CHAPTER- II

PREPARATION OF THE SAMPLES

AND

DIELECTRIC HYSTERESIS

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PREPARATION OF THE SAMPLE AND DIELECTRIC HYSTERESIS

: Part I : Preparation of the Sample :

2.1 Introduction:

Since the days of Rochelle salt the existence of a hydrogen bond had been considered as one of the necessary conditions for the occurance of ferroelectricity. The ferroelectricity of barium titanate ($BaTiO_3$) was now a radical departure from this hypothesis. Barium titanate is, to date the most extensively investigated ferroelectric material. Barium titanate is extremely interesting to study because it is chemically and mechanically very stable and secondly because it exhibits ferroelectric properties at and above room temperature. Barium titanate is again so studied because it can be easily prepared and used in the form of ceramic polycrystalline samples.

The anamolous dielectric properties of barium titanate were, in fact, discovered on ceramic specimens through studies carried out independently from each other around 1943 by Wainer and Salomon in the United States, Ogawa in Japan and Wul and Goldman in Russia. The ferroelectric activity of $BaTiO_3$ was reported in 1945-46 by Von Hippel and co-workers, and independently by Wul and Goldman. Barium titanate differs from the other ferroelectrics in that other phase transitions occur at lower temperatures. The Curie point of $BaTiO_3$ is at 120°C and the phase below 120°C is tetragonal, with point group 4 mm. The tetragonal phase is stable from 120°C to about 5°C. Below 5°C, a new phase appears, which has orthorhombic symmetry belonging to point group mm. This phase is still ferroelective, but the direction of spontaneous polarization is now parallel to one of the original cubic $\langle 110 \rangle$ directions.

The first single crystals of barium titanate were produced in Switzerland in 1947. The publication of Remeika's method in 1954 made available the large single crystals easily. Measurements of many physical quantities were carried out on single crystals. Nevertheless, a very considerable amount of work has been and is being done on polycrystalline specimens ("ceramic") of $BaTiO_3$ and its modifications. The predominant reason for these studies, however, stems from the many applications of ceramic $BaTiO_3$ in various fields of engineering.

Lead titanate belongs to the perovskite family of ferroelectrics like barium titanate. $PbTiO_3$ is terroelectric at room temperature and has the highest Curie temperature (490°C) known among perovskite-type ferroelectrics as reported first by Shirane et al (1950). Most of the experimental results were obtained on ceramic samples. Single crystals can be grown with flux methods but not as easily as in the case of $BaTiO_3$, mostly because of the loss of PbO at higher temperatures. Both the specific heat and specific volume exhibit large anomalies at the transition. The dielectric constant of $PbTiO_3$ has been measured as a function of temperature, only with ceramic samples. As for spontaneous polarization P_s , no reliable data are available to date, although it is known that the value of P_s is considerably larger than that for $BaTiO_3$. More quantitative treatments of the ferroelectric phenomenon in $PbTiO_3$ have been carried out by the Russian workers. The theory indicates that the character of the internal field distribution in $PbTiO_3$ is qualitatively the same as in $BaTiO_3$, but that the fields are stronger in the former case. The calculated value of spontaneous polarization of $PbTiO_3$, at room temperature, is 81×10^{-6} C/cm^2 and is thus about three times larger than for $BaTiO_3$. For $PbTiO_3$, the ferroelectric to paraelectric transition is of first order, and transition temperature T_c decreases with pressure with an initial slope, reported by G. A. Samara (1972) of U.S.A. Latent heat associated is 350 ≠ 45 Cal/mole and corresponding entropy change 0.46 ≠ 0.05 cal/mole°K.

A great number of solid solution systems involving $PbTiO_3$ have been investigated. Concentration of Pb ions greatly affects two lower transition temperatures of $BaTiO_3$ in a system $(Pb, Ba)TiO_3$. In the system $(Pb, Ca)TiO_3$ the composition $(Pb_{0.5}, Ca_{0.5})TiO_3$ has been studied more recently by Sawagnchi et al (1956,59) with particular attention to the problem of aging of ferroelectric ceramics. Properties of dielectrics (dielectric nonlinearity) in $(Pb,Sr)TiO_3$ which offer promise in applications such as voltage variable capacitors in automatic matching circuits and are reported by C. R. Griffiths (1977). Sawaguchi and Charter (1959) studied the aging effect in ceramic samples of $(Pb_{0.5}, Ca_{0.5})TiO_3$, whose Curie point lies in the vicinity of room temperature. They found that the effect could be explained by the slow separation of the solid solution into two phases in the course of time.

2.2 Preparation of the Sample:

In the present study we aim to prepare ferroelectric solid solutions and systems of $PbTiO_3$, $CaTiO_3$, $SrTiO_3$ in the ceramic form. $PbTiO_3$ has the highest Curie temperature known among perovskite type ferroelectrics. Almost any substitution of Pb or Ti with suitable atoms which are likely to form perovskite type lattice causes a lowering of the Curie point. Number of solid solution systems involving $PbTiO_3$ were studied. Curie temperature depends upon composition when Pb is replaced by Ba, Ca or Sr. In all three cases considered the Curie point decreases almost linearly with increasing concentration of the substituting atoms. The axial ratio c/a of the tetragonal solid solutions at room temperature decreases accordingly. The problem of preparation of ceramic ferroelectrics was dealt in the third international conference held at Edinburgh, Scotland on 10-14September,1973. A hard ceramic body can be easily prepared by way of standard sintering procedures at temperatures of the order of 1350-1450°C and the shape of the ceramic body can be easily modified to suit a number of practical requirements. Under suitable conditions, the ceramic can be polarized in any given direction by the application of a strong d.c. field. These ceramics can then be used as electromechanical transducers in a number of applications. If we compare the properties of ceramics with those of single crystals we will meet some which are, obviously, almost identical in the two cases, and some which are not. Among the former we might include the transition temperatures, the specific heat, the lattice constants and generally, most of the physical properties measured in the cubic phase, such as the Curie constant. It should be noted that, however, most of the result obtained with ceramic samples must be corrected for porosity before they can be considered representative of the material investigated. It is evident, for example, that the dielectric constant actually measured on a ceramic specimen will be a function of the number, the shapes, and the dielectric constant of the pores. Correction formulac have been worked out, and tested experimentally, by Rushman and Strivens (1947). Roberts (1950) has shown, for the cases of

$BaTiO_3$ and $PbZr\ O_3$, that the Curie constant is also a function of porosity.

2.3 Preparation of ($PbTiO_3$ + $SrTiO_3$) :

In order to prepare $PbTiO_3$, the mixture of lead carbonate and titanium dioxide were taken in 1:1 molar proportion, i.e. 13.365 gm. of $Pb\ CO_3$ and 3.99 gm. of TiO_2, in platinum crucible and kept in a globar furnace which was heated to 900°C. This temperature is to be maintained constantly by two hours. At this temperature lead carbonate gets decomposed and CO_2 (carbon dioxide) easily escapes. The reaction can be shown as.

$$PbCO_3 + TiO_2 \longrightarrow PbTiO_3 + CO_2$$

The remaining melt is $PbTiO_3$ which is cooled slowly. This melt after cooling was well powdered by agate mortar so as to be a fine powder. Similarly strontium titanate ($SrTiO_3$) was prepared, viz. 7.39 gm. of $Sr\ CO_3$ and 3.99 gm of TiO_2 were mixed and heated in a furnace to a temperature of 900°C. The carbon dioxide easily leaves and remaining melt is $SrTiO_3$. The reaction taking place is

$$Sr\ CO_3 + TiO_2 \longrightarrow Sr\ TiO_3 + CO_2$$

Now these fitauate solid solutions in 1:1 molar ratio by well powdering were throughly mixed and heated in a furnace to temp. of 900°C. At such a high temperature the mixture becomes uniform because any trace of CO_2 if it remains, gets easily removed. The remaining mixture or is ($PbTiO_3$ + $SrTiO_3$). This solid solution is again well powdered by agate mortar so as to become a homogeneous mixture. The homogeneous powder was introduced in the pellet dye to prepare pellets. For the pellet formation a pressure of 5 tonns was given by Brahma's pressure machine. These pellets were sintered and then used for experimental purpose.

2.4 Preparation of ($PbTiO_3$ + $CaTiO_3$) :

For the preparation of $CaTiO_3$, 5.001 gm of $CaCO_3$ and 3.99 gm of TiO_2 were mixed and heated in a furnace to 900°C. Carbon dioxide gets removed and decomposition takes place as

$$CaCO_3 + TiO_2 \longrightarrow CaTiO_3 + CO_2 \quad .$$

Well powdered Ca TiO_3 and $PbTiO_3$ were mixed uniformly in 1:1 molar ratio and heated to 900°C. The melt remained was ($PbTiO_3$ + $CaTiO_3$). In a similar manner pellets were prepared for the use of experimental purpose.

The samples, i.e. individual carbonates and titanium dioxide taken for the preparation of solid solution titanates were of BDH and of L.R. grade.

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Part II : DIELECTRIC HYSTERESIS

2.5 Introduction:

$PbTiO_3$ (lead titanate), $CaTiO_3$ (Calcium titanate), and $SrTiO_3$ (strontium titanate) belong to the family ABO_3 of ferroelectrics as perovskite type. Their solid solutions, ($PbTiO_3$ + $CatiO_3$) and ($PbTiO_3$ + $SrTiO_3$) have Curie temperature 490°C each, Mitsui T.(1969). The dielectric of (Pb,Sr) solid solutions at low temperature and high pressure (the range $\kappa < 0.1$) near the ferroelectric transition were also investigated and revealed several quantum effects and demonstrated that these resulted in a deviation from the Curie-Weiss law. The pressure of lead ions in perovskite solid solutions affects their physical properties. The dielectric constant along the ferroelectric direction obeys the Curie-Weiss law.

$$\epsilon = \frac{C}{T - T_C}$$

upto some hundredth of degree above the Curie temperature T_C. C = Curie-Weiss constant. The dielectric constants under different conditions were reported for perovskite type crystals like barium titanate by many research workers.

2.6 Coercive Field:

Coercive field is given from the figure of hysteresis loop for the fermagnetic substances (Fig.1.2, Chapter I) by measuring the length OD is generally identified with the threshold field at which almost all domain walls can begin to more. For ferroelectric substances, on the contrary the threshold field is fairly lower than the coercive field as is observed for most crystals. For $BaTiO_3$ single crystal, for example, the threshold field is written a few hundreds of volts/cm at room temperature, while corresponding coercive field is several hundred volts/cm or higher for 50 Hz alternating field. Thus for ferroelectric substances the coercive field is not deyermined by the threshold field, but will be determined by the characteristics of the movement of domain wall under external field.

The coercive field can be represented in terms of the movement of domain walls, and hysteresis loop can be related with movement of domain walls. These above statements can be explained by taking simple example of $BaTiO_3$. For $BaTiO_3$ single crystal which has only 180° domains, the dependence of the coercive field on applied field, crystal thickness and temperature was observed. Furthermore, it has been found the imperfections affect the hysteresis loop, and double loop may be formed, if the crystal is heavily stressed, Shirane (1955). These effects have been used in interpreting the various features of the damage in crystals such as 'Rochelle Salt' and triglycine sulfate caused by r-ray irradiation as showed by Chynoweth (1959).

2.7 Theoretical Expression fof Coercive Field:

Theoretical expression for coercive field can be obtained by considering the following:

Let us assume that the growth of the 180° domain is mainly caused by the forward growth of the domain i.e. the growth in the direction of applied field. This assumption is based on the direct observation of the forward growth by Merz (1954). It is assumed further that the switching time of the domain is determined mainly by velocity of the forward growth, the 'coercive field' can be determined as follows.

Now let us call the velocity of the forward growth of the domain V_C . Assuming that all domains have nearly the same magnitude of polarization and behave similarly in the applied external field, the following relations can be obtained.

$$d_0 = \int_0^{t_s} V_c \, dt = \int_0^{E_c} V_c \frac{dt}{dE} \, dE.$$

Where d_0 is the thickness of the crystal, t_s is the switching time and E_c is the coercive field. E is related with t, by certain functional relation. For the sinusoidal wave $E = E_0 \sin Wt$, where E_0 is the amplitude of the applied field and W is the angular frequency. Then using the relation

$$\frac{dE}{dt} = E_0 W \sqrt{1 - \left(\frac{E}{E_0}\right)^2}$$

then this equation becomes

$$d_o E_o W = \int_0^{E_c} V_c \frac{dE}{1 - (E/E_o)^2}$$

From this relation the coercive field can be calculated if the dependence of V_c on E is known.

2.8 Hysteresis Loop:

Since the hysteresis loop is a feature common to all ferroelectrics. Thus it is convenient to study their phenomenological properties by studying the loop. The hysteresis loop of good single crystals of $BaTiO_3$ exhibit rather sharp corners and a marked rectangular appearance. The following parameters describe a hysteresis loop.

1) The spontaneous polarization P_s , which is the polarization present in the ferroelectric crystal in the absence of external fields. P_s obviously equals the product of the number of dipoles per unit volume multiplied by the moment of one single dipole. When the temperature is decreased P_s usually increases rapidly on crossing the curie point and reaches a saturation value at low temperatures.

2) The coercive field strength E_c which is detined in Fig. (1.2) of chapter I, as the value of the external field required to make the reverse spontaneous polarization zero. E_c depends not only on the temperature but also on the measuring frequency and on the wave form of the applied voltage.

3) The slope of the hysteresis loop connecting P and E for the value E = o of the applied field, this slope equals the susceptibility X_F obtained by measuring the polarization and applying the field along the ferroelectric axis.

The field at which the polarization reverses its direction depends also upon the time that it is permitted to take for the reversal. Thus the shape of hysteresis loop depends on the rate at which the loop praversed. On the basis of exponential law found experimentally by Merz (1954), the formula is

$$\frac{dP}{dt} = F(P)\, e^{-\alpha/E(t)}$$

Where the function F (P) takes into account the fact that the switching rate depends on the extent to which the crystal has already reversed its polarization.

2.9 Effect of Internal Stress on Hysteresis Loop:

We know that internal stresses influence the stability of domains. Suppose, at first there are no internal stresses in the crystal. Since in the experimental condition when the external field is applied by a constant voltage source, the polarizing charges on the surfaces which are caused by the movement of domains are always compensated by the charges on the electrodes, then the state of the crystal which is fully polarized in one direction will not be stable. Because by the appearance of domain walls the free energy of the crystal is increased by the energy of the boundaries. On the contrary, if certain internal stresses exist in the crystal, the state with a certain domain configuration may become most stable, because the internal stresses will be relaxed by the appearance of domains. Therefore, for such crystals the original state with a certain domain configuration may be restored, when applied field has been removed. Thus the internal stresses will act on the domain walls as a sort of restoring forces.

2.10 Experimental Details:

The ferroelectrics are the class of pyroelectric crystal for which the direction of spontaneous polarization is reversed. Thus the basic criteria for the ferroelectric materials is the appearance of proper hysteresis loop on the Cathode Ray Oscilloscope (C. R. O.) connected in the Sawyer and Tower circuit. The modified form of the Sawyer and Tower circuit (1930) Fig. (2.1) was used for the observation of the dielectric hysteresis. Hysteresis loops can be observed very easily on the screen of C. R. O. by introducing the pellet in a crystal holder in the modified circuit using a.c. field (usually 50 Hz). According to Fig. (2.1), C_x- the capacity of the crystal, C_o the oil filled condensers, and C the gang condenser which is connected in series with the crystal. The voltage across the crystal C_x is applied to

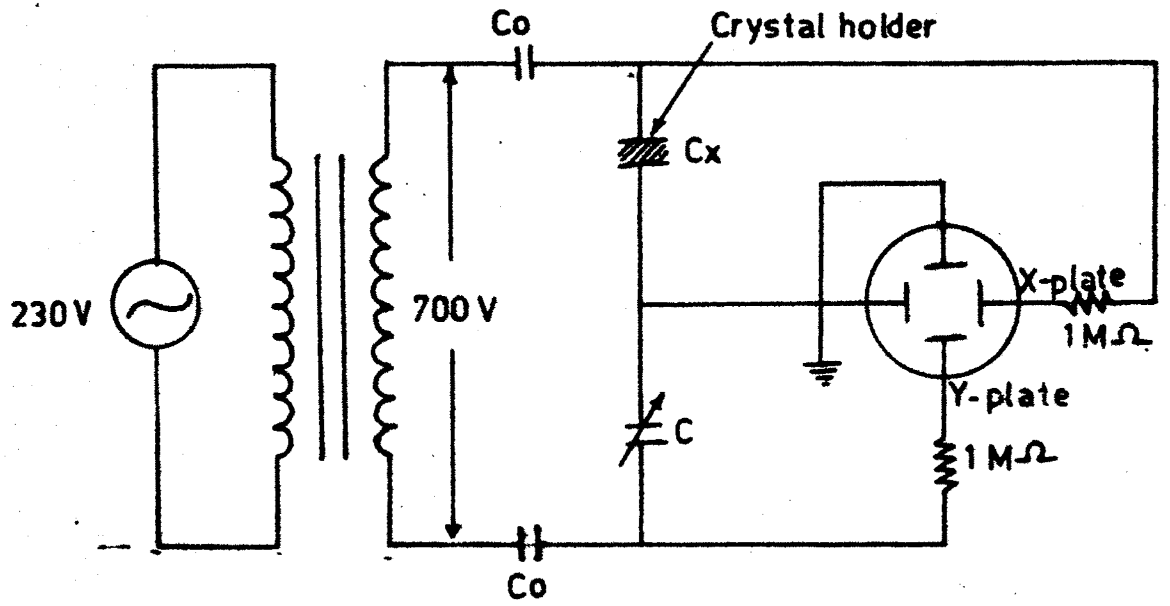


Fig.21:Sawyer-Tower circuit for the display of the hysteresis loop (Modified form).

horizontal plates of the oscilloscope. The horizontal deflection is proportional to the field across the crystal. And the voltage across the gang condenser is therefore proportional to the polarization of the crystal Cx . This voltage is applied to the vertical plates of the oscilloscope.

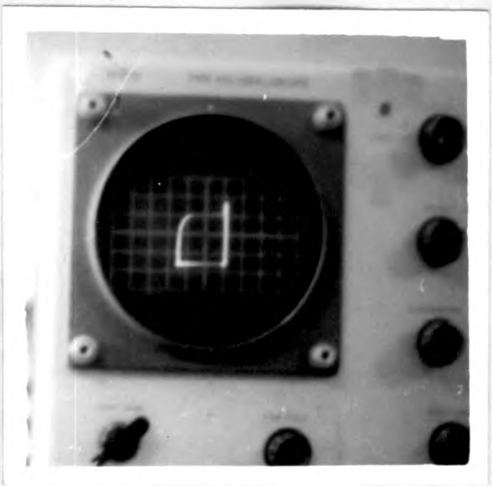
The Sawyer and Tower circuit allows not only the display of the ferroelectric hysteresis loop on the oscilloscope but also the measurement of important quantities such as spontaneous polarization P_s and coercive field E_c .

In The modified form of the circuit two oil filled condensers are used in series. The output of a step up transformer gives output voltage 700^{o}V. A step condenser is used in series with the crystal. The crystal or pellet is mounted in a designed, so called crystal holder. The surfaces of the pellet were made conducting by using a thin paint of silver paste. Two resistances, each one megohm, are used to **avoid** damage of C. R. O. The voltage across the crystal is 1500 Volt/cm. The experimental set-up is shown in Fig. (2.2).

2.11 Hysteresis Loop Of ($PbTiO_3$ + $SrTiO_3$):

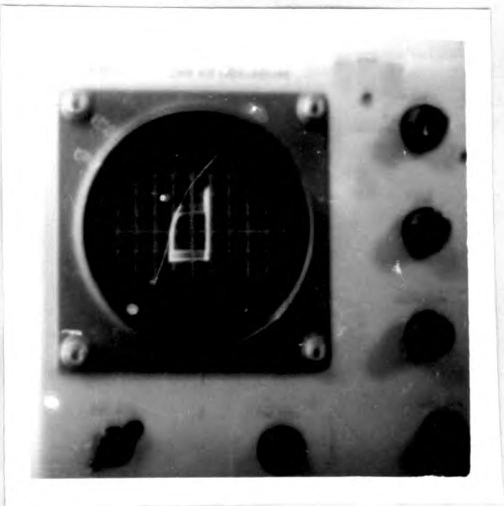
$PbTiO_3$, $CaTiO_3$ and $SrTiO_3$ belong to the family of $BaTiO_3$. The hysteresis loop at different temperatures for $PbTiO_3$ is shown in the photographic figures. Fig. (2.3). The Curie temperature of $PbTiO_3$ is 490°C.

FIG.(2.2)



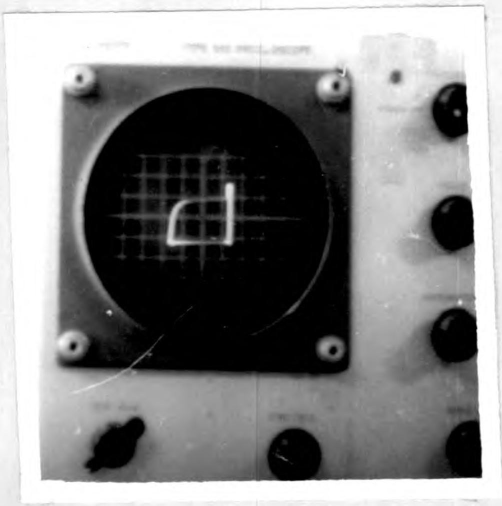
25 °c

100 °c

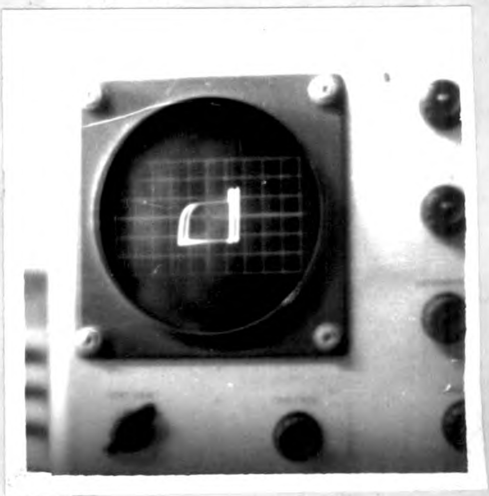


300 °c

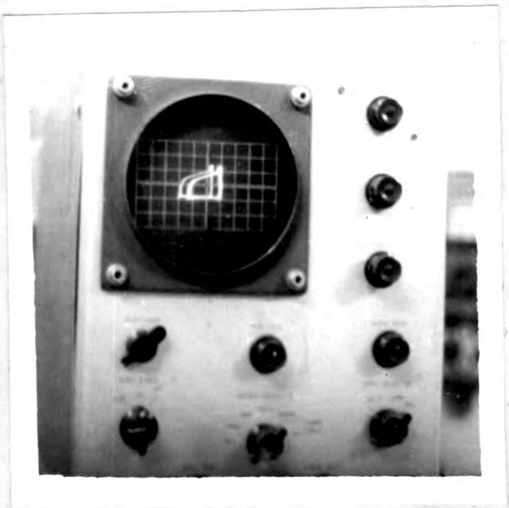
FIG. (2.3)



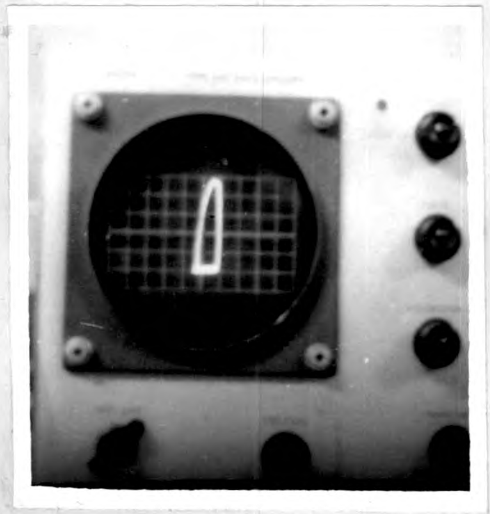
25°c



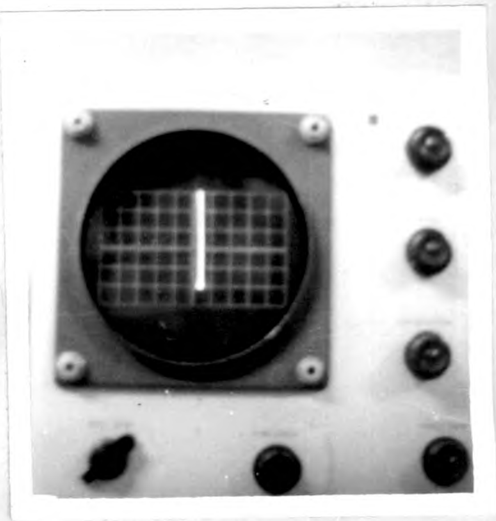
100°c



400°c

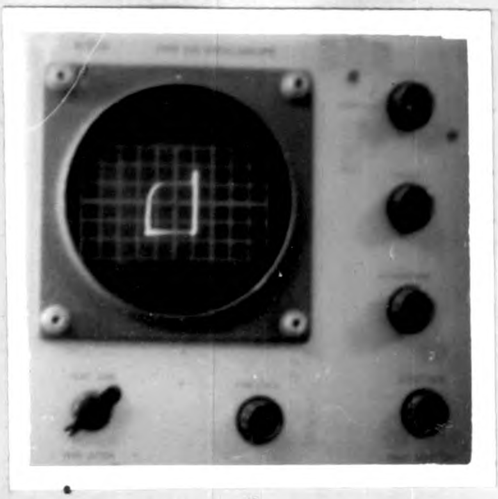


475°c

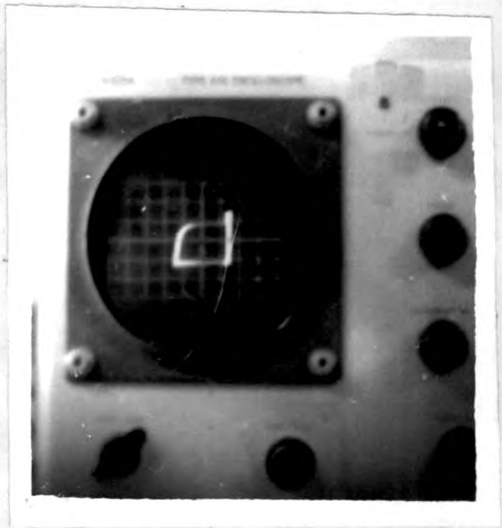


< 490°c

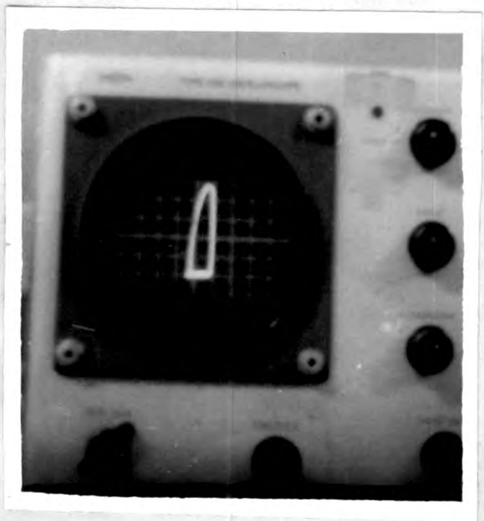
FIG. (2.4)



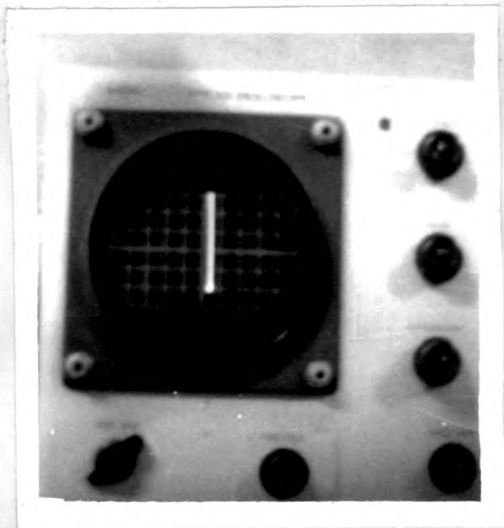
25°c



200°c



475°c



< 490°c

FIG. (2.5)

Hysteresis loop at different temperatures for the solid solution system ($PbTiO_3$ + $SrTiO_3$) is shown in the photographic figures. Fig. (2.4). At room temperature the shape of the loop for the system is also rectangular as for lead titanate single crysal.

The Curie temperature for this system is less than 490°C. As the temperature increases the shape of the loop changes, and at Curie temperature the loop vanishes completely.

2.12 Hysteresis Loop Of ($PBTiO_3$ + $CaTiO_3$):

Hysteresis loop at different temperatures for the solid solution system ($PbTiO_3$ + $CaTiO_3$) is shown in the photographic figures. Fig. (2.5). At room temperature for this sytem also the shape of the hysteresis loop is rectangular. The Curie temperature is less than 490°C. The shape of the loop changes as the temperature increases.

As for the solid solution systems even, the shape of the hysteresis loop is rectangular at toom temperature. As the temperature increases the shape of the loop gets disturbed. In the vicinity of Curie temperature, the near vanish of the loop is observed. At Curie temperature it totally vanishes. From this we can conclude that coercive field is strongly dependent upon the temperature just as it is dependent upon the amplitude and frequency of the applied field. The coercive field decreases as temperature increases. It reduces to zero at Curie temperature. Similarly the case of spontaneous polarization, as the hysteresis loop vanishes at the Curie temperature, the spontaneous polarization decreases as the temperature increases. It reduces to zero at Curie temperature.

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