
CHAPTER - II

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FERRITES AND FERROELECTRICS

SECTION – A

FERRITES

2A.1 INTRODUCTION

Ferrite is the recent name given to some oxide magnetic materials. The first magnetic material known to man, lode-stone or magnetite also happens to be a ferrite. The chemical formula for, lode-stone is Fe_3O_4 (i.e. $\text{FeO} \cdot \text{Fe}_2\text{O}_3$) in the form of double oxide of iron studies on Fe_3O_4 helped the development of other ferrites[1].

Ferrites are ferrimagnetic substances and are mixed crystals of various magnetic oxides, with ferric oxide. Ferrites possess very high electrical resistivity (greater than 10^5 ohm-cm) and extremely low dielectric loss, but large hysteresis loop [2].

Ferrites can be prepared by the standard ceramic method and in any desired shape according to variety of applications in various fields. The properties of ferrites depend upon the preparation method, preparation conditions, cation distribution and magnetic interactions etc. [3].

First section of this chapter deals with structure, theories of magnetisation, properties of ferrites and applications of ferrites.

2A.2 HISTORICAL DEVELOPMENT

The naturally synthesized ferrite prepared ferrite Fe_3O_4 aroused immense interest in man. The ancient people living in 600 B.C. believed that lode stone possesses an inherent living force, which accounts for the observed attraction between magnetite and iron. The first measurement of the saturation magnetization of magnetite was made by Du-Bios (1890)[4]. Pierre Weiss (1907)[5] went further to determine curie temperature and suggested its possible use in reducing eddy current loss in inductors and transformers.

The first synthetic ferrite was prepared by Hilpert (1909) [6] and then a large number of ferrites were prepared. He established the basic formula for ferrite as MOFe_2O_3 where M is divalent metal ion. Barth and Posnjak (1932) [7] carried out x-ray analysis of ferrites. They found that it is necessary to assume that the divalent and trivalent metal ions interchange positions in crystals and thus discovered inverse spinel structure.

Verwey and Heilmann (1947) [8] and Verwey, de Boer and Van Santen (1948) [9] carried out their x-ray studies on a number of oxides having spinel structure and concluded that Mn, Fe, Co, Mg, Cu and Ni ferrites which were magnetic had an inverted spinel structure whereas Zn and Cd ferrites which were non magnetic had a normal spinel structure.

Neel (1948) [10] was the first to give the basic theory of ferrimagnetism. Applying the molecular field theory to ferrites, he introduced the concept of magnetic sub-lattices. Yafet and Kittel (1952) [11] extended Neel's theory of magnetic sub-lattices in ferrites by postulating a triangular or canted arrangement of these sub-lattices. In order to explain a. c. conductivity in ferrites, Koops proposed a model to explain the dielectric dispersion [12]. Gilleo proposed the formula to correlate the observed curie temperature, magnetization and cation distribution [13]. Smart and Gorter [14] worked independently and correlated the cation distribution found by microwave resonance and magnetization [15].

2A.3 CRYSTAL STRUCTURE OF SPINEL FERRITES

In general ferrites show four different types of crystal structure :

- 1) Spinel structure
- 2) Hexagonal structure
- 3) Garnet structure
- 4) Perovskite structure

In the present work, we are concerned with the spinel structure of ferrite. The detailed discussion about spinel structure of ferrite is given below.

2A.3.a Chemical Structure of Spinel Ferrites

The general chemical formula for ferros spinel is MFe_2O_4 , where M is divalent metal ion and Fe is trivalent metal ion. In fact MFe_2O_4

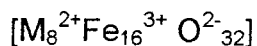
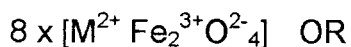
is a combination of two oxides MO and Fe_2O_3 where M is a metallic ion such as Mn , Co , Ni , Cu , Cd , Mg etc.

Ferrites prepared by single divalent atoms such as $NiFe_2O_4$, $CdFe_2O_4$ etc. are called simple ferrites. Those in which divalent ions are partially replaced by one metal ion and partially by other metal ion are called binary or mixed ferrites e.g. $Ni_xCo_{1-x}Fe_2O_4$, $Mg_xCd_{1-x}Fe_2O_4$ etc.

2A.3.b Lattice Structure of Spinel Ferrites

The spinel is a cubic crystal of F.C.C. type. The unit cell of ferrite contains 8 formula units i.e. $8MFe_2O_4$ or $M_8Fe_{16}O_{32}$. The oxygen ions are physically bigger than the other ions greatest and they form a face centered cubic lattice. The lattice parameter 'a' is found to vary from 8.3 Å to 8.6 Å.

The unit cell formula is



In this case 32 oxygen ions are arranged on a closely packed face centered cubic lattice. There are 96 interstitial sites available between the 32 oxygen ions. Out of which only 24 interstitial positions are occupied by metal ions, out of which 8 tetrahedral (A site) and 16 octahedral (B site) sites are occupied by cations. The close packed face centered cubic structure with

oxygen ions is shown in fig. 2.2 with two types of interstices. The 96 interstitial positions are divided into two distinct types.

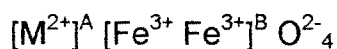
2A.4 Classification of ferrites

Ferrites can be classified on the basis of cation distribution into three groups :

- a) Normal Spinel Ferrite
- b) Inverse Spinel Ferrite
- c) Random Spinel Ferrite

2A.4.a Normal Spinel Ferrite

In normal spinel ferrites, all the divalent metal ions occupy A sites and all the trivalent iron ions occupy B sites. The structural formula for such a ferrite can be written as



Ferrites like $CdFe_2O_4$ and $ZnFe_2O_4$ etc. have this type of structure and they are non-magnetic in nature.

2A.4.b Inverse Spinel Ferrite

In the inverse spinel ferrite, all the divalent metal ions $[M^{2+}]$ occupy B sites and the trivalent ions $[Fe^{3+}]$ are equally divided between A and B sites. The general cation distribution may be written as

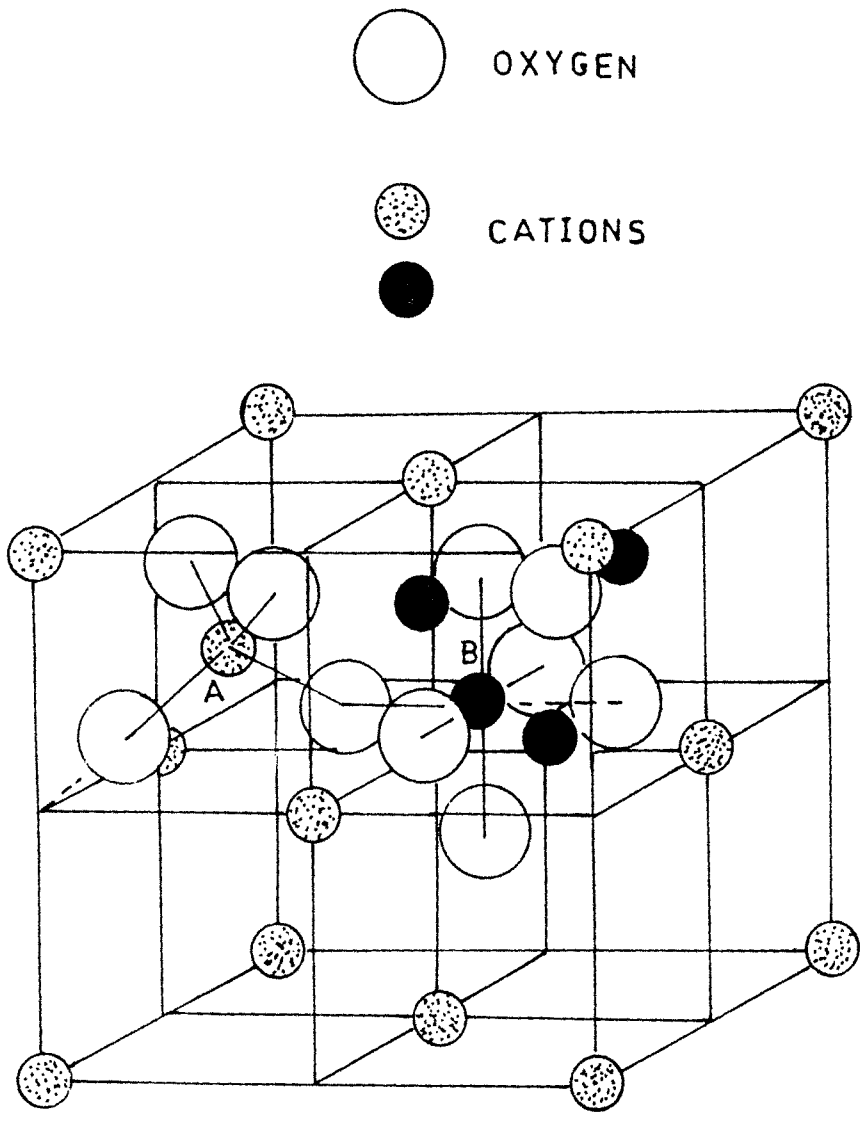


FIG. 2A.1 - THE SPINEL STRUCTURE .

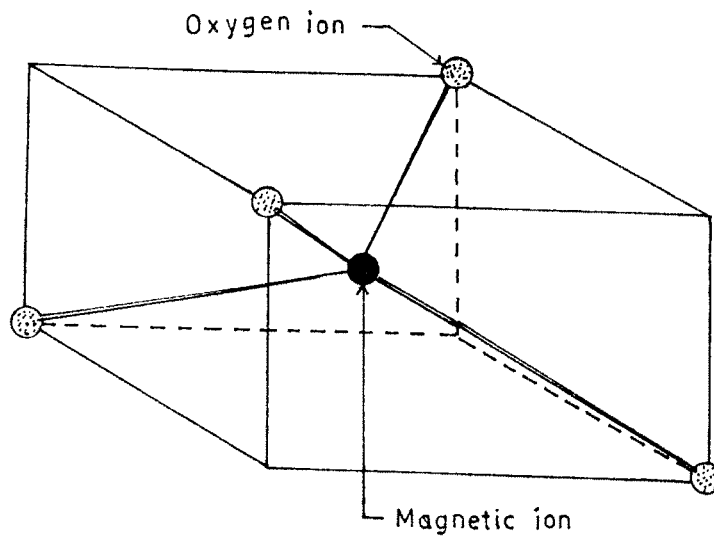


Fig 2A·2(a) – THE MAGNETIC ION OCCUPIES A TETRAHEDRAL LATTICE SITE WHERE IT IS SURROUNDED BY FOUR NEAR NEIGHBOUR OXYGEN IONS .

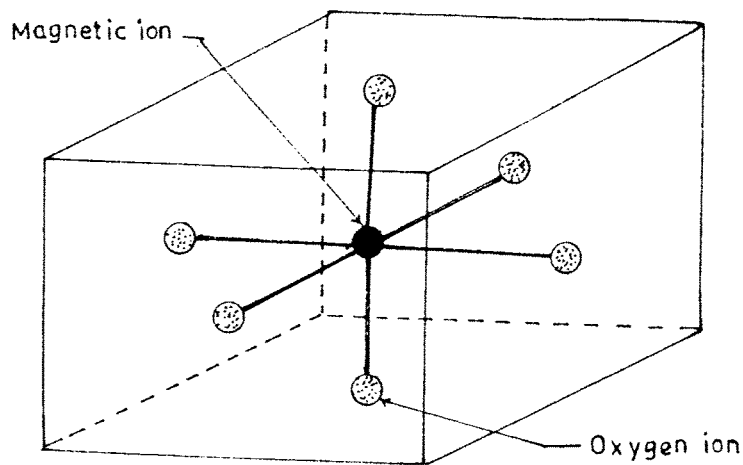
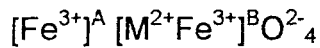


Fig. 2 A·2(b) – THE MAGNETIC ION IS SAID TO OCCUPY AN OCTAHEDRAL LATTICE SITE WHERE IT IS SURROUNDED BY SIX NEAR NEIGHBOUR OXYGEN IONS .

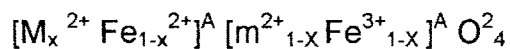


Ferrites like CoFe_2O_4 , Fe_3O_4 , NiFe_2O_4 , CuFe_2O_4 etc. have this type of structure and they are magnetic in nature.

2A.4.c Random Spinel Ferrite

The divalent $[\text{M}^{2+}]$ and trivalent $[\text{Fe}^{3+}]$ metal ions are randomly distributed over A and B sites depending on their physicochemical conditions of preparation and compositional variation. Such a ferrite is partially inverse.

The general cation distribution may be represented as



where, x = Coefficient of normalcy

$1-x$ = Coefficient of inversion

For eg. MnFe_2O_4 , CuFe_2O_4

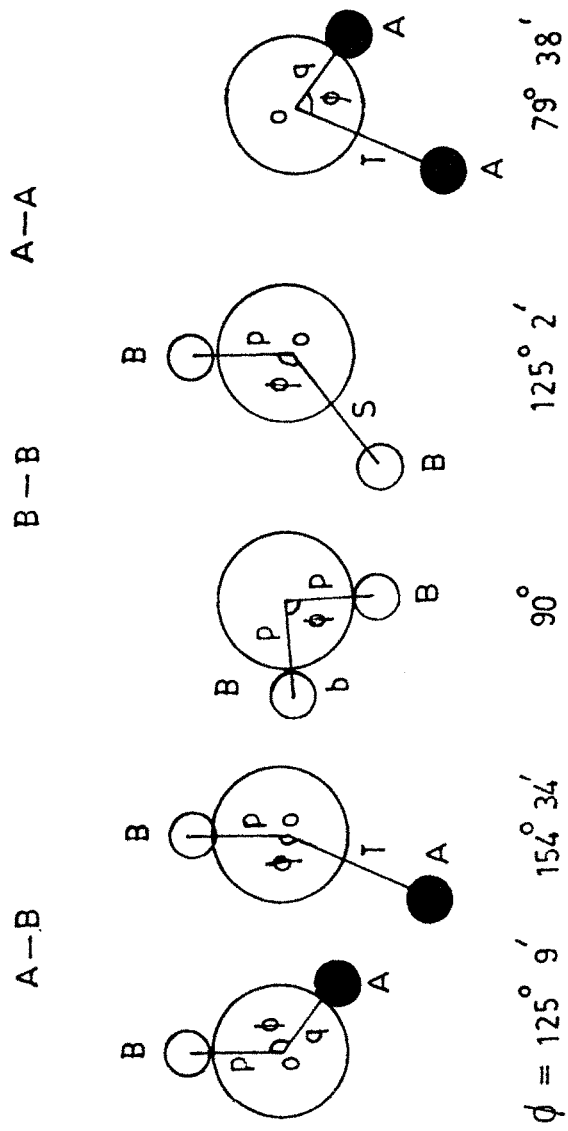
2A.4.2 Magnetic Interaction

In the spinel ferrites every oxygen ion is surrounded by three B cations and one A cation. The angles between A-O-A and A-O-B are [16]

$$\angle \text{A-O-A} = 79^\circ 9' 1''$$

$$\angle \text{B-O-B} = 90^\circ \text{ and}$$

$$\angle \text{A-O-B} = 125^\circ 9' 1''$$



ANGLE BETWEEN A-A, B-B & A-B CATIONS IN A SPINEL STRUCTURE .

FIG. 2 A.3

The angle between A-A and B-B is shown in fig. 2.3 when the distance between M-O-M is small and the angle $\angle \text{MOM}$ is 180° [17] the interaction is expected to be strong. Thus we can conclude that B-B interaction is weak, the A-A interaction is weaker while the A-B interaction is strong.

2A.5 Ferrimagnetism

Neel has introduced the term ferrimagnetism by considering the properties of ferrites. Antiferromagnetism and ferrimagnetism are observed in the magnetic materials showing indirect exchange interaction. The intervening ions give rise to the two sublattices characterised by different oxygen environments for the magnetic atoms. Magnetic interactions within the sublattice give rise to sublattice magnetisation. At any temperature magnetisations of the two sublattices are not equal. However they are opposite in nature and the net magnetisation results as in the case of ferromagnetic materials. Therefore ferrites exhibit almost all the properties of ferromagnetic materials.

The properties of ferrites can be classified into two groups, intrinsic and structure sensitive. Saturation magnetization, magnetostriction anisotropy and curie temp are basically the intrinsic properties while permeability, hysteresis resistivity and dielectric constant are very much structure sensitive. The structural aspects like grain size, porosity, impurities and inclusions of non-magnetic ions, size distribution of inclusion affect the

structure sensitive properties. The magnetic behaviour of ferrites is explained on the basis of Neel's two sublattice model, which is rather well known [2,3,10]

2A.8 APPLICATIONS OF FERRITES

The electrical and magnetic properties make the ferrite material as unique substance in the electric, magnetic and electronic applications. Ferrites can operate with virtually no eddy current losses at high frequencies. Hence ferrite materials are used in certain fields such as microwave communication data processing devices, radar, television etc. Modern electronic industry needs the inductors and transformers on miniature scale and ferrites can efficiently serve this purpose. Ferrites are also used in MW antenna in radio receivers, mechanical filters, circulators, broad band transformers, ultrasonic generators, isolators, modulators, phase shifters, direction couplers, tape recorders, television, radio etc[14,15]. Besides these other important applications are

In digital computers the ferrite cores are used as the switching and memory elements for transmitting, storing, and recording the signal pulse in few micro second. Due to high resistivity of ferrites they find applications in audio devices such as recording and erasing heads in the tape recorder. Ferrites having permeability in the range of 50 KHz to 150 KHz are used in filter inductor for band pass filter in telephone circuits. Ferrites with large magnetostriction or lower permeability are used in accelerators, filter and

ultrasonic generators. Hexagonal ferrites being permanent magnetic materials are used in loud speakers. Ferrites are used for manufacture of microwave integrated circuits in an electronic field. The ferrite plating is a new technique used for the preparation of film devices in which not heat resistant materials such as plastics are used.[16]

SECTION – B

FERROELECTRICS

2B.1 INTRODUCTION

A crystal is said to be ferroelectric when there are two or more orientational states in the absence of an electric field and can be shifted from one to another of these states by external electric fields.

The ferroelectric materials exhibit hysteresis property, which is the basic feature to use them for the applications of computer memory devices just as ferromagnets and they offer remarkable scope for the production of solid state integrated versions of memory devices. During the last few years, the field of ferroelectricity is expanding fast and extensive investigations on the properties of ferroelectrics have been carried out especially on a single crystal. The theory of ferroelectricity is rather different from that of ferromagnetism, but both of them analogous possess domains, exhibit hysteresis loops and show curie weiss behaviour near their phase transition temperature. The reversible nonlinear behaviour of ferroelectric substances makes them useful in dielectric amplifiers, voltage regulators, pyroelectric detectors etc. and these promising applications render them attractive for further research [18,19].

2B.2 CRYSTALLOGRAPHIC CONSIDERATIONS AND DEFINITION OF A FERROELECTRIC

Ferroelectric materials have a high dielectric constant which is non-linear, i.e. it depends to a considerable extent on the intensity of the electric field. Such materials exhibit hysteresis loops i.e. the polarization is not a linear function of applied electric field. If the centre of gravity of the positive and negative charges in a body do not coincide in the absence of an applied electric field, the substance has an electric dipole moment and is said to be spontaneously polarized. Such a substance is called ferroelectric.

Ferroelectrics exhibit polarization under the influence of dielectric field. The polarization is affected in elastic optical, thermal behaviour of the material. It is well known that any one crystal can be classified in one or another of 32 crystal classes (point groups) according to the symmetry elements, which it possesses. Twenty one of 32 classes are piezoelectric in which a polarization can be induced by an applied mechanical stress and eleven of them are characterized by the existence of a centre of symmetry, which are thus called centrosymmetric. These can of course possess no polar properties. Nearly half of piezoelectric classes exhibit the very important property that a finite and permanent value of polarization known as spontaneous polarization.

If these polar materials are subjected to a change in temperature, then there is associated a change in value of dipole moments. This results

in a detectable current, known as pyroelectric current and the materials are called as pyroelectrics. These materials possess domains, showing Curie-Weiss behaviour near their phase transition temperature.

Above certain temperature, called transition temperature the ferroelectric materials are no longer ferroelectrics and show normal dielectric behaviour.

In some ferroelectrics the temperature dependence of the dielectric constant can be described fully by Curie-Weiss law

$$\epsilon = \epsilon_0 + [C/(T - T_c)]$$

where ϵ_0 = Part of dielectric constant independent of temperature.

C = Curie temperature

T_c = Curie-Weiss temperature.

The dielectric constant become very high in the vicinity of Curie-Weiss temperature, when the crystal undergoes a transition from the polar state to non-polar state at the transition temperature. The phase transition may be of the first order or of the second order. The ferroelectric materials show piezoelectric and pyroelectric properties below transition temperature. Ferroelectrics possess domain structure, which can be made visible under polarizing microscope.[18].

2B.3 CLASSIFICATION OF FERROELECTRICS

The ferroelectrics are classified according to their physical properties, chemical composition, center of symmetry and phase transitions. The classification based on the nature of phase transition is rather ingenious and explanatory of the phenomena.

Accordingly the ferroelectric crystals are divided into two groups. A first group of ferroelectrics which undergo a transition of the order disorder type, as in KH_2PO_4 , consists of triglycine sulfate and probably some of the alums. A second group of compounds, undergoing a transition of the displacive type consists of BaTiO_3 and most of the double oxide ferroelectrics. This classification is practically equivalent to that done on the basis of the existence of permanent or induced dipoles in the non-polar phases of the crystals. A characterization of the nature of the phase change in the sense mentioned above (order-disorder verses displacive) can, in principle, be met on the basis of accurate structural investigation. In some cases, however, this information is already available from the results of dielectric investigations.

2B.4 DIELECTRIC PROPERTIES OF FERROELECTRICS

A consequence of the small atomic shifts occurring in ferroelectric crystals is the behaviour of the dielectric constant of these crystals

as a function of temperature. The dielectric constant is normally defined as the derivative of the dielectric displacement D with respect to the field E .

When a solid dielectric in the form of flat slab is kept in a uniform electric field with its normal to field, the dielectric displacement D in CGS system of units is expressed by

$$D = \epsilon_0 E_0 = \epsilon E = E + 4\pi P \quad \dots\dots\dots(1)$$

where E_0 and E are field strengths outside and inside the dielectric ϵ_0 and ϵ are dielectric constant of surrounding medium and of the dielectric respectively.

Similarly the derivative of polarization P with respect to the field E , $\partial P / \partial E$ is taken to be unity since surrounding medium is air or vacuum usually. Ignoring spontaneous polarization (P_0) can be given as

$$P = KE \quad \dots\dots\dots(2)$$

where K is dielectric susceptibility. From equation (1) the dielectric constant of an isotropic medium can be defined as

$$\epsilon = D / E = [E + 4\pi P] / E \quad \dots\dots\dots(3)$$

In an isotropic cubic system P is always parallel to E and hence all quantities in above equation for expressed as scalars [20].

2B.5 FERROELECTRICS – THEORY AND APPLICATIONS

In view of the unique properties exhibited by ferroelectric and the wide technological applications to which they are being put to, numerous attempts have been made to explain the phenomenon of ferroelectricity in crystals and purpose a number of theories have been accordingly proposed. It was Slater (1941) who proposed the molecular theory of ferroelectricity based on the actual crystal structure to explain ferroelectric phase transition in KH_2PO_4 . The most successful and challenging theory due to Cochran (1960-61) [21,22] is based on lattice dynamics. A thermodynamic theory of BaTiO_3 type ferroelectrics has been developed by Devonshire (1941, S1, S4) and Ginzburg 1945, 44) [23,24,25].

The theory is based on the following assumptions :

- 1) The free energy of a ferroelectric crystal is regarded as a function of temperature, stress and polarization.
- 2) The polarized phase is regarded as slightly distorted unpolarised by the same free energy function.
- 3) The anomalous piezoelectric and elastic properties and considered to be a result of the anomalous dielectric behaviour. Thus the coefficient of polarization in the free energy functions bear the significant temperature dependence.

- 4) The second order piezoelectric coefficients i.e. the electrostrictive coefficient are of main important because the crystal is not piezoelectric in the unpla5rized state.
- 5) The free energy functions contain three components of polarization vector. The free energy 'G' of polarized crystal is expressed by elastic Gibb's function.

$$G = U - TS = X_i X_j$$

where U = Internal energy of crystal under external stresses

T = Temperature S = Entropy

X_i = the i^{th} component of mechanical stress

X_j = the j^{th} component of mechanical strain

Ferroelectrics are the materials with strong anomalies in man of their physical properties, such as dielectric constant, electro-optical coefficients, piezoelectric coefficient etc. Some of these properties are actually used to build special devices. For ferroelectrics the anomalies observed are very large dielectric constant, piezoelectric and pyroelectric coefficients. The very large dielectric constant makes them useful, in ceramic form to make high capacitance condensers. Their large piezoelectric coefficients make them particularly suitable as transducers.

a) Linear Properties

Ferroelectric transducers have high coupling constant but comparatively high dielectric losses. The purpose of a transducer is in some cases to convert a. c. fields or sudden changes of field into corresponding mechanical motions, as in ultrasonic generators, loudspeakers or pulse generators for use with sonic delay lines. In other cases, a transducer uses the piezoelectric effects to convert small motions into electric changes, as in ultrasonic detectors, strain gauges, microphones, pickups and devices to measure the extent of vibrations. Ferroelectrics are used in capacitors, because of their high permittivity values. Ferroelectrics are also used in frequency controls, filters miniature capacitors, thermal meters, modulating devices, frequency multipliers, switches etc. [26].

b) Non Linear Properties

The ferroelectrics are strongly non linear at low frequency region and near the transition temperature. Bias changes the value of permittivity in ferroelectrics. Therefore ferroelectrics condensers have values which can be changed electrically called 'Variconds'. Ferroelectric condensers have been used for tuning in superhets and for frequency modulation. Ferroelectrics can replace varactor and diodes, which are expensive.

It can be used as dielectric amplifier and as low frequency amplifier. This type of amplifier could be used for remote controls, servo systems, stabilization of supplies and autofrequency amplification. Some polar materials and particularly ferroelectrics show increase in resistivity with the increase in temperature. However drastic changes have been observed in several ferroelectric materials near their curie point. This property has been successfully employed for fabricating positive temperature coefficient (PTC) transducers. Switching thermistors (PTC) are used mostly in control applications such as in TV set, in single phase electric motor, as over charge protection devices in batteries, thermal overload protection devices etc. The existence of a hysteresis loop makes it possible for the ferroelectric to be used as memory elements.

Some of devices mentioned above such as capacitors and piezoelectric transducers are of great commercial importance. Others, such as optical holographic storage media and colour projection TV system (Marie 1976) are still at a developmental stage, but may prove to be economically very significant in future [27].

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