

CHAPTER II

CHAPTER – II FERRITES AND FERROELECTRICS

SECTION – A : FERRITE MATERIALS

2A.1. INTRODUCTION

Ferrites are oxide magnetic materials with iron oxide as their main component. The first magnetic material known to man, lodestone or magnetite, also happens to be a ferrite. The chemical formula for lodestone is Fe_3O_4 (i.e. $\text{FeO} \cdot \text{Fe}_2\text{O}_3$), double oxide of iron. Studies on Fe_3O_4 helped the development of other ferrites [1].

Ferrites show semiconducting properties with their resistivity varying from 5×10^{-3} for Fe_3O_4 to $10^{11} \Omega\text{-cm}$ in NiFe_2O_4 . Ferrites have the chemical formula MFe_2O_4 or $\text{Mo} \cdot \text{Fe}_2\text{O}_3$, where M is a divalent metal ion and Fe^3 is a trivalent iron ion.

Ferrites continue to evoke interest as they happen to be the most important electronic and magnetic ceramics. The simultaneous twin requirements of optimal electronic and magnetic properties in the advanced electronics, microwave and computer technologies have focussed the attention of research works on these materials. The technological importance of ferrites can be gauged from the wide spectrum of their applications. The properties of ferrites depend upon the preparation method, preparation conditions, cation distribution and magnetic interactions [2].

2A.2 HISTORICAL DEVELOPMENTS

The natural ferrite, Fe_3O_4 , aroused considerable interest in the early days. The ancient people (600 B.C.) believed that lodestone 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 [3]. Weis [4] went further to determine Curie temperature and suggested its possible use in reducing eddy current losses in inductors and transformers.

The first synthetic ferrite was prepared by Hilpert [5]. He established the basic formula of ferrite to be $MO.Fe_2O_3$, where M is divalent metal ion. Barth and Posnjak [6] carried out x-ray analysis of ferrites. They assumed that the divalent and trivalent ions interchange their positions in the crystals and thus discovered inverse spinel structure.

Verwey and Heilman [7] and Verwey, De Boer and Van Santen [8] carried out their x-ray studies on a number of oxides having spinel structure. They concluded that Mn, Fe, Co, Mg, Cu and Ni ferrites which are magnetic have an inverse spinel structure whereas Zn and Cd ferrites which are nonmagnetic have a normal spinel structure.

Neel [9] was the first to give the basic theory of ferrimagnetism. Applying the molecular field theory to ferrites, he introduced the concept of magnetic sublattices. Yafet and Kittle [10] extended Neel's theory of magnetic sublattices in ferrites by postulating a triangular or canted arrangement of these sublattices. Koops [11] proposed a model to explain the dielectric dispersion. Gilleo [12] correlated the observed Curie temperature with cation distribution. Smart [13] and Gorter [14] worked independently and correlated the cation distribution found by microwave resonance and magnetization.

2A.3 CRYSTAL STRUCTURE

In general ferrites show four different types of crystal structures :

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

Out of these four structures, the ferrites used in the preparation of present composites are of spinel type. Hence the spinel structure is only discussed here.

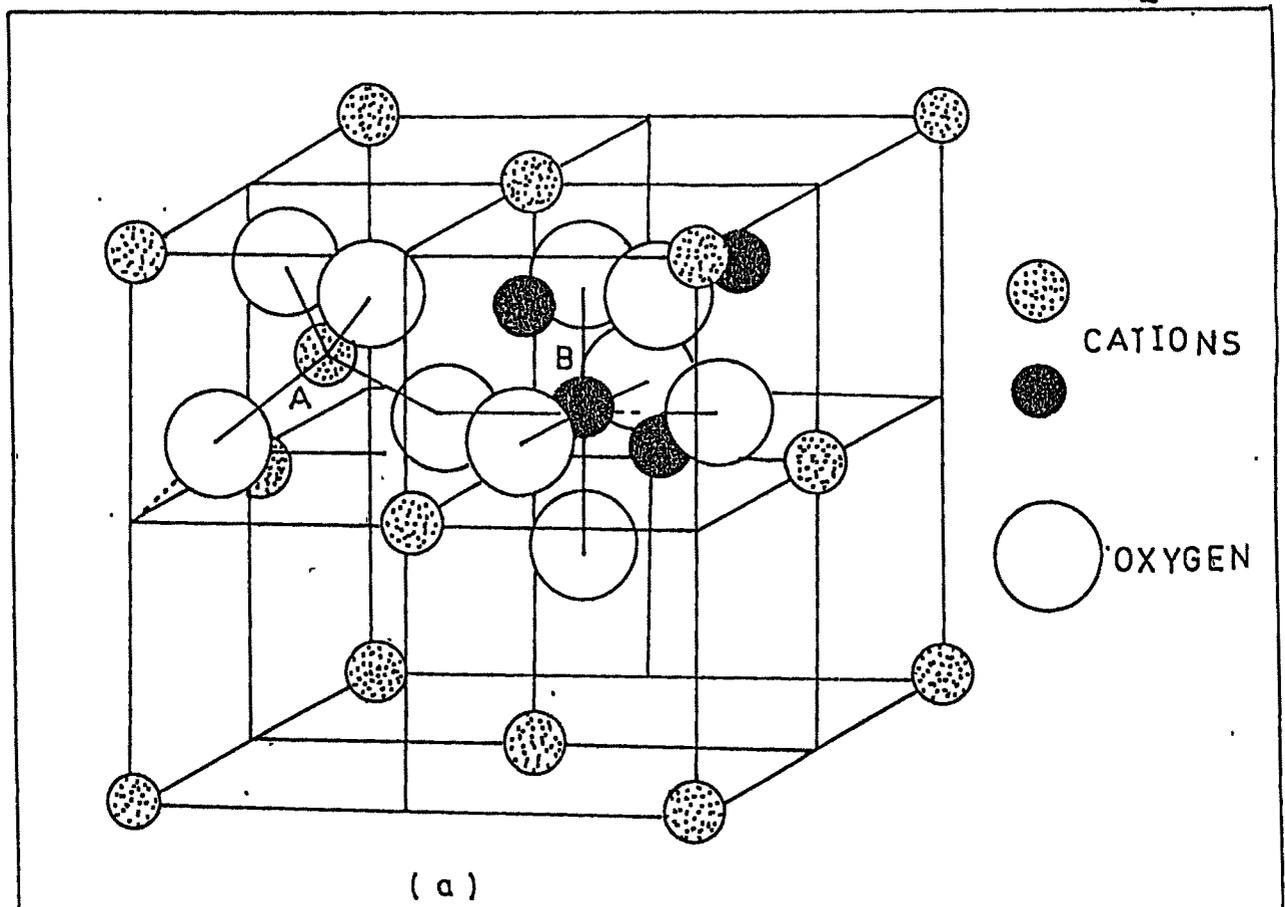
2A.4 CHEMICAL STRUCTURE OF SPINEL FERRITES

Ferrites crystallize into a spinel structure, which is named after the mineral spinel, $MgAl_2O_4$, i.e. magnesium aluminate. Its structure was first determined by Bragg [15] and Nishikawa [16]. The compounds having similar formula and lattice arrangement as that of magnesium aluminate are chemically termed as "spinel". Thus, the ferrites with spinel structure have, the general formula MFe_2O_4 . 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.

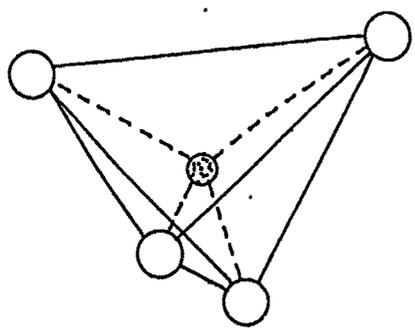
Ferrites prepared by single divalent atoms such as $NiFe_2O_4$, $CdFe_2O_4$ etc. are called simple ferrites. Those in which divalent ions are partially replaced by one metal ion and partially by other metal ion are called binary or mixed ferrites e.g. $Ni_xCo_{1-x}Fe_2O_4$, $Mg_xCd_{1-x}Fe_2O_4$ etc.

2A.5 LATTICE STRUCTURE OF SPINEL FERRITES

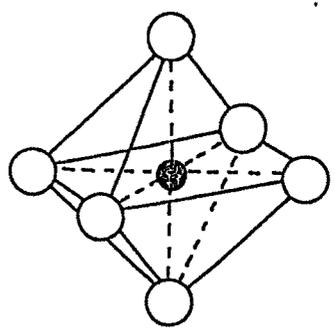
The ferrite crystal is ionic having cubic face centered crystal structure with the space group $Fd_{3m} - O_h^7$. The unit cell consists of 8 formula units of MFe_2O_4 . Hence an unit cell of ferrite contains $8M^{2+}$ ions, $16 Fe^{3+}$ ions and $32 O^{2-}$ ions. The 32 oxygen ions are arranged in a closely packed face centered cubic structure. These are assumed to be rigid spheres of ionic radius equal to $1.38A^0$. There are 96 interstitial sites available between the 32 oxygen ions. There are two kinds of lattice sites available for M^{2+} and Fe^{3+} cations. The tetrahedral or 'A' site and octahedral or 'B' site. A sites are surrounded by four oxygen anions situated at the corners of a tetrahedron. Only 8 out of 64 sites available are occupied. B sites are surrounded by 6 oxygen anions situated at the corners of a octahedron.



THE SPINEL STRUCTURE (SCHEMATIC)



TETRAHEDRAL SITE



OCTAHEDRAL SITE

FIG. 2-1

Only 16 out of 32 sites available in each unit cell are occupied. Thus only 24 out of 96 available interstitial sites are occupied. The spinel structure is shown in the Fig. 2.1(a) and the closely packed face centered cubic structure with oxygen ions is shown in Fig. 2.1(b) and 2.1(c).

2A.6 CATION DISTRIBUTION

Out of 24 metallic cations there are 16 Fe^{3+} ions and 8 divalent metal ions. Out of these some Fe^{3+} ions go to A or B site and correspondingly some metallic ions go to A or B site. It is nothing but cation distribution. In an apparently simplest way, 'cation distribution' depends upon the site preference energies of different ions. In order to explain the preference of a particular cation, it is necessary to apply the molecular orbital theory as there happens to be some tendency of mixing of electronic orbitals and the bondings are somewhat covalent in certain directions. Such bonding is known as coordination bonding and forms co-ordination complex molecule, which is a ligand containing hybrid orbitals. In spinels, we find three types of interpenetrating orbitals, viz. 1) tetrahedral orbitals 2) octahedral orbitals 3) square orbitals, which give rise to splitting up of orbital energy with degeneracy of energy states resulting in lowering of total energy of the system. The lowering of total energy due to the splitting of energy levels is crystal field stabilisation energy (CFSE). When a transition metal ion is surrounded by a regular octahedron of anions, the 5 d-electrons are split by the electrostatic field into two groups. (i) a lower triply degenerate t_{2g} and (ii) upper doubly degenerate e_g orbitals. There occurs a preference for an ion in spinel depending on whether the value of CFSE for that particular ion is larger or smaller or zero in either tetrahedral co-ordination or octahedral co-ordination [17]. The cation distribution can be studied from x-ray diffraction, neutron scattering or by measurements of saturation magnetisation.

2A.7 CLASSIFICATION OF FERRITES

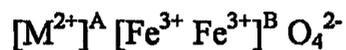
Ferrites can be classified on the basis of cation distribution into three groups –

- a) Normal spinel ferrites
- b) Inverse spinel ferrites
- c) Random spinel ferrites

a) Normal Spinel Ferrites

When all the divalent metal ions occupy A sites and all the trivalent iron ions occupy B sites, then the resulting ferrite is termed as normal spinel.

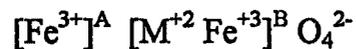
The cation distribution is –



e.g. $CdFe_2O_4$ and $ZnFe_2O_4$. These ferrites are non-magnetic in nature.

b) Inverse Spinel Ferrites

When all the 8 divalent metal ions occupy B site and 8 out of the 16 trivalent ions occupy A site and the remaining 8 occupy B site, i.e. the trivalent ions $[Fe^{3+}]$ are equally divided between A and B sites, then the resulting ferrite is termed as inverse spinel. The cation distribution is –

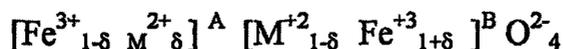


e.g. $CoFe_2O_4$, Fe_3O_4 and $NiFe_2O_4$

These are magnetic in nature.

c) Random Spinel Ferrites

Completely normal or inverse spinel are the extreme cases. When the divalent and trivalent metal ions get randomly distributed over A or B sites, then random spinel results. The cation distribution is –



Where, δ is the measure of degree of inversion and $0 \leq \delta \leq 1$.

When $\delta = 1$, we get normal spinel and for $\delta = 0$, we get inverse spinel.

2A.8 MAGNETIC INTERACTION IN FERRITES

As metal ions in ferrites occupy two different sites viz. octahedral and tetrahedral sites, three different kinds of magnetic interactions between metal ions are possible via intermediate O^{2-} ions by superexchange mechanism, namely, A-A, A-B and B-B interactions. It is observed that the interaction energies between two magnetic ions M^{I} and M^{II} depend on the distance of these ions from the oxygen ions through which interactions occur and the angle between $\text{M}^{\text{I}}\text{-O-M}^{\text{II}}$ represented by ϕ . The angle ϕ of about 180° between the cations gives maximum interaction energy. The exchange energy decreases rapidly with increasing distance of the cations from the oxygen anion.

The various possible configurations of the ion pairs in spinel ferrites with favourable distances and angles for an effective magnetic interaction as envisaged by Gorter [18] are given in Fig. 2.2. Based on the values of the distances and angle ϕ , it may be concluded that B-B interaction is weak, the A-A interaction is weaker while the A-B interaction is the strongest [19].

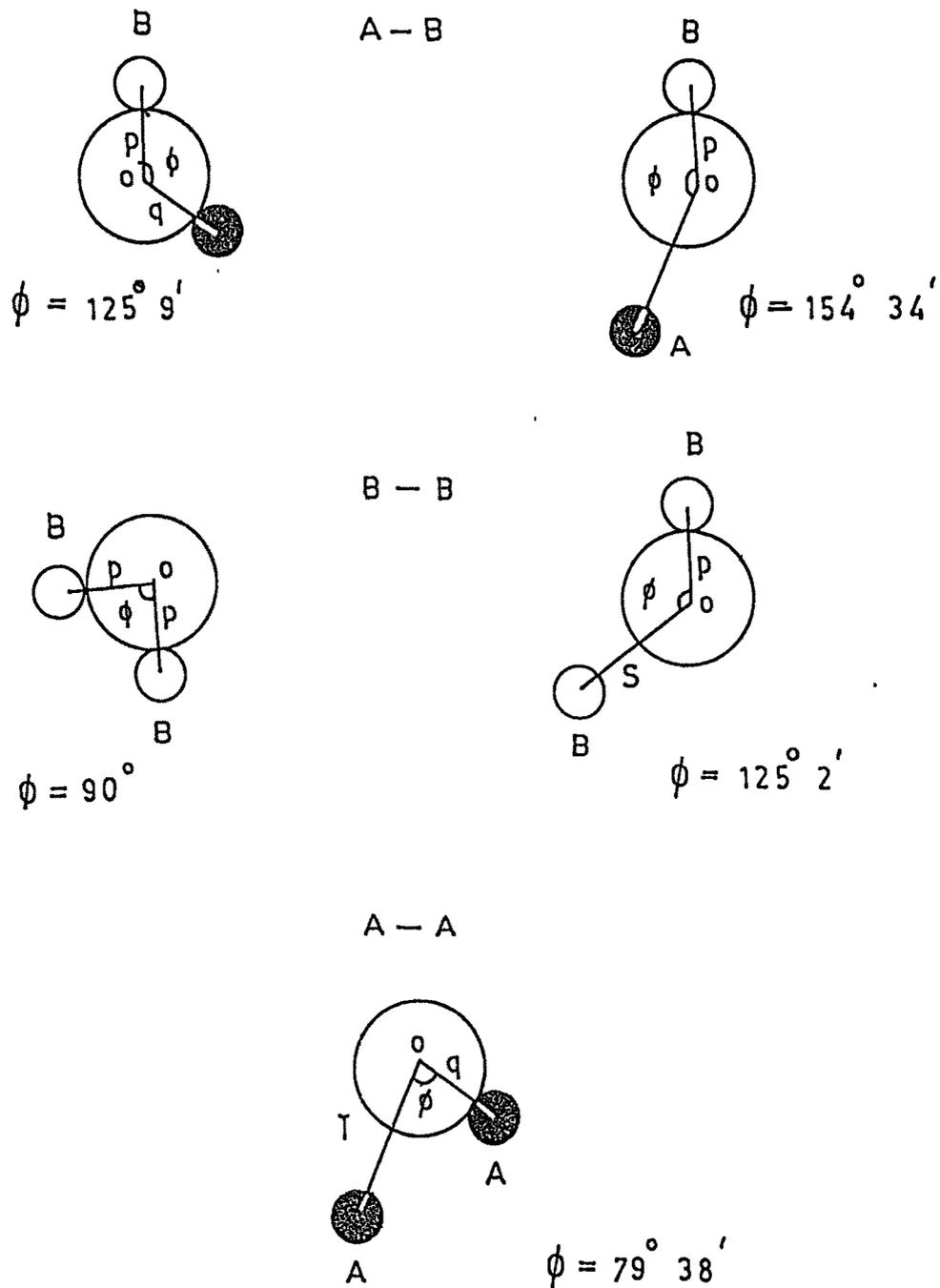


FIG. 2.2 — ANGLE BETWEEN A-A, B-B & A-B
DIRECTIONS IN A SPINEL STRUCTURE.

2A.9 THEORIES OF FERRIMAGNETISM

2A.9.1 NEEL'S THEORY

The term 'ferrimagnetism' was coined by Neel [20] to describe the properties of materials like ferrites, which below a certain temperature exhibit spontaneous magnetization from an uncompensated antiparallel arrangement of atomic magnetic moments. Neel assumed a partitioning of the moments into two sub-lattices, which because of their mutual interactions get aligned antiparallel to each other, thus producing a total magnetic moment equal to the difference between their individual magnitudes. The difference may occur when octahedron becomes tetragonal. The c-axis is parallel to one of the former cube edges, [100]. The tetragonal deformations are found on macroscopic scale if the concentration of Jahn-Teller ions is large. An example is CuFe_2O_4 , which is tetragonal [18, 21] below $T=1030\text{k}$ with $c/a = 1.06$. Both these T and c/a data depend on the distribution of Cu^{2+} over the octahedral and tetrahedral sites [22]. Other ions like Cr^{2+} (d^4) [23] and Ni^{3+} (d^7 in low spin state) [24], on tetrahedral sites Ni^{2+} (d^8) [25] and Fe^{2+} (d^6) [26] also show Jahn-Teller effect by giving rise to tetragonal deformations.

2A.9.2 YAFET-KITTLE THEORY OF FERRIMAGNETISM

Experimental data on some magnetic spinels were found to be incompatible with this above simple type of spin ordering as postulated by Neel. In 1952, Yafet and Kittle [10] extended Neel's model and the method of calculation based on a Weiss Molecular Field treatment of the exchange interactions between the several spin lattices. When A-B interactions are predominant, then the spin ordering of Neel-type will occur. But, when the AB interactions is equal to or smaller than that of AA interactions and BB interactions, the two sublattice model is no longer applicable and triangular model becomes energetically favourable.

When the atoms (or ions) B_1 and B_2 are in the sub-lattice B and the atom (or ion) A is in the sub-lattice A, superexchange interaction $J_{AB} \approx J_{AB}$ is negative and predominant, then the spins B_1 and B_2 will be oriented parallel to each other, even if the J_{BB} is negative. Now, if $J_{AB} \approx J_{BB}$ and both are negative, the parallel alignment of B_1 and B_2 will no longer be possible. The spins in B sub-lattice are not antiparallel but orient themselves such that at equilibrium, the total energy of the system is minimum. This is a practical problem in materials containing ferrites, because of one of the sub-lattice can be diluted by substituting non-magnetic ions such as Cd and Zn. The AB interactions are usually dominant but in competitive situations canted spin arrangements can arise either through substitution or by change in temperature.

2A.10 ELECTRICAL PROPERTIES OF FERRITES

The properties like electrical conductivity, thermo-electricity and dielectric dispersion in ferrites are very well explained in terms of the polaron hopping theory [27]. This theory can be proposed as long as the ions of the same parent atom but in different valence states are to be found in crystallographically similar positions in the lattice.

2A.11 APPLICATIONS OF FERRITES

The electrical and magnetic properties of ferrites make them unique in the electrical, magnetic and electronic applications. Ferrites can operate with virtually no eddy current losses at high frequencies. Hence they are used in microwave communications, 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 radio receivers, mechanical filters, circulators, broad band transformers, ultrasonic generators, isolators,

modulators, phase shifters, direction couplers, tape recorders, television, radio etc. [13, 14].

In digital computers the ferrite cores are used as the switching and memory elements for transmitting, storing and recording the signal pulse in few microseconds. 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 to 150 are used in filter inductor for band pass filters 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 (MICS) in an electronics field. The ferrite plating is a new technique used for the preparation of film devices in which heat resistant materials such as plastic are used [28].

SECTION – B : FERROELECTRIC MATERIALS

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 field.

The ferroelectric materials exhibit hysteresis property. It is the basic feature to use them in computer memory devices. 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 rapidly and extensive investigations on the properties of ferroelectrics have been carried out especially on single crystals. The theory of ferroelectricity is rather different from that of ferromagnetism, but both of them 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 [29,30].

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. 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 and 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. 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, thus called centrosymmetric. These can of course possess no polar properties. Nearly half of piezoelectric classes exhibit the very important property that of 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 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 constant

T_c = Curie-Weiss temperature

The dielectric constant becomes very high in the vicinity of Curie-Weiss temperature, where the crystal undergoes a transition from the polar state to non-polar state. 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 [29].

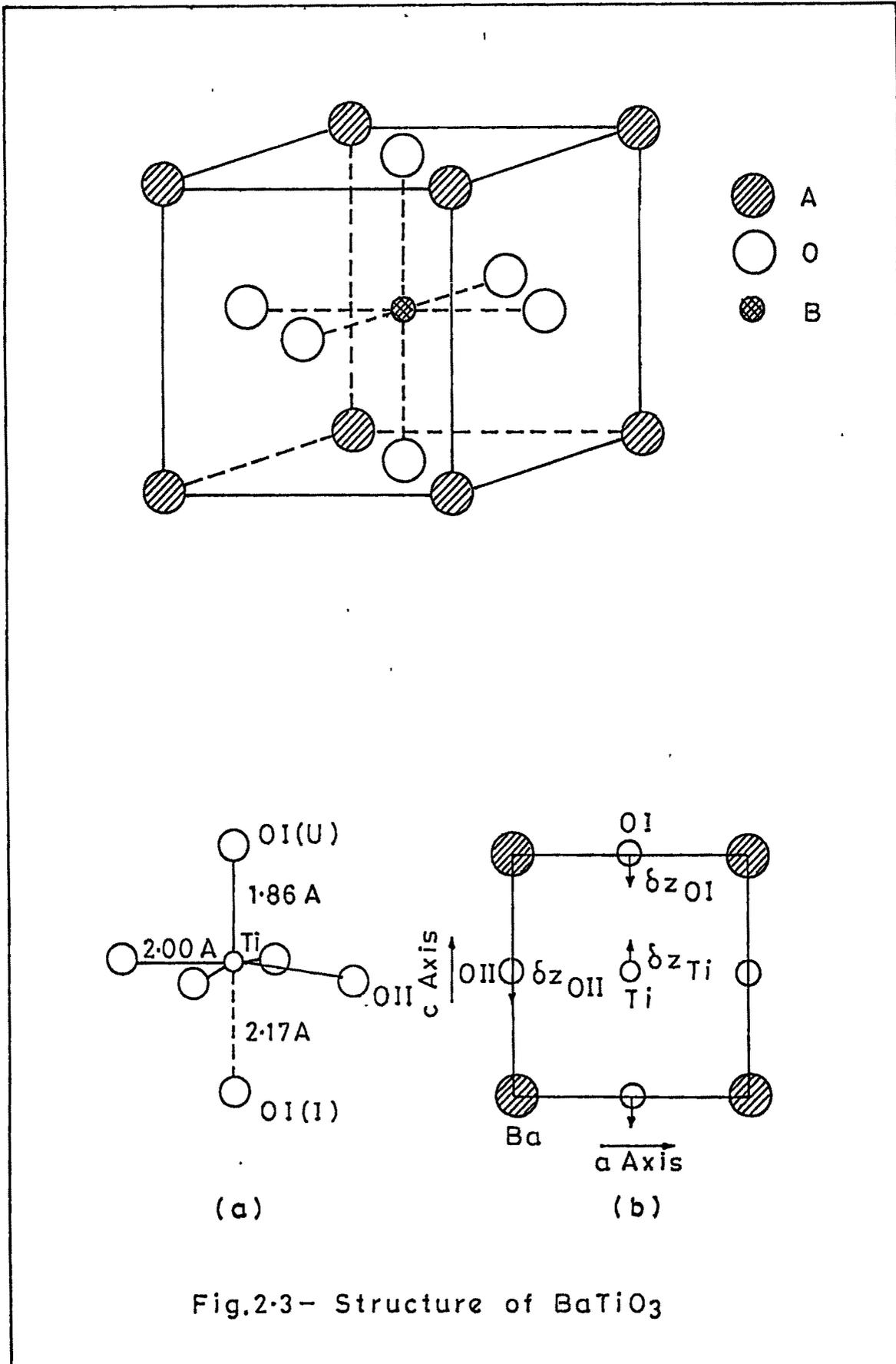
2B.3 CLASSIFICATION OF FERROELECTRICS

The ferroelectrics are classified according to their physical properties, chemical composition, centre 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 sulphate 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 can be made on the basis of accurate structural investigations.

2B.4 CRYSTAL STRUCTURE OF BaTiO_3

Barium Titanate (BaTiO_3) is the most extensively used ferroelectric material owing to its simpler structure, mechanical and chemical stability and exhibition of ferroelectric properties at and above room temperature. BaTiO_3 belongs to a large family of compounds with general formula ABO_3 , whose representative in nature is the mineral CaTiO_3 , called perovskite. The structure of BaTiO_3 above the Curie temperature is an ideal perovskite structure as depicted in the Fig. 2.3 and the space group is $\text{Pm}\bar{3}\text{m}$. The co-ordinates of the atoms in the non-polar phase are as follows-



Ba at (0 0 0), Ti at $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ and 3O at $(\frac{1}{2} \frac{1}{2} \frac{1}{2} 0)$, $(\frac{1}{2} 0 \frac{1}{2})$, $(0 \frac{1}{2} \frac{1}{2})$, where the cell edge is about 4Å . Typical for BaTiO_3 and all other members belonging to this group is the arrangement of the highly polarisable oxygen ions in the form of an octahedron with a small metallic ion at the centre.

Below the Curie point (i.e. polar phase), the atoms are displaced from their original symmetric positions along one of the $\langle 001 \rangle$ axes. The structure becomes tetragonal with the cell dimensions $a = 3.992\text{Å}$, $c = 4.036\text{Å}$, space group is $P4mm$ and one formula unit per unit cell. The coordinates of the atoms in this structure can be expressed in terms of three parameters, δ_{ZTi} , δ_{ZOI} and δ_{ZOII} . These three parameters represent the shifts of the atoms from the symmetrical positions. Thus Ba at (0, 0, 0), Ti at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + \delta_{ZTi})$ and OI at $(\frac{1}{2}, \frac{1}{2}, \delta_{ZOI})$ and 2OII at $(\frac{1}{2}, 0, \frac{1}{2} + \delta_{ZOII})$, $(0, \frac{1}{2}, \frac{1}{2} + \delta_{ZOII})$. These parameters are indicated schematically in Fig. 2.3(a) [31]. Neutron diffraction studies on BaTiO_3 at room temperature reveal the values of δ_{ZTi} , δ_{ZOI} and δ_{ZOII} . Choosing the origin at z level of OII, the table 1 gives the results concerning atomic shifts and the bond distance.

Table 1

Atomic shifts (Å)	Bond distance (Å)	
$\delta_{zBa} = + 0.05$	Ti - OI $\left\{ \begin{array}{l} 1.86 \\ 2.17 \end{array} \right.$	Ba - OII $\left\{ \begin{array}{l} 2.80 \\ 2.88 \end{array} \right.$
$\delta_{ZTi} = + 0.10$		
$\delta_{ZOI} = - 0.04$	Ti - OII 2.00	Ba - OI 2.82

The environment of Ti is depicted schematically in Fig. 2.3(b). This implies a slight distortion of oxygen octahedron surrounding the Ti atom. Assuming completely ionic-character of the crystal, the positional parameters of ions allow an estimate of the maximum possible contribution

of the ionic polarization. The result is $17 \mu\text{c}/\text{cm}^2$ implying that even the minimum contribution of electronic polarisation ($9\mu\text{c}/\text{cm}^2$) is considerable.

2B.5 FERROELECTRIC DOMAINS

The region of the crystal with uniformly oriented spontaneous polarisation called as domains and the region between the two domains is called as domain wall [32]. The walls which separate the domains with oppositely oriented polarisation are called 180° domain walls and those which separate regions with mutually perpendicular polarisation are called 90° walls. Because the C_T and a_T axes in a tetragonal crystal are different, the angle between polarisation directions on each side of a 90° wall is slightly smaller than 90° [33].

Ferroelectric domains form to minimise the electrostatic energy of the depolarising fields and the elastic energy associated with the mechanical constraints to which the ferroelectric specimen is subjected as it is cooled through paraelectric-ferroelectric phase transition [34]. Onset of the spontaneous polarisation of the transition temperature leads to the formation of a surface charge. This surface charge produces an electric field, called a depolarising field, E_d , which is oriented oppositely to P_s . The depolarising field will form whenever there is a nonhomogeneous distribution of spontaneous polarisation. The depolarising field often cannot be completely compensated as the grown ferroelectric crystals often exhibit reduced or even zero pyroelectric and piezoelectric effects due to the presence of ferroelectric domains. Splitting of a ferroelectric crystal into domains may also occur due to an influence of the mechanical stresses [35]. A combination of electric and elastic boundary conditions to which a crystal is subjected as it is cooled through the ferroelectric phase transition temperature usually leads to a complex domain structure with many 90° and 180° walls.

Domain walls which differ in orientation to the spontaneous polarisation vector are called ferroelectric domain walls and those which differ in orientations to the spontaneous strain tensor are called as ferroelastic domain walls [35]. Criteria which may be used to derive possible type of domain walls in a ferroelectric material were derived by Fousek and Janovec [36]. Ferroelectric domains are much narrower than domain walls in ferromagnetic materials.

2B.6 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

$$D = \epsilon_0 E_0 = \epsilon E_{\square} = E + 4\pi P \quad \dots (2.1)$$

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

The derivative of polarization P with respect to the field E is taken to be unity since surrounding medium is usually air or vacuum. Spontaneous polarization (P) can be given as

$$P = kE \quad \dots (2.2)$$

Where K is dielectric susceptibility. From equation (2.1), the dielectric constant of an isotropic medium can be defined as

$$\epsilon = D/E = (E + 4\pi P)/E \quad \dots (2.3)$$

In an isotropic cubic system P is always parallel to E and hence all quantities in above equation are expressed as scalars [37].

2B.7 FERROELECTRICS THEORY

In view of the unique properties exhibited by ferroelectric and the wide technological applications to which they are being put to, numerous attempts to explain the phenomenon of ferroelectricity in crystals were made and a number of theories have been accordingly prepared but none of these was found to be satisfactory. The most promising, modern and challenging theory due to Cochran is based on lattice dynamics, and the concept of so called soft modes [34, 38, 39].

Ferroelectric phase transitions are a special case of structural phase transitions, and can thus be interpreted in terms of stability of the crystal lattice dynamics. In a structural phase transition, the order parameter (polarisation in case of ferroelectric phase transition) may be associated with a lattice vibrational mode which exhibits an instability at the transition temperature. For a second order transition, for example, the frequency spectrum of the lattice vibrations related to the order parameter is proportional to $T - T_c$, so that this mode 'softens' to (its frequency goes to zero) as the material is cooled towards T_c . Freezing of the vibrations at T_c gives rise to non-zero order parameter and the corresponding reduction in symmetry. A soft mode is an optic mode and can be studied experimentally by infrared spectroscopy and neutron scattering [38]. The lattice dynamics approach and its recent extensions [40] have been very successful in describing qualitatively ferroelectric phase transitions. A detailed discussion of the theoretical approach can be found in book by Lines and Glass [34]. However, the theory is briefly outlined here.

2B.7.1 COCHRAN THEORY

Cochran's theory [39] is based on the assumption that the ferroelectric phase transition is the result of instability of crystal lattice with respect to one of the homogeneous (wave vector $g = 0$) transverse optical

mode (ω_T). Essentially the theory is based on the assumption that if the crystal is wholly or partially ionic, lattice vibrations are accompanied by polarisation oscillations of equal frequency, which create a local field interacting with the ions through long range coulomb forces. If for one particular mode of vibration these long range forces have the magnitude equal and opposite in sign to the short range forces, the crystal becomes unstable for this mode. The dielectric constant, which is connected to the frequency of the critical mode becomes large as it happens at the Curie temperature.

A Lydanne-Sachs-Teller (LST) theory [41] gives the relation between the ferroelectric properties and the thermodynamic properties of the crystals. For $g = 0$ mode of the diatomic crystal, LST relation gives the ratio of frequencies of the longitudinal optical (ω_L) and transverse optical (ω_T) mode of the infinite wavelength in terms of the ratio of the static dielectric constant (ϵ_s) of the crystal to the high frequency dielectric constant (ϵ_∞) as :

$$\epsilon_s / \epsilon_\infty = \omega^2 L / \omega^2 T \quad \dots (2.4)$$

where $\omega^2 T = 0$. Hence, $\epsilon_s = \infty$, as ϵ_s is equal to refractive index.

Cochran obtained the more general case in which there are n atoms in the elementary cell as :

$$\epsilon_s / \epsilon_\infty = 11 \sum_{j=2}^n \omega_j^2 L / \omega_j^2 T \quad \dots (2.5)$$

This equation produces one essential anomaly needed to explain ferroelectric transition. In order to have a complete understanding of the ferroelectric behaviour it is necessary to investigate the temperature dependence of $\omega^2 T$. In ferroelectrics, ϵ_s follows Curie-Weiss law above the transition temperature.

$$\epsilon_s = \epsilon_0 + \frac{4\pi c}{T - T_c}, \quad T > T_c \quad \dots (2.6)$$

where ϵ_0 is the temperature independent part of the dielectric constant. This equation (2.6) through equation (2.4) implies that the transverse optical modes of infinite wavelength have an anomalous temperature dependence given by

$$\omega^2 T = G (T - T_c), \quad \text{for } T > T_c \quad \dots (2.7)$$

where G depends on short range force constant.

The softening of the transverse optical mode ω_T by polarisation and the rapid rise of static dielectric constant offers an explanation for the onset of ferroelectricity. The temperature dependence of ω_T follows Curie-Weiss law and is related to ϵ_s through LST relation.

This theory provides an explanation of ferroelectric phase transition in diatomic crystal Cochran has used the data on lattice dynamics in an analysis of some characteristics of transitions in BaTiO_3 and estimated the dielectric constant value equal to 14,000 and spontaneous polarisation equal to $19.5 \mu\text{c}/\text{cm}^2$ for BaTiO_3 at the Curie temperature. The values are very close to those obtained experimentally by Merz in 1953 [42]. The prediction of absolute value of the frequency ω_T of the transverse optical mode with wave vector (g) zero for perovskite materials is the most interesting new result of this theory. Infrared studies by Ballantyne (1964) [43] on BaTiO_3 above the Curie temperature show that within the experimental error, the results are in agreement with Cochran theory.

The lattice dynamic theory has been successful in describing ferroelectric phase transitions qualitatively but for quantitative predictions difficulties originate in model simplification which are often unavoidable in many body problems. However, the phase transition sequence, effective

charge of ions and polarisation can now be fairly calculated for many pure ferroelectrics. Whereas the predictions of piezoelectric behaviour based on microscopic theories are still not available for any ferroelectrics [35].

2B.8 APPLICATIONS OF FERROELECTRICS

Ferroelectrics are the materials with strong anomalies in some 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 and 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.

Ferroelectrics are used in capacitors because of their high permittivity values. They are also used in frequency controls, filters, miniature capacitors, thermal meters, modulating devices, frequency multipliers, switches etc. They can be used as dielectric amplifiers and as low frequency amplifiers. These type of amplifiers could be used for remote controls, servo systems, stabilization of supplies and autofrequency amplification. Some polar materials and particular ferroelectric show increase in resistivity with increase in temperature. However drastic changes have been observed in several ferroelectrics near the Curie point. This property has been successfully employed for fabricating positive temperature coefficient transducers. Switching thermistors (PTC) are used mostly in control applications such as in TV sets, single phase electric motors, overcharge protection devices in batteries, thermal overload protection devices etc. The existence of a hysteresis loop makes it possible for them to use as memory elements.

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