
Chapter II

THEORETICAL BACKGROUND

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2.1 Introduction

Preparation of the samples is an important stage in material science. This is a process in which one mixes chemical component in different proportions following different chemical procedures and subjects the same to a series of treatments. The type of chemicals or metal salts and steps involved could vary from method to method. There are many processes as depending on many methods of sample preparation available. The method of sample preparation could be simple like co-precipitation method of sample preparation or highly complex and complicated like plasma method. Not all methods of sample preparation yield nano particle samples, moreover many times the method of preparation differs from sample to sample depending upon the type of material ~~one has to prepare~~. There are solid state methods, chemical methods as well as methods employing the combination of both. Each method has its own merits and demerits. The suitability of a particular method for preparing the required sample is mainly depends on the properties one expects to get or aims at.

Ceramic method:

This is the common method for preparing metal oxides and other solid materials. This involves grinding powders of oxides, carbonates or other compound containing relevant methods and heating mixture at desired temperature. Several oxides, phosphides and sulphides have been prepared by this method. Platinum, silica and alumina containers are used for the synthesis of metal oxides, while graphite containers are used for sulphides and other chalcogenides. Most of the ceramic preparations require very high temperatures, which are generally attained by resistant heating. This method suffers from many disadvantages such as: (I) no simple way of monitoring the progress of the reaction in ceramic method, (II) Sometimes it becomes

better to say
contents
or
components.

What
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difficult to obtain the compositionally hydrogenous products by the ceramic techniques even when reaction proceeds almost to completion

whether it
homogenous

Sol-gel synthesis:

Sol-gel method is one of the most important methods of preparing inorganic oxides. It is wet chemical method and a multi step process involving both chemical and physical process such as hydrolysis, polymerization, gelation, drying, dehydration and densification. The name "sol-gel" is given to the process because of distinctive viscosity increase that occurs at particular point in the sequence of the steps. A sudden increase in viscosity is the common feature of sol gel processing. The important features of the sol gel methods are better homogeneity, high purity, lower processing temperature, more uniform phase distribution in multi component systems, better size and morphological control.

Co-precipitation method:

In chemistry, the co-precipitation is the carrying down by a precipitate of substances normally soluble under the conditions employed. Analogously, in medicine, coprecipitation is specifically the precipitation of an unbound "antigen along with an antigen-antibody complex". Co-precipitation is an important issue in chemical analysis, where it is often undesirable, but in some cases it can be exploited. In gravimetric analysis, which consists on precipitating the analyte and measuring its mass to determine its concentration or purity, co-precipitation is a problem because undesired impurities often co-precipitate with the analyte, resulting in excess mass. This problem can often be mitigated by "digestion" (waiting for the precipitate to equilibrate and form larger, purer particles) or by redissolving the sample and precipitating it again.

On the other hand, in the analysis of trace elements, as is often the case in

radiochemistry, co-precipitation is often the only way of separating an element. Since the trace element is too dilute (sometimes less than a part per trillion) to precipitate by conventional means, it is typically co precipitated with a carrier, a substance that has a similar crystalline structure that can incorporate the desired element. An example is the separation of francium from other radioactive elements by co-precipitating it with cesium salts such as cesium perchlorate.))

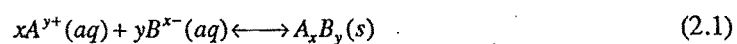
2.2 Basics of co-precipitation:

Theory and Thermodynamics of co-precipitation:

Co-precipitation reactions tend to exhibit the following characteristics:

- The products of precipitation reactions are generally sparingly soluble under the conditions of high super saturation.
- Such conditions indicate that the nucleation will be a key step of the precipitation process and that a large number of small particles will be formed.
- Secondary process such as Oswald ripening and aggregation, will dramatically affect the size, morphology and properties of the products.
- Super saturation conditions necessary to induce precipitation are usually the result of a chemical reaction. Although precipitation can be induced in any number of ways, chemical reactions are by far the most common methods for the synthesis of nanoparticles. Generally chemical reactions are chosen that results in products with low solubilities such that the solution quickly reaches a super saturation condition.

Consider a simple addition reaction for the formation of an electrolyte,



The equilibrium relationship between the products and its reactants is expressed as the solubility product constant, K_{sp} .

$$K_{sp} = (a_A)^x (a_B)^y \quad (2.2)$$

where, a_A and a_B are the activities of cation A and anion B in aqueous solution. K_{sp} values tend to be very low for many hydroxides, carbonates, oxalates and chalcogenides in aqueous solutions, solubility data for compounds in solvents other than water are substantially sparser.

When the product contains only one or two elements (e.g. metal, binary oxide, etc.), precipitation reactions are relatively straightforward. In more complicated ternary and quaternary systems, the process becomes more complex as multiple species must be precipitated simultaneously. ~~(Hence the term co-precipitation)~~ Co-precipitation reactions involve the simultaneous occurrence of nucleation, growth, coarsening, and/or agglomeration processes. //

Nucleation- The key to any precipitation process is the degree of super saturation, S given by

$$S = \frac{a_A a_B}{K_{sp}} \quad (2.3)$$

where a_A and a_B are the activities of solutes A & B and K_{sp} solubility product constant, or alternatively by $S = \frac{C}{C_{eq}}$ where, C and C_{eq} are the solute concentrations at saturation and at equilibrium, respectively.

← As nucleation begins in a supersaturated solution there exists equilibrium critical radius, R^* //

$$R^* = \frac{\alpha}{\Delta C} \quad (2.4)$$

The term α is given by

$$\alpha = \left(\frac{2\sigma_{SL}}{kT \ln S} \right) v C_{\infty} \quad (2.5)$$

where, σ_{SL} is the surface tension at the solid – liquid interface, v is the atomic volume of solute, k is Boltzmann constant, T is temperature and S is super saturation.

Nucleated particles with $R > R^*$ will continue to grow, while those with $R < R^*$ will dissolve. The activation energy of the cluster formation is given by [1]

$$\Delta G^* = \frac{4\pi\sigma_{SL}R^{*2}}{3} = \frac{16\pi\sigma_{SL}^3 v^2}{3k^2 T^2 \ln^2 S} \quad (2.6)$$

Thus for stationary conditions, the homogeneous nucleation rate, R_N is given by

$$R_N = \left(\frac{dN}{dt} \right) \frac{1}{V} = A \exp \left[\frac{-(\Delta G^*)}{kT} \right] \quad (2.7)$$

where, N is the number of nuclei formed per unit time per unit volume, V and A is a pre-exponential factor typically ranging from 10^{25} to $10^{56} \text{ S}^{-1} \text{ m}^{-3}$.

Combining equations (2.6) and (2.7)

$$R_N = A \exp \left[\frac{-16\pi\sigma_{SL}^3 v^2}{3k^3 T^3 \ln^2 S} \right] \quad (2.8)$$

Revealing that R_N is an exponential function of S . R_N remains negligible until certain critical supersaturation S^* is reached.

Growth: The growth process of the precipitated particles is complicated. The process can be either diffusion-limited or reaction-limited. Majority reactions are diffusion-limited. As such, concentration gradients and temperature become the predominant factors determining growth rate as new material is supplied to the particle surface via long distance mass transfer. The balance of that material as monomer, crossing the surface of spherical crystallite is given by

$$\frac{dr}{dt} = D\Omega \left(\frac{1}{\delta} + \frac{1}{r} \right) (C_b - C_i) \quad (2.9)$$

where, r is the crystal radius, t is time, D is the diffusivity of the monomer, Ω is the molar volume, and δ_i is the thickness of the layer over which the concentration changes from C_b , the bulk solute concentration, to C_i the solute concentration in the vicinity of crystal surface [2-3]. The relation between monomer concentration and crystal structure is given by the Gibbs – Thomson equation [4]

$$C_e(r) \cong C_\infty \left(\frac{1 + 2\Omega\gamma}{R_G T R} \right) \quad (2.10)$$

C_∞ is constant, γ is the interfacial tension, T is temperature and R_G is universal gas constant. The relation between the rate of growth G and super saturation ratio, S can be expressed as a power law equation [5].

$$G = \frac{dL}{dt} = k_G S^g \quad (2.11)$$

where k_G is the growth rate constant and g is the growth order.

Ostwald ripening: Ostwald ripening is the phenomena by which smaller particles are essentially consumed by larger particles during the growth process [6-7]. A detailed mathematical description of Ostwald ripening was developed by Wagner; their combined models are today referred as LSW theory. The principles of LSW theory are summarized as follows.

I) For a diffusion-controlled process, the average radius of the precipitate particles r as a function of time, t is [8],

$$\bar{r}(t) = \sqrt[3]{kt} \quad (2.12)$$

where, k is the coarsening rate and D is the diffusion current of solute across the grain

boundary. Particle size is thus proportional to the cube – root of time.

II) During diffusion –controlled ripening, number density N of nucleated particles decays as

$$N(t) = \frac{0.22Q_0}{\bar{r}(t)^3} = \frac{0.22}{2D\alpha t} \quad (2.13)$$

where, Q_0 is the total initial super saturation. The number of solute particles decreases as r^{-1} during ripening.

III) The size distribution of particles is given by

$$f(R,t) = \left[\frac{N(t)}{\bar{R}(t)} \right] \rho_0(\rho(t)) \quad (2.14)$$

$\rho(t) = R/\bar{R}(t)$ and $\rho_0(\rho)$ is a time-independent function of the absolute dimension of the grains.

Growth termination and nanoparticles stabilization: The agglomeration of small particles precipitated from solutions is practically inevitable in the absence of a stabilizer. It should be pointed out that agglomeration can occur at any stage during synthesis. There are generally two approaches to nanoparticles stabilization (a) steric repulsion between particles caused by surfactants, polymers or other organic species bound to the nanoparticles surfaces, (b) Electrostatics repulsion resulting from the chemisorption of charged species.

2.3 Mechanism of co-precipitation

There are three main mechanisms of co-precipitation: inclusion, occlusion, and adsorption [9]. An inclusion occurs when the impurity occupies a lattice site in the crystal structure of the carrier, resulting in a crystallographic defect; this can happen when the ionic radius and charge of the impurity are similar to those of the carrier. An

adsorbate is an impurity that is weakly bound (adsorbed) to the surface of the precipitate. An occlusion occurs when an adsorbed impurity gets physically trapped inside the crystal as it grows.

Besides its applications in chemical analysis and in radiochemistry, coprecipitation is also potentially important to many environmental issues closely related to water resources, including acid mine drainage, radionuclide migration in fouled waste repositories, metal contaminant transport at industrial and defense sites, metal concentrations in aquatic systems, and wastewater treatment technology [10]. Coprecipitation is also used as a method of magnetic nano particle synthesis [11].

2.4 Characterisation techniques

2.4.1 X-ray diffraction (XRD) technique

A given substance always produces a characteristic diffraction pattern, whether that substance is present in the pure state or as one of the constituent of a mixture of substances. This fact is the basis for the diffraction method of chemical analysis. Qualitative analysis for a particular substance is accomplished by identification of the pattern of that substance. Quantitative analysis is also possible, because the intensities of the diffraction lines due to one phase of a mixture depend on the proportion of that phase in the specimen. Detailed treatments of chemical analysis by X-ray diffraction are given by Klug and Alexander [12] and Zwell and Danko [13]. Charles, Nenadic and Crable [14] have reviewed diffraction methods of determining quartz, asbestos and talc in industrial dust; all of these minerals can cause lung disease.

Basic principle of X-ray diffraction technique

The crystallographic features are studied by the process of X-ray diffraction. The X-ray technique based on monochromatic radiation is generally more important

because the spacing of the planes (d-spacing) can be deduced from the observed diffraction angles. The phenomenon of X-ray diffraction can be considered as a reflection of X-rays from the crystallographic planes of the material and is governed by Bragg's equation

$$2d\sin\theta = n\lambda \quad (2.15)$$

where 'd' is the lattice spacing, λ is the wavelength of monochromatic X-rays, n is the order of diffraction and θ is the diffraction angle.

Generally, the powder technique in conjunction with diffractometer is most commonly used. In this instrument, the diffracted radiation is detected by the counter tube, which moves along the angular range of reflections. The intensities are recorded on a computer system. The 'd' values are calculated using relation 2.15 for known values of θ , λ and n . The X-ray diffraction data thus obtained is printed in tabular form on paper and is compared with Joint Committee Powder Diffraction Standards (JCPDS) data to identify the structure of the material.

2.4.2 Scanning electron microscopy (SEM)

Scanning electron microscopy is used for inspecting topographies of specimen at very high magnifications using piece of equipment called scanning electron microscope. SEM magnifications can go to more than 30000x. But some semiconductors manufacturing applications require magnification less than 300x only. SEM inspection is often used in the analysis of die/package cracks and failure surfaces, bond failures and physical defects on the die or package surface. To produce the SEM image, the electron beam is swept across the area being inspected, producing many signals. During SEM inspection, a beam of electrons is focused on the spot volume of the specimen, resulting in the transfer of energy to the spot. These bombarding electrons, also referred to as primary electrons, dislodge electrons from the specimen

itself. The dislodged electrons, also known as secondary electrons are attracted and collected by a positively biased grid or collector and transferred into signal. These signals are then amplified, analyzed and translated into images of the topography being inspected. Finally the image is shown on a cathode ray tube (CRT) or any other display device. The SEM is used primarily for the examination of thick (i.e. electron opaque) samples. Electrons which are emitted or back scattered from the specimen are collected to provide: (1) Topological information (i.e. detailed shape of specimen surface) if the low energy secondary electrons (≤ 50 eV) are collected, (2) atomic number or orientation information if the high-energy back scattered electrons are used or if the leakage current to earth is used. Imaging of magnetic samples using secondary and or back-scattered electrons reveals magnetic domain contrast. In addition, two other signals can be collected; the electron beam induced current and light cathodoluminescence. The convergence angle of the probe at the specimen is controlled by the diameter of the final aperture and this angle determines the depth of field of an SEM. ~~Thus~~ ^{In fact,} the large depth of field that is commonly associated with SEM images is ~~in fact~~ due to small convergence angle at the specimen, which is much smaller than the corresponding angle in optical microscopes. A very large value of depth of field for high-resolution image, which underlines the value of high magnification SEM images of rough surfaces. Figure 2.1 shows the schematic diagram of scanning electron microscope.

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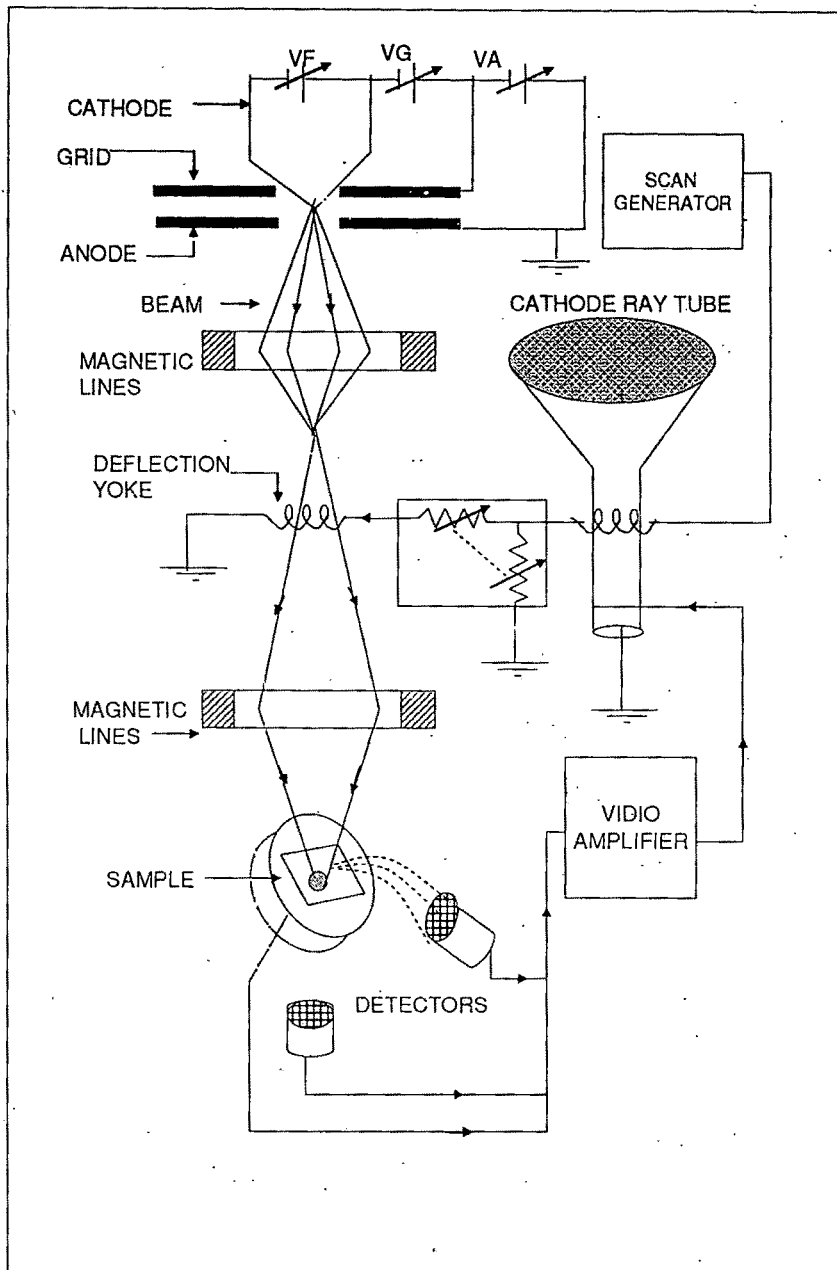


Fig. 2.1 Schematic diagram of Scanning Electron Microscope

2.4.3 Dielectric properties

A) Introduction

Dielectrics are materials that are poor electrical conductors. In most instances the properties of Dielectric are due to polarization of the material. When the dielectric is placed in an electric field, the electrons of an atom or ions of a unit cell reorient themselves. As a result of this polarization, the dielectric is under stress and it stores energy this becomes available when an electric field is removed. This polarization is analogous to the polarization that takes place when a magnetic material is magnetized. The effectiveness of a dielectric material is measured by its relative ability, to store energy, and is expressed in terms of a dielectric constant or permittivity (ϵ). The term dielectric constant is actually frequency dependent function of real and imaginary parts. The ratio of the imaginary part to the real part of the dielectric constant is called loss tangent [15]. The ability of a dielectric to withstand electric fields without losing insulating properties is its dielectric strength. A good dielectric must return a large percentage of energy stored in it when the field is reversed. Dielectrics exhibiting high dielectric constants at high frequencies, high dielectric strengths and have low loss tangents are desirable for an application point of view [16].

B) Polarization of Dielectrics:

- **Electronic Polarizability:** - Electrons and positively charged nucleus will be displaced such a way that electrons move in the positive field direction and nuclei in opposite direction.
- **Ionic Polarizability:** - If the bonding is ionic, cations and anions will get displaced with respect to one another.
- **Orientalional Polarizability:** If the material contains complex ions or molecules possessing permanent dipole moment, the dipoles will tend to align

themselves in the field direction. The net effect will be to induce a dipole moment within the solid. This Polarizability is absent in the non-polar materials [17]. A polar material may exhibit a zero dipole moment due to thermal randomization of dipoles and an applied electric field will induce a net dipole moment. Thus the polarization is inherently associated with thermal motion of molecules which depends on temperature. Dipole reorientation polarization can follow only up to MHz-GHz (10^6 - 10^9 cycle/sec). The average degree of orientation is given by the Langevin function,

$$\alpha_{or} = \frac{\rho^2}{(3K_B T)} \quad (2.16)$$

where, K_B denotes the Boltzmann constant and T the absolute temperature. This is why ferroelectric materials with permanent dipoles cannot be used for microwave dielectrics materials, their permittivity are typically high at low frequencies (KHz), but decreases significantly with increasing applied electric field frequency. Below microwave frequency, the polarization is due to the microstructure of polycrystalline materials followed by the migration of free charges. This polarization is referred as interfacial polarization or space charge polarization. It exists in heterogeneous materials containing semiconducting impurities. This is field distortion due to space charge and it increases dielectric permittivity [18].

- **Space charge polarization:** - Space charge polarization exists in a dielectric material, which shows spatial homogeneities of charge carrier densities. Space charge polarization effects are not only of importance in semiconductor field-effect devices but also occur in ceramic with electrically conducting grains and insulating grain boundaries (so called Maxwell- Wagner polarization). A drift of mobile electrons or ions, which are confined, to outer or inner surfaces, causes the space charge polarization. Depending on the local conductivity, the space

charge polarization may occur over a wide frequency range Hz to MHz. The total polarization of the dielectric material results from all the contributions discussed above and given by equation,

$$\epsilon = \epsilon_{elec} + \epsilon_{ion} + \epsilon_{or} + \epsilon_{sc} \quad (2.17)$$

The contributions from the lattice are called intrinsic contributions, in contrast to extrinsic contributions

C) Dielectric constant:

The relative dielectric constant is the ratio between the charges stored on an electrode slab of material brought to a given voltage to the charge stored on a set of identical electrodes separated by vacuum. In the usual MKS notation, it is the ratio between the Permittivity in farads per meter and that of free space, $\epsilon_0 = 8.85 \times 10^{-12}$ F/m.

D) Dielectric Loss (Tan δ)

With alternating voltages, the charge stored on a dielectric has both real (in phase) and imaginary (out of phase) components caused by either resistive leakage or dielectric absorption. The loss is expressed by the ratio of out of phase component to the in phase component. This is the dissipation factor or the dielectric loss, also frequently called loss tangent (Tan δ).

E) Frequency dependence of Dielectric Constant

Total polarization is contributed by the electronic, ionic and orientational and space charge polarizability. The response of each type to the frequency dependence is different. The electronic polarization can be quickly built up in 10^{-14} - 10^{-15} s, ionic polarization requires a time as long as 10^{-11} - 10^{-13} s i.e. both electronic, ionic polarizability responds in the regions from the microwave to infrared. The total polarization and dielectric constant decreases in steps as frequency is steadily

increased. Koop [19] gave phenomenological theory of dispersion based on Maxwell [20]-Wagner [21] interfacial polarization model for inhomogeneous dielectric structure. It was assumed that the solid consists of well conducting grains separated by poorly conducting layers. This model explains strong dispersion for dielectric constant ϵ and a relaxation peak in the dielectric loss ($\text{Tan}\delta$) at low frequency. It is seen that the dielectric constant at higher frequencies is due to the presence of low conducting surface layers of the grains. The dielectric constant (D) found in a dielectric material when subjected to an alternating field (E) is given by

$$D = \epsilon^* E \quad (2.18)$$

where, ϵ^* is a dielectric constant of a material which is a complex quantity involving a real (ϵ') and an imaginary parts (ϵ''),

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (2.19)$$

The physical significance of an imaginary part is the energy dissipation in the system called dielectric loss. Loss factor ($\text{Tan}\delta$) is given as

$$\text{Tan}\delta = \frac{\epsilon''}{\epsilon'} \quad (2.20)$$

The power loss per unit the volume of the material is given by,

$$P = \epsilon E^2 \epsilon_0 \epsilon' \tan \delta \quad (2.21)$$

where, referred symbols have their usual meaning.

The dielectric constant is a function of frequency of alternating electric field. As a consequence, with increasing frequency dielectric constant decreases in steps. At high frequencies only electron polarizability contributes to the polarization and hence a dielectric constant attains a constant but small value.

F) Temperature dependence of Dielectric Constant

In a solid polar dielectric with Curie temperature $T_{1c} > 0$, the dielectric constant increases with increase in temperature due to growing effect of ionic polarization. The gradual increase in temperature reduces the relaxation time. A further increase in temperature adds to random vibration motion of molecules, which becomes less susceptible to orientation in the field direction and hence the dielectric constant decreases. In non polar dielectrics, the polarizability is independent of temperature. However, the influence of heat leads to expansion and results in decrease of number of polarized molecules per unit volume. Thus the dielectric constant decreases with increase in temperature. At Curie temperature maximum value of the dielectric constant is observed and it decreases above the Curie temperature. It indicates the phase transition from ferroelectric to paraelectric. However the phase transition in ferroelectrics is to paraelectric is of three kinds (i) spontaneous polarization abruptly drops to zero at the curie temperature T_C , so that Curie-Weiss temperature $T > T_C$, (ii) spontaneous polarization smoothly decrease to zero, so that $T = T_C$, dielectric constant extends to infinity and (iii) The phase transition takes place within a broad temperature range and spontaneous polarization gradually decreases showing a diffused (broad maxima). This type of transition is commonly found in ferroelectrics [22]. It is reported that the diffused phase transition (DPT) is caused due to chemical inhomogeneity from the cation disorder in complex perovskites. It is related to the nanoscale ordered micro regions exhibiting a material acting as location of spontaneous polarization above the transition temperature [23]. It was suggested that thermal treatment makes the distribution of ordered micro regions to diffuse and it tends to increase the width of the DPT.

G) A.C. Conductivity:

A capacitor when charged under a.c. voltage will have some loss current due to ohmic resistance or impedance by heat absorption. If Q be the charge in coulomb due to a difference potential of (V) volt between two plates of a condenser of area A, and separated by distances d, then a.c. conductivity ($\sigma_{a.c.}$) due to a.c. voltage $v (v_0 e^{i\omega t})$ is given by the relation,

$$\sigma_{a.c.} = \frac{J}{E} \quad (2.22)$$

J is current density and E the electric field strength vector. But electric field Vector, $E = D/\epsilon$, where D is displacement vector of the dipole charges, ϵ is the complex permittivity of this material. For a parallel plate capacitor the electric field intensity (E) is the ratio of potential difference between plates of a capacitor to the inter plate distance i.e.

$$E = \frac{V}{d} \quad (2.23)$$

Since the current density $J = \frac{dq}{dt}$, but q is given by

$$J = \epsilon' \frac{Vj\omega}{d} \quad (2.24)$$

Substituting for E and J in (equation 2.25)

$$\sigma_{a.c.} = \frac{J}{E} = \epsilon' j\omega \quad (2.25)$$

Since, ϵ being a complex quantity

$$\sigma_{a.c.} = (\epsilon' - j\epsilon'')j\omega = j\omega\epsilon' + \omega\epsilon'' \quad (2.26)$$

The a.c. conductivity may be a real quantity; the term containing j has to be neglected hence,

$$\sigma_{a.c.} = \omega\epsilon'' \quad (2.27)$$

In any dielectric material there will be some power loss because of the work done to overcome the fractional damping forces encountered by the dipoles during their

rotation. If an a.c. field is considered, then in an ideal case the charging current I_c will be 90° out of phase with the voltage. But in most of capacitors due to absorption of electric energy some loss current I_L will also be produced, which will be in phase with the voltage. Charging current I_c , and loss current I_L , will makes angles δ and θ , respectively with the total current, I , passing through the capacitor. The loss current is represented by $\sin\delta$ of the total current.

1) generally, $\sin\delta$ is called loss factor but when δ is small then,

$$\sin \delta \cong \delta \cong \tan \delta$$

But the two components of the complex dielectric constant ϵ , will be frequency dependent and is given by

$$w\epsilon' = \frac{D \cos \delta}{E} \quad (2.28)$$

$$w\epsilon'' = \frac{D \sin \delta}{E} \quad (2.29)$$

Since the displacement vector in the time varying field will not be in phase with E and hence there will be phase difference δ between them. We have

$$\tan \delta = \frac{\omega\epsilon''}{\omega\epsilon'} \quad (2.30)$$

$$\sigma_{a.c.} = w\epsilon' \tan \delta \quad (2.31)$$

where $w = 2\pi f$ and $\epsilon' = \epsilon_0 \epsilon_r$. Here ϵ_r is the relative permittivity of the material and ϵ_0 is the permittivity of free space. So

$$\sigma_{a.c.} = 2\pi f \epsilon_0 \epsilon_r \tan \delta \quad (2.32)$$

This equation is used to calculate the a.c. conductivity using dielectric constant and $\tan\delta$ at a given frequency. It is to be noted that both $\tan\delta$ and ϵ_r are available from dielectric measurements [24].

2.4.4 Electrical resistivity

Electrical Resistivity is an important physical property of dielectric crystals, not only for practical applications but also for the interpretation of various physical phenomena. It is important for understanding the electrical transport mechanism in any solid. There are different methods of determining the nature of conductivity. The simplest way is to measure dc conductivity as a function of time using electrodes, which blocks ionic conduction. In case of pure ionic conduction dc conductivity decreases with time and tends to become zero after sufficiently long time, whereas for pure electronic conductor it is essentially independent of time.

The electrostatics interaction between conduction electrons (or holes) and nearby ions results in the displacements of ions causing the polarization in the surrounding region. The charge carrier is situated at the center of polarization potential well. The carriers can be transferred to the neighboring site by thermal activation. The process of jumping of electrons (or holes) by thermal activation has been described as the hopping mechanism. Heikes and Johnson have derived an expression for the mobility of a charge carrier subject to hopping mechanism.

$$\mu = \frac{e^2 a^2 w_0}{KT} \exp\left(-\frac{\Delta E}{KT}\right) \quad (2.33)$$

where, w_0 is the frequency of vibration of crystal lattice, 'a' is the distance between nearest neighbour cations, ΔE is the activation energy and K is Boltzmann constant.

For mixed samples conductivity decreases with time but tends to stabilize at some finite constant value. This is the electronic contribution [25-26]. The dc electrical conductivity of a material is an intrinsic or inherent property of the materials. It denotes its ability to conduct electric charge. The conductivity of the solid dielectric depends on

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