Advanced laboratory report

Pyroelectricity:

Triglycine sulfate crystal growth and characterization

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Introduction

Ferroelectric crystals are an interesting class of materials. They are similar phenomenologically to ferromagnetic materials in that they exhibit hysteresis loops, spontaneous polarization, and coercive field. Ferroelectric crystals have a number of practical applications, and one of those is a pyroelectric infrared (PIR) detection.

PIR devices can detect a person moving into or through a detection zone with high reliability. The slightest positive or negative thermal radiation change in contrast to a background, focused by the appropriate optics, triggers the sensor element. There is no interference between neighboring units due to the passive nature of the detection principle [1].

At the heart of every PIR detector is the pyroelectric crystal. Typical detectors use materials, such as triglycine sulfate (TGS) or lithium tantalite. They are ferroelectric crystals, which have a maximum pyroelectric sensitivity at room temperature and therefore do not require the cooling for detection of temperature changes. And both TGS and lithium tantalite exhibit a large spontaneous electrical polarization below their Curie points.

Triglycine sulfate is a water-soluble crystal and it is a joint in the armour of this crystal from the point of view its stability in the environment. But indeed for this reason we chose to grow a triglycine sulfate crystal. A water solubility of TGS allows growing it from the water solution by evaporation. So we plan to obtain a TGS crystal and make a PIR detector from it.

Theoretical background

Ferroelectricity

Ferroelectricity is a property of certain non-conducting crystals, or dielectrics, that exhibit spontaneous electric polarization (separation of the center of positive and negative electric charge, making one side of the crystal positive and the opposite side negative) that can be reversed in direction by the application of an appropriate electric field.

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The main problems which arise in the theory of dielectric crystal are concerned with the polarization that can be induced in such non-conducting materials be means of an externally applied electric field. The polarization values, which can be measured in normal dielectrics upon application fields, are usually small. Although rather large but limited number of crystals exhibit polarization values which are many orders of magnitude larger than those observed in most dielectrics. It became customary to call "ferroelectricity" the phenomenon exhibited by these crystals. The reason for this denomination is historical and is due to a formal similarity of the ferroelectric phenomenon with ferromagnetism. The similarity is mainly phenomenological: just as ferromagnetic materials exhibit a spontaneous magnetization and hysteresis effects in relationship between magnetization and magnetic field, ferroelectric crystals show a spontaneous electric polarization and hysteresis effects in the relation between dielectric displacement and electric field. This behavior is mostly observed in the certain temperature regions delimited by transition (or Curie) points above which the crystal is no longer ferroelectric and show normal dielectric behavior [2].

In order to describe the essential features of the ferroelectric phenomenon, we will use a model of a hypothetical ferroelectric crystal and see what kind of dielectric behavior it would show. The model, which has no general validity and is extremely oversimplified, is that of a two-dimensional crystal having the chemical formula A B and a fictitious structure depicted in Fig. 1
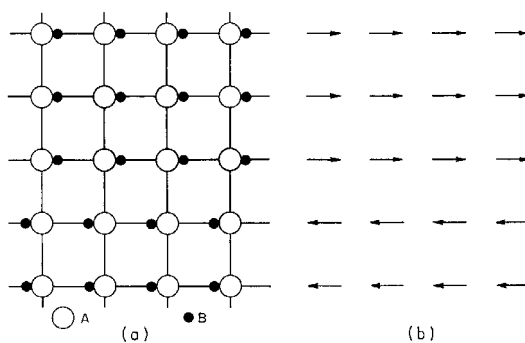

Fig. 1 Schematic structure of a fictitious ferroelectric crystal [2]

The A ions, which we will assume to carry a negative charge, are located on the lattice points of a simple square net. The B ions, carrying a positive charge, are located on the horizontal lines joining the A ions; their equilibrium positions are such that they always lie closer to one of the two adjacent A ions than to the other. Such a situation is possible if the potential between two adjacent A ions is of the type sketched in Fig.2: there are two equilibrium positions, corresponding to the same minimum value of the energy, for a B ion on the line joining two A ions. The B ions can jump from one equilibrium position to the other but in order to do so they must be provided with the energy necessary to overcome the energy barrier A E.

Suppose now that, at a given temperature T, all B ions are closer to their A partners on the left. We can visualize every group AB as an electric dipole and the structure can then be schematically represented by an assembly of dipoles pointing all in the same direction, as in the three upper rows of Fig.1. We say that the crystal is spontaneously polarized: the spontaneous polarization is measured in terms of dipole moment per unit volume, or, with reference to the charges induced on the surfaces perpendicular to the polarization, in terms of charge per unit area. The crystals having a spontaneous polarization are called pyroelectric and the direction of the spontaneous polarization is called the polar axis.

Alignment of the electric dipoles may extend only over a region of the crystal, while in another region the direction of the spontaneous polarization may be reversed, as in the lower portion of Fig.1. Such regions of uniform polarization are called domains, a term borrowed again from ferromagnetism. We are going to see in the following that energy considerations require the formation of domains.

Suppose now that we apply an electric d.c. field in the horizontal direction of Fig.1. The dipoles, which are already oriented in the direction of the field, will remain so aligned, but those, which are oriented in the direction opposite (antiparallel) to the field, will show a tendency to reverse their orientation. If the applied field is sufficiently large, the B ions of our model will be able to overcome the barrier ΔE, and in so doing will cause the corresponding dipole to flip (or switch) over into the direction of the field.
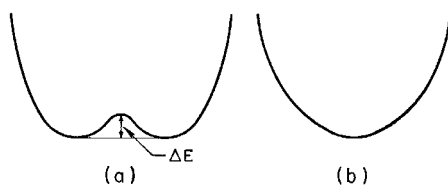

(a) ΔE (b)

Fig. 2 Schematic potential walls [2]

Suppose that our crystal is initially composite of an equal number of positive and negative domains (i.e. domains oriented to the right and domains oriented to the left), which means that the overall polarization of the crystal is equal to zero. If we first apply a small electric field directed say, in the positive direction, we will have only a linear relationship between P and E because the field is not large enough to switch any of the domains and the crystal will behave like a normal dielectric. In the plot of P vs. E, shown schematically in Fig. 3, we obtain the portion OA of the curve. If we increase the electric field strength, a number of the negative domains will switch over in the positive direction and the polarization will increase rapidly (portion AS), until we reach a state in which all the domains are aligned in the positive direction: this is a state of saturation (portion BC) and the crystal consists now of a single domain. If we now decrease the

field strength, the polarization will generally not return to zero but rather follow the path CD of Fig. 3. When the field is reduced to zero, some of the domains will remain aligned in the positive direction and the crystal will exhibit a remnant polarization Pr(OD). The extrapolation of the linear portion BC of the curve back to the polarization axis represents the value of the spontaneous polarization PS(OE).
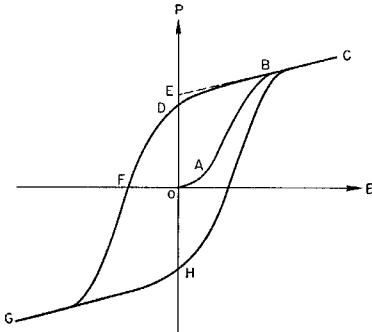

Fig. 3 Ferroelectric hysteresis loop

In order to annihilate the overall polarization of the crystal, we find it necessary to apply an electric field in the opposite (negative) direction. The value of the field required to reduce P to zero (OF) is called the coercive field E_c. Further increase of the field in the negative direction will, of course, cause complete alignment of the dipoles in this direction (FG), and the cycle can be completed by reversing the field direction once again (GHC).

The relation between P and E is thus represented by a hysteresis loop (CDGHC), which is the most important characteristic of a ferroelectric crystal. The essential feature of a ferroelectric is thus not the fact that if has a spontaneous polarization, but rather the fact that this spontaneous polarization can be reversed by means of an electric field.
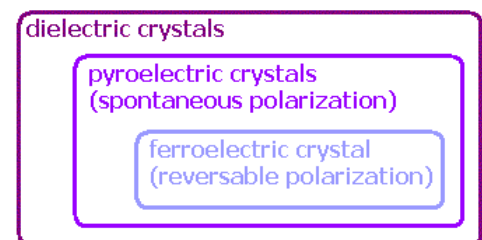
It may be noted that, owing to the relation between dielectric displacement D, electric field E, and polarization P, $D = E + 4\pi P$, the relation between D and E is also characterized by a hysteresis curve.

The fact that an applied field can cause the polarization to alter its orientation has some important consequences. In the first place, it means that the shift of the B ions is small, and this small relative shift turns the crystal into its electrical twin. It is not illogical to expect, then, that if the energy barrier ΔE (Fig. 2 a) is so low as to be accessible with the help of an electric field, then it may also be affected by other factors, such as temperature changes.

With increasing temperature, the thermal motion of the atoms in the lattice may increase to such an extent that the B ions of our fictitious crystal may be able to overcome the energy barrier ΔE without the help of an external field, and may therefore jump from one equilibrium position to the other.

Another possibility is that the shape of the potential curve between adjacent A ions changes to the point of becoming as indicated schematically in Fig. 2 b. In the latter case, there is only one equilibrium position possible for the B ions, i.e. midway between two A ions. In the former case, the statistical

distribution of the B ions will be symmetrical with respect to the A ions. The result is the same: our crystal is no longer polar, and will behave rather as a normal dielectric material.

The temperature at which such a transition from the polar into the non-polar state occurs is often referred to as Curie temperature (or Curie point), again in analogy with ferromagnetism.

Crystallographic Considerations and Definition of a Ferroelectric

It is well known that any one crystal can be classified in one or another of thirty-two crystal classes (point groups) according to the symmetry elements, which it possesses. A study of these thirty-two classes reveals that eleven of them are characterized by the existence of a center of symmetry: they are thus called centrosymmetric. A centrosymmetric crystal can of course possess no polar properties. If, for example, we apply a uniform stress to such a crystal, we will indeed cause a small displacement of the charges within the lattice, but the existence of a center of symmetry will bring about a compensation of the relative displacements. If we apply an electric field to a centrosymmetric crystal, we will indeed change its shape, but the strain will remain unchanged if we reverse the direction of the electric field. In other words, the strain is proportional to the square of the applied field: the effect is quadratic. This is the effect called electrostriction, which occurs actually in all substances, whether crystalline or amorphous, solid or fluid [2].

The remaining twenty-one crystal classes do not have a center of symmetry; they are non-centric. The absence of a center of symmetry makes it possible for crystals in these classes to have one or more polar axes and thus to show vectorial or tensorial properties. With one exception, all classes devoid of a center of symmetry exhibit the piezoelectric effect. The single exception is the cubic class 432, which, although without a center of symmetry, nevertheless has other symmetry elements that combine to exclude the piezoelectric activity. Piezoelectricity is the property of a crystal to exhibit electric polarity when subject to stress. The piezoelectric effect is a linear effect; application of pressure to a piezoelectric crystal plate between two electrodes causes a charge to flow in a certain direction through a measuring circuit. If the pressure is replaced by a tension, the charge will flow in the opposite direction. Also, if we apply an electric field to the crystal plate, it will be stretched; if we reverse the field direction, it will be compressed. This is the converse piezoelectric effect.

Out of the twenty piezoelectric classes, ten are characterized by the fact that they have a unique polar axis, i.e. an axis which shows properties at one end different from those at the other. Crystals in these classes are called polar because they are spontaneously polarized. Generally, this spontaneous polarization cannot be detected by charges on the surface of the crystal because these charges have been compensated through external

32 groups of the symmetry
dielectric crystals
12 are non-centric
piezoelectric crystals
10 have unique polar axis
pyroelectric crystals
reversable polarization
ferroelectric crystals

or internal conductivity, or by twinning. The value of the spontaneous polarization, however, is dependent on temperature; thus, if the temperature of the crystal is altered a change in the polarization occurs and electric charges can be observed on those crystal faces, which are perpendicular to the polar axis. This is
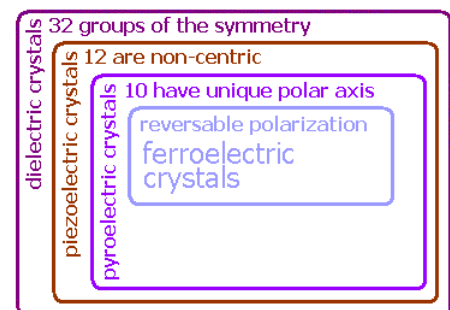
the pyroelectric effect. The ten crystal classes, which have a unique polar axis are also called pyroelectric classes.

The ferroelectric crystals belong to the pyroelectric family. They constitute only that part of it, however, for which the direction of the spontaneous polarization can be reversed by application of an electric field. It is thus a necessary condition for a ferroelectric crystal to belong to any one of the ten polar classes (in its ferroelectric phase) but not a sufficient condition, as reversibility of the polarity must also occur. We can thus define a ferroelectric crystal as a pyroelectric crystal with reversible polarization.

This definition brings about an interesting difference between ferroelectricity and ferromagnetism. In the case of ferromagnetism, whenever the moments are spontaneously aligned they can also be reversed by means of an external field. Thus, the magnetic phenomenon is interesting because the moments are spontaneously aligned. The phenomenon of ferroelectricity, on the other hand, is interesting only when the moments are loosely aligned, i.e. when the interactions are so delicately balanced as to allow reversal of the spontaneous polarization.

Triglycine sulfate

The ferroelectric activity of triglycine sulfate, $(NH_2CH_2COOH)_3 \cdot H_2SO_4$, (abbreviated TGS), was discovered by Matthias et al. in 1956. It has immediately attracted the attention of many researchers because it exhibits ferroelectric properties at room temperature, and it can be grown easily in large samples. Chemically and crystallographically, it is by far not the simplest ferroelectric known, but its phenomenological behavior is simple. It represents, in fact, one of the most typical examples of a ferro-electric.
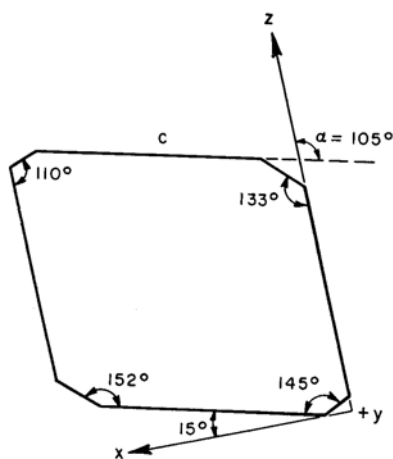

Fig. 4 Ferroelectric face of TGS crystal .The ferroelectric axis coincides with Y-axis. [2]

The Curie temperature lies at 49 °C. The phase above the transition has monoclinic symmetry and belongs to the centrosymmetrical class 2/m. Below the transition temperature, the mirror plane disappears and the crystal belongs to the polar point group 2 of the monoclinic system. Ferroelectricity is found along the direction of the twofold polar axis (monoclinic b axis). The transition is of the second order.

However, the investigation of the dielectric, piezoelectric and pyroelectric properties requires the choice and the identification of a reference system of co-ordinates. Since the most convenient monoclinic angle β is approximately equal to 105° and the predominant face is often the c face, the following

orientation of a reference system of orthogonal co-ordinates is selected in relation to the most common crystal habit. The Y axis is parallel to the polar axis, the Z axis is parallel to the natural edge which forms an angle 105° with the predominant (c) face of the crystal, and the X axis is perpendicular to Y and Z to form a right-handed system, as indicated in Fig.4

The components of the dielectric constant tensor of TGS have the following values at 23°C (measuring field 1 V/cm, frequency 500 kc/s): ε_a=8.6, ε_b=43, ε_c=5.7. The temperature dependence of these quantities, measured at 1 kc/s and 1 V/cm is shown graphically in Fig. 5.
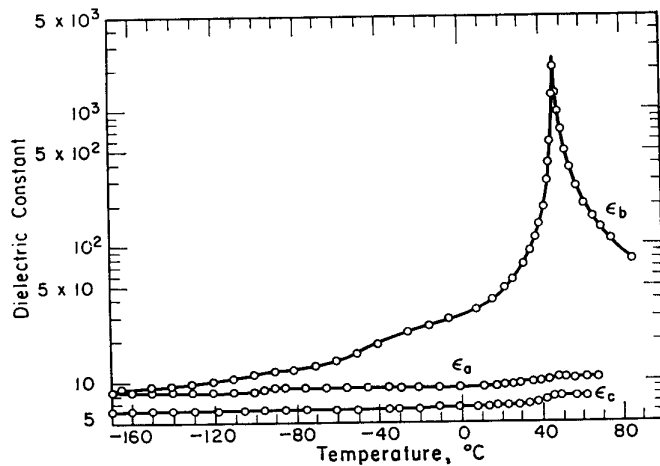

Fig. 5 Dielectric constant as a function of temperature [2]

The temperature dependence of the spontaneous polarization Ps is depicted in Fig. 6, and is typical of a transition of the second order. The value of P_s at room temperature is about 2.8 x 10^{-6} C/cm^2, but the data reported by different authors may fluctuate within ± 20% of this value. Below 0 °C, the spontaneous polarization increases only slowly with decreasing temperature, reaching a value of approximately 4.3x10^{-6} C/cm^2 at - 140 °C [2].
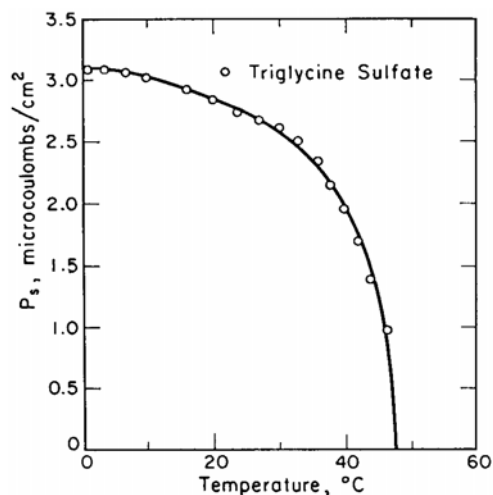

Fig. 6 Spontaneous polarization of TGS as a function of temperature [3]

Measurements of the coercive field E_c of TGS have been carried out by a number of authors. This quantity is strongly dependent upon the amplitude and frequency of the applied field, at any given

temperature below the Curie point. At room temperature, the value of E_c measured with a field of 1500 V/cm and a frequency of 50c/s is equal to 430V/cm. The dependence of the 50c/s coercive field upon the amplitude of the applied field has been tentatively written by Toyoda et al. in the form where the exponent b equals 0.5 at 20 °C and 0.4 at -73 °C [2]. The temperature dependence of E_c measured with a 50 c/s field of 1500 V/cm is depicted in Fig. 6. The sharp increase occurring below -10°C is not indicative of phase transitions, but of the fact that the relaxation time associated with the reversal process increases rapidly with decreasing temperature.
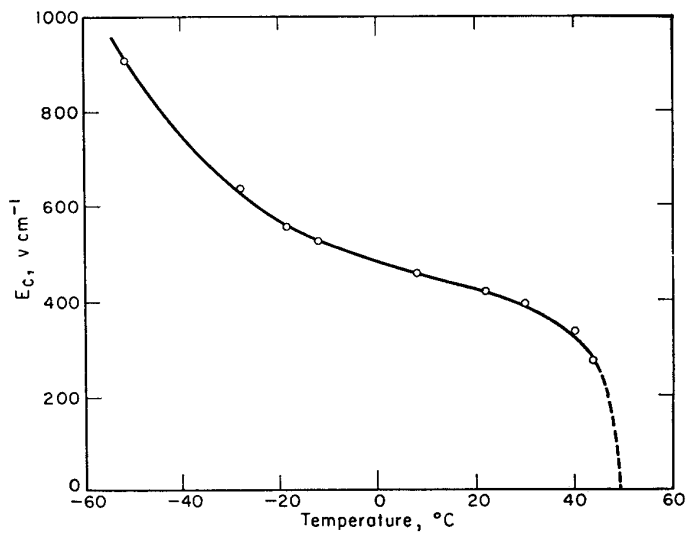
Coercive field E_c of tri-glycine sulfate, measured with a field of 1500 V/cm at 50 c/s as a function of temperature

Fig. 7 Coercive field of TGS [2]

Experimental studies of ferroelectric properties

Ferroelectric properties

Ferroelectric hysteresis loops can be observed very easily on the screen of an oscilloscope by inserting the crystal in a simple circuit first described by Sawyer and Tower and using an a.c. field (generally 50 Hz) [3]. The circuit is depicted schematically in Fig. 8: the voltage lying across the crystal C_x is put on the horizontal plates of the oscilloscope, thus plotting on the horizontal axis a quantity which is proportional to the field lying across the crystal. The linear capacitor C_0 is connected in series with the crystal C_x and the voltage lying across C_0 is therefore proportional to the polarization of the crystal C_x. This voltage is laid across the vertical plates of the oscilloscope. The Sawyer and Tower circuit allows not only the display of the hysteresis loop on the scope screen, but also the measurement of important quantities such as the spontaneous polarization P_s and the coercive field E_c.
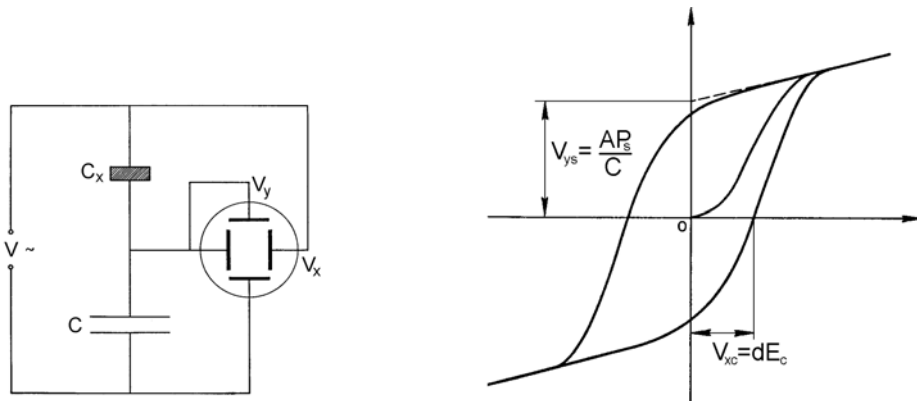

Fig. 8 Experimental circuit for hysteresis loop measurement [4]

The voltage V_y across the vertical deflection plates of the oscilloscope is given by [4]:

$$V_y = \frac{1}{C} \int I dt = \frac{1}{C} \int \frac{dQ_x}{dt} dt = \frac{Q_x}{C}.$$

By Gauss' law the free charge Q_x on the crystal electrodes is given in mks units by:

$$Q_x = AD = A\left(\varepsilon_0 E + P\right) = A\left(\varepsilon_0 E + \chi\varepsilon_0 E + P_f\right) = A\left(\varepsilon\varepsilon_0 E + P_f\right),$$ where A is the electrode area, χ and ε are the electric susceptibility and dielectric constant characterizing the linear part of the polarization P and P_f is the nonlinear part of the polarization associated with the ferroelectric behavior.

$$V_y = \frac{Q_x}{C} = \frac{A\left(\varepsilon\varepsilon_0 E + P_f\right)}{C} = \frac{A}{C}\left(\varepsilon\varepsilon_0 \frac{V_x}{d} + P_f\right)$$

For linear dielectric P_f is zero, and oscilloscope will display a straight line with slope proportional to the dielectric constant ε and the capacitance C_x of the sample: $\dfrac{dV_y}{dV_x} = \dfrac{\varepsilon\varepsilon_0 A}{Cd} = \dfrac{C_x}{C}$

Pyroelectric properties

Usually the pyroeffect is determined by measuring the charge freed at the electrodes by a change in temperature, with an electrometer: a method, which is neither accurate nor reliable [5]. However, another,

dynamic method has been devised by Chynoweth [6]. The crystal under investigation, heated by exposure to a strong light pulse, produces a pyroelectric current whose value is given by: $i = \dfrac{dP_s}{dt} = \left(\dfrac{\partial P_s}{\partial T}\right)\left(\dfrac{\partial T}{\partial t}\right)$,

where Ps is spontaneous polarization, t the time, and T the temperature. The term is $\dfrac{dT}{dt}$ the rate of change of temperature and is independent of initial crystal temperature, provided the specific heat at constant stress is assumed to be constant in the temperature range under consideration. It is sufficient, therefore, to measure the initial value i_0 of the pyroelectric current in order to measure the pyroelectric coefficient in arbitrary units. To determine the pyroelectric coefficient in absolute units from i_0, it is necessary to know the initial rate of change of the temperature$\left(\dfrac{dT}{dt}\right)_0$, which is difficult to measure accurately.

From the value of the pyroelectric constant measured in a certain interval of temperatures (T_1-T_2) it is possible to calculate, by means of integration, the difference $P_s(T_1)$-$P_s(T_2)$ between the spontaneous polarization. The value so calculated can be compared with that determined from measurements on the hysteresis loop [5].
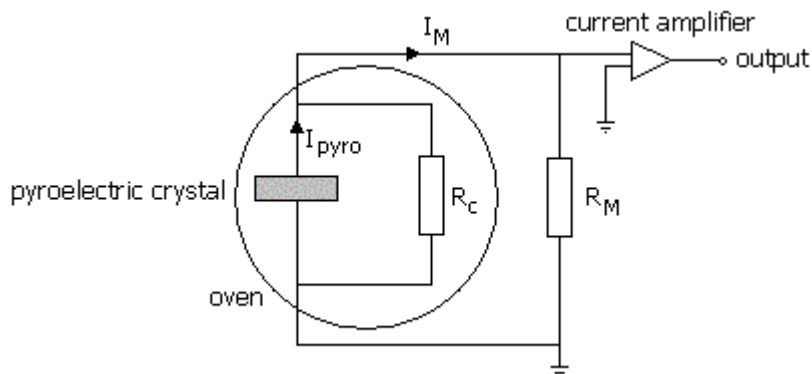

Fig. 9 Experimental circuit for pyroelectric current measurement [7]

A pyrocurrent can be calculated as: $I_{pyro} = I_M\left(1 + \dfrac{R_M}{R_C}\right)$, where I_M is the measured current, R_M and R_C are the input resistances of the amplifier and the leakage resistance of the element, respectively [7].

TGS crystal growth

The crystal obtaining for its next investigation is a separated problem, which was solved by different researchers by the different ways. There two common used methods of TGS crystal growth: evaporation at constant temperature [14] and slow temperature lowering [8,9,10,11]. The raw solution one can easily obtain by reacting a water solution of glycine with proper amount of the sulfuric acid.

Solution preparation

The reaction which product is triglycine sulfate follows next:

$$3NH_2CH_2COOH + H_2SO_4 \rightarrow (NH_2CH_2COOH)_3 \cdot H_2SO_4.$$
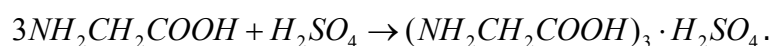
In literature we found two detailed preparation recipes others authors read that "solution easily can be obtained". The W.W Duley and P.J. Finnegan [8] proposed the next recipe: "Large crystals of TGS were grown from a supersaturated (See Fig.10) solution of glycine (Fisher reagent grade). Sixteen hundred grams of glycine in a solution of 10 liters of water at temperature 55^0C are reacted with cP (chemical pure) sulfuric acid until the final solution was in equilibrium at pH 4". This way is not suitable for us because we did not have accurate equipment in the laboratory for measurements of dynamic changing pH.
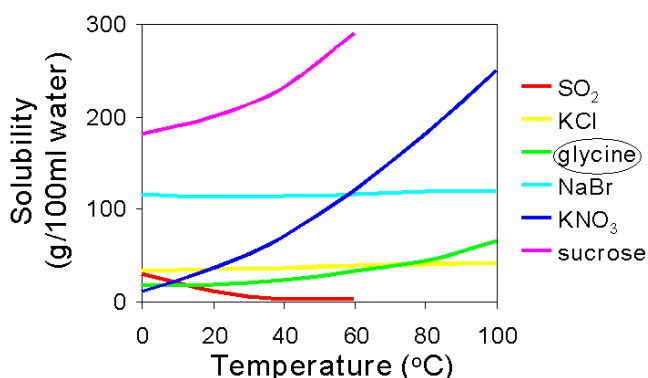

Fig. 10 Solubility of glycine as a function of solution temperature [12]

Another source of the recipe we found in the instruction for doped TGS compounds preparation. Form the German it was translated as [13]: "To the solution of 700 ml of water (deionazed) and 88 ml sulfuric acid one have to add 348.3 g of glycine dissolved in 1.5 liter of deionazed water. Do not exceed temperature 60^0C, better to hold temperature around 55^0C".

In the table that follows we summarized the parameters of the TGS solution preparation and growing for two methods that we found in the literature.

	Method	Temperature	Solution
[8]	Slow temperature lowering	Starting with 55^0C, decreasing to 48^0C	TGS solution is not saturated at 55^0C but very fast evaporates because of high temperature of solution.
[9]	Slow temperature lowering	Starting with 42^0C, decreasing by 0.2^0C/day	TGS solution saturated at 40^0C
[10]	Slow temperature lowering	Starting with 37^0C, decreasing by 0.1^0C /day	TGS solution saturated at 35^0C

[11]	Slow temperature lowering	Starting with 45.9^{0}C, decreasing by 0.4^{0}C /day	-
[13]	Slow temperature lowering	Starting with 55^{0}C, decreasing to 41^{0}C	TGS solution is not saturated at 55^{0}C but very fast evaporates because of high temperature of solution.
[14]	Evaporation at constant temperature	35 ^{0}C	TGS solution saturated at 35^{0}C

We had decided to apply a constant evaporation method for more simplicity and keep a temperature at 35 ^{0}C because this temperature is a nearest to the room temperature and it, on our opinion, leads to the less temperature fluctuation that can disturb a normal growth.

Obvious that it is useful to prepare the solution of the TGS saturated at temperature of its growth for more rapid crystallization. Following the TGS saturation graph (Fig.11) we analyzed the preparation recipes.
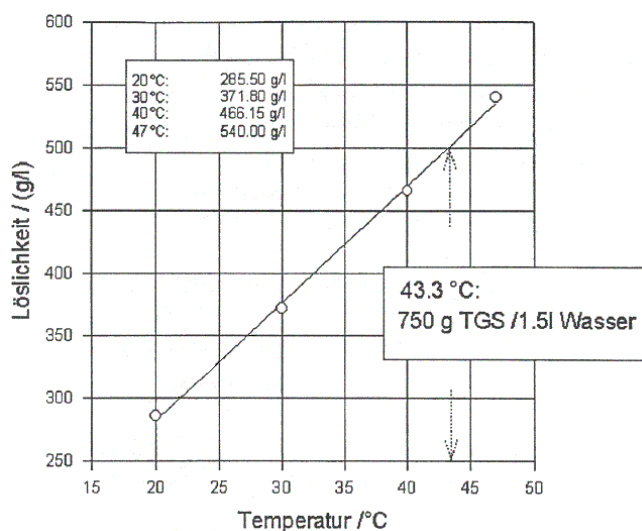

Fig. 11 Solubility of triglycine sulfate as a function of solution temperature [13]

For crystallization we want to get saturated solution of TGS at temperature of 35^{0}C. It means that we want to get in 1 liter of water $\approx 425g$ of TGS. Form the chemical equation we know that $\approx 425g$ of TGS is consisted of 296.1g of glycine and 128.9 g (or 70ml) of sulfuric acid. So we've modified the recipe and now new instruction says: dissolve in 1 liter of water 296 g of glycine and after that add to it 70 ml of sulfuric acid.

	Molecular weight	Comments
Glycine (NH$_2$CH$_2$COOH)	75.07 g/mol	
Sulfuric acid (H$_2$SO$_4$)	98.08 g/mol	Density -1.84 g/sm^2

We take to the account that nuclei of the crystals in saturated solution can appear in a moment and for its prevention we will heat all components to the higher temperature that we need, to a temperature at which the solution is not saturated, for example, 55^{0}C and after successful reaction slowly during (3 days) we will decrease a temperature to 35^{0}C.

Crystal growth method and equipment

We applied a constant temperature evaporation method and for it we had designed and made the crystallizer.
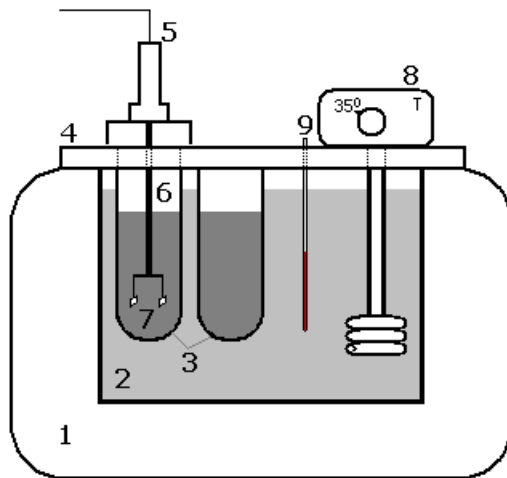

Fig. 12 Schematic diagram of crystallizer: 1 - thermal isolation (foam plastic box filled by plastic foam), 2 – plastic aquarium with water for thermal stability, 3 – crystallizing plastic bottles with TGS solution, 4 – cover from foam plastic for prevention water evaporation from aquarium, 5 – rotating motor[1] for spinning crystals in the solution, 6 – plastic rod for crystal settling down into the solution with thread for crystal holding, 7 – crystal seeds, 8 – thermocontroller with heater and water mixer (Fried-TEP-3), 9 – mercury thermometer.

Processing

- Heat water in crystallizer to 55^0C and keep it for 1 day for thermocontroller stabilization
- Wash up all needed glassware for mixing, plastic spoons, thermometer, crystallization bottles with soap and rinse thoroughly all ware in deionized water
- Heat at hot plate deionized water for glycine dissolving up to 55^0C
- Dissolve in hot water proper amount of glycine
- Add to the solution needed amount of sulfuric acid
- Wait for final reaction about hour
- Place solution in crystallizer's bottle
- Close the cover and keep solution for 3 day for stabilization gradually decreasing the temperature to 35^0C [11][2]
- Take away the cover and let to solution to be freely evaporated
- Collect first seeds of crystals
- Filter the solution[3], add some deionized water, repeat procedure from 8 to10

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[1] It is known that rotation of growing crystal helps to researchers [8,9,10,11] to obtain equal growth for all crystal faces and averts sticking together of monocrystals.

[2] In [13] researchers propose that thermal stabilization and step temperature decreasing to the temperature of crystallization prevents unwanted centers of crystallization.

- Locate 2 small[4] seeds of crystal in solution using crystal holder wire[5]
- Switch on the spinning motor[6]
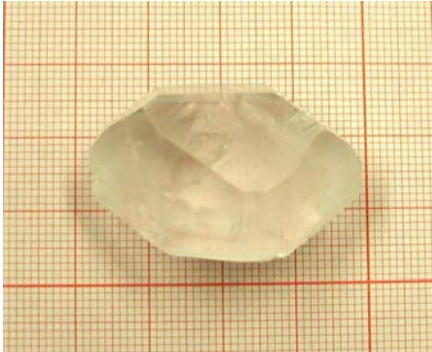- Let to crystals freely grow about 10-15 days

Fig. 13 The grown crystal of TGS (sample 1)

Crystal form and preparation of ferroelectic capacitor

For ferroelectric properties characterization it is necessary to carefully examine the form of obtained crystal so that the crystal can be sectioned along the correct plane. The permanent polarization vector P of TGS is perpendicular to the (010) face of the crystal. Grown crystals must be cleaved along the (010) face [8].

For grown crystal we determined its basic faces by superimposing the crystal on the outline of its faces. The small crystal had only some basic faces (Fig.14a), when the big crystals had quite sophisticated form (see Fig.14b).

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[3] In [11] researcher declare that number repeated filtrations will purify the solution from impurities that have raw materials.

[4] Noted in the experiments that the best quality crystals with more precise face coincidence are grown from the smallest seeds.

[5] We used a plastic wires (wax dental floss) which are sufficient smother than other tried wires.

[6] The speed of rotating is about 42 cycles per minute clockwise. It is about that was kept in [10]. We adapt for rotation used motor from flea market.
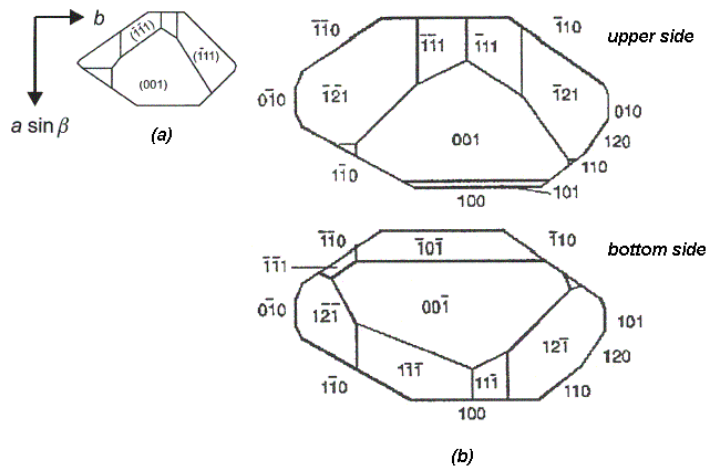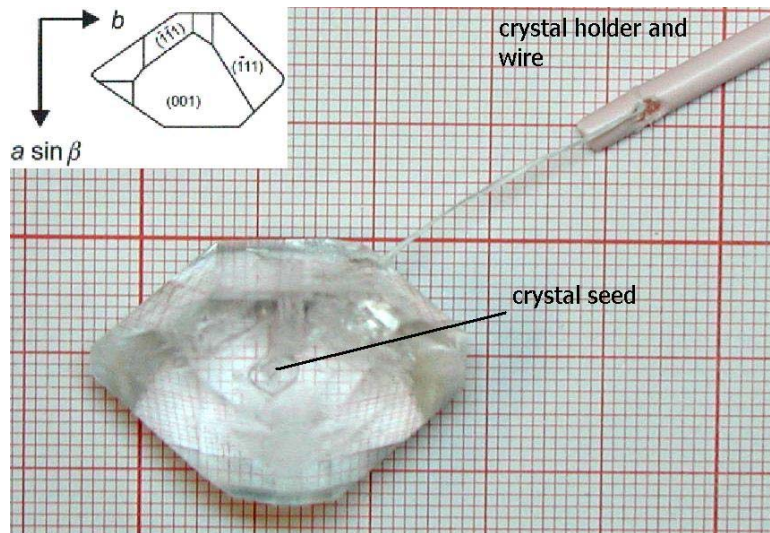
Fig. 14 TGS faces outline [11,13]

Fig. 15 Crystal faces determination

The cleavage along the (010) face (perpendicular to the axis b) brought to obtaining the crystal slices with thickness about 3-4mm.

On the next stage of capacitor preparation we have to polish the slices to the smallest thickness that we can reach. In [8] suggested: "Crystals may be polished satisfactory using fine mineral oil and various meshes of carborundum powder (actually 400-1000 mesh) on a glass flat. A final polish may be accomplished by working on a flat of freshly poured bee wax coated with mineral oil". And in [11] written: "the crystal was sliced by ware-saw on disks with thickness about 2mm. By diamond brush paste the disks were polished to the thickness about 0.3 mm". We have reached the thickness about 0.5-0.9mm by gentle rubbing across medium –fine metal sandpaper and after that polishing by water moisten tissue paper.

Fig. 16 crystal cleavage and thin slide polishing

Electrodes that are needed for capacitor "it is absolutely necessary to paint or evaporate onto the faces" [4]. We deposited electrodes by silver paint.
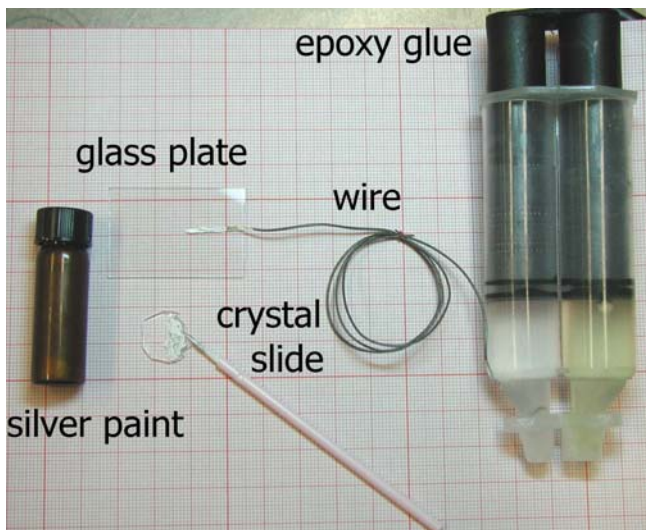

Fig. 17 Capacitor electrodes preparation

And at the end we have placed capacitor and its wires on a glass plate and cover it by epoxy glue (for the prevention all possible damages). The finished TGS capacitor depicted on Fig.18
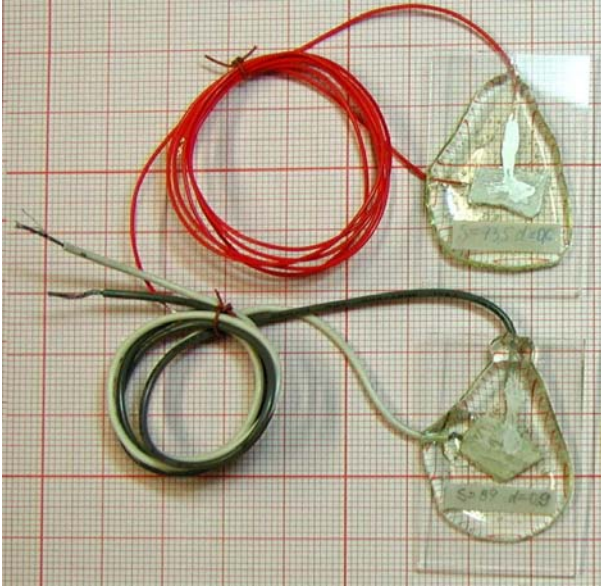
Fig. 18 Finished capacitors

Experimental data

Crystal growth

We have made 5 full process experiments in which we obtained 8 TGS crystals.

Experiment 1

First of all we had tried to grow the crystal *on hot plate without thermal isolation*.

	Comments
Solution	We mixed all ingredients and during the growth we have note that there were a lot of impurities in the solution after first seeds appearing. We supposed that it happened because of dust falling down from ventilation.
Single seed growth	We hold the seed on the cotton thread that has not been rotated. It brought about adhering on a thread undesired secondary crystals.
Final crystal	The crystal had reached a size 20mmX15mmX16mm but it was not a mono crystal but conglomerate of mono crystals that did not have a right form.

Experiment 2

We had made a crystallizer (see on Fig.19) and repeated and experiment.

Fig. 19 Crystallizer

	Comments
Solution	We mixed all ingredients and placed it in the crystallizer and also placed a cover under a bottle with solution but during the growth we have note again that there were a lot of impurities in the solution after first seeds appearing. We supposed that it needed to filter the solution.

Single seed growth	We hold the seed on the cotton thread that had not been rotated.
Final crystal	We got mono crystal and tried to split it but we did not right define a face of ferroelectricity.
Capacitor	The capacitor that we made did not show the hysteresis loop.

Experiment 3

|	Comments
Solution	We had filtered the solution using paper filter. During the growth we have note that still there are a lot of impurities (that we can to see) in the solution.
Single seed growth	We held the seed on the cotton thread and switched on the rotation. On a wire there were undesired secondary crystals but it became less.
Final crystal	We've get one crystal. The crystal reached satisfactory sizes.
Capacitor	We have right determined the ferroelectric face, cleaved it, and made the capacitor but did not cover it by epoxy glue for capsulation. It was nominated as sample 1.
Measurement	We have measure the hysteresis loops for different temperatures.
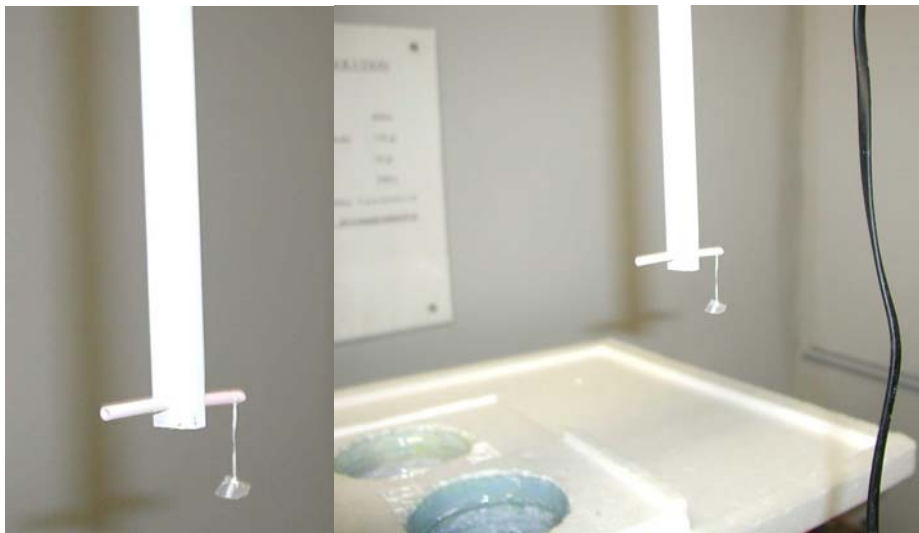
Fig. 20 Crystal holder

Fig. 21 Motor for crystal rotation

For purpose to measure hysteresis loop at different temperatures we had made two measurement units: one for measurements below room temperature, the second –above room temperature. For below room temperature measurements we used the first unit, water in which was cold with ace. For above room temperature measurements we used the second unit, water in which was heated by hot plate.
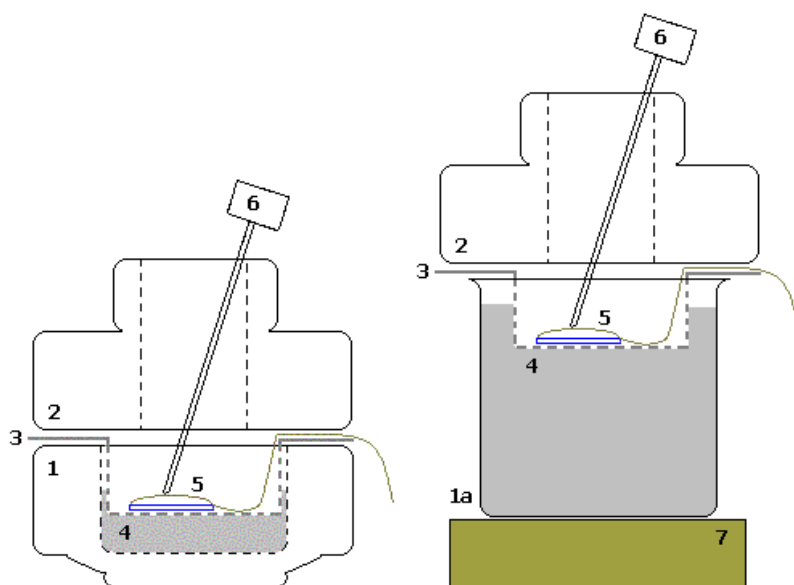

Fig. 22 Thermo isolated units: 1-plastic foam bottom unit, 1a- glass bottle, 2 –plastic foam upper box, 3 – aluminum foil, 4 – water, 5 – TGS capacitor, 6- digital contact thermometer, 7- hot plate.

Experiment 4

	Comments
Solution	We have filtered the solution using tissue paper hand made filter. The solution was quite transparent.
Single seed growth	We held the seed on the plastic thread and switched on the rotation. On a wire there were sufficiently less undesired secondary crystals.
Final crystal	We obtained 2 crystals. The crystals had reached satisfactory sizes. But during the evaporation solution was over and we added supersaturated solution, which was prepared later. It entailed the appearance the layers of different transparency in the crystal.
Capacitor	We have right determined the ferroelectric face and made the capacitor covered it by epoxy glue for capsulation. The slides of crystal are very fragile. For example, from the 8 slides obtained by cleavage two crystals only 2 were saved during the rubbing to desired thickness. Samples 2 and 3.
Measurement	We have measure the hysteresis loops for different temperatures

Experiment 5

	Comments
Solution	We have filtered the solution using tissue paper hand made filter. The solution was quite transparent.
Single seed growth	Before placing the seeds of the crystal in the crystallization bottle we keep solution in the bottle 3 days at temperature 55^0C gradually decreasing to 35^0C for stabilization fluctuation in the solution. We held the seed on the plastic thread and switched on the rotation. On a ware there were sufficiently less undesired secondary crystals.
Final crystal	We obtained 2 crystals. The crystals had reached satisfactory sizes and transparency.

Capacitor	We had not made a capacitor and saved it a whole.

Hysteresis measurement

Data acquisition

The final measurement set up is depicted on Fig.23,24. It consists of: thermo isolated unit, capacity circuit, power supply (we used transformer that converted a grid voltage to an appropriated), and data acquisition instrument (in our case it was oscilloscope Tektronix TDS3012 with hardcopy unit). Within the experiment we heat the sample to the 50°C and keeping it to cold we periodically acquire the data from oscilloscope that was in X(Y) mode (it helps us to see if the hysteresis is disappeared). When a temperature nears to the room temperature we change the thermo-isolated unit and use an ice for the next cooling.
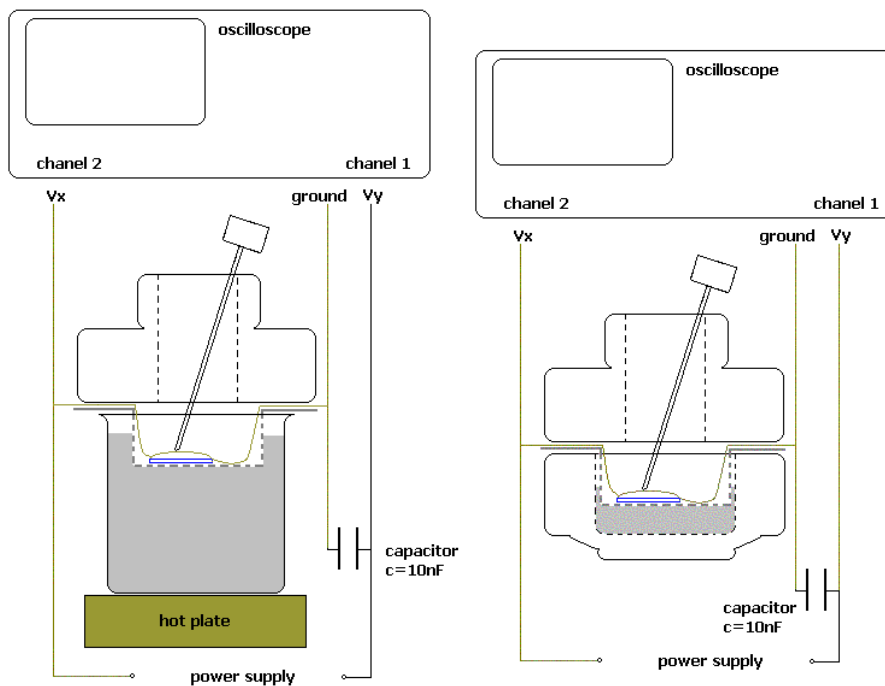

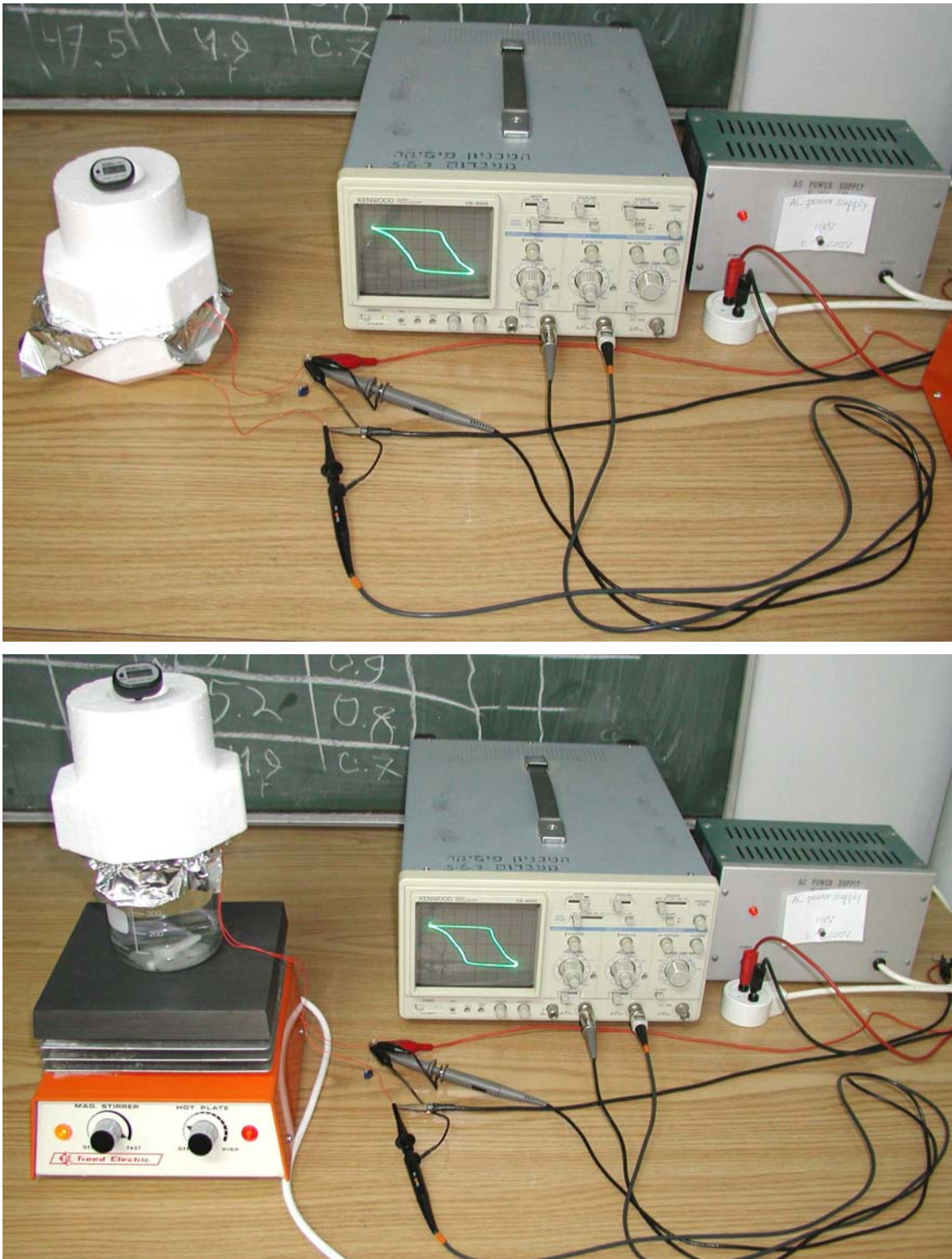**Fig. 23 Measurement sets (schematically)**

Fig. 24 Measurement sets

Fig.25 shows hysteresis loop for the sample that we had obtained in the growth experiment #3. It was capacitor without epoxy capsule and therefore in the time of experiment for temperatures below room temperature capacitor was damaged by condensation vapor from the air. We did not present the data for those temperatures.
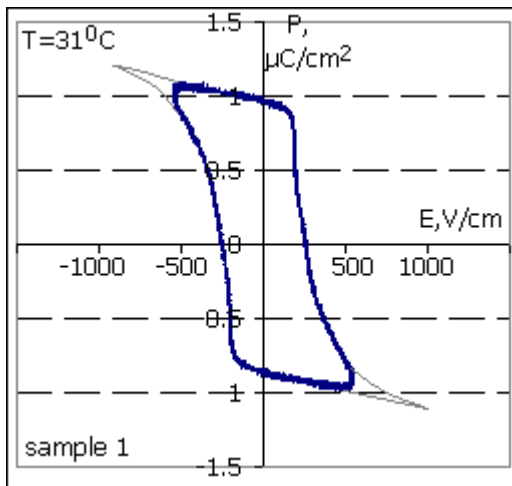
Fig. 25 Hysteresis loop for crystal sample 1.

As it can be seen obtained loop has a hysteresis form. After data analysis for sample 1 we decided to increase a applied field from 1500 V/cm, that we read about it in [2], to 1900V/cm[7] because as you can see it can be assume that field that is equal to 1500 V/cm is not enough (if we look at Fig. a it seems that polarization can amount to the higher value). So we changed the external field to the others samples[8] and polarization loops shown on Fig.26 demonstrate that our assumption was right and for the higher field we may see a "saturation".
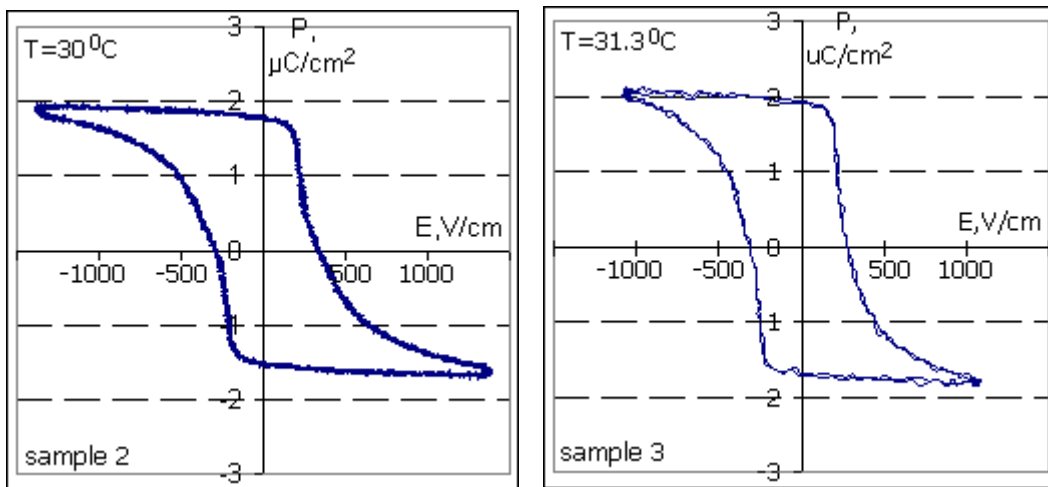

Fig. 26 Hysteresis loops for sample 2 and 3

On the Fig.27 we can see a characteristic form of the polarization curve. From the data we can say that for sample 1 Curie temperature is 44 ± 2 ^{0}C and polarization at room temperature is a $1.04\pm0.1\mu C/cm^2$. Those values do not adjust with literature very much, but they have a sense.

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[7] It is known that a magnitude of this field is not very important, but it must be sufficient for saturation of the polarization curve.

[8] We increased the field for the sample 2 and sample 3 only because in the time of measurement we damaged the sample 1 by water vapors (It was capacitor without capsulation)
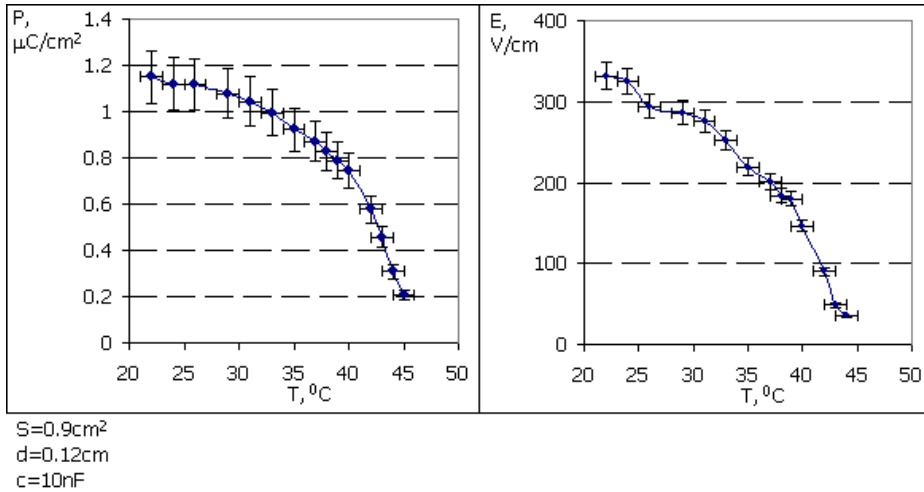
P,
μC/cm²

E,
V/cm

S=0.9cm²
d=0.12cm
c=10nF

Fig. 27 Spontaneous polarization Ps of TGS and Coercive field Ec as a function of temperature (measured with a field of 1500V/cm at 50Hz). Sample 1.

The spontaneous polarization dependence on temperature for the sample 2 and sample 3 are shown on Fig.28. We see a better agreement in the values of spontaneous polarization:

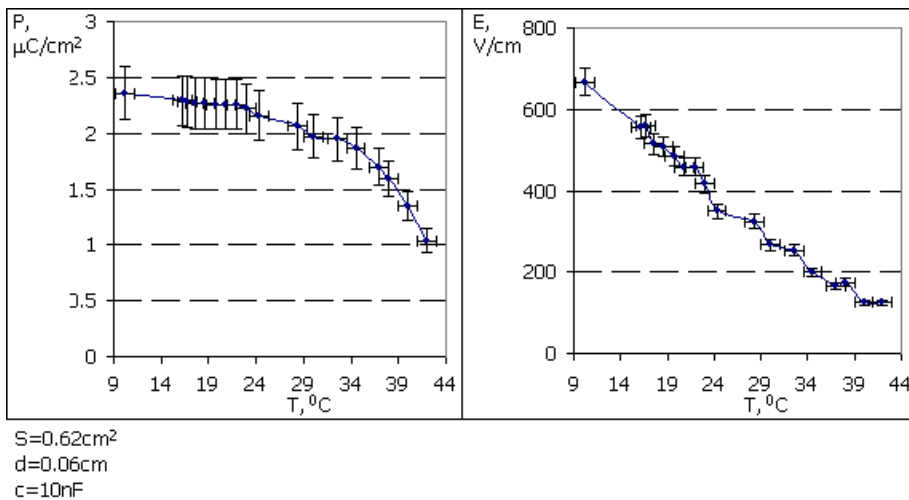|	$T_{curie}, {}^0C$	P_s, μc/cm² at room temperature	E_c, V/cm at room temperature
Expected [2, 5]	49	2.8±0.54	430±80
Sample 2	42±1	2.26±0.39	458±51
Sample 3	40±1	2.30±0.40	475±53

P,
μC/cm²

E,
V/cm

S=0.62cm²
d=0.06cm
c=10nF

Fig. 28 Sample 2: Spontaneous polarization Ps of TGS and coercive field Ec as a function of temperature (measured with a field of 1900V/cm at 50Hz).
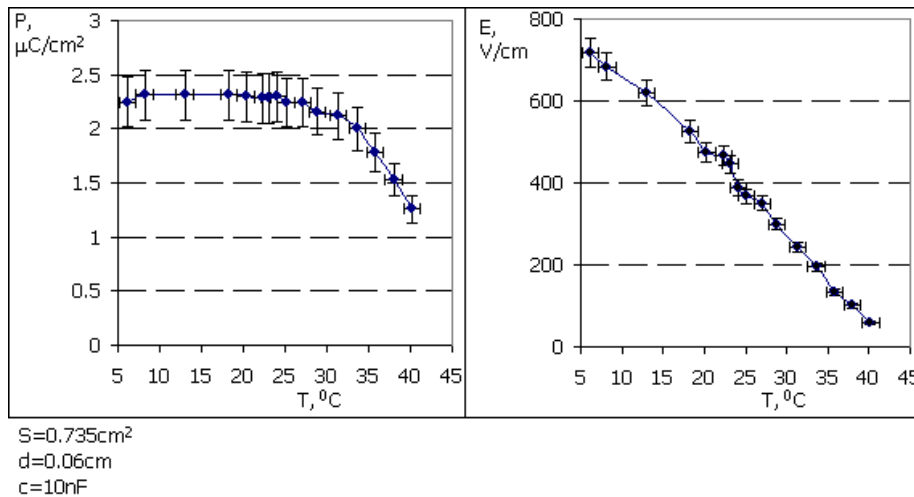
S=0.735cm²
d=0.06cm
c=10nF

Fig. 29 Sample 3: Spontaneous polarization Ps of TGS and Coercive field Ec as a function of temperature (measured with a field of 1900V/cm at 50Hz).

Data analysis and conclusions

We think that we had obtained the data that have a sense. The reasons why we have deviation from the literature results are following:

1. Solution preparation. We suppose that impurities in solution leaded to imperfect results. Our assumption we can confirm by observation presented in [14]. Researchers doped the solution of TGS by different dopants for detailed investigation the TGS pyroelectric properties. They tried to make better, from the point of view of its application as an active element of pyroelectric infrared detector, electric properties of TGS by doping it with lysine. They perform the graph of spontaneous polarization (see Fig.30). We can note that doping changes the magnitude of spontaneous polarization sufficiently.
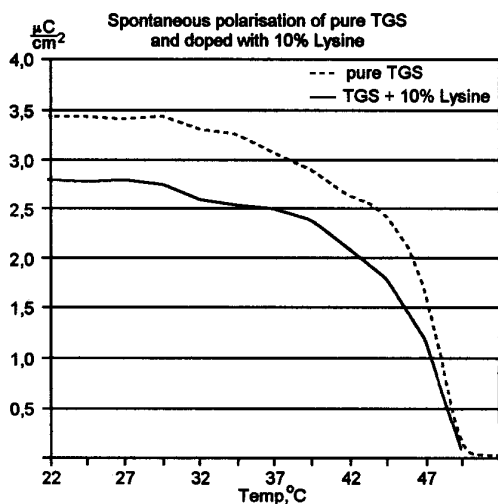

Fig. 30 Spontaneous polarization doped TGS crystals [14]

In the other article [15] we can read that one doping material in the different condition of growth can change the electrical properties by different ways (see Fig.31).
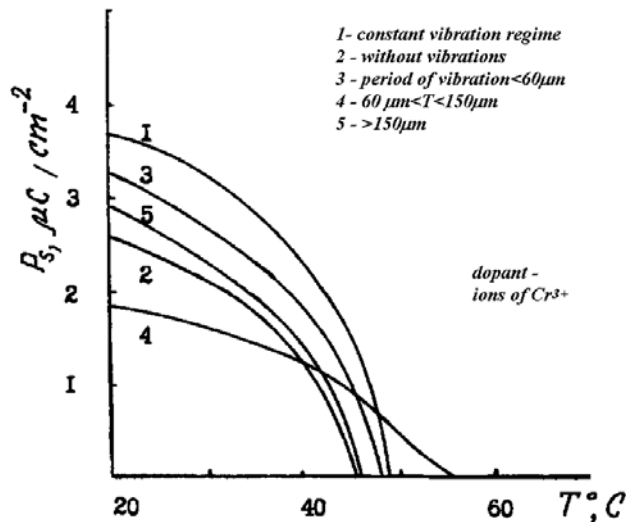
Fig. 31 Spontaneous polarization doped TGS crystals [15]

So we can say that the strong impact of impurities does not clearly understood and forecasted. We think that there are some possible sources of impurities in our experiments:

- Raw material (Glycine has % of initial impurities, sulfuric acid was chemically pure)
- Water (we used a deionized water that had acid reaction)
- Paper Filter (we used tissue paper that did not be special cleaned from dust)
- Thread (cotton or plastic were not specially cleaned)

2. Crystal growth. Also possible that constant temperature evaporation is not the best method and using another method more perfect results may be achieved.

3. Capacitor. Errors in ferroelectric face determination can also have effect on spontaneous polarization magnitude. An additional errors are appeared when we rubbed the crystal manually without control that plates of the slides are parallel one each other and to the ferroelectric face. We have to note that capsulation with epoxy glue also is not especially reliable, because in the dried up glue there are a lot of bubbles with air that may leak.

4. Measurement. It is absolutely clear that more stable control and measurement of temperature permits to improve the results.

Pyroelectric current measurement

Measurements can be made with crystal placed in the sample chamber [16] shown on Fig.32. for noise prevention.
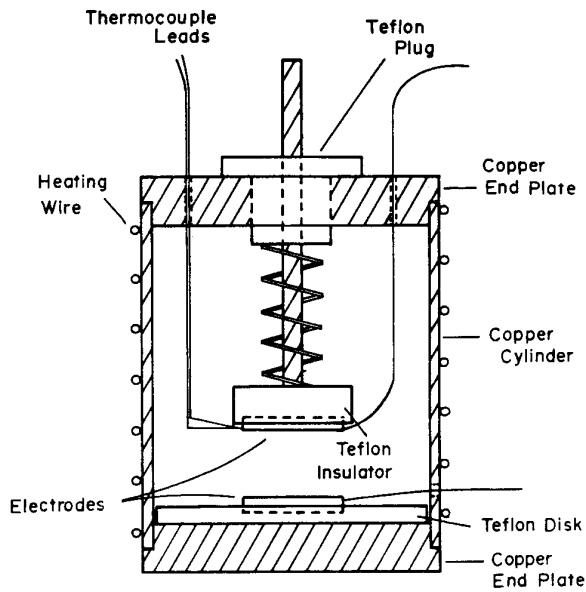
Fig. 32 Experiment chamber for measurement pyroelectric current [16]

We had tried to use capacitors that we made for previous experiments. We expected that in the circuit with current amplifier we could detect the pyroelectric current.

In practice, the pyroelectric element is coupled to the outside world by means of an integrated low-noise buffer amplifier. Because the detectors behave like capacitors with very large impedance and low signal levels, the design of these amplifiers is critical. Two techniques for amplification are commonly used: voltage mode and current mode. In the voltage mode scheme, the output signal or current from the pyroelectric element produces a voltage across the buffer amplifier's input resistor. This high impedance level signal is transformed with an FET source follower into a signal with more usable low impedance. In this configuration, the frequency response of the detector is determined by the RC constant of the detector and the input load resistor, and the output signal level is simply the product of the pyroelectric current and the "lumped" impedance of the detector and the load resistor. The current mode amplification scheme uses an operational amplifier connected as a current-to-voltage converter where the current gain or output voltage is determined by the impedance of the feedback loop. Each amplification scheme has limitations; the application should determine the choice.
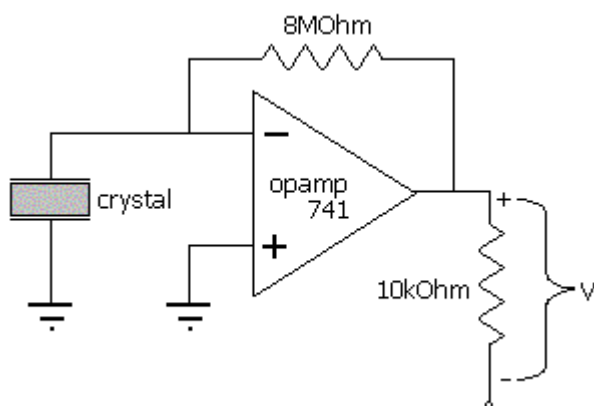

Fig. 33 Experimental circuit (current-to-voltage mode) [17]

We assemble the circuit on demonstration plate but it was misfired. The noise from different sources disturbed the signal.

Conclusions

- We have built the crystallizer
- We have made 5 growth experiments
- We have grown 8 TGS crystals
- We have made 7 capacitors
- We have made 2 measurement isolated sets
- We have made 3 measurements of hysteresis loop for different temperatures
- We have achieved quite good results in comparison with literature [2]
- We tried to make a pyroelectric current detection circuit but did not be successful.

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