causing a polarity flip or simply increasing the charging of the crystals. The results of the water and baking treatments are summarized in figure 4. The altered charging behavior with water addition and removal combined with the similarly-achieved results with non-fluorides demonstrates that fluorides are not immune to the effects of surface contamination by water without some sort of baking process.

At this time no claim can be made that the surfaces under test were better controlled than with some other macroscopic single crystals.

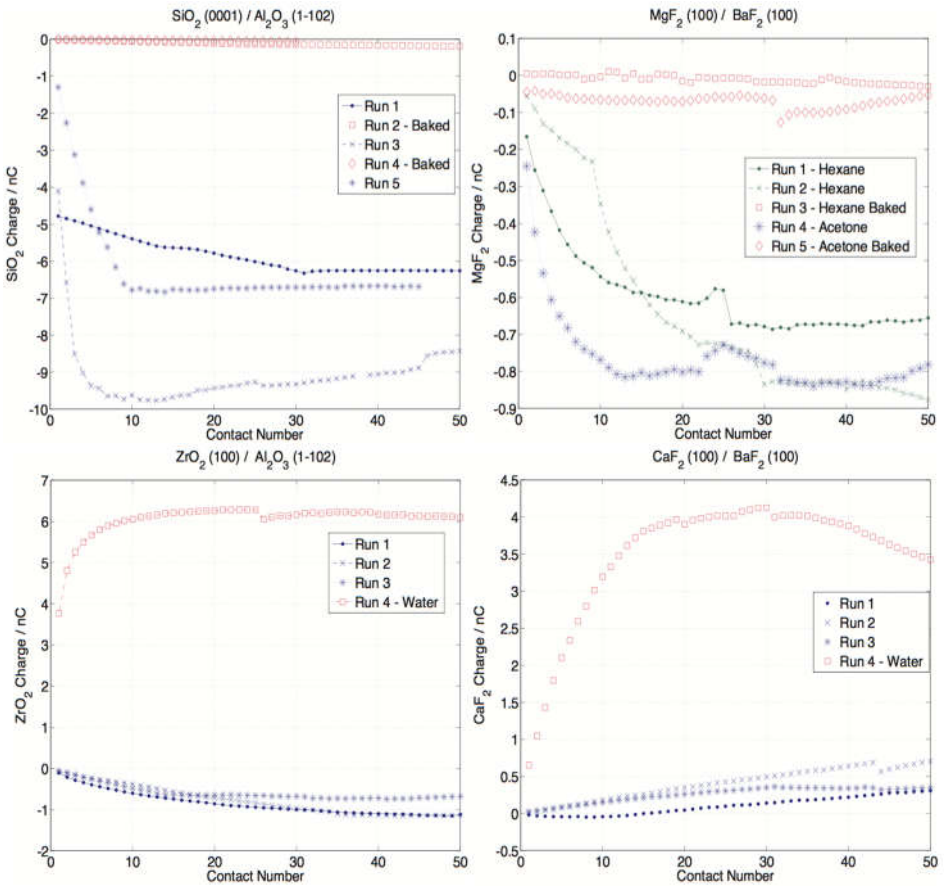


Fig. 4. Top: The difference in charging behavior after being baked is shown for quartz and sapphire on the left and for magnesium fluoride and barium fluoride on the right. The fluorides are slightly affected by baking whereas the non-fluorides show a dramatic drop in charging behavior. Bottom: data shown for the effect of water on fluorides and non-fluorides. Both show a dramatic increase in the magnitude of charging, with a polarity flip for the non-fluorides. A similar interpretation cannot be made for the fluorides as the polarity flips in the absence of water render the results ambiguous.

In addition, by measuring electromagnetic radiation it is clear that for non-fluorides the plateau in charging curves is due, at least in part, to discharge between the crystals rather than reduction in charging by the underlying mechanism. For the fluorides there is not enough X-ray flux to determine if discharging is a substantial contributor. Since the total charging between the fluorides is much lower than other pairs where X-ray analysis proved useful, it is possible that the crystals are still discharging, but the lower voltage between

the crystals prevents electromagnetic radiation from reaching the energy threshold of the detector used (5 keV).

V. CONCLUSION

An attempt was made to establish a triboelectric series for fluorides using macroscopic single crystals. It was established that among the tested fluorides (MgF_2 , CaF_2 , LiF , and BaF_2) that MgF_2 will charge negatively against the other three, though no quantitative claims are made. Further, no triboelectric series could be established for the remaining crystals due to polarity flips, which could be indicative of multiple mechanisms behind the charging behavior. Additionally, repeatable behavior of the polarity flip for the BaF_2 / CaF_2 pair suggests that understanding of the competing charging mechanisms may be achieved by analyzing charging characteristics in the distinct regions where one mechanism is dominating the other. Once one charging mechanism is accurately modeled its contribution to the total charging can be isolated and subtracted to give a clearer view of charging trends of any competing mechanisms. Repeating this procedure would allow for all mechanisms to be accounted for separately, and the apparent variation caused by their mixed contributions could be reduced to a point where a quantitative description of tribo-electrification can finally be put forward.

By moving forward with the preliminary results from this experiment and single crystals that have better-defined surfaces, progress towards understanding of the underlying mechanisms behind contact charging and establishment of a quantitative triboelectric series can be accomplished. Particularly, running experiments with new equipment designed to mitigate factors that lower repeatability should help by reaching high vacuum which can minimize charge loss to gas in the chamber, and vibration isolation and precise motor control of the stages to reduce variability between contacts and runs. Lastly, an effort should be made to better characterize the surfaces of the crystals both before and after the experiment using, for example, Kelvin probes to examine charge distributions, Atomic Force Microscopy to characterize the surface geometry, and X-ray and electron scattering techniques to probe for contamination and material transfer. The results presented here show a promising path towards understanding triboelectrification and in particular the importance of material selection and discharge monitoring, combined with high levels of environmental control to ensure repeatability.

IV. ACKNOWLEDGEMENTS

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