CHAPTER 1

FERROELECTRICS

1.1 INTRODUCTION

The ferroelctricity is an interesting field of the spontaneous electric polarization. The name "Ferroelctrics" arose from the analogy with ferromagnetics. The ferroelctricity is rapidly growing field and efforts are devoted to ferroelectric devices, using dielectric and pyroelectric properties of these materials. The ferroelectrics are a subgroup of the pyroelectrics in which the direction of spontaneous polarization can be reversed by an electric field.

Historically, the first ferroelectric material discovered, has been the Rochelle salt i.e. Sodium Potassium Tratrate tetrahydrate ($NaKC_4H_4O_6$ -$4H_2O$). Rochelle salt was prepared around 1655 by Seignette in La Rochelle (France) It is also known a "Seignette salt". Its anamalously large piezoelectric effect was noticed by the Curie brothers(1) in their pioneer investigation of piezoelectricity. The quantative measurements of its piezoelectricity and electro-optic effect were carried by Pockels (2). Valasek (3 ,4) recognized ferroelectricity by detalied studies in Rochelle Salt and he was First to Point out the analogy between the dielectric properties of Rochelle salt and magnetic properties of ferromagnetic materials. Mueller (5) called this phenomenon as ferroelectricity because of this analogy with ferromagnetism.

Busch and Scherrer (6) discovered ferroelctricity in potassium dihydrogen Phosphate, KH_2PO_4 and its properties were studied by the Zurich group. Slater (7) Published a theory of the phase transtion of KH_2PO_4, which stimulated interest and inspiration in ferroelectricity for many physicists.

Wainer and Saloman (8) in United states, Wul and Goldman (9) in Russia and Ogawa (10) in Japan independently discovered the anomalous dielectric properties of Barium titanate ($BaTiO_3$). Lateron the ferroelctric activity of $BaTiO_3$ was confirmed by Von Hipple and his co-workers (11) and independently by Wul and Goldman (12). Since the discovery of ferroelectricity in $BaTiO_3$ compounds with persovskite structure have been studied extensively, these studies have resulted in the discovery of several ferroelectric titanates, niobeates and tantalates particularly by Matthias (13).

The ferroelectric activity in Lead titanate ($PbTiO_3$) was reported independently by Shirane et al (14) and Smolenskii (15). Lead titanate and several ceramics of isomorphous oxides possess some of the most interesting porperties such as dielectric, piezoelelric and electrical, which are more significant from the applications view point.

Jona and Shriane (16) have given an useful table of seventy six ferrocelctric crystals which were known up to January 1961. Mitsui et al (17-a) have given comprehensive compilation of the nearly 450 pure compunds and solid solutions of ferroelectric character so far known. Structure and property data on large number of perovskite type compounds is provided by Glass (18).

Subbarao (19) has compiled in concise from ferroelectric and antiferroelectric materials, known upto 1971. This compilation provides an excellent source of data on the spontaneous polarization and curie temperature of ferroelectric and antiferroelectric materials.

Mitsui et al (17-b) have been identified almost 700 ferroelectric pure compounds and solid solutions. Major sources of bibliographic information on polar materials are provided by Mitsui (17-a, 17-b), Lang (20,21) Toyoda (22), Conolly et al (23,24).

1.2 Ferroelectric Materials and Their Characteristic Properties:-

Ferroelectrics are all solids and all are non-metallic. The properties of ferroelectrics are most simply studied when a material is in a single crystal form. A ferroelectric crystal is defined as a crystal which belongs to pyroelectric family (i.e. shows a spontaneous electric polarisation), and direction of the spontaneous polarisation of which can be reversed by an electric field. Experimentally reversal of the spontaneous polarization in ferroelectric is observed as a normal hysterisis loop shown in fig 1.1.

A dielectric is a material whose electrical and often optical properties are influenced by electric fields A subclass of dielectrics is piezoelectrics. These are the materials which when mechanically stressed produce an electric charge and vice versa. A subclass of piezo electrics is pyroelectrics. These are polar materials, which have a spontaneous polarization. This subclass of polar materials is known as ferroelectrics.

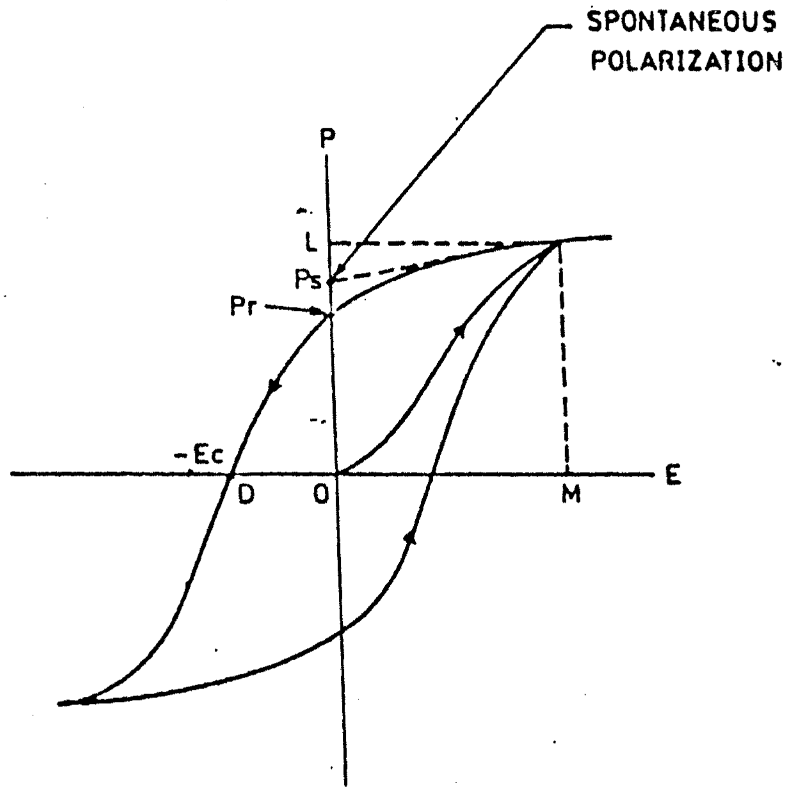

FIG. 1·1 SCHEMATIC REPRESENTATION OF FERROELECTRIC HYSTERESIS LOOP, THE COERCIVE FORCE IS OD (Ec).

Three prominent properties of ferroelectrics are, their reversible polarization, their anomalous properties and their non linearities. Most of the ferroelectric cease to be ferroelectrics above temperature Tc known as transition temperature. The an~~o~~amalous behaviour near transition temperature is probably as significant as the reversible polarization, but it is not definitive of a ferroelectric. The permittivity rises sharply to a very high peak value at the temperature Tc; the very high values in this neighbourhood are referred to as an~~o~~amalous values.

In some ferroelectrics, the temperature dependence of the dielectric constant above the transition tempterature can be described fairly accurately by simple law from its ferromagnetic analogue.

$$\epsilon = \epsilon_o + \frac{C}{T - Tc} \qquad (1.1)$$

Where

C --> Curie constant

T_c--> Curie-weiss tempterature

ϵ_0--> The part of delielctric dielectric constsnt independent of temperature

The dielectric constant becomes very large in the

Vicinity of Curie-weiss temperature.

With increasing temperature, ferroelectricity usually disappears above certain temperature called 'transition temperature'. The crystal undergoes a tranisition from the polar state at the transition temperature. The phase tranisition can be of the first order or of the higher (usually second) order.

In first order transition, volume and energy of a crystal change discontinuously at transition point, the energy apeearing as Latent heat in an infinitely narrow temprerature range. In the second order transition, volume and energy change continuously at the transition point. Therefore in the second order transition there is no release of "Latent heat" but the expansion coefficient and specific heat show anomalies extending over a finite range of temperature-

Most of ferroelectric crystals possess the following properties.

1 They exhibit a dielectric hysterisis loop between polarization and applied electric field below a certain on critical temperature; this termperature is called ferroelectric transition temperature.

2 They have ferroelectric domain structure which may be visible in polarised light.

3 They have high dielectric constant along the polar axis, which is a function of temperature and rises to a peak value at the curie temperature.

4 They possess a pseudo-symmetric structure. In the ferroelectric fase the structure belongs to polar class.

5 They have transition at the curie temperature to form structure of higher symmetry .

6 The curie temprature is raised by application of a biasing field, or a hydrostatic pressure.

7 They show piezoelcetric and pyroelectric properties below the curie temprature .

8 There is a sudden appearance of surface charge at the transition.

1.3 Dielectric properities and polarizability

a) Dielectric Properities

When a flat slab of any solid dielectric is placed in a uniform field $\bar{E}o$, with it's normal parallel to the field the dielectric displacement $\bar{D}$ in CGS system of units is given by

$$D = \epsilon o \, \bar{E}o = \epsilon \, \bar{E} = E + 4 \pi P \qquad \text{-- (1.2)}$$

Where $\overline{Eo}$ and $\overline{E}$ are field strengths outside and in th dielectric ϵ_0 and ϵ are dielectric constant of the surrounding medium and of the dielectic respectively, and P is the polarization. Usually surrounding medium is air or vacuum hence ϵ_0 is taken to be unity. Ignoring spontaneous polarization the relation between field strength $(\overline{E})$ and polorization $(\overline{P})$ can be written as

$$\overline{P} = n\,\overline{E} \qquad \ldots.(1.3)$$

Where n is the dielectric susceptibility.

In isotropic cubic system $\overline{P}$ is always parallel to E, then all quantities in the above equations are written as scalers, from eq^n (1.2) the dielectric constant of an isotropic medium is defined as :-

$$\epsilon = \frac{D}{E} = \frac{E + 4\pi P}{E}$$

$$= 1 + 4\pi n \qquad \ldots.\ (1.4)$$

OR

$$n = \frac{\epsilon - 1}{4\pi} \qquad \ldots.\ (1.5)$$

Equation (1.5) gives the relation beween n and ϵ

In a non cubic crystal the dielectric response is described by the components of the susceptibility tensor or of the dielectric constant tensor

$$P_j=n_{jk}E_k \qquad \ldots(1.6)$$

$$\epsilon_{jk}=1+4\pi n_{jk} \qquad \ldots(1.7)$$

1.3 (b)Polarizability:

The dielectric behaviour of ferroelectric crystals depend on poloarizability and internal field. The actual field in a dielectric varies greatly from point to point, over distances comparable with molecular dimensions. The interanal field F, also called the local or molecular field, is defined as that field in a very small spherical cavity from which the molecules have been removed.

According to Lorentz equation

$$F = E + Y P - E (1 + Y\Omega) \qquad (1.8)$$

Where E is the statistical field, in the dielectric, P is the polarization and Y is the internal field constant.In an iosptropic medium, $Y = \frac{4\pi}{3}$. The internal field constant Y differs from $\frac{4\pi}{3}$ in the crystals of lower symmetry. It is usually considered as independent of temperature.

In the field F, each molecule becomes polarized and acquires the dipole moment P. The polarizability of an atom is defined by

$$P = \alpha F \qquad (1.9)$$

where α is the polarizability, which is an atomic property.

The polarization in the crystal may be expressed as (Kittel, 1971).

$$P = \sum_j N_j P_j = \sum N_j \alpha_j F_j (j) \qquad \ldots. (1.10)$$

where N_j is the concentration and α_j the polarizability of atom j and F(j) is the local field at atom sites j.

Taking local field as

$$F = E + \frac{4\pi}{3} P \qquad \ldots.(1.11)$$

we get

$$P = N_j \alpha_j \left(E + \frac{4\pi P}{3} \right) \qquad \ldots.(1.12)$$

Hence the dielectric susceptibility is given by

$$n = \frac{P}{E} = \frac{\Sigma N_j \alpha_j}{1 - 4\pi/3 \, \Sigma N_j \alpha_j} \qquad \ldots.(1.13)$$

Since $\epsilon = 1 + 4\pi n$

in CGS system we get

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \Sigma N_j \alpha_j \qquad \text{....(1.14)}$$

This is the well known Clausius -Mossotti, relation.

The total polarizability is usually separated into three parts.

(i) Electronic polarizability (α_e) :- This is due to displacements of electrons within the atoms or ions.

(ii) Atomic polarizability (α_a) :- It is due to displacements of atoms or ions within the molecule.

(iii) Dipolar polarizability (α_d) :- This arises from molecules with a permanent electric dipole moment that can change orientation in an applied field.

The electronic and atomic polarizabilities are independent of temperature and hence, the portion of the dielectric constant dependent on them is essentially independent of temperature. The dipolar polarizability is a function of temperature. The dipolar polarizability is a function of temperature. According to Debye's theory (1954) the dipolar polarizability per molecule in a week field is given by

$$\alpha_d = \frac{p^2}{3\ kT}$$

where p is dipole moment of a polar molecule. k is Boltzmann constant and T is the absolute temperature.

The contributions to the total polarizability are shown in fig. (1.2). The dielectric constant at optical frequencies is entirely due to the electronic polarizability. The atomic and dipolar contributions are small at high frequencies because of the intertia of the molecules and ions, polarizability is the function of freqency of the applied field. At low frequency of the applied field all types of polarization are equal to the value in the steady field.

1.4 Classification of Ferroelectrics:

In recent years the phenomenon ferroelectricity has been discovered in a large number of materials. As investigations in recent years have shown that ferroelectricity is a more common phenomenon than had been considered for a long time. Hence the classification of these materials has become very difficult. However, classification of ferroelectrics has been proposed according to different criteria as follows.

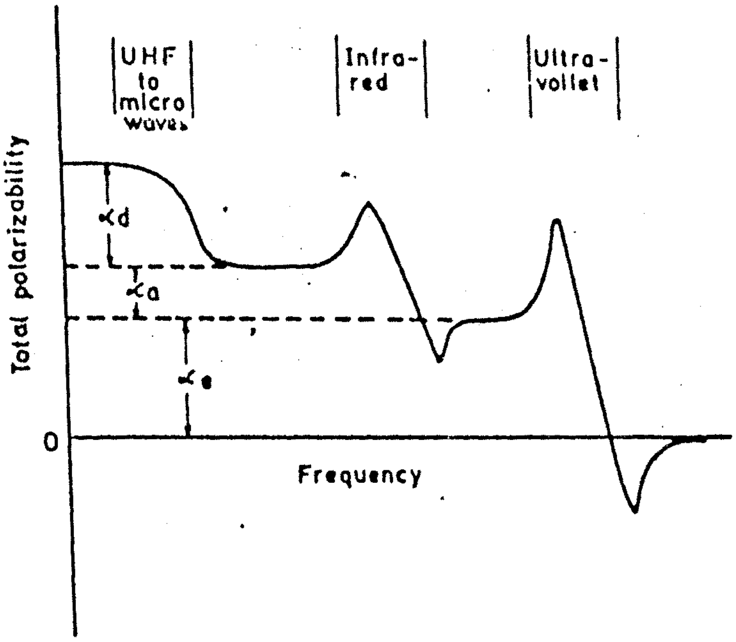

FIG. 1.2 SCHEMATIC REPRESENTATION OF FREQUENCY DEPENDENCE OF THE SEVERAL CONTRIBUTIONS TO THE TOTAL POLARIZABILITY.

1) **Crystal chemical classification**:

This classification divides ferroelectric compounds into two groups. The first group includes hydrogen-bonded crystals, such as potassium dihydrogen phosphate, Rochelle salt, triglycine sulfate. The second group includes the double oxides, such as $BaTiO_3$, $PbTiO_3$, $KNbO_3$, $Cd_2Nb_2O_7$ etc.

2) **Classification according to the number of directions allowed to the spontaneous polarization**:

This kind of classification also divides the ferroelectrics into two groups. The first group comprises those ferroelectrics that can polarize along only one axis, such as Rochelle salt, KH_2PO_4-type ferroelectrics, Colemanite Triglycine sulfate and Triglycine selenate. The second group includes thsoe ferroelectrics that can polarize along several axes that are equivalent in non-polar phase, e.g. $BaTiO_3$-type ferroelectrics, $PbNb_2O_6$, ferroelectric alums etc.

This classification is useful for the study of ferroelectric domains. In the polarized phase both classes show piezoelectric effect. Ferroelectrics of the second group often have transition points below their Curie temperature at which the spontaneous polarization changes in magnitude and direction. This type of classification is particularly useful for the study of ferroelectric domains.

3)**Classification according to the existence or lack of centre of symmetry in the point group of their non-polar phase**:

The first group consists of those ferroelectrics that are piezoelectric in the unpolarized phase such as Rochelle salt and related tartrates, KH_2PO_4-type ferroelectrics. The second group consists of those ferroelectrics which are not piezoelectric in unpolarized kphase, such as $BaTio_3$, $Cd_2Nb_2O_7$ $PbNb_2O_6$ etc. This classification is particularly useful for the thermodynamic treatment of the ferroelectric transitions.

4)**Classification according to the nature of the phase change at the Curie point**:

According to this classification the ferroelectric crystals are divided into two groups, order-disorder group and displacive group. The order-disorder group of ferroelectrics includes crystals with hydrogen bonds, such as KH_2PO_4 and isomorphous slats & triglycine sulfate. The ferroelectrics in this group undergo a transition of the order disorder type.

The displacive group of ferroelectrics include ionic crystals whose structures are closely related to the perovskite and ilmenite structures, such as those of $BaTiO_3$ and most of the double oxide ferroelectrics. The simplest ferroelectric crystals of this group is GeTe (Powley et al 24a) with sodium chloride structure.

5) Classification according to the predominant nature of atomic displacements required by polarity reversal

Abrahams and Keve (25) have examined the properties of ferroelectric crystals and have divided ferroelecric crystals into three classes according to the predominant nature of the atomic displacements reuquired by polarity reversal.

The one-dimentional class includes those ferroelectric crysrtals in which the atomic displacement vectros $(\overset{\rightarrow}{/\backslash})$ and all Loci (L) followed by the atoms during reversal, are linear and parallel to the polar axis. $BaTiO_3$, $PbTiO_3$ $KNbO_3$, $LiNbO_3$ and SbSi are the examples of this group.

The two-diemensional class includes those ferroelectric crystals in which the atomic displacement vector $(/\backslash)$ or the actual Loci (L) followed by atoms during reversal lie in paralllel planes containing the polar direction. Examples of some two dimensional ferroelectrics are $BaCOF_4$, HCl, HBr, $NaNO_2$.

The three dimensional class includes those ferroelectric crystals in which the displacement vector (/\) and the Loci (L) followed by atoms during reversal, have essentially random orientations. Examples are $(NH_4)_2SO_4$, KH_2PO_4.

1.5 **Spontaneous Polarization**:

The existence of dielectric hystersis loop indicates spontaneous polarization p_s, which is defined as dipole moment per unit volume. The experimental methods for observation of the hysterisis loop on the screen of a Cathode Ray Oscilloscope are based on the Sawyer and Tower circuit(26). The hystersis loop is schemitically shown in fig. (1.1). Liner extrapolation from the saturation region to zero field gives the spontaneous polarization Ps. The intercept on polarization axis is Pr (remenant polarization) and the intercept OD on the E-axis gives the coercive field. The total polarization of the ferroelectric in the saturation field OM is represented by the intercept OL.

The main defect of the Sawyer and Tower circuit is the phase difference introduced between the applied field and the polarization of the crystal, because the impedance of the crystal is variable. A modification to the Sawyer and Tower circuit was proposed by Sinha (27). The circuits which are commonly used are similar in principle to the modified circuit.

Other methods which are commonly used for measuring the magnitude of Ps are polarity reversal techniques (Camlible, 28), charge interation technique (Glass,18) and pyroelectric measurement using claibration for scaling (Glass, 18).

The type of phase transition governs the nature of the temperature dependence of Ps. The spontaneous polarization Ps suddenly falls to zero in a ferroelectric crystal which undergoes the first-order phase transition. The transition in barium titanate ($BaTiO_3$) is an example of first-order transition (Merz, 29). In a ferroelectric crystal which undergoes the second-order phase transition, Ps decreases continuously to zero at the transition temperature The example of second-order transition is triglycine silfate (Jona amd Shirane 16).

1.6 **Ferroelectric Domains**

The first direct optical observation of domains in KH_2PO_4, with polarized light, was made by Zwicker and

Scherrer (30). The domain structure in single crystals of $BaTiO_3$ was reported for the first time almost simultneously. by Kay (31), Blattner et al (32), Matthias and Von Hikplle (33) and Mitsui and Furuchi (34). Marutake (35) made direct observations of the domain structure in Rochelle salt.

In general, a ferroelectric crystal consists of domains, which are regions of homogenous polarization that differ only in a direction of the polarization. All the spontaneously polarized unit cells within a domain in a ferroelectric crystal are oriented identically. Consequently each domain has a macroscopic spontaneous polarization. The directions of spontaneous polarization of neighbouring domains in a ferroelectric crystal make definite angle with one another. A line of separation between two neighbouring domains is called a domain wall. A domain wall is usually considered to be thin that it has a much smaller volume than the bulk material in the domains. A domain wall is electrically neutral and corresponds to a minimum of the energy of a crystal. Consequently, the dipoles in the neighbouring domains are oriented in such a way that, at a wall the projection of the polarization vector of one domain is equal in magnitude and oppoiste in sign to the projection of polarization vector of the neighbouring domain.

A single crystal may contain a number of domain reginons although, by definition, it cannot contain more than one crystallite. A single crystal has domain walls, but no grain boundaries. In a polycrystalline material, there may be several domains in each crystallite. The reasons for occurrence of domains in a ferroelectric crystal are now fairly well understood. In paraelectric phase i,e. above the Curie temperature the direction along which the polarization is to occur cannot a unique direction. But even in ferroelectric phase, there must be at least two equivalent directions along with the same probability .

The paraelectric crystal consists of uniformly polarized regions,because at the Curie temperature different regions of the crystal can polarize in different direction. Below Tc the crystal must belong, by its symmetry, to one of the paraelectric classes and the domains differ in the direction of P_s. Therefore, when a ferroelectric is cooled below the Curie temperature, in absence of external electrical and mechanical stress, it breaks up into domains of different orientation. It means that from the crystallogrphic point of view, the domain structure is identical with the Twining structure. Twin operations of ferroelectic domains have been discussed by Zheludev and Scuvalov (36,37).

1.7 Literature survey and Orientation of the Present work:-

An excellent account of the detailed dielectric, optic and elastic properties of $BaTiO_3$ was given by Jona and Shirane (38). The most detailed the inelastic neutron scattering study of $BaTiO_3$ was carried out by Yamada et al (39), Shirane et al (40), and Harada et al (41). The sintering process for semiconducting ceramics was investigated via measurement of density and porosity, observation of the cerramic microstructures and DTA by Yoneda et al (42). Large PTCR (positive tenperature coefficient of resistivity) effects of more than several orders of magnitude have been observed in porous semiconducting $BaTiO_3$ ceramics by Kuwabara (43). Study of structural phase transition by hyper - Raman scattering in $BaTiO_3$ and $SrTiO_3$ was carried out by Inoue (44). The effect of an external magnetic field on ferroelectric characteristics of $BaTiO_3$ type crystal was discussed by Konsin et al (45). recently Koschek and Kubalek

(46) have suggested that the electron microscopy and cathodonuminescence measurement technique can be used for experimental confirmation of some important aspects of existing theories of PTC effect and for the quality control of commercial $BaTiO_3$ ceramics.

The $BaTiO_3$ assumes the perovskite structure. The structure is extreemly simple with a general formula ABO_3 where A is monovalant or divalant metal ion and B is pentavalnt or tetravalent metal ion. Ion in position A is of larger radius, while the one in position B is smaller, e.g. ionic radius of Ba is 1.3 A° while that of Ti is 0.68 A°.

With the aim to study the effect of substitution in A as well as in B position, number of solid solutions have been synthesised and studied. A detailed report of which is available even in the text, Piezoelectric, ceramics by B. Jatteetal (47) tien etal (48) have generalised that with single cation substitution in both A and B positions, the curie point shows a minimum, in the corresponding binary system. the effects of off-valency substitutions or doping are also well investigated for $BaTiO_3$ composition.

A range of solid solutions which is not investigated in details as yet is the compensated off-valarcy substitution. A few reports available are on replacement of $2Ba^{2+}$ by K^{1+} + La^{3+} (49), replacement of $2Ti_{4+}$ by Fe^{3+} + Nb^{5+} Na^{1+} + Nb^{5+} replacing Ba^{2+} and Ti^{4+} (50), La^{3+} + Al^{3+} replacing Ba^{2+} and Ti^{4+} (51), 2 Ti getting replaced by Fe^{3+} + Ta^{5+} (52).

Constraint of matching the ionic size and valency are both important while selecting the ions to form the solid solutions. Further, as almost always one shall adopt the ceramic process of synthesis oxides or carbonates(sec 2.3) of the selected ion should not dissociate at the sintering temperature.

From the background discussion above it appears that yet there exist a wide range of solid solutions to be investigated. To illucidate the available scope of formation of solid solutions, a few examples are sited in table(1.1&1.2) Ionic radii of the elements are also indicated in the table.

In our opinion these substitution will modify the ferroelectric and the transport properties of $BaTiO_3$ drastically, as a result of modification of the inter atom covalant or ionic interaction. Additional ferroelectric

TABLE 1.1

Possible Replacement Of Ti

Type	Possible Combinations
1+7	Li + Re, Li + Tc 0.60 0.62 0.60 0.61
2+6	Mg + W, Mg + MO, Cu + W, Cu + MO 0.65 0.62 0.65 0.62 0.72 0.62 0.72 0.62
3+5	Cr + Ta, V + Sb, V + Nb, Cr + Sb 0.69 0.68 0.74 0.62 0.74 0.69 0.62 Cr + Nb, Fe + Sb, Fe + Nb Fe + Ta 0.69 0.64 0.62 0.64 0.64 0.68 V + Ta 0.74 0.68

TABLE 1.2

Possible Replacement Of Ba

Type	Possible Combinations
1+3	Rb + Ac, Tl + Ac, In + Ac 1.48 1.18 1.48 1.18 1.32 1.18 K + AC 1.32 1.18

TABLE 1.2

Possible Replacement Of BaTi

Type	Possible Combinations
3+3	Ac + Cr, Ac + Fe, Ac + Ga 1.18 0.69 1.18 0.64 1.18 0.62

Ac <---------Symbol

1.18 <---------Ionic Size in A°

phases may also appears as a result this modified interaction.

In view of investigating the effect of partial Ti replacement we have selected two compositions viz.

1) Ba $Fe_{x/2}$ $Sb_{x/2}$ Ti $_{1-x}$ O_3 and 2) Ba $Cr_{x/2}$ $Sb_{x/2}$ Ti_{1-x} O_3
The effects of substitututtion would be prominant for very low levels and therefore we have selected the values of x as = 0.025, 0.05, 0.1, 0.2, 0.4. Purposely the x is not varied linearly. After an elementary cycle of investigations, a range of substitution could be marked where the physical properties of the binary system, show a minimum or maximum. Then one may study the phenomenon in detail by preparing solid solutions with closely space d values of x in that region.

Similar studies are performed and reported for $PbTiO_3$ based solid solution. These investigations may provide potential information about the phenomenon of ferroelectricity may result to be as well as of commercial importance. Recently Prasad etal (53) and Ichinose etal (54) have investigated the.

Pb_{1-x} Ca_x $Mn_{0.05}$ $W_{0.05}$ $Ti_{0.9}$ O_3 and $Pb_{1-x}ca_x$ $Co_{0.02}$, $W_{0.02}$, $Ti_{0.96}$ O_3 compositions respectively to achieve ferroelectric compositions with improved electrical performance, these studies have stimulated us to investigate the effect of Fe^{3+} Sb^{5+} and Cr^{3+} Sb^{5+} substtitution in $BaTio_3$ system.