

The Piezoelectric Effect in Quartz and Barium Titanate

Nikita Sichov - nsichov@ethz.ch

Supervisor: Somayeh Saghamanesh - ssaghamanesh@phys.ethz.ch

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Abstract

This experiment verifies our theoretical model of the piezo effect for the quartz and barium titanate crystal. Identifying the gauge constant to be $\eta_g = 30290 \pm 1292 \text{ F}^{-1}$, we found evidence implying quartz is temperature independent, and doesn't stray far from our theoretical value for the piezo module at room temperature as $2.3 \cdot 10^{-12} \text{ C/N}$ over different temperatures. We also observed the piezo electric effect in Barium Titanite when it was polarized and unpolarized. The former case was an order larger than the latter and that there is a temperature independence where the piezo module would rise up until around 365K and then drop. The measurement did well in depicting key qualitative features of the piezo effect, and helped us conclude where improvements to the method of the measurement could be applied to give further statistically-rigid quantitative conclusions.

Introduction

The piezoelectric effect occurs when an electrical field is generated in solid matter due to mechanical stress. This process can also be reversed, where an electric field creates mechanical stress in the material.[2]

The Piezoelectric effect

In a crystal lattice where inversion symmetry is not present the center of mass of negative charge is shifted and leads to polarization P_i . This polarization is dependent on the symmetric stress tensor T_j :

$$P_i = \sum_{j=1}^6 d_{ij} T_j \quad i = 1, 2, 3 \quad (1)$$

where d_{ij} are the piezo modules. This relation is only true as a linear approximation for small deformations. Higher order terms become relevant with larger deformations and 1 is no longer valid.

The inverse effect occurs when putting the piezoelectric crystal into an electric field causing a subsequent deformation from stress.

An alteranative way of writing 1 comes from applying maxwell equations:

$$Q_i = \sum_{j=1}^6 d_{ij} K_j \quad i = 1, 2, 3 \quad (2)$$

Quartz

The quartz symmetry group is D_{3d} meaning the matrix of the piezo module has the simplified form:

$$(d_{ij}) = \begin{pmatrix} d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (3)$$

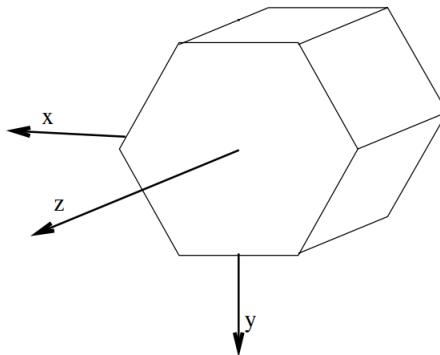


Figure 1: Unit cell of quartz in the 3 coordinate system.[1]

Figure 1 shows us how the quartz unit cell looks like in the matrix coordinate system 3. Additionally, looking at Figure 2, we see how stress in the x -direction affects the unit

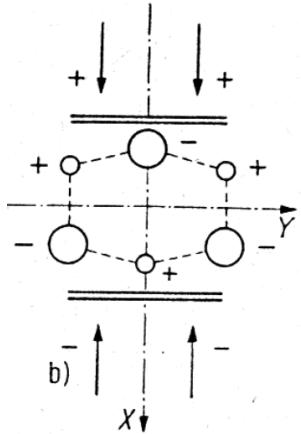


Figure 2: Deformation of the quartz unit cell under a force K_x . The subsequent polarity is visible.[3]

cell and induces a charge difference in the unit cell in the same direction. We focus on the following relation for our experiment:

$$Q_x = d_{11}K_x \quad (4)$$

due to 3 and 2, so if we were to look for d_{11} we know what orientation we need (an x crystal cut).

Barium Titanat

In the range of 5°C and above, Barium Titanate (BaTiO_3) has two phases: tetragonal for 5°C–120°C and cubic for 120°C and onwards. In the cubic phase, the atoms are in a perovskite-like structure, and in the tetragonal phase the atoms of the compound are shifted along the z-axis as: $\text{Ba} \sim 5\text{pm}$, $\text{Ti} \sim 10\text{pm}$, $\text{O}_I \sim -4\text{pm}$ and $\text{O}_{II} \sim -9\text{pm}$ as shown in Figure 3. This shift creates interatomic polarity due to the negative and positive differences of the atoms in the compound.

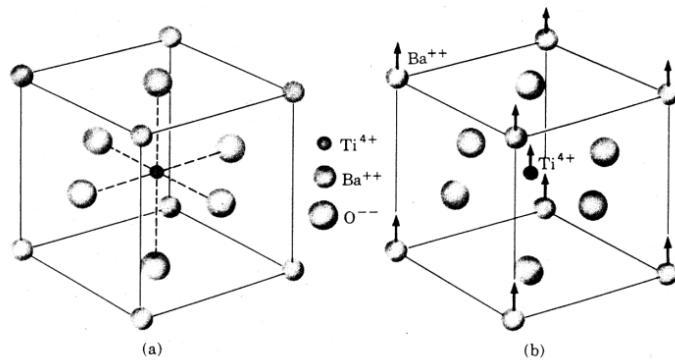


Figure 3: Cubic and Tetragonal phase structure of Barium Titanate unit cell. [1]

Note that the Barium Titanate sample is sintered from a lot of ceramics, therefore all possible polarization vectors arise during the cubic phase. Therefore, there is no

piezoelectric effect above 120°C. We can "reset" the polarization by heating the sample to a cubic phase, then polarizing it while cooling it down in order to induce a "pure" polarization¹. Also, to depolarize the crystal, one may heat it to 120°C and observe the sample in a "pure" unpolarized state.

Experiment

Setup

We plan on measuring the piezoelectric effect of Quartz and Barium Titanate with the setup shown in Figure 4. Either Quartz or Barium Titanate is set in the "Kristall" part where it is lodged between and held together by two copper pieces that are capable of creating a voltage difference and measure temperature. This crystal, a heating apparatus and the copper pieces are contained in a ceramic that thermally isolates the system. Then from above, a force is applied by an oscillating eccentric mechanism attached to a lever.

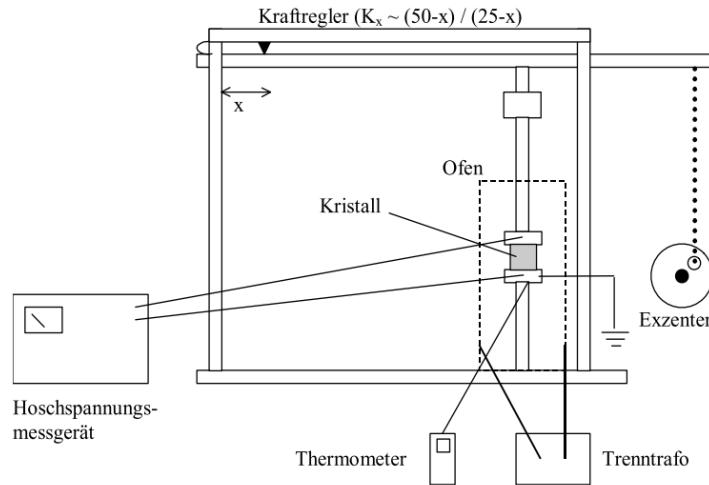


Figure 4: A Diagram of the Measuring Device used for the Experiment.[1]

Measuring

Firstly, we want to measure the relation between the current and the force applied to see if our linear approximation of the relation is valid. For this we put a quartz sample into "Kristall" from Figure 4 and measure over different forces.

Secondly, for measuring the piezo module d_{11} we have to define the charge Q in 4 in a more practical manner. Considering the circuit model of the amplifier we see that most of the current is going through the capacitor, therefore $Q = C \cdot V$. Considering the force K_x from 4 we know it is oscillatory and position dependent, so we take the time average $\langle K(x, t) \rangle_t$ where the positional dependence is proportional to $K(x, t) \propto \frac{50-x}{25-x} f(t)$ where $f(t)$ is proportional to a periodic motion of frequency $\omega = 2\pi \cdot 5\text{Hz}$. In the end, from 4

¹This polarization is pure compared to just applying a high voltage because during the time the crystal isn't used it gets polarized from exterior sources and can be more prone to error.

we get:

$$V_x = d_{11} \cdot \frac{\langle K(x) \rangle_t}{C} = R \cdot I$$

where $R = \frac{1}{g}$ is the amplification factor and $\eta_g = \frac{1}{C}$ is the gauge constant. We therefore measure the current:

$$I = d_{11} \langle K(x) \rangle_t g \eta_g \quad (5)$$

We can then use the piezo-module of quartz at room temperature to define the gauge constant and give a well defined function of $d_{11}(x) = \frac{I}{\langle K(x) \rangle_t} \cdot \frac{1}{g \eta_g}$. It is important to note here that the coefficient $\frac{I}{\langle K(x) \rangle_t} = \frac{dI_{eff}}{dK_x}$ by our linear approximation, because of this we can discard any additive constant of the current.

Thirdly, with the definition of η_g we can see how the piezo-module of quartz changes with respect to temperature by measuring the current-force dependence at several fixed temperatures.

Then, we do the same to Barium Titanate. However, we must consider that its ferroelectric structure is prone to external polarization. This can and will affect our result. Therefore we want to see how the piezoelectric effect manifests in a purely polarized and unpolarized state. We begin by heating our sample to above 120°C where the phase of Barium Titanate is cubic and therefore completely unpolarized. From there, as it cools back to the tetragonal phase, we apply a high voltage (1500V) through the copper clamp of the crystal. We measure the piezo-module at five different temperatures as the sample cools down, and measure five similar temperatures as it heats up again. Then we again, heat above 120°C celsius, depolarize the sample, and measure the unpolarized piezo-module at five constant temperature as it cools, and five as it heats.

Results

We measure the force-current relation of quartz at room temperature as Figure 5 and get a slope of $13.93 \pm 0.59 \mu\text{A N}^{-1}$.

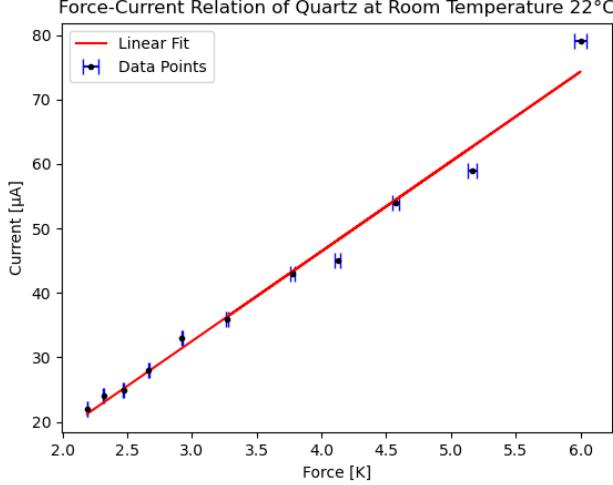


Figure 5: Force-Current relation of a Quartz in room temperature (temprature of our literature value).

We then consider the piezo-module of quartz at room temperature to be $d_{11} = 2.3 \cdot 10^{-12} \text{ CN}^{-1}$. Thereby, using 5, we find the gauge constant to be $\eta_g = 30290 \pm 1292 \text{ F}^{-1}$ or $3.3703 \pm 0.1438 \cdot 10^{-24} \text{ cm}$ in CGS units[5].

We then observe how the piezo module changes with respect to temperature in Figure 6. The force-ampere relation that was used for calculating this result is found in Figure 9

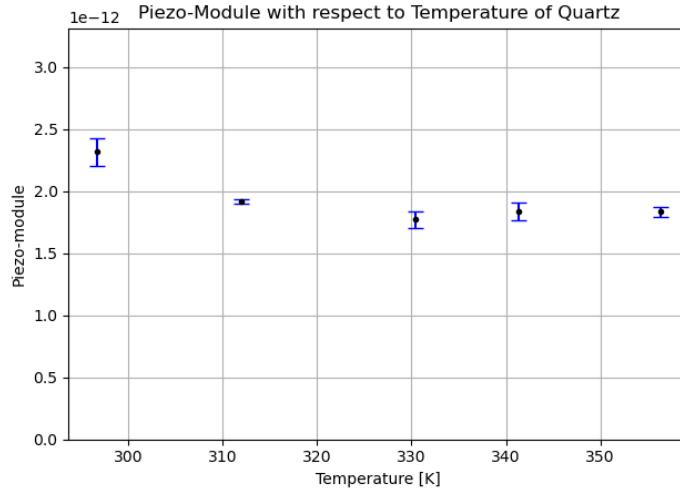


Figure 6: Piezo-Module Change with respect to the temperature of Quartz.

Finally, we find the piezo-module of polarized Barium Titanate in Figure 7 and

unpolarized Barium Titanate in Figure 8 with results summarized in 1 and 2. An analysis of the force-current relation is found in 10.

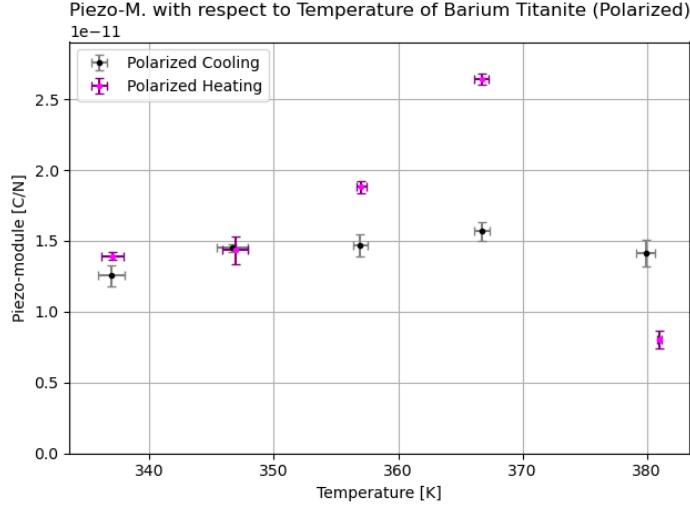


Figure 7: Piezo-Module Change with respect to the temperature of Polarized Barium Titanate.

| Temperature (K) | Polarized Piezo-Module (C/N) |
|-------------------|-------------------------------------|
| <i>Cooling</i> | |
| 379.90 ± 0.75 | $(1.414 \pm 0.094) \times 10^{-11}$ |
| 366.75 ± 0.60 | $(1.568 \pm 0.065) \times 10^{-11}$ |
| 356.95 ± 0.60 | $(1.469 \pm 0.075) \times 10^{-11}$ |
| 346.70 ± 1.25 | $(1.450 \pm 0.029) \times 10^{-11}$ |
| 336.95 ± 1.10 | $(1.255 \pm 0.076) \times 10^{-11}$ |
| <i>Heating</i> | |
| 337.05 ± 0.90 | $(1.394 \pm 0.031) \times 10^{-11}$ |
| 346.90 ± 1.05 | $(1.434 \pm 0.099) \times 10^{-11}$ |
| 357.05 ± 0.40 | $(1.881 \pm 0.043) \times 10^{-11}$ |
| 366.70 ± 0.55 | $(2.640 \pm 0.039) \times 10^{-11}$ |
| 381.00 ± 0.15 | $(0.800 \pm 0.062) \times 10^{-11}$ |

Table 1: Polarized piezoelectric module measurements over temperature during cooling and heating cycles.

Discussion

The force-current relation of quartz has a slope of $13.93 \pm 0.59 \mu\text{AN}^{-1}$. This is a relatively low error and shows on Figure 5 that at least under these conditions and with Quartz, we have nice linear behaviour. It is important that this particular set of measurements shows nice properties with low error because we need to define the gauge constant $\eta_g = 30290 \pm 1292 \text{ F}^{-1}$, a value that we will have to use for all other measure-

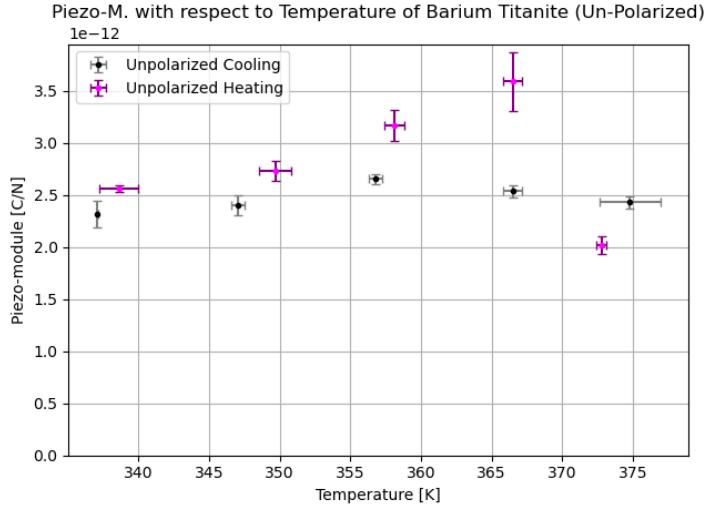


Figure 8: Piezo-Module Change with respect to the temperature of unpolarized Barium Titanate.

ments.²

Another key thing that influenced the measurement method from this result is noticing that when picking equidistant points on the force lever, due to the relation $K(x)_t \propto \frac{50-x}{25-x}$ larger distances need to have a higher density of measurements to give a better linear fit. But it is also worth keeping in mind that the error will tend to be larger there.

Next, we observe the piezo module with respect to the temperature of quartz (Figure 6). Firstly, we see that the first "room temperature" value, which we used to calibrate and find the gauge constant, has a large error and strays far from the rest of the points. This is problematic as it should technically be our most accurate result. Nonetheless, since the data points are somewhat oscillatory, it does seem to approach a temperature-independent behaviour.

Despite this, a linear fit would have a negative gradient. The range of results sits in about a range of size $5 \cdot 10^{-3}$ whereas the result is of the order of 10^{-12} . The data alone doesn't decisively conclude on a temperature-independence.

A key improvement would be to have more results over a large temperature range. A more precise gauge constant would also have a vital effect on this result.

Bringing our attention to the results of the Barium Titanate (Figure 7 and 8), we notice that the polarized measurements are almost a whole order larger. In fact the unpolarized results are similar to quartz' behaviour. A potential reason for this is the polarized structure (with the shifted atoms) have a strong piezo effect due to the stronger interatomic polarity from the shift. Then applying the force K_x only further strengthens this polarity (by deformation), thereby giving us a larger piezo module.

We can say with strong confidence that the piezo module is temperature dependent in both cases, and act in a similar manner whether polarized, not polarized, during heating or cooling. We see a consistent increase up to around 365K where afterwards we see a strong dip. This happens in both the cooling and heating phases, but it is always a more aggressive trend in the heating phase. The temperature dependence and the dip

²For this we used the literature value that the piezo module of quartz at room temperature is $2.3 \cdot 10^{-12} \text{ C/N}$.[4]

| Temperature (K) | Unpolarized Piezo-Module (C/N) |
|-----------------|-------------------------------------|
| <i>Cooling</i> | |
| 374.80 ± 2.15 | (2.431 ± 0.057) × 10 ⁻¹² |
| 366.50 ± 0.65 | (2.540 ± 0.059) × 10 ⁻¹² |
| 356.80 ± 0.45 | (2.653 ± 0.047) × 10 ⁻¹² |
| 347.05 ± 0.50 | (2.404 ± 0.095) × 10 ⁻¹² |
| 337.10 ± 0.05 | (2.315 ± 0.129) × 10 ⁻¹² |
| <i>Heating</i> | |
| 338.60 ± 1.35 | (2.560 ± 0.029) × 10 ⁻¹² |
| 349.70 ± 1.15 | (2.732 ± 0.095) × 10 ⁻¹² |
| 358.15 ± 0.70 | (3.171 ± 0.148) × 10 ⁻¹² |
| 366.50 ± 0.65 | (3.592 ± 0.280) × 10 ⁻¹² |
| 372.80 ± 0.35 | (2.017 ± 0.088) × 10 ⁻¹² |

Table 2: Unpolarized piezoelectric module measurements during temperature cycling. First section: cooling cycle; second section: heating cycle.

are interesting properties that seem to happen due to a threshold being reached. A hypothesis could be that the temperature of the piezo module peak is where the titanium atoms are excited enough to have the kinetic energy to position itself far away enough from its static point (at low potential) and in a positive position to maximize the piezo effect, while at the same time the barium atoms aren't excited enough to leave their static potential and make the interatomic structure dynamic (and therefore less consistently piezo effective over the entire lattice). The key reasoning behind this hypothesis (other than the results) is the fact that Barium is almost 3 times heavier than titanium, making it harder to put into motion.

When heating, the piezo module peak is higher than when cooling. This implies there isn't just a temperature (internal energy) dependence, but also a Power (Energy input over time) dependence. When heating, the absolute power is higher than when cooling, implying if we want to induce a stronger piezo effect we want to have a higher Watt. To confirm this we'd want a similar rate of cooling or perhaps lower the heating rate. Either way this is an interesting and consequential parameter which should lend itself to further analysis.

Looking at the results of Figure 10 we see the data points of the fits we used for finding the piezo module values of Figure 7 and 8. On these graphs, we clearly see when our presupposed linearity is violated and begins to explain certain errors we see in the previous temperature-piezo relation. We see that over all force values, the largest one mostly strays from the linearity. This can be related to the fact that new non-linear terms are introduced due to the higher energy level. The same argument can be used when we look at high temperature values where again, more energy is introduced into the system which add non-linear terms to 1 and make our theoretical assumption no longer valid. A key improvement would therefore be to use lower temperatures and forces so as to keep our linear approximation accurate. Keeping an eye over the linearity of our data points is vital to finding the appropriate range. Again, other key improvements of would be to use more data points, more ranges and keeping the temperature more stable during fix-temperature data collection.

Conclusion

In conclusion, we successfully verified the linear relation between force and charge of quartz at room temperature with a relatively low error as $13.93 \pm 0.59 \mu\text{AN}^{-1}$ but our

gauge constant ended up having a higher error $\eta_g = 30290 \pm 1292 \text{ F}^{-1}$. This increases the error of almost all subsequent measurements.

We see that the piezo module of quartz with respect to temperature implies temperature independence but cannot be statistically justified with our measurements alone.

We see that for Barium Titanate, whether the crystal is polarized or not plays a massive role (a difference of a whole order) but generally the behaviour is still quite similar. There is also a clear temperature dependence, implying a rise until a peak at around 365K after which there is a strong dip. These trends are amplified if the quartz is being heated instead of it naturally cooling. Finally, we saw that our theoretical assumptions of linearity (as originally stated in 1) are less accurate at high temperature and with higher forces.

Therefore, we included, if we want better results to characterise the piezo effect, we want to work in lower temperatures, a larger range, and more frequently distributed data points, the only real limit of achieving these goals being time.

In general, the experiment did well to identify key phenomena of the piezo effect in Quartz and Barium, additionally we managed to roughly identify the temperature dependence of the two materials. Nonetheless, the results aren't statistically deterministic and spending a lot more time on the experiment would give a stronger verification to our results.

Appendix

This report benefitted from ChatGPT and DeepSeek for LaTeX table formatting and python syntax recollection. However, it was not used to write text or code.

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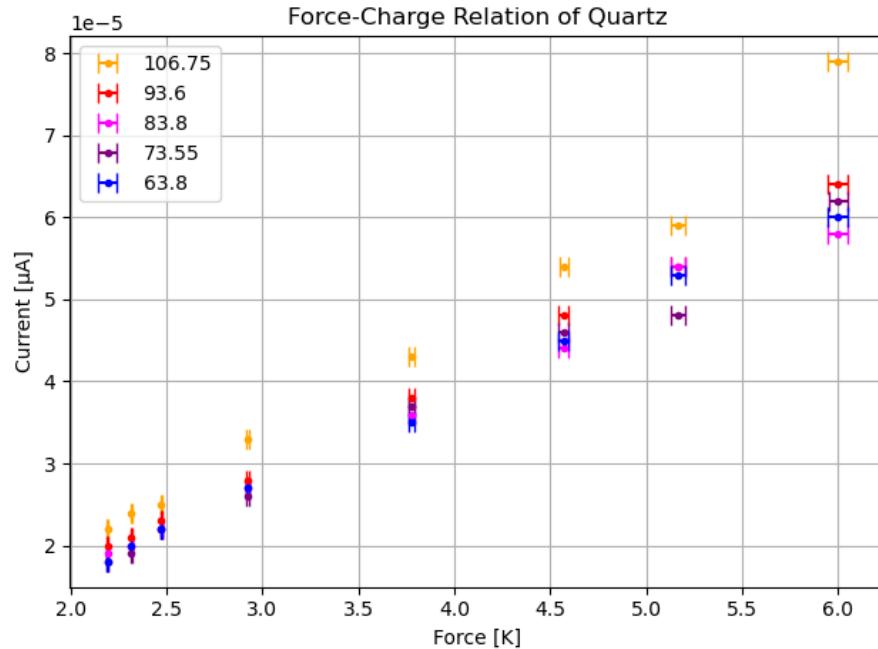


Figure 9: Force-Ampere relation for the quartz crystal at different temperatures.

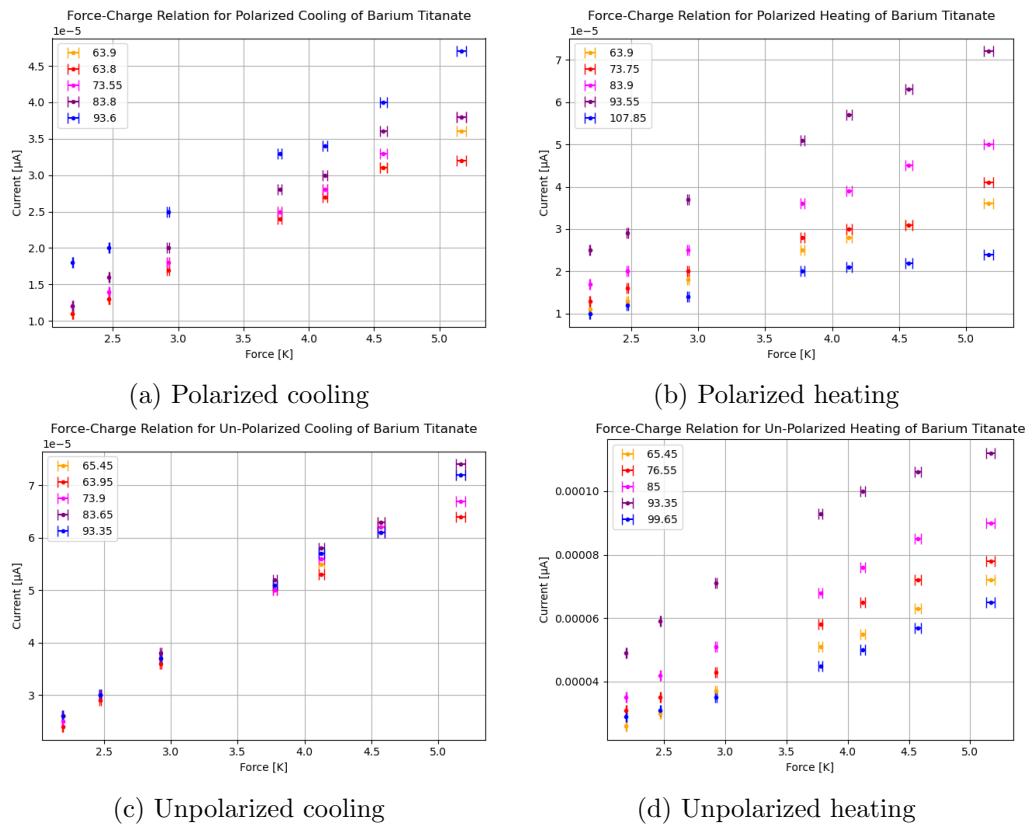


Figure 10: Charge measurements for polarized and unpolarized samples during cooling and heating cycles. (a) Polarized sample during cooling, (b) polarized sample during heating, (c) unpolarized sample during cooling, (d) unpolarized sample during heating.