The ferroelectric study of the Triglycine Sulfate

Tiago David da Silva Ferreira Nº201305729

Abstract: In this work it was studied the ferroelectric properties of the Triglycine Sulfate. The critical temperature was determined and its value is $T_C = 46.21$ºC. The dependence of the reminiscent polarization with the temperature was determined and the results are in agreement with the predictions of the Landau theory. A study of the dependence of the coercive field with the temperature was also made. In the introductory part of this report a brief description of ferroelectrics and a simple deduction of the Landau theory for continuous phase transitions is given.

I. Introduction

The ferroelectricity was discovered during the study of the Rochelle salt, Sodium potassium tartrate tetrahydrate [1]. In 1912, Peter Debye, constructed a theory to explain the results obtained in experiments with the Rochelle salt and with this theory he predicted the existence of a critical temperature below which the material had a permanent dielectric polarization. The lack of experimental evidence of this conclusion made him reject the result. In 1920, Joseph Valasek, presented to the scientific community the first hysteresis curve, proving, therefore, the result obtained by Peter Debye [2]. Since then many ferroelectric materials were discovered and its applications have been vast. One of these materials is the Triglycine Sulfate, TGS. The TGS is a ferroelectric crystal that is used for infrared detector applications at room temperature and some pyroelectric sensors are based on this material because of its sensitivity to a large spectrum width, from ultra-violet to far infrared, and for not needing a cooling system [3]. In this work it will be studied some of the ferroelectric properties of the TGS.

II. Theory

A ferroelectric is a material that have a permanent dielectric polarization, and its name appears from the analogy with the ferromagnetic materials. This permanent polarization appears in the material in a domain structure and as a whole, because of the random orientation of the dipole moments of the domains, the material has no net polarization. In a domain all the dipoles are parallel and the orientation of the directions of the domain dipoles can be changed by applying an electric field to the sample. Materials with this structure are non-linear dielectrics and as a consequence these materials show a ferroelectric hysteresis when the polarization is plotted against the electric field. This hysteresis loop is due to the fact that some dipole moments have to overcome a potential barrier before they can align with the electric field. One example of a ferroelectric hysteresis loop can be seen in the Figure 1.

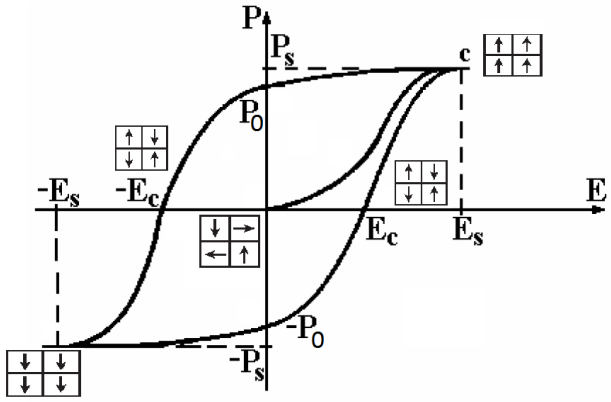


Figure 1: Hysteresis loop of a ferroelectric. E is the electric field applied to the material and P is the polarization induced in the material; P_S is the polarization saturation. Its the polarization of the material when the domains dipoles are all aligned. In this situation the ferroelectric can be consider as single domain; P_0 is the reminiscent polarization. It's the polarization with which the material stays when the applied field is reduced to zero; E_C is the coercive field and is the field that needs to be applied to eliminate the polarization of the material; E_S is the saturation field. The field that induces a saturation polarization in the sample.

As it can be seen, from Figure 1, as the applied field is increased the dipole moments tend to align with the field. This alignment go on until all the dipoles are align and at this point the saturation is reached. When the applied field is reduced to zero some dipoles stay aligned and a reminiscent polarization is present in the material. A electric field in the opposite direction is necessary to eliminate this saturation. If the electric field continues to grow the dipoles start to align, now in the opposite direction, and again a saturation state is reached.

These cycles are temperature dependent and above a certain temperature, the critical temperature T_C, the polarization vanishes. This change is associated with a change in the internal order of the crystal, other wise known as a phase transition. As the temperature of the sample is increased the thermal effects start to overcome the effect of the applied electric field

and the area of the loops and the reminiscent polarization decreases. Above the T_C the material goes through a phase transition and this can be of two types: first or second order. According to Landau and in a simple way [4], a first order transition is characterized for having a abruptly change in the phase of the material while a second order is characterized to have a continuous transition between phases. The theory behind these phase transitions is phenomenological and was invented by Landau. First it is considered that: a continuous phase transitions are driven by the internal order; The amount of this order is measured by an order parameter, in the present case the parameter is the polarization, chosen so that $P = 0$ if $T > T_C$ and $P \neq 0$ otherwise; In the neighborhood of the transition, the thermodynamic potential can be expanded as a Taylor series in the order parameter. The thermodynamic potential that will be used is the Gibbs Free Energy and this potential is given by the equation 1

$$\phi \equiv G = U - TS - \overrightarrow{E} \cdot \overrightarrow{P} \tag{1}$$

where U is the internal energy, S is the entropy, P is the polarization, and E is the electric field. Expanding the potential in a Taylor series one obtains:

$$\phi = \phi_0 + \frac{1}{2}\phi_1 P^2 + \frac{1}{4}\phi_2 P^4 + O\left(P^4\right) \tag{2}$$

Notice that only the even terms are considered because the odd terms lead to discontinuous phase transitions and in this work only the continuous case is of interest. From the equation 2 the thermodynamic equilibrium implies that ϕ is a minimum. From this the equations 3 and 4 can be written.

$$\left(\frac{\partial \phi}{\partial P}\right)_{P_0} = 0 \tag{3}$$

$$\left(\frac{\partial^2 \phi}{\partial P^2}\right)_{P_0} > 0 \tag{4}$$

P_0 is the reminiscent polarization. The equation 3 allows to write the reminiscent polarization as function of the temperature and the equation 4 allows to write dielectric permittivity as function of the temperature. Using the equilibrium equation 3 it can been written that:

$$\left(\phi_1 + \phi_2 P_0^2\right) P_0 = 0 \tag{5}$$

and the equation 5 has two solutions:

$$\begin{cases} P_0 = \sqrt{\frac{-\phi_1}{\phi_2}} & T < T_C \\ P_0 = 0 & T \geq T_C \end{cases} \tag{6}$$

Consider now the case for $T < T_C$ and looking again for the equation 2 it can be assumed that ϕ_1 has a dependency on temperature as follows:

$$\phi_1 = a\left(T - T_C\right) \tag{7}$$

The equation 7 allows to conclude that:

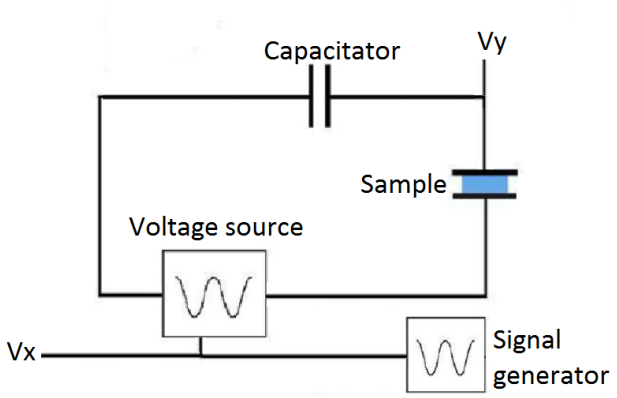
$$P_0 \sim \left(T_C - T\right)^{\frac{1}{2}} \tag{8}$$

This result is valid for temperatures close to the critical temperature.

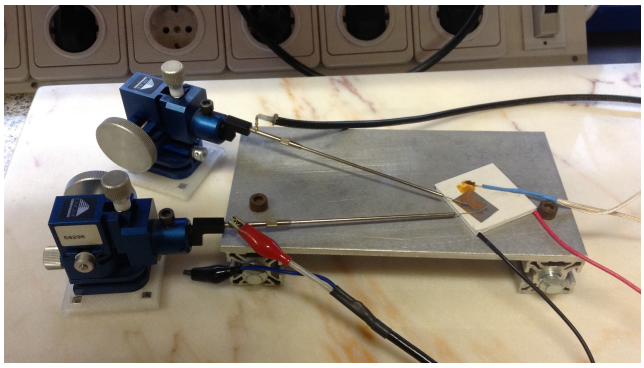
The material under study is the Triglycine Sulfate and has a continuous phase transition for $T_C = 49.35$ºC, as it can bee seen in [5].

III. Experimental setup

The experiment consisted in to apply an electric field to the sample and then measure the voltage on one of the surfaces of the sample. The voltage that created the electric field was also measured. The experimental setup that was used is the following:



(a) Simple schematic of the experimental setup. The voltage source that generated the tension for the creation of the electric field was modulated by a signal generator with a sinusoidal wave of 2Hz and an amplitude of 1V. A capacitor of $1.5\mu F$ was used to compensate the phase between the two measured signals. V_X and V_Y were measured through a digital oscilloscope and data was saved directly in the computer. The sample was heated through a peltier.



(b) A photo of the sample from a part of the setup. The white square is the peltier. A little surface of copper was used to facilitate the connection with the base. The white wire with blue at his end is the thermocouple used for controlling the temperature.

Figure 2: Experimental setup.

One peltier was used to heat the sample and a thermocouple, with a sensitivity of $41\mu V/$ºC, was used to control the temperature of the sample, as it can be seen in the Figure 2b. This thermocouple was referenced a 0ºC. The sample of TGS used had a thickness $d = 0.95mm$ and a surface area $S = 8.24 \cdot 10^{-6} m^2$.

During the experiment several hysteresis[1] loops were measured for different temperatures on heating and cooling.

IV. Results and discussion

One of the several hysteresis loops that was measured can be seen in the Figure 3.

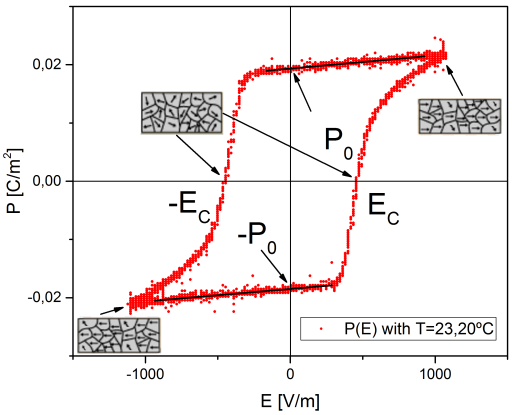


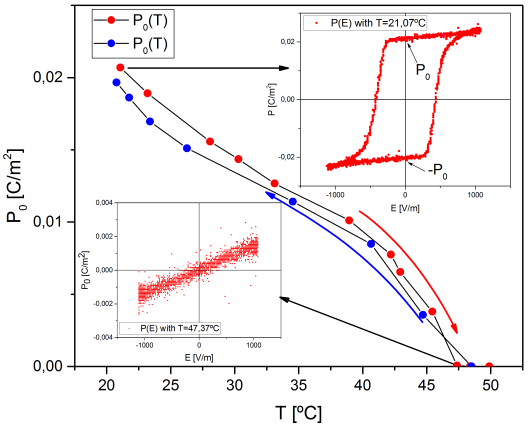
Figure 3: Hysteresis loop for $T = 23.20$ºC. The black lines are the linear fit that was made to determinate the reminiscent polarization. The value obtained was $P_0 = 0.02069 C/m^2$.

Figure 3 shows the dipoles alignment along the cycle. Notice that the saturation is not fully reached. It is difficult to align all the dipoles and high fields are necessary to reach full alignment. Also, other factors may be contributing to this phenomenon.

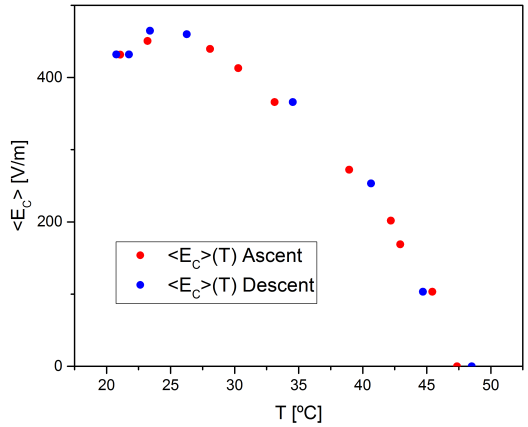
The reminiscent polarizations were calculated from all the cycles measured and from that resulted the Figure 4a. The coercive fields were also calculated and the results can be seen in the Figure 4b.

The first thing to notice in the Figure 4a is that the ascent and descent curves are almost the same. The difference is very small. As shown in the inset of the Figure 4a, after the sample passes is phase transition, the loop disappears and the data is almost linear. In this region the TGS is in its paraelectric phase. In this phase the material is centrosymmetric and has zero dipole moment. The data in the Figure 4b shows how the coercive field varies with the temperature. This results are important when one is considering to use ferroelectrics to create memories. From the Figure 4a it can also be seen that the data appears to obey to the Landau theory. This is better seen in the graph of $P_0^2(T)$, as can be seen in the Figure 5.

[1]The electric field was calculated this way: $E = \frac{V_X}{d}$, where d is sample thickness. The polarization was calculated as this way: $P = \frac{CV_Y}{S} - \epsilon_0 E$, where C is the capacitance of the capacitor and S is the surface area of the sample.



(a) Graph with $P_0(T)$ for the case where the temperature is increasing (red) and for the case where the temperature is decreasing (blue). The inset in the upper right corner is the hysteresis loop for the first temperature measured. The inset in the lower left corner is the hysteresis loop after the phase transition. Notice that at this temperature there is no loop and the data is almost linear.



(b) The mean coercive field as function of the increasing and decreasing temperature. The mean values were calculated through an arithmetic mean of the modulus of the positive and negative coercive fields.

Figure 4: The dependence on the temperature of the reminiscent polarization and the coercive field.

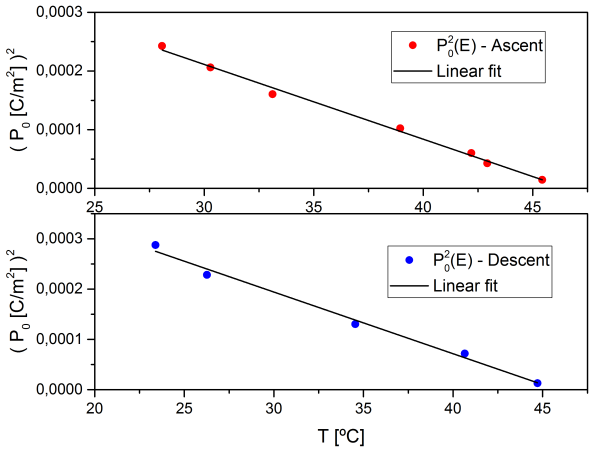


Figure 5: Graph with $P_0^2(T)$.

The experimental data in the Figure 5 is in agreement with the theory deduced in the section 2. This is seen from the good fits obtained for the two cases. This result also permits to conclude that the phase transition is of the second order, as mentioned in [6]. Notice that only the points close to T_C were considered to the linear fit, the other are in a region of temperatures where the approximation starts to fail. From the linear fits, the critical temperature is calculated and is $T_C = 46.21^{\circ}\text{C}$. This temperature is the mean of the critical temperatures in the ascent and descent cases[2]. The value obtained does not differ much from the value presented in the literature, as can be seen in [5]. The error is $\sim 6\%$, which is a good result.

V. Conclusion

The critical temperature of TGS sample under study was determined to be $T_C = 46.21^{\circ}\text{C}$ and this result is in agreement with the values presented in the literature and with the values obtained by other colleagues. The results also allowed to verify the Landau theory for continuous phase transitions. The critical temperature of the TGS is very close to room temperature and this makes this material not good to be used as a memory, where the temperatures can raise above the 50°C. Despite this, the TGS is good to be used on infrared detector applications at room temperature and on pyroelectric sensors. In the future, the study of the TGS with impurities or with different methods of growing is necessary to try to expand the applications of this material.

References

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[2]For the ascent case the value obtained was $T_C^{\uparrow} = 46.58^{\circ}\text{C}$ and for the descent case the value obtained was $T_C^{\downarrow} = 45.84^{\circ}\text{C}$.