C H A P T E R - II

PREPARATION OF A SAMPLE AND DIELECTRIC HYSTERESIS

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: Part - I Preparation of a Sample :

2.1 Introduction:

Sodium vanadate is one of the ferroelectric crystals. It does not exhibit ferroelectric properties at room temperature but at higher temperature its properties are well observed. Recently it has been pointed out that several kinds of crystals of XVO_3 type exhibit the ferroelectric properties similar to those of barium titanate. In the field of ferroelectrics research, the physical properties of single crystals of $NaVO_3$ have been studied and it has been reported that this substance is perhaps a ferroelectric. But ferroelectric properties of $NaVO_3$ below $380^{\circ}C$ were reported by Sawada et al (1951). No further evidence on ferroelectricity of this compound seems to have been presented by any other workers.

Sawada et al(1951) had reported that dielectric constant at room temperature is small and only a slight hump was observed near its Curie temperature, $380^{\circ}C$. The shape of hysteresis loop was irregular. The twin structure similar to the domain structure of $BaTiO_3$ was observed. The data concerning the spontaneous polarization at Curie temperature was not reported by Sawada and Nomura (1951).

The structure of $NaVO_3$ has often been classified as one of the perovskite type but it is actually quite different

as was shown by Sorum (1948). The lattice contains VO_4 tetrahedra which shows two corners, and can be regarded as being constructed of infinite linear chains of VO_3^- ions. The importance of this compound in the ferroelectric family is that it seems to be the only example amongst the ferroelectric oxides that does not crystallize with a framework of oxygen octahedra.

Metavanadates of the alkali metals XVO_3 , exist over the entire range from lithium through cesium. Small crystals of all have been grown by slowly cooling stoichiometric melts. Large crystals, allowing extensive property, evaluation were not produced. However, recently, Baughman and Farnum (1970) produced sizeable crystals of KVO_3 .

The first study of solid-liquid equilibria in the system Li_2O-V_2O_5 was made by Canneri (1928), who reported the formation of two intermediate compounds, one a 1:1 salt which melts congruently at about 618°C. Reisman and Mineo (1962), found other additional compounds and confirmed the existence of $LiVO_3$.

A number of compounds also exist in the Na_2O -V_2O_5 system including a composition at 50 mole% Na_2O sodium metavanadate, like $LiVO_{31}$ melts congruently; but at a slightly higher temperature (627 - 638°C), Glazyrin and Fotiev (1964) determined that $NaVO_3$ was monoclinic using

optical techniques, which confirmed the earlier work of Sorum, who reported the space group to be C 2/C and the lattice constants a = 10.14 A°, b = 9.45 A°, C = 5.86 A° and $\beta = 69.58^{\circ}$. Strusievici (1962) reported a polymorph of $NaVO_3$, prepared by dehydration of the crystal hydrate. Sawada and Namura (1950) reported that sodium metavanadate became a ferroelectric above room temperature and exhibited a domain structure and hysteresis in electric fields. Pulvari and Miller et al(1960) however, conjectured that $NaVO_3$ may be antiferroelectric rather than ferroelectric above room temperature.

Potassium metavanadate has been more widely studied which includes highly refined crystal structure analysis and optical studies. Compound formation and phase diagrams for the $K_2O - V_2O_5$ system are also available. From these studies it was evident that KVO_3 melts congruently at a temperature of 520°C, and has an orthorhombic crystal structure with lattice constants $a_o \pm 570$ A°, $b_o = 10.82$ A°, $C_o = 5.22$ A°.

The variation of refractive index and birefringence as a function of cation radius for the alkali metal metavanadate series was studied by Glazyrin (1964). A steep almost linear decline of birefringence was observed with increasing cation radius. The index of refraction also decreased with increasing cation radius, reaching a minimum.

Recently, Hellicar and White (1960) have observed ferroelectric properties in silver vanadate ($AgVO_3$). The Curie temperature is 170°C - 180°C; hence below this temperature it is ferroelectric and becomes Paraelectric above this temperature. The compound, however, is probably not isomorphous with $NaVO_3$.

2.2 Compound Preparation:

In the present study, our aim is to prepare ferroelectric compounds sodium vanadate and potassium vanadate. Since these are alkali metals, the method of preparation of sodium vanadate is similar to that of potassium vanadate.

Plate-type single crystals of $NaVO_3$ were obtained by Sawada S. and Nomura S. (1951) and K. Ramani and M. A. Viswamitra (1974). They obtained plate-like crystals of $NaVO_3$ by slow cooling of the molten 1:1 mixture of V_2O_5 and Na_2CO_3 from 630°C. The crystals were yellowish brown in colour with well developed {100} good cleavage planes. The external forms of crystals are of various kinds of types, i.e. square, rectangular and other ones. Therefore for the preparation of $NaVO_3$ and KVO_3 ferroelectric compounds above method can be adopted.

In our method of preparation of compounds, the mixture of Na_2CO_3 or K_2CO_3 and V_2O_5 in 1:1 molar proportion was heated in the platinum crucible kept in the furnace upto 630°C. Then this molten mixture at this temperature was allowe d

to cool slowly; so that a crystalline solid was obtained. This crystalline solid was then powered in the mortar and that powder was introduced in the pellet-dye to prepare pellets. For the preparation of pellets a pressure of 5 tone is required which is available from Brahma's pressure machine.

2.3 Preparation of $NaVO_3$:

In order to prepare $NaVO_3$, the mixture of 4.24 gms. of Na_2CO_3 and 7.35 gms. of V_2O_5 was heated at 630°C in the platinum crucible kept in the furnace. Na_2Co_3 and V_2O_5 were purchased from the companies K. Chem. Chemicals and Sarabhai M. Chemicals, Baroda, respectively. Both the chemicals were of L-R grade. The mixture gets melted at this high temperature and melt was allowed to cool slowly. At above high temperature sodium carbonate gets decomposed and evolution of CO_2 takes place leaving behind the crystalline solid having yellowish brown colour. This crystalline solid of $NaVO_3$ was observed to be transparent and hard. The chemical reaction that takes place at high temperature can be written as:

$$Na_2CO_3 + V_2O_5 = 2\ NaVO_3 + CO_2 \uparrow$$

The crystalline solid of $NaVO_3$ was then powdered in the mortar and that powder was introduced in the pellet-dye to prepare pellets. For the pellet formation a pressure of 5 tone required which is available from Brahma's pressure machine. These pellets were sintered and then used for experimental purpose.

2.4 Preparation of KVO_3 :

For the preparation of KVO_3 compound, a mixture of 5.52 gms. of K_2CO_3 and 7.35 gms. of V_2O_5 was heated at about 750°C in the platinum crucible kept in the electrical furnace. These chemicals K_2CO_3 and V_2O_5 were purchased from the company Sarabhai M. Chemicals, Baroda. Both the chemicals were of LR grade. Then the molten mixture was cooled slowly. At the temperature 750°C, potassium carbonate gets decomposed and evolution of CO_2 takes place leaving behind the crystalline pink solid. We can write the chemical reaction for above process as follows:

$$K_2CO_3 + V_2O_5 = 2KVO_3 + CO_2\uparrow$$

The crystalline solid of KVO_3 was then powdered in the mortar and powder was introduced in the pellet-dye to prepare pellets. The preparation of pellet requires the pressure of about 5 tone; for which Brahma's pressure machine dan be employed. These pellets were sintered and used for experimental purpose.

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DIELECTRIC HYSTERESIS

2.5 Introduction:

The basic criterion for the identification of the ferroelectric material is that it must show hysteresis loop on the CRO connected in the Sawyer-Tower circuit. Ferroelectric properties of $NaVO_3$ below 380°C were reported by Sawada et al (1951). The dielectric constant at room temperature is amall and hysteresis loop reported, was irregular. The dielectric constant along the ferroelectric direction obeys the Curie-Weiss law:

$$\epsilon = \frac{C}{T - T_c} \qquad \text{- - - -} \qquad (2.1)$$

We know that ferroelectrics are the materials which possess a spontaneous electric polarization P_s which can be reversed by applying a suitable electric field E. This process is known as switching, and is accompanied by hysteresis. See Fig. 1.2. In many ways these materials are electrical analogues of ferromagnetics, in which the magnetization I may be reversed by a magnetic field H.

2.6 Coercive Field:

For ferromagnetic substances " coercive field " is obtained from the figure of the hysteresis loop (Fig. 1.2, Chapter-I). This coercive field obtained by measuring E_c is

identical with the threshold field at which almost all the domain walls can begin to move. On the other hand for ferroelectric substances, threshold field is fairly lower than the coercive field. 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 determined 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 example of $BaTiO_3$. $BaTiO_3$ single crystal has only $180^{o}C$ domains. The coercive field depends on applied field, crystal thickness and temperature. It has been found that the imperfections affect the hysteresis loop, and double loop may be formed, if the crystal is heavily stressed. The theoretical expression for coercive field is given by:

$$do\ Eo\ W = \int_{o}^{E_c} V_c \frac{dE}{\sqrt{1 - (E/Eo)^2}} \qquad ----- \qquad (2.2)$$

Where,

do = thickness of the crystal.

E_o - amplitude of the applied field.

W - angular frequency.

E_c - coercive field.

V_c - Velocity of the forward growth of the domain.

2.7 Effects of Internal Stresses on Hysteresis Loop:

We know that the stability of domains is influenced by internal stresses of the substance. By application of the external field, the polarizing charges are developed on the surface of the substance and these charges are compensated by the charges on the electrodes. The fully polarized state of the crystal will be the most stable, if depolarizing field is completely neglected. This is 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 substance, 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 substances 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 force.

2.8 Experimental Details:

The dielectric hysteresis curve can be obtained on the CRO by using Sawyer and Tower circuit. The modified form

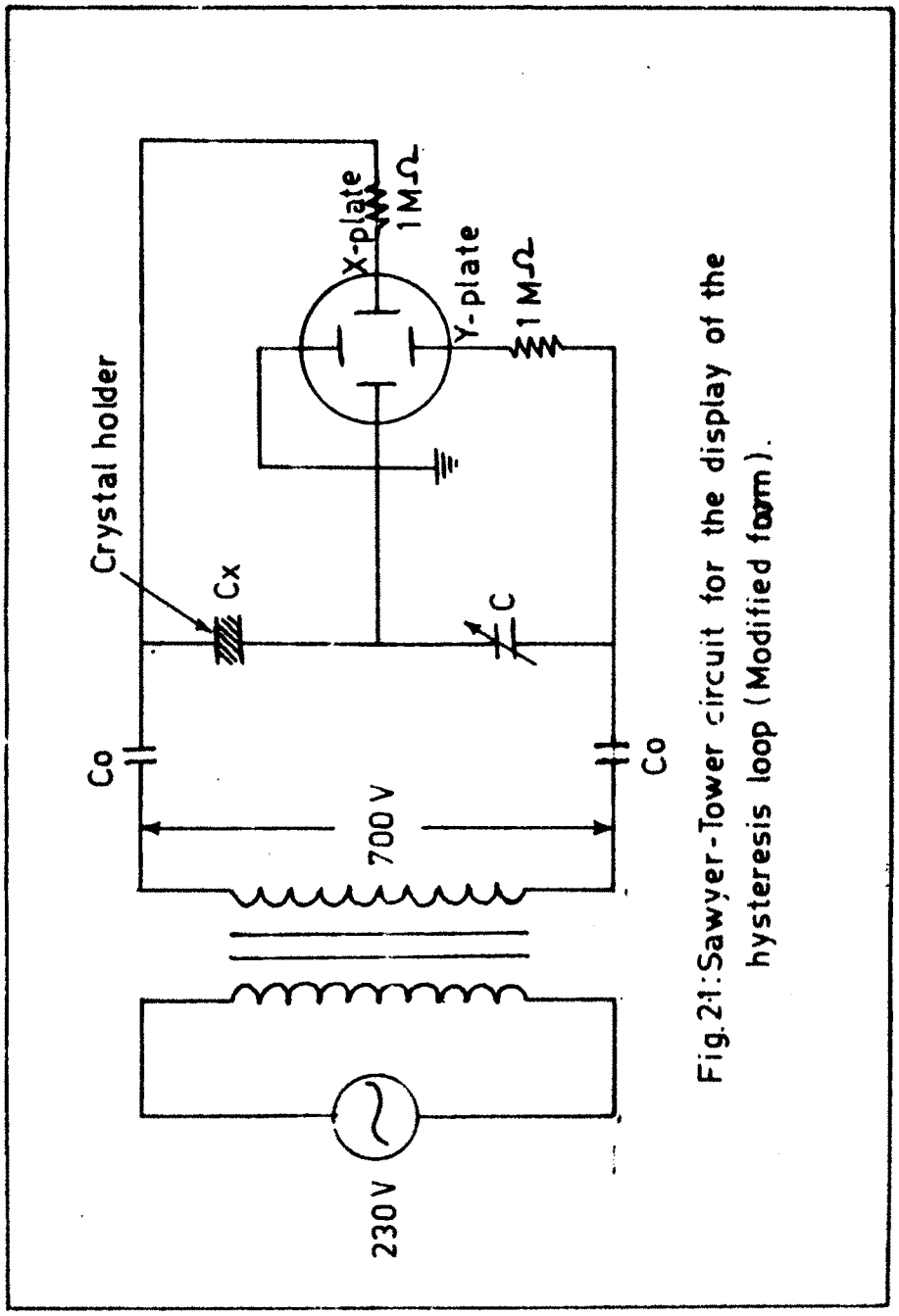


Fig.21:Sawyer-Tower circuit for the display of the hysteresis loop (Modified form).

of Swyer and Tower (1930) circuit is as shown in Fig. 2.1. Hysteresis loops can be observed very easily on the screen of an oscilloscope by inserting the crystal in the modified circuit a.c. field (generally 50 c/s). The voltage across the crystal C_x is applied to horizontal plates of the oscilloscope. The capacitor C_o is connected in series with the crystal C_x. Thus, the horizontal deflection is proportional to the field across the crystal and voltage across C_o is therefore proportional to the polarization of the crystal C_x. This voltage is applied to the vertical plates of the oscilloscope.

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

The experimental set up is shown in Fig. 2.2. In the circuit of Fig. 2.1, two oil filled condensers are used in series. The output of a step up transformer gives output voltage of 700 volts. A gange condenser is used in series with the crystal. The pellet is mounted in a specially designed crystal holder. The surfaces of pellet were made conducting by using silver-paste. Two resistances, each one meg. ohm, are used to avoid damage of CRO. The voltage across the pellet was 1 KV/cm.

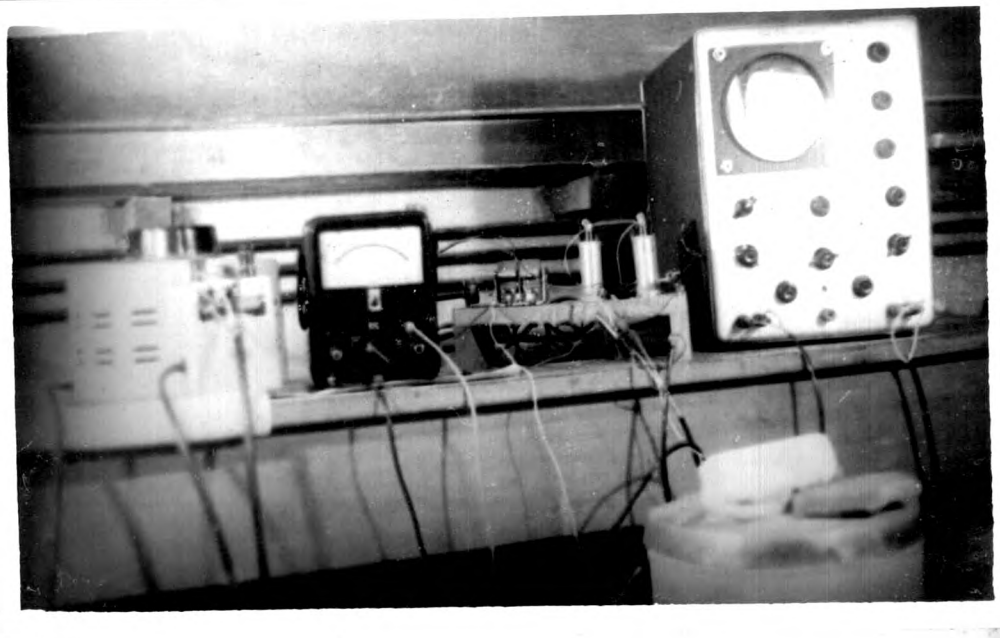
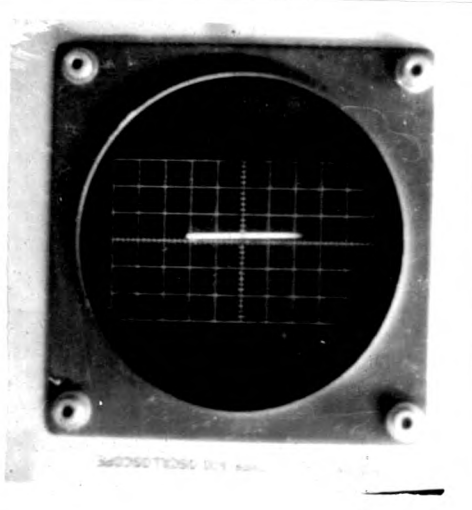
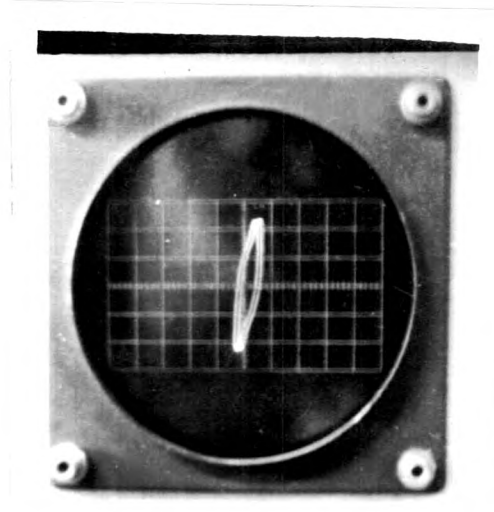


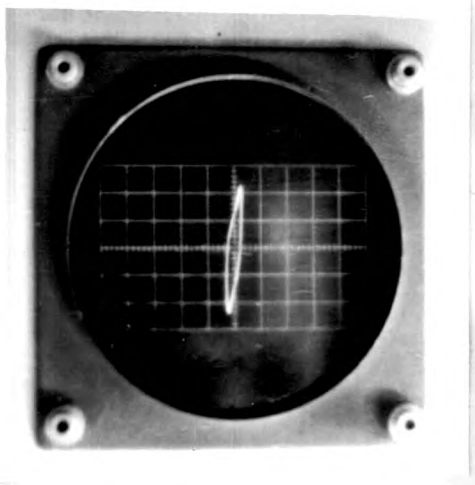
Fig: 2·2



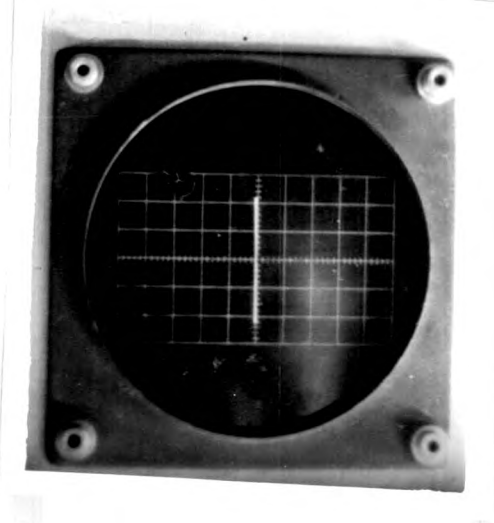
(a) Room Temperature



(b) 220°c

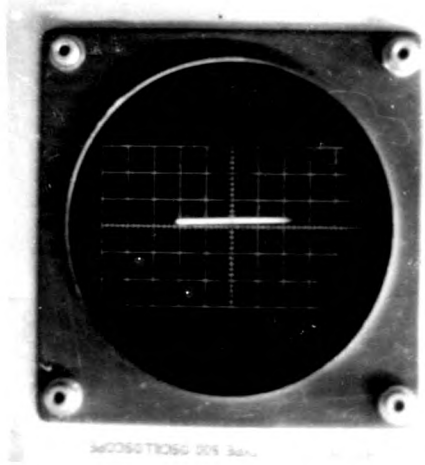


(d) 200°c

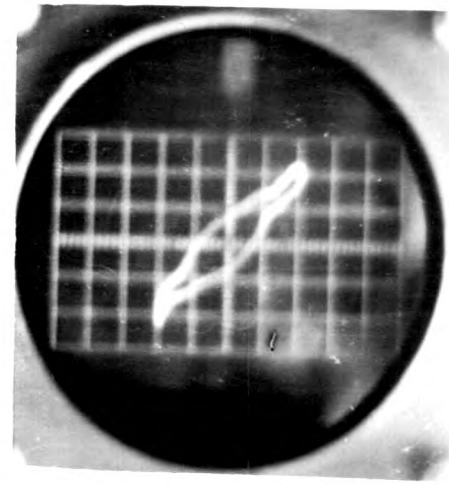


(c) 450°c

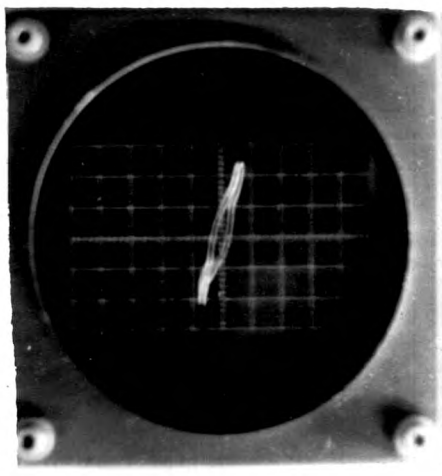
Fig: 2.3



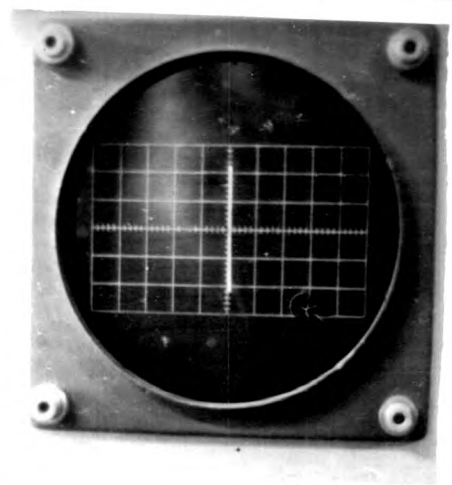
(a) Room Temperature



(b) 275°c



(c) 300°c



(d) 325°c

Fig: 2.4

2.9 Hysteresis Loop of $NaVO_3$:

By using Sawyer and Tower circuit as shown in Fig. 2.1, the hysteresis loops can be observed on the cathode ray oscilloscope. At room temperature the hysteresis loops are not observed for sodium vanadate. In case of sodium vanadate well defined hysteresis loop is observed at 220°C as shown in Fig. 2.3(b). Hysteresis loop disappears at 450°C and again appears at 200°C as shown in Fig. 2.3(d).

2.10 Hysteresis Loop of KVO_3 :

When the pellet of KVO_3 is placed in the crystal holder connected in the Sawyer-Tower circuit, the hysteresis loop is observed on the screen of CRO. Hysteresis curves for KVO_3 at different temperatures are as shown in Fig. 2.4. In case of KVO_3 loop is observed at 275°C, which vanishes at temperature 325°C as shown in Fig. 2.4 (d).

Sawada S. and Nomura S. (1951) had reported that the hysteresis loop which broadens at definite temperature, decreases with the increase of the impressed voltage. The observation of the hysteresis curves for $NaVO_3$ and KVO_3 gives an idea that as the temperature increases, the shape of the loop gets disturbed and vanishes at the Curie temperature.

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