CHAPTER II
THEORETICAL BACKGROUND

This chapter presents the theoretical background about dielectric properties and the related electrical response in materials. The first section of this chapter gives the relationship between a dielectric response and polarization mechanisms in materials; a dielectric relaxation theory is also included in the chapter as well. The basic theory and mechanism of the polarizations related to giant dielectric properties of materials are revealed. Orientational, hopping, and space charge polarizations are briefly discussed; in addition, the dielectric response in the time- and frequency-domains that relate to these polarizations is also represented. Some models of the dielectric relaxation are expressed to describe the dielectric response behavior of dielectric materials through the polarization mechanism. Moreover, a conductivity term is added into these models in order to obtain the most suitable model to ascribe the real dielectric response behavior. The temperature dependence of the polarizations is also investigated. The basic of impedance spectroscopy is suitably ascribed in the second section of the chapter. The last section of the chapter demonstrates the microstructure model of inhomogeneous dielectric materials, which may be related to their giant dielectric properties.

2.1 Basic dielectric theory

When insulator materials such as ceramics or glasses are used either as a capacitive element in electronic applications or as insulation, dielectric properties are of special importance. For such applications, the dielectric properties of a particular material (e.g., dielectric constant, dielectric factor or loss tangent, and dielectric strength) are usually used to determine the ability and suitability. Although the important dielectric property names as "*dielectric constant*", this property is never constant; it varies with several factors such as frequency, field strength, temperature, humidity, and radiation as well as other dielectric properties (Hence, West, 1990). Moreover, dielectric properties of some materials also depend strongly on the kinds and preparation methods of electrodes (Krohns et al., 2007; 2008). Thus, it is necessary and important to examine dielectric theory in terms of materials response, circuit response, and environmental response.

It is well known that the basic definitions concerning about dielectric properties are usually treated from a simple parallel-plate capacitor, as illustrated in figure 2.1. The positive charge (+*Q*) and negative charge (-*Q*) can be introduced by applying a dc voltage across the plates and charging the system as a capacitor. Important relationships can be created by considering the effect of filling the free space between the plates with a dielectric material (Hence, West, 1990; Moulson, Herbert, 2003; Wahab, 2005). According to Gauss's law (Johnk, 1988), which simply states that the electric flux outward from a volume is equal to the net charge enclosed inside, surface charge density (σ'_{s0}) and the electric filed ($\vec{E}$) that normal to the plates separated by a vacuum are related to each other as

$$E = \frac{\sigma'_{s0}}{\varepsilon_0}, \tag{2.1}$$

where, ε_0 is the permittivity of free space, vacuum permittivity or electric constant and is equal to 8.854187871 ... × 10^{-12} $\mathrm{Fm^{-1}}$. Note that, the value of ε_0 is defined from the formula, $\varepsilon_0 = 1/\mu_0 c_0^2$, where μ_0 and c_0 are the magnetic constant or vacuum permeability and the speed of light in vacuum, respectively.

Similarly, when the dielectric material is inserted into the gab between the plates as seen in figure 2.1, the correlation between surface charge density (σ'_s) and the electric filed ($\vec{E}$) can be expressed as

$$E = \frac{\sigma'_s}{\varepsilon_{permit}}, \tag{2.2}$$

where ε_{permit} is the permittivity of the dielectric material. As a result, the capacitance of the free-space capacitor (C_0) is enhanced with the capacitance of C (Hence, West, 1990; Moulson, Herbert, 2003; Wahab, 2005). In addition, a dielectric constant (ε'), the most important definition of dielectric materials, can be defined as

$$\varepsilon' = \frac{C}{C_0} = \frac{\varepsilon}{\varepsilon_0}. \tag{2.3}$$

The ratio of the permittivity of the material to the permittivity of free space is, therefore, the dielectric constant of such material; as a result, the dielectric constant can also be called the '*relative permittivity*', which is unitless.

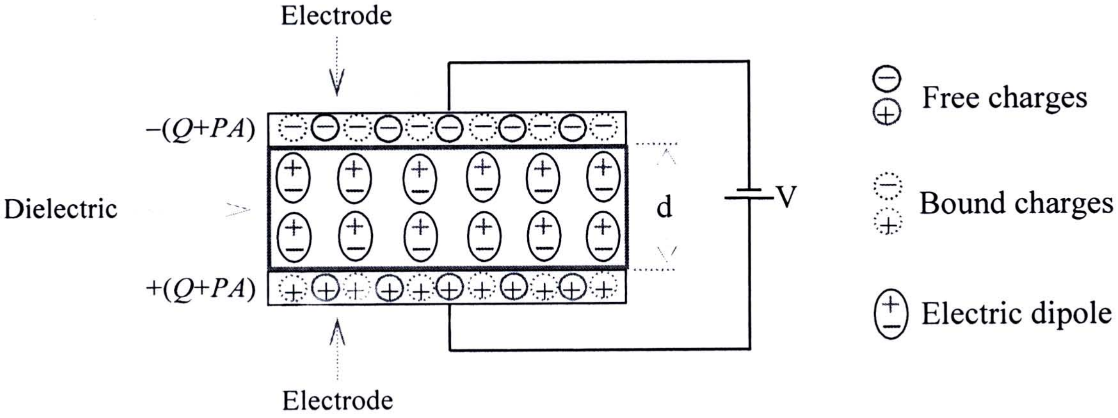

Figure 2.1 Charge on a parallel-plate capacitor with dielectric material between plates (Adapted from Hence, West, 1990).

2.2 Polarizations in dielectrics

Although the energy band structure of a dielectric or an insulator is similar to that of a semiconductor, the forbidden gab in the dielectric is comparatively larger. Thus, electrons in the valence band of the dielectric material cannot surmount the forbidden energy gab in dielectric. Consequently, they cannot move into the conduction band even though they are activated by thermal energy kT available at room temperature unlike the semiconductor. This is why the dielectric material is the insulator; electrons cannot move trough the material. Under an applied electric field, however, these electrons in the dielectric can only move a bit within the molecules. For dielectric theory, therefore, dielectric properties of materials usually comprise the short-range conducting electrical characteristics. Furthermore, the dielectric responses result not only from the short-range motion of electrons, but also from the short-range motion of all charge carriers (atoms, molecules, ions, holes, and vacancies) under the influence of the applied electric field (Hence, West, 1990). The displacement of the charge carriers in the dielectric generates an electric dipole moment ($\bar{\mu}$) and is called to be '*polarized*'. The electric dipole comprises two equal and opposite point charges ($\pm Q$) separated by a small distance, δx. The dipole moment of the electric dipole is defined as

$$\bar{\mu} = Q\delta\bar{x} . \tag{2.4}$$

Certainly, the dipole moment is a vector and directed from the negative charge to positive charge. In the case of an applied alternating electric field, the electric dipoles can be aligned in the direction of the field. The dipole moment per unit volume of the dielectric material is termed the polarization ($\bar{P}$), i.e.

$$\bar{P} = \frac{\sum_{i=1}^{n} \bar{\mu}_i}{\Delta V} . \tag{2.5}$$

Usually, the direction of $\bar{P}$ is exactly the same as that of $\bar{\mu}$. If the number of the displaced molecules per unit volume in the dielectric is N, and if each has the same moment ($\overline{\mu}$) or the average moment of the these displaced molecules is $\overline{\mu}$, then the polarization is given by

$$P = N\overline{\mu} . \tag{2.6}$$

As illustrated in figure 2.1, the insertion of the dielectric inside the space between the metallic plates causes the potential between the plates induced by the original charges ±Q on the plates to decrease to a smaller value. In fact, the charges ±Q remain constant; however, one portion of σ_s' is used to compensate the polarization charges on the surfaces of the dielectric in contact with the metallic plates (Kao, 2004). This portion is the bound charge density (σ_b'), which is bound at the locations with its charge opposite in the polarity and equal to the magnitude of the polarization charges of the dielectric. The polarization P can also be defined as

$$P = \sigma_b' . \tag{2.7}$$

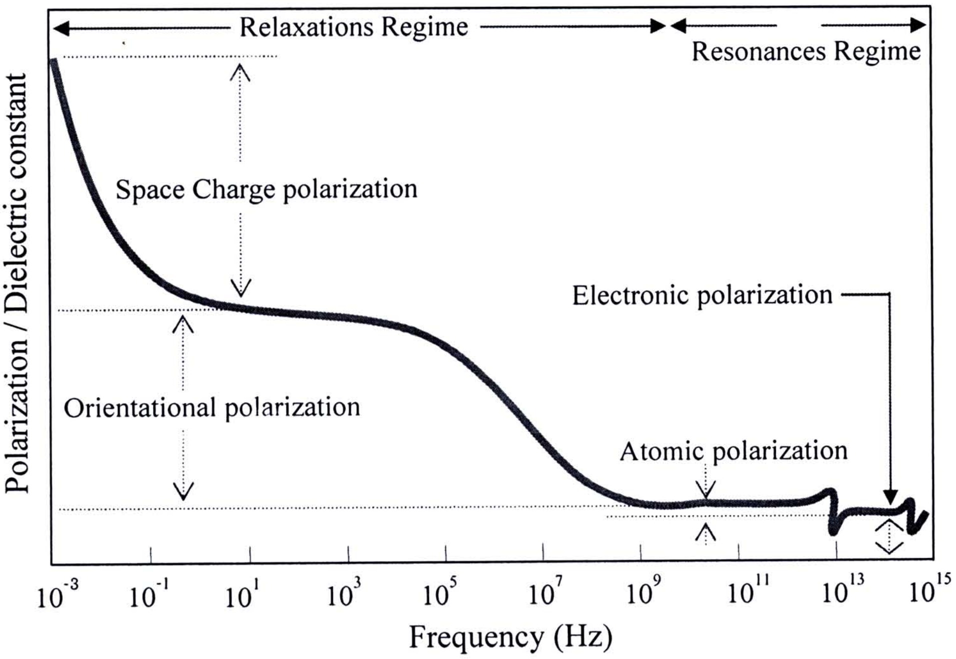

Figure 2.2 Frequency dependence of the polarization mechanisms in dielectrics (Adapted from Hence, West, 1990).

In general, the mechanisms of polarization in dielectric ceramics and glasses can be divided into four primary groups: electronic, atomic, orientational, and space charge polarizations. All of the mechanisms contribute to the total polarization of the dielectrics, resulting from the short-range motion of charge carriers. Figure 2.2 illustrates the frequency dependence of the polarization mechanisms in dielectrics. Each of these polarization mechanisms dominates at different frequencies range; moreover, the polarization intensities of these four mechanisms are different. The interfacial and dipolar polarizations are low-frequencies electrical responses and their intensities are considerably larger than those of the electronic and atomic polarizations. Detailed descriptions of the polarization mechanisms are as following.

2.2.1 Electronic polarization

It is the displacement of the valence electron cloud of the ion within a material with respect to the positive nucleus. This polarization mechanism can occur at very high frequencies in the ultraviolet optical range, 10^{15} Hz. This mechanism is related to the optical properties of the material, i.e., the index of refraction.

2.2.2 Atomic polarization

It is owing to the shift of positive and negative ions in a material with respect to each other. The atomic polarization can occur at high frequencies up to the range of about 10^{12}-10^{13} Hz, which is in the infrared range. The board peak of the infrared absorption can reveal to the several types of ions in the dielectric or a distribution in bond strengths.

2.2.3 Orientational polarization

It is also called '*dipole polarization*' and is an especially important contribution to the dielectric properties of ceramics and glasses at room temperature. In solid dielectric materials, especially for ferroelectric materials, the dipole polarization resulting from permanent dipole moments exhibited in the materials can usually be responsible for the dielectric constant values of 10^3 or more in the frequency range of 10^2-10^6 Hz. The nonlinear polarization behavior of the ferroelectric materials is certainly associated with this polarization, which is due to the spontaneous alignment of dipoles in one of the equilibrium position. Interestingly, in ionic crystal, complex defect dipoles can be formed by Schottky defects, which are exhibited by impurity (doping) atom–vacancy associations. The complex defect dipole polarization is used to ascribe the giant dielectric properties of the NiO-based ceramics in this thesis.

2.2.4 Space charge polarization

It is also called '*Interfacial polarization or Maxwell-Wagner polarization*', the polarization occurs when mobile charge carriers are restricted by a physical barrier; therefore, charge migration is inhibited. When an ac electric field is of sufficiently low frequency, less than 10^{-3} Hz, a net oscillation of charge can be induced between barriers as far apart as 1 cm, producing a very large capacitance and dielectric constant. If the distance between the adjacent barriers in a dielectric is small in the orders of sub-micron or micron, and/or the density of charges contributing to the interfacial polarization is sufficiently large, the frequency range of sensitivity for such interfacial polarization may extend into the kilocycle (10^3) range (Hence, West, 1990). As a result, it is very difficult to distinguish the frequency responses between dipolar and interfacial polarizations.

Generally, electronic and atomic polarizations are concerned with optical properties of materials; hence, the high dielectric constant of materials is only related to the orientational and space charge polarizations. The details of these polarizations are discussed in the next section of this chapter in the thesis.

2.3 Dielectrics in alternating electric fields

The application of a sinusoidal voltage, $V = V_0 \exp(j\omega t)$, to an ideal dielectric, i.e., one without losses, the charge must vary with time and will result in a charging current (I_c) given by

$$I_c = \frac{dQ}{dt} = C\frac{dV}{dt} = j\omega CV = \omega CV_0 \exp[j(\omega t + \pi/2)], \tag{2.8}$$

where $Q = CV$ and $j = \exp(j\pi/2)$. The charging current in an ideal dielectric, therefore, leads the applied voltage by $\pi/2$ as illustrated in figure 2.2. This charging current is associated with storage of electric charge by the dipoles (Moulson, Herbert, 2003; Hence, West, 1990).

Equation (2.8) is only valid for the ideal dielectric. In fact, the charges are never totally in phase and the loss current can be induced by two sources: (1) the dissipation of energy due to the inertia of the moving charges, which have a specific mass, or the oscillation of dipoles and (2) the long-range migration of charges, i.e., Ohmic conduction. For the first contribution to the dielectric loss, electrical energy from the applied electric field is lost in the overcoming of this inertia during polarization. A loss current (I_l) in a dielectric resulting from the ac conduction from the inertial resistance and the dc conduction, which are in phase with the applied voltage, can be expressed as

$$I_l = I_{ac} + I_{dc} = \left(G_{ac}(\omega) + G_{dc}\right)V , \qquad (2.9)$$

where G is the conductance in units of Siemens, mho, or ohm^{-1}. The total current (I_{total}) for a real dielectric material can be written as

$$I_{total} = I_c + I_l = j\omega CV + \left(G_{ac}(\omega) + G_{dc}\right)V . \qquad (2.10)$$

It is clearly seen in figure 2.3 that the total current induced in the real dielectric is a complex quantity, and it leads the applied voltage by an angle $90 - \delta$. Thus, δ is called the '*loss angle*'.

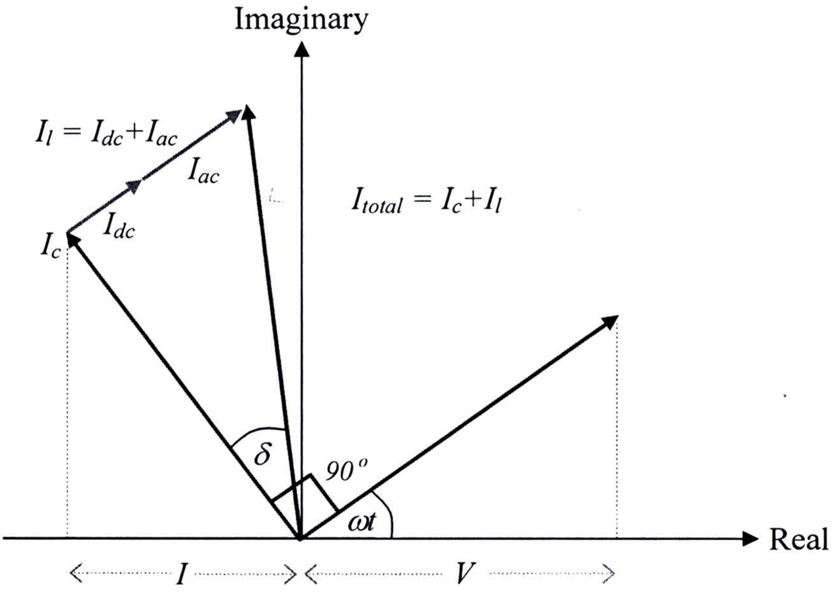

Figure 2.3 Vector diagram of charging, loss, and total current in a dielectric (Adapted from Hence, West, 1990).

The total current in the real dielectric can be expressed in both terms of charging and loss currents. In addition, a complex dielectric constant (ε^*) should also be used to describe the dielectric properties of materials:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' , \tag{2.11}$$

where ε' and ε'' are the dielectric constant and dielectric loss of the dielectric materials. Therefore, from equation (2.3), we can obtain

$$Q = CV = \varepsilon^* C_0 V , \tag{2.12}$$

and

$$i = \frac{dQ}{dt} = \varepsilon^* C_0 \frac{dV}{dt} = \varepsilon^* C_0 (j\omega V), \tag{2.13}$$

and thus

$$i = j\omega C_0 V\varepsilon' + \omega C_0 V\varepsilon'' . \tag{2.14}$$

The first term on the right-hand side of equation (2.14) explains charge storage in the dielectric; therefore, the dielectric constant (ε') can be called the '*charging constant*', while ε'' is referred to as the '*dielectric loss factor*'. According to equation (2.11), it is important to note that the imaginary part of complex dielectric permittivity (ε'') represents only the dielectric loss due to the friction in the polarization processes associated with the oscillation of dipoles. Therefore, the second term on the right-hand side ascribes the dielectric loss, which does not associate with the loss due to the Ohmic conduction. The *loss tangent*, $\tan\delta$ or *dissipation factor* is defined as

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{I_l}{I_C} . \tag{2.15}$$

The dissipation factor represents the relative expenditure of energy to obtain a given amount of charge storage. The product, $\varepsilon' \tan\delta$, is sometimes termed the total loss factor, and provides the primary criterion for evaluating the usefulness of a dielectric as an insulator. To minimize ε'', the losses in the insulator, it is desirable to have a small dielectric constant and most importantly a very small loss angle. The effect of Ohmic conduction on electrical response of dielectric materials is discussed in the next section of this chapter.

2.4 Relationship between complex dielectric constant and polarization

To more understand dielectric properties of a dielectric material, it is important to create a correlation between the complex dielectric constant (ε^*) and the polarization ($\vec{P}$) in the dielectric material. The relation can be performed by considering the total electric displacement field $\vec{D}$ in the material, which is used to establish such relation. In the dielectric material, the presence of an electric field causes the bound charges in the material to slightly separate, including a local electric dipole moment as demonstrated in figure 2.1. The total electric displacement field can be defined as

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P} = \varepsilon^*_{permit} \vec{E}, \tag{2.16}$$

where ε^*_{permit} is the complex permittivity of the dielectric material. The total electric displacement field is the sum of the polarization field within the dielectric material and the product of an electric field between the plates without the dielectric between them and ε_0. The polarization can be revealed as

$$\vec{P} = \vec{E}\left(\varepsilon^*_{permit} - \varepsilon_0\right), \tag{2.17}$$

since

$$\varepsilon^* = \varepsilon^*_{permit} / \varepsilon_0 . \tag{2.18}$$

Note that ε^* is the complex dielectric constant. The polarization can be rearranged as

$$\bar{P} = \bar{E}\left(\varepsilon_0\varepsilon^* - \varepsilon_0\right) = \left(\varepsilon^* - 1\right)\varepsilon_0\bar{E} \tag{2.19}$$

and then

$$\varepsilon^* - 1 = \frac{\bar{P}}{\varepsilon_0\bar{E}}. \tag{2.20}$$

Because of $\bar{P}$ and $\bar{E}$ are in the same direction, equation (2.20) can be presented in scalar form,

$$\varepsilon^* - 1 = \frac{P}{\varepsilon_0 E} \tag{2.21}$$

or

$$\varepsilon^* = 1 + \frac{P}{\varepsilon_0 E} \tag{2.22}$$

and defining

$$P / \varepsilon_0 E \equiv \chi \tag{2.23}$$

where χ is the electric susceptibility.

$$\varepsilon^* = 1 + \chi \tag{2.24}$$

Equations (2.22) and (2.24) give a correlation desired between the dielectric constant and the total polarization in the material. Moreover, it would be even more useful to have a relationship between ε^* and the electric susceptibility of the charge mechanism contributing to the total polarization.

The polarization $\vec{P}$ can be defined as

$$P = N_i \overline{\mu}_i , \tag{2.25}$$

where N_i is the number of dipoles of type i per unit volume and $\overline{\mu}_i$ is the average dipole moment, which is proportional to the local electric field (E'). The ratio of average dipole moment to the local electric field can be defined as the *polarizability* (α),

$$\alpha_i = \frac{\overline{\mu}_i}{E'} \tag{2.26}$$

Thus, the total polarization can be written as

$$P = N_i \alpha_i E' \tag{2.27}$$

In the case of system with little molecules interaction such as gases, the locally acting field E' is the same as external applied field, E_a. In the case of insulating dielectric solids, polarization of the surrounding medium substantially has enough to affect the magnitude of the local field. The local field contribution was firstly derived by Mosotti via the integration of the normal component of the polarized vector over the surface of a spherical cavity in the material (Kao, 2004). The obtained result is

$$E' = E_a + \frac{P}{3\varepsilon_0} \tag{2.28}$$

Since $N_i \alpha_i = P / E'$ from equation (2.27) then

$$N_i \alpha_i = \frac{P}{E_a + P / 3\varepsilon_0} \tag{2.29}$$

By substituting equations (2.17) and (2.18) into equation (2.29), we obtain

$$\frac{\varepsilon^* - 1}{\varepsilon^* + 2} = \frac{1}{3\varepsilon_0} N_i \alpha_i . \tag{2.30}$$

Equation (2.30) can be called as the classical Clausius-Mosotti equation, which describes the relationship between the complex dielectric constant of a material and the number of polarizable species N_i as well as the polarizability of the species α_i. According to figure 2.2, there are four major classes of polarizable species in the ceramics and glasses; consequently,

$$\frac{\varepsilon^* - 1}{\varepsilon^* + 2} = \frac{1}{3\varepsilon_0} \left[N_e \alpha_e + N_a \alpha_a + N_{or} \alpha_{or} + N_{sc} \alpha_{sc} \right], \tag{2.31}$$

where α_e, α_a, α_{or}, and α_{sc} are electronic, atomic, orientational, and space charge polarizabilities, respectively.

2.5 Electric polarization and relaxation in time-varying electric field

As described in the previous section, each of these polarization mechanisms dominates at different frequency ranges, indicating that each polarization requires different times to perform. This is why the degree of the total polarization depends on the time variation of the electric field, as revealed in figure 2.4. The dynamic response under time-varying electric fields can give the important information about the dielectric behavior for basic studies as well as for technological applications. In this time-domain approach, after a step-function electric field is applied, the time-dependent polarization is measured immediately. This time-dependent polarization can also be measured from the decay of the polarization from an initial steady state value to zero after an initial polarizing field is removed suddenly, as shown in figure 2.5. This decay is usually referred to as dielectric relaxation.

In general, electronic and atomic polarizations and depolarizations require a short time (<10^{-10} s), as shown in figure 2.4. These deformations of electronic and ionic polarizations are associated with the resonance process because they involve vibrating modes. As well know that resonance of an oscillating system occurs when a frequency of an electric field is equal to the natural frequency of the system. Unlikely, the times required for orientational, hopping, and space charge polarizations are longer than those of the two previous polarizations; moreover, they vary in a wide rang of time. Because these polarization processes involve a relaxation time, they are sometimes referred to as relaxation processes. A relaxation phenomenon is exhibited when restoring action tends to bring the excited system back to its original equilibrium state.

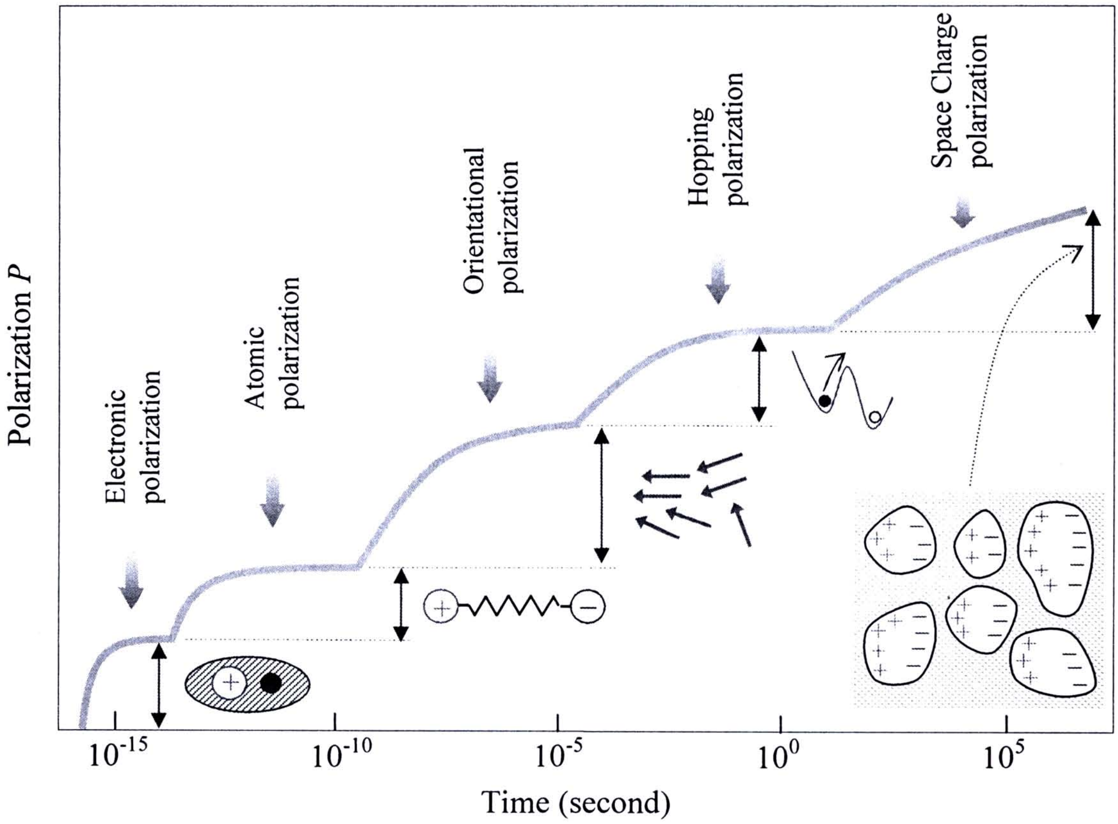

Figure 2.4 The variation of different types of polarization with time under a step-function electric field (Adapted from Kao, 2004).

Sometimes, the dielectric spectra resulting form the hopping or space charge polarizations and the orientational polarization are quite similar. Furthermore, if the intensity of the interfacial polarization (hopping and space charge) is sufficiently large, the interval time required for the interfacial polarization can be extended to the interval time required for the orientational polarization. For simplicity, the hopping and space charge polarizations are, therefore, ignored. The total polarization of dielectrics can be expressed as

$$P_{total} = P_e + P_a + P_{or} \,. \tag{2.32}$$

It is important to note that the response time for the electronic and atomic polarizations is very shot, which can be estimated it is independent on the frequency range of 0-10^{12} Hz. Consequently, these two polarizations can be included as the high-frequency polarization (P_∞):

$$P_\infty = P_e + P_a \,. \tag{2.33}$$

From equation (2.22), P_∞ can be approximated as

$$\varepsilon'_\infty \approx 1 + \frac{P_\infty}{\varepsilon_0 E} , \tag{2.34}$$

where ε'_∞ is the dielectric constant at a high frequency range or the unrelaxed high-frequency dielectric constant, and then,

$$P_\infty = (\varepsilon'_\infty - 1)\varepsilon_0 E \,. \tag{2.35}$$

These two types of polarization (P_e and P_a) are considered to follow instantaneously the excited field E without lag, P_∞ and E are in phase. Similarly, the low-frequency dielectric constant or the relaxed static dielectric constant (ε'_s) can be expressed as

$$\varepsilon_s' = 1 + \frac{P_{total}}{\varepsilon_0 E} = 1 + \frac{P_{or} + P_\infty}{\varepsilon_0 E}. \tag{2.36}$$

By replacing equation (2.35) into (2.36) and simplifying, the orientational polarization can be written in terms of ε_∞' and ε_s' as

$$P_{or} = (\varepsilon_s' - \varepsilon_\infty')\varepsilon_0 E. \tag{2.37}$$

From equations (2.35) and (2.37), P_{total} can be written as

$$P_{total} = P_\infty + P_{or} = (\varepsilon_\infty' - 1)\varepsilon_0 E + (\varepsilon_s' - \varepsilon_\infty')\varepsilon_0 E. \tag{2.38}$$

Note that there is a phase difference between P_{or} and E.

As shown in figure 2.5, after an initial polarizing field is removed suddenly, the decay of the orientational polarization is exhibited from an initial steady state value ($P_\infty + P_{or}$) to zero. Such polarization will decay at a rate,

$$\frac{dP_{or}(t')}{dt'} = -\frac{P_{or}(t')}{\tau}, \tag{2.39}$$

where τ is the macroscopic relaxation time. By using the boundary condition, at $t = 0$, $P_{or} = (\varepsilon_s' - \varepsilon_\infty')\varepsilon_0 E$; consequently, the solution of equation (2.39) is

$$P_{or}(t') = [(\varepsilon_s' - \varepsilon_\infty')\varepsilon_0 E]\exp(-t'/\tau). \tag{2.40}$$

Similarly, if the step-function excited field is applied to the dielectric system, $P_{or}(t) = 0$ at $t = 0$, and then $P_{or}(t)$ increases with increasing time. The orientational polarization will increase at a rate,

$$P_{or}(t) = (\varepsilon_s' - \varepsilon_\infty')\varepsilon_0 E[1 - \exp(-t/\tau)]. \tag{2.41}$$

In this case, $dP_{or}(t)/dt$ provides the orientational polarization rate. The approximate time required for the polarization is display in figure 2.4.

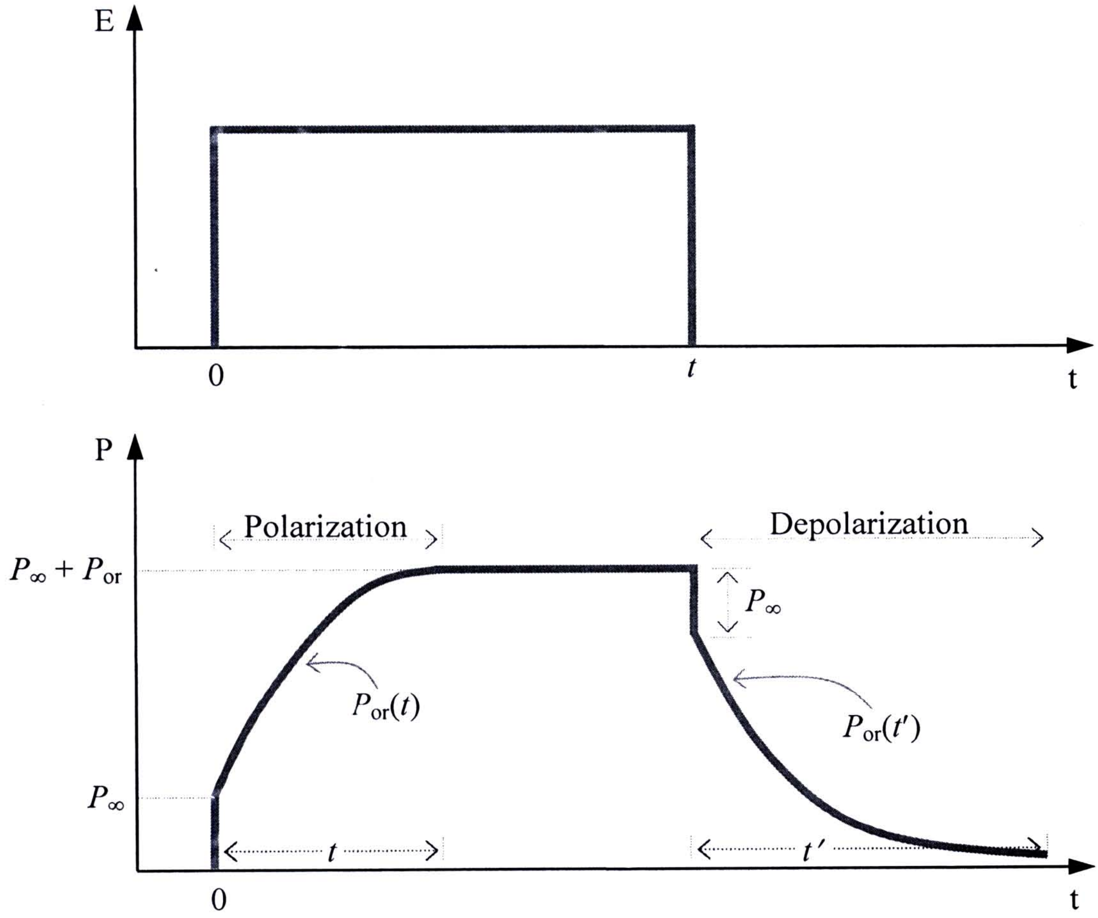

Figure 2.5 The variation of different types of polarization with time under a step-function electric field (Adapted from Kao, 2004).

As demonstrated in figure 2.6, supposing that during the time interval between u and du, an excited field $E(u)$ is applied to the dielectric system. At $t < u$ and $t > u + du$, $E = 0$; consequently, $P_{or}(t)$ will take time to respond and will change for $t > u$. Then, $P_{or}(t)$ reaches the value of $P_{or}(u + du)$ at $u = t + du$; eventually, the polarization decays gradually to zero at $t \geq u + du$. In the interval time of $u \leq t \leq u + du$, the variation of the polarization can be expressed as (Kao, 2004)

$$P_{or}(t-u)=(\varepsilon_s'-\varepsilon_\infty')\varepsilon_0\left\{1-\exp\left(-\frac{t-u}{\tau}\right)\right\}E(u). \tag{2.42}$$

The term of $1-\exp\{-(t-u)/\tau\}$ can be referred to a response function. From equation (2.38), the total P_{total} consists of P_∞ which can be responded to the excited field immediately and $P_{or}(t)$ which is governed by equation (2.42). The increment of total polarization, dP_{total} is

$$dP_{total}(t-u)=dP_\infty(t-u)+dP_{or}(t-u). \tag{2.43}$$

By considering equations (2.35) and (2.42), equation (2.43) can be shown as

$$dP_{total}(t-u)=(\varepsilon_\infty'-1)\varepsilon_0 dE(u)+(\varepsilon_s'-\varepsilon_\infty')\varepsilon_0\left\{1-\exp\left(-\frac{t-u}{\tau}\right)\right\}dE(u). \tag{2.44}$$

According to the superposition principle, the total polarization at time t is a superposition of all increments dP; therefore, P_{total} can be obtained as

$$P_{total}=(\varepsilon_\infty'-1)\varepsilon_0 E(t)+(\varepsilon_s'-\varepsilon_\infty')\varepsilon_0\int_0^t\left[1-\exp\left(-\frac{t-u}{\tau}\right)\right]dE(u). \tag{2.45}$$

Integrating by part, equation (2.45) can be obtained as

$$P_{total}=(\varepsilon_\infty'-1)\varepsilon_0 E(t)+(\varepsilon_s'-\varepsilon_\infty')\varepsilon_0\int_0^t\frac{E(u)}{\tau}\exp\left(-\frac{t-u}{\tau}\right)du, \tag{2.46}$$

where the term of $\exp[-(t-u)/\tau]$ is the decay function that tends to approach zero at $t\to\infty$. If E is the step-function electric field with $E=0$ at $t=0^-$ and $E=E$ at $t=0^+$, then equation (2.46) is expressed as

$$P_{total} = (\varepsilon'_\infty - 1)\varepsilon_0 E + (\varepsilon'_s - \varepsilon'_\infty)\varepsilon_0 E[1 - \exp(-t/\tau)]. \tag{2.47}$$

The first term on the right hand side of equation (2.47) is a time-independent electric polarization function, whereas the second term is a function that depends on time. The variation of the total polarization (P_{total}) with time (t) is revealed in figure 2.5.

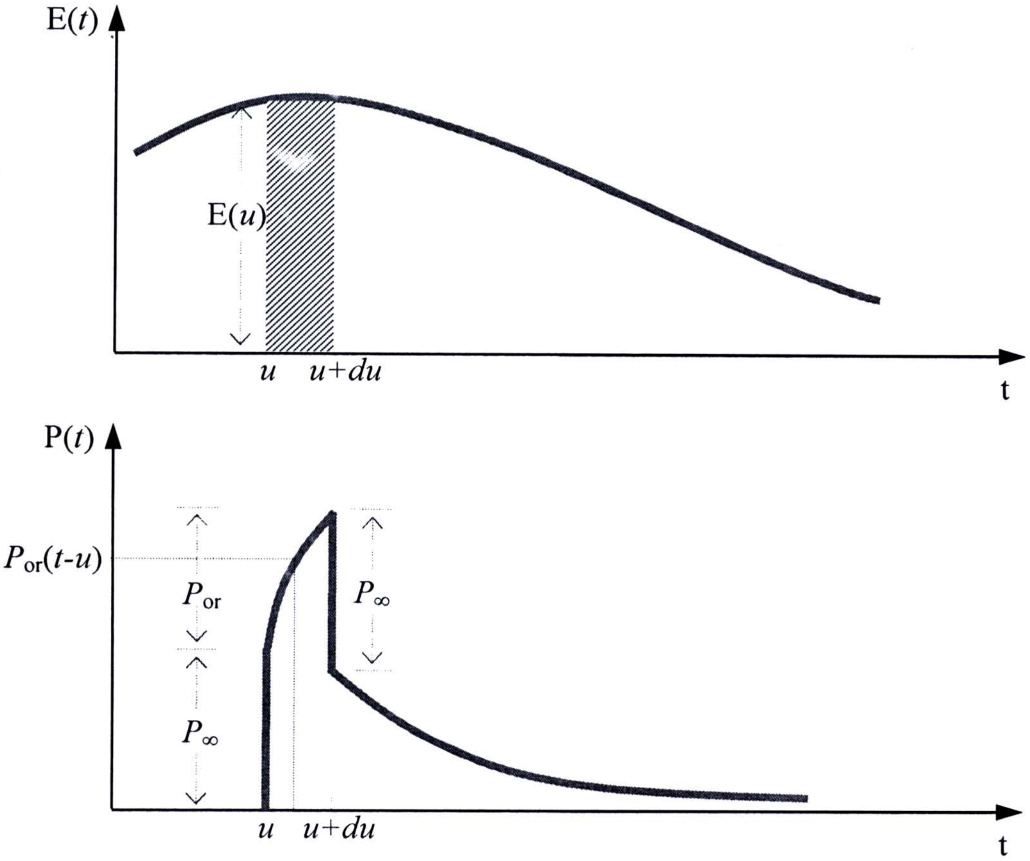

Figure 2.6 The time response of $P(t)$ to a delta function electric field $E(u)$ of strength $E(u)$ within the time period of $u \le t \le u + du$ (Adapted from Kao, 2004).

2.6 Electric polarization and relaxation in alternating electric fields

As previous discussion, if a sinusoidal ac electric field,

$$E(t) = E_0 \cos \omega t = \mathrm{Re}\left[E_0 \exp(j\omega t)\right], \tag{2.48}$$

is applied into a dielectric system, the total polarization of the dielectric will vary with a frequency of electric field. To study the effect of an applied alternating electric field into the dielectric on its polarization behavior and dielectric properties as a function of frequency, P_{total} is assumed that it has reached its dynamic steady state at $t = 0$. Thus, the bottom limit of the integral in equation (2.46) must be changed to $-\infty$, where $P = 0$. The total polarization can be expressed as

$$P_{total} = (\varepsilon'_\infty - 1)\varepsilon_0 E_0 \cos \omega t + (\varepsilon'_s - \varepsilon'_\infty)\varepsilon_0 \frac{E_0}{\tau} \mathrm{Re}\left[\int_{-\infty}^{t} \exp(j\omega u) \exp\left(-\frac{t-u}{\tau}\right) du\right], \tag{2.49}$$

or,

$$P_{total} = (\varepsilon'_\infty - 1)\varepsilon_0 E_0 \cos \omega t + (\varepsilon'_s - \varepsilon'_\infty)\varepsilon_0 E_0 \,\mathrm{Re}\left[\frac{\exp(j\omega t)}{1 + j\omega\tau}\right], \tag{2.50}$$

and then,

$$P_{total} = (\varepsilon'_\infty - 1)\varepsilon_0 E_0 \cos \omega t + \frac{(\varepsilon'_s - \varepsilon'_\infty)\varepsilon_0 E_0 \cos \omega t}{1 + (\omega\tau)^2} + \frac{(\varepsilon'_s - \varepsilon'_\infty)(\omega\tau)\varepsilon_0 E_0 \sin \omega t}{1 + (\omega\tau)^2}. \tag{2.51}$$

The second term on the right hand side, which is in phase with the applied field, is the lossless component. While the third term, which is out of phase with the applied field with $\pi/2$, is the loss component. It is clearly seen from equation (2.51) that the electric dipoles in the dielectric cannot follow the oscillation of field when $\omega \geq 1/\tau$. As a result, the intensity of the total polarization gradually decreases to the values of electronic and atomic polarization intensities as the frequency of the field increases

(Kao, 2004; Hence, West, 1990). If the three components are denoted as P_∞, P_1, and P_2, respectively, equation (2.51) can be reduced to

$$P_{total} = (P_\infty + P_1)\cos\omega t + P_2 \sin\omega t\,. \tag{2.52}$$

This variation of dielectric parameters (ε'_∞, ε'_s and τ) is one of the most important properties of materials for fundamental studies and technological applications.

In fact, no material is free of dielectric loss, implying that there is no material having frequency-independent ε' and ε''. The dispersion in these two parameters is generally an intrinsic property of all dielectric materials; hence, it is related to other properties of the dielectric materials. Up to now, it is widely known that the dielectric dispersion of the dielectric can simply be ascribed by the Debye relaxation model. By expressing, $E_0 \cos\omega t = \mathrm{Re}[E_0 \exp(j\omega t)]$, $E_0 \sin\omega t$ can be written as

$$E_0 \sin\omega t = \mathrm{Re}[E_0 \exp(j(\omega t - \pi/2))] = \mathrm{Im}[E_0 \exp(j\omega t)]\,. \tag{2.53}$$

Equation (2.51) can be rearranged as

$$P_{total} = \left[(\varepsilon'_\infty - 1) + \frac{(\varepsilon'_s - \varepsilon'_\infty)}{1 + (\omega\tau)^2}\right]\varepsilon_0 E_0 \exp(j\omega t) - j\left[\frac{(\varepsilon'_s - \varepsilon'_\infty)(\omega\tau)}{1 + (\omega\tau)^2}\right]\varepsilon_0 E_0 \exp(j\omega t)\,. \tag{2.54}$$

According to equations (2.11) and (2.22), the complex total polarization P_{total} can be presented as

$$P^*_{total} = (\varepsilon^* - 1)\varepsilon_0 E^* = [(\varepsilon' - 1) - j\varepsilon'']\varepsilon_0 E_0 \exp(j\omega t)\,. \tag{2.55}$$

As results, the Debye equation can be obtained by comparing equation (2.54) with equation (2.55),

$$\left(\varepsilon^{*}-1\right)=\left[\left(\varepsilon'_{\infty}-1\right)+\frac{\left(\varepsilon'_{s}-\varepsilon'_{\infty}\right)}{1+\left(\omega\tau\right)^{2}}\right]-j\left[\frac{\left(\varepsilon'_{s}-\varepsilon'_{\infty}\right)\left(\omega\tau\right)}{1+\left(\omega\tau\right)^{2}}\right], \tag{2.56}$$

$$\varepsilon^{*}=\varepsilon'-j\varepsilon''=\varepsilon'_{\infty}+\frac{\varepsilon'_{s}-\varepsilon'_{\infty}}{1+j\omega\tau}. \tag{2.57}$$

The dielectric constant (ε') and dielectric loss (ε'') can be separated as

$$\varepsilon'=\varepsilon'_{\infty}+\frac{\varepsilon'_{s}-\varepsilon'_{\infty}}{1+\left(\omega\tau\right)^{2}}, \tag{2.58}$$

$$\varepsilon''=\frac{\varepsilon'_{s}-\varepsilon'_{\infty}}{1+\left(\omega\tau\right)^{2}}\omega\tau, \tag{2.59}$$

and

$$\tan\delta=\frac{\varepsilon''}{\varepsilon'}=\frac{\left(\varepsilon'_{s}-\varepsilon'_{\infty}\right)\omega\tau}{\varepsilon'_{s}+\varepsilon'_{\infty}\left(\omega\tau\right)^{2}}. \tag{2.60}$$

Equations (2.57) through (2.60) are the desired frequency-dependent relationships of the charging and loss component as well as the loss tangent of the dielectric material. These equations are generally called the Debye equations for dynamic polarization; assuming that the relaxation time of each dipole in the dielectric is the same in value (Cole, Cole, 1941). It is worth to recognize that these equations are based on the assumption that the polarization in the dielectric decays exponentially. In fact, Debye relaxation model is satisfactory only for the condition $\varepsilon'_{s}-\varepsilon'_{\infty}<1$, which is fulfilled only in dilute solutions because there is no the interaction between particles or dipoles in these solutions (Kao, 2004).

According to equations (2.59) and (2.60), the angular frequencies of the applied electric field at which ε'' and $\tan\delta$ are maximal can be obtained by setting $d\varepsilon''/d\omega = 0$ and $d(\tan\delta)/d\omega = 0$. For example, it can be shown that

$$\frac{d\varepsilon''}{d\omega} = \frac{d[\Delta\varepsilon'\omega\tau/(1+\omega^2\tau^2)]}{d\omega} = \frac{\Delta\varepsilon'(\tau+\omega^2\tau^3) - 2\Delta\varepsilon'\omega^2\tau^3}{(1+\omega^2\tau^2)^2}, \tag{2.61}$$

where $\Delta\varepsilon' = \varepsilon'_s - \varepsilon'_\infty$. Therefore, $d\varepsilon''/d\omega$ will be zero when

$$\Delta\varepsilon'(\tau+\omega^2\tau^3) = 2\Delta\varepsilon'\omega^2\tau^3. \tag{2.62}$$

From equation (2.62), the frequency at which ε'' is maximal will occur at $\omega = \omega_{p(\varepsilon'')}$,

$$\omega_{p(\varepsilon'')} = \frac{1}{\tau}. \tag{2.63}$$

Similarly, it can be proved that the frequency at which $\tan\delta$ is maximal will occur at $\omega = \omega_{p(\delta)}$,

$$\omega_{p(\delta)} = \frac{\sqrt{\varepsilon'_s/\varepsilon'_\infty}}{\tau}. \tag{2.64}$$

At the frequency of $\omega = \omega_{p(\varepsilon'')}$ and $\omega_{p(\varepsilon'')}\tau = 1$ the dielectric parameters of the dielectric are given by

$$\varepsilon' = \frac{\varepsilon'_s + \varepsilon'_\infty}{2}, \tag{2.65}$$

$$\varepsilon'' = \frac{\varepsilon'_s - \varepsilon'_\infty}{2}, \tag{2.66}$$

$$\tan\delta = \frac{\varepsilon_s' - \varepsilon_\infty'}{\varepsilon_s' + \varepsilon_\infty'} . \tag{2.67}$$

At the frequency of $\omega = \omega_{p(\delta)}$, $\tan\delta$ is given by

$$\tan\delta = \frac{\varepsilon_s' - \varepsilon_\infty'}{2\sqrt{\varepsilon_s'\varepsilon_\infty'}} . \tag{2.68}$$

The frequency dependence of the dielectric parameters is demonstrated in figure 2.7. These dielectric spectra are obtained by assuming $\varepsilon_s' = 600$, $\varepsilon_\infty' = 100$, and $\tau = 10^{-5}\, s$ and taking into equations (2.58), (2.59), and (2.60). The results reveal that the angular frequency of the applied electric field (ω), at which ε'' is maximal, is 10^5 Hz corresponding to equation (2.63). At this frequency, the values of the dielectric constant (ε') and dielectric loss (ε'') are 350 and 250, respectively. In general, ε_s' is always larger than ε_∞' and $\left(\sqrt{\varepsilon_s'/\varepsilon_\infty'} > 1\right)$ consequently, the frequency at the peak of $\tan\delta$ should be higher than that of ε'' by

$$\Delta\omega = \omega_{p(\delta)} - \omega_{p(\varepsilon'')} = \frac{1}{\tau}\left(\sqrt{\frac{\varepsilon_s'}{\varepsilon_\infty'}} - 1\right) . \tag{2.69}$$

As shown in figure 2.7, $\Delta\omega$ is about 1.45×10^5 Hz; hence, $\omega_{p(\delta)} = 2.45\times10^5$ Hz.

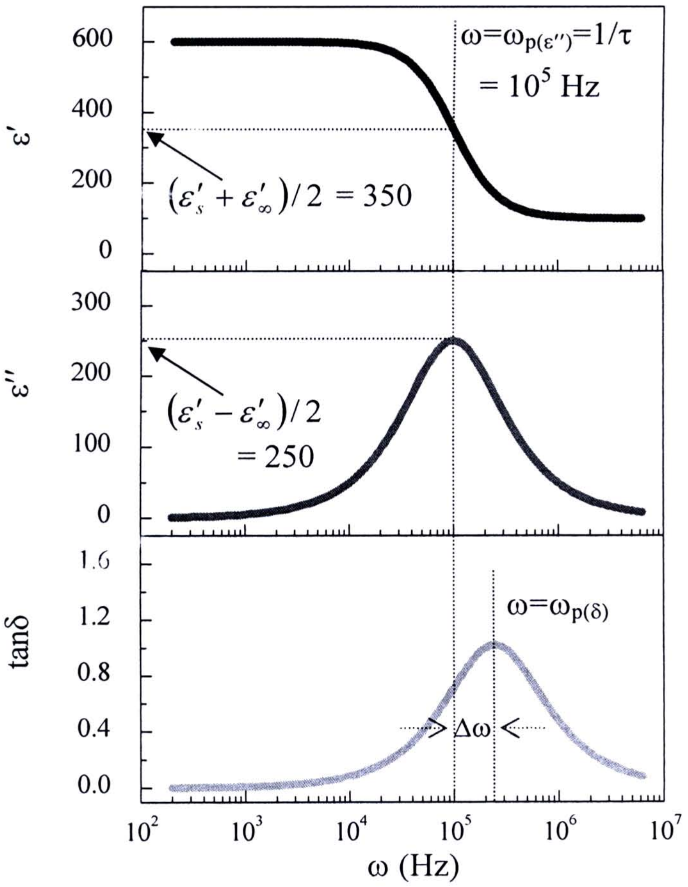

Figure 2.7 Frequency dependence of dielectric properties of dielectric materials (plotted using equations (2.58)-(2.60)).

2.7 Hopping polarization relaxation

As previous discussion, the electronic polarization can always be found in all kinds of non-conducting materials such as semiconductors and insulators. Ionic polarization can only occur in some materials consisting of two or more different kinds of atoms that behave as ions due to the exchange of the valence electrons with the others. From these points of view, both polarizations are induced by an applied electric field, and can also be called the '*induced polarizations*'. In contrast, the orientational polarization is due to the presence of permanent electric dipoles in materials, the applied electric field just forces them to orient toward the direction of the field. The first two polarizations are slightly dependent on temperature and independent on the frequency below 10^{12} Hz. On the other hand, the orientational polarization depends strongly on the frequency range of 0-10^{12} Hz depending on temperature. Although the induced and orientational polarization are quite different, they are similar in a way; the positive and negative charges or ions cannot be separated forming the bound positive and negative charges within the atom or molecule itself. However, some electric polarizations can also occur from mobile and trapped charges (electrons, holes, vacancies, or ions). In this thesis, the polarizations that relate to the mobile charges and do not associate with the bound positive and negative charges are grouped as the '*space charge polarization*'. This polarization consists of hopping and interfacial polarizations. As revealed in figure 2.4, the times required for the orientational and hopping polarization processes are in range of about 10^{-9} to 1 s, or in the frequency range of about 1-10^9 Hz, which is the relaxation regime. This implies that the hopping polarization can exhibit a dielectric relaxation behavior also.

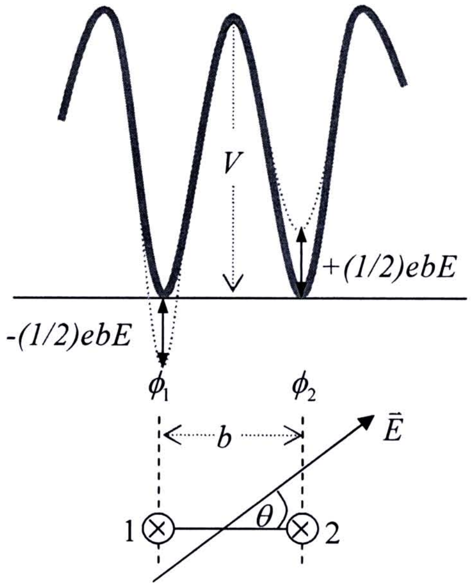

Figure 2.8 Potential well energy configuration in materials. The solid lines indicate energy without field; dot lines indicate energy with applied field (Adapted from Hence, West, 1990).

With applied an electric field into a non-conducting ionic material, ions and vacancies as well as electrons and holes can usually be localized by hopping from one site to the adjacent site, depending on the width and the height of potential barrier. These localized charge carriers hopping between the potential barriers not only produce conductivity but also give rise to dipolar effects, creating the hopping polarization in the material or can be called '*Polaron relaxation*' (Wang, Zhang, 2007). This hopping polarization behavior can be described by considering the two schematic potential energy wells, as displayed in figure 2.8. The probability of a jump, P', between energy wells is exponentially related to the temperature and the energy barrier V. Without an applied electric field, the probabilities for an ion to hop from site (1) to site (2) ($P'_{1\rightarrow 2}$) and from site (2) to site (1) ($P'_{2\rightarrow 1}$) are equal, as following,

$$P' = P'_{1\rightarrow 2} = P'_{2\rightarrow 1} = A\exp\left(-\frac{V}{k_B T}\right), \tag{2.70}$$

where V represents the maximum barrier in the path of the least resistance in the glass or ceramic, T is absolute temperature (K) and k_B is Boltzmann constant and is equal to 1.38×10^{-23} J/K. When an electric field is applied, the ion coordination is slightly distorted and the potential energy of the two sites will become unequal by an amount

$$\phi_2 - \phi_1 = e(bE) = ebE\cos\theta, \tag{2.71}$$

where b is the distance separating the potential well and θ is the angle between the field vector and the jump vector. Therefore, this model is equivalent to a turn of 180° of a dipole with a dipole moment of

$$\mu = \tfrac{1}{2} zeb, \tag{2.72}$$

where z is valence of the ion. With applying the electric field, the potential on the right will now be smaller by an amount $\frac{1}{2}zebE$ (Moulson, Herbert, 2003; Hence, West, 1990; Kao, 2004). As a result, the potential barrier at site (1) is changed to $-V+(-\mu E)$; consequently, the probability of jumps from site (1) to site (2) can be expressed as (assume that $\cos\theta = 1$ and $V \geq k_B T$)

$$P'_{1\to 2} = A\exp\left(-\frac{V+\mu E}{k_B T}\right) \tag{2.73}$$

or

$$P'_{1\to 2} = A\exp\left(-\frac{V}{k_B T}\right)\exp\left(-\frac{\mu E}{k_B T}\right). \tag{2.74}$$

By using a Taylor series

$$e^{-x} = 1 - x + \frac{x^2}{2!} - \ldots \tag{2.75}$$

and assume that $\mu E / k_B T \leq 1$, the last term in equation (2.74), $\exp(-\mu E / k_B T)$, can thus be expanded as

$$\exp\left(-\frac{\mu E}{k_B T}\right) = 1 - \frac{\mu E}{k_B T}. \tag{2.76}$$

As a result, equation (2.74) can be rewritten as

$$P'_{1\to 2} = A\exp\left(-\frac{V}{k_B T}\right)\left(1 - \frac{\mu E}{k_B T}\right). \tag{2.77}$$

Considering equation (2.70), we can obtain,

$$P'_{1\to 2} = P\left(1 - \frac{\mu E}{k_B T}\right). \tag{2.78}$$

Similarly, the probability for the ion to hop in the reverse direction from site (2) to site (1) can be expressed as

$$P'_{2\to 1} = A\exp\left(-\frac{V - \mu E}{k_B T}\right). \tag{2.79}$$

By using the Taylor series, equation (2.79) can be rewritten as

$$P'_{2\to 1} = P\left(1 + \frac{\mu E}{k_B T}\right). \tag{2.80}$$

Without the applied electric field, the number of ions in well (1) and well (2) cannot change with time. Assume that N are ions, which relate to dipoles per unit volume and there are less enough that there will be no dipolar interaction; consequently, the ions going to well (1) must come out of well (2) and vice versa. Therefore, we can obtain

$$N_1 P'_{1\to 2} = N_2 P'_{2\to 1}, \tag{2.81}$$

where N_1 and N_2 are the number of the ions in well (1) and well (2), respectively. By substitution equations (2.78) and (2.80) into equation (2.81), we can express as

$$N_1 P'\left(1 - \frac{\mu E}{k_B T}\right) = N_2 P'\left(1 + \frac{\mu E}{k_B T}\right). \tag{2.82}$$

Equation (2.82) can be rearranged as

$$N_1 - N_2 = (N_1 + N_2)\frac{\mu E}{k_B T}. \tag{2.83}$$

The total number of wells N occupied per unit volume must be constant; thus, the static polarization is defined as

$$P_{s(hopping)} = (N_1 - N_2)\mu. \tag{2.84}$$

By using the definition expressed in equation (2.84), equation (2.83) can thus be illustrated in the static polarization term due to the hopping of charges as

$$P_{s(hopping)} = \frac{N\mu^2 E}{k_B T}, \tag{2.85}$$

where $N_1 + N_2 = N$, and N is constant.

With an applied ac electric field, the variation of the number of dipoles (ions) in site (1) is equal to the outflow from site (1) minus the inflow to site (2) (Hence, West, 1990). Thus,

$$\frac{dN_1}{dt} = -N_1 P'_{1\to2} + N_2 P'_{2\to1}, \tag{2.86}$$

and the rate of a decrease in the ions at one site should be equal to the rate of an increase at another site,

$$\frac{dN_2}{dt} = -\frac{dN_1}{dt}. \tag{2.87}$$

Based on the change in the number of dipoles induced by the jumping of ions, it can be demonstrated that

$$\frac{d(N_1 - N_2)}{dt} = 2\frac{dN_1}{dt}. \tag{2.88}$$

By comparing equations (2.86) and (2.88), we can show that

$$\frac{1}{2}\frac{d(N_1 - N_2)}{dt} = -N_1 P'_{1\to 2} + N_2 P'_{2\to 1} = -N_1 P'\left(1 - \frac{\mu E}{k_B T}\right) + N_2 P'\left(1 + \frac{\mu E}{k_B T}\right). \tag{2.89}$$

Equation (2.89) can be rewritten as

$$\frac{1}{2}\frac{d(N_1 - N_2)}{dt} = -P'(N_1 - N_2) + P'(N_1 + N_2)\frac{\mu E}{k_B T}. \tag{2.90}$$

By taking μ / μ into both sites of equation (2.90) and using the concept of equation (2.84), we will obtain the new equation that is in a form of the time dependence of polarization:

$$\frac{1}{2\mu}\left(\frac{dP_{hopping}(t)}{dt}\right) = -\frac{P'}{\mu}P_{hopping}(t) + P'N\frac{\mu E}{k_B T}. \tag{2.91}$$

Equation (2.91) can be rearranged as

$$\frac{1}{2P'}\left(\frac{dP_{hopping}(t)}{dt}\right) + P_{hopping}(t) = \frac{N\mu^2 E}{k_B T}. \tag{2.92}$$

Equation (2.92) is a relaxation equation with a relaxation time τ, which is equal to $1/2P'$. According to equation (2.58), the relaxation equation (2.92) can be written as

$$\tau\frac{dP_{hopping}(t)}{dt} + P_{hopping}(t) = P_{s(hopping)}, \tag{2.93}$$

where $P_{s(hopping)}$ is the zero-frequency value of the hopping polarization. When an alternating electric field is applied, $P_{(hopping)}$ will differ from $P_{s(hopping)}$. The hopping polarization will increase to the static value of $P_{s(hopping)}$ with a rate of change of $dP_{hopping}(t)/dt$. According to equation (2.37), $P_{or} = (\varepsilon'_s - \varepsilon'_\infty)\varepsilon_0 E$, if we assume that the static polarization of the system is due to the hopping polarization and there is no orientational polarization in the system, we can therefore express the static hopping polarization as

$$P_{s(hopping)} = (\varepsilon'_s - \varepsilon'_\infty)\varepsilon_0 E. \tag{2.94}$$

By inserting equation (2.94) into equation (2.93), we can obtain

$$\tau \frac{dP_{hopping}(t)}{dt} + P_{hopping}(t) = (\varepsilon'_s - \varepsilon'_\infty)\varepsilon_0 E \tag{2.95}$$

To make progress, we can assume that the applied polarizing field is $E^* = E_0 e^{j\omega t}$; thus, equation (2.95) can be modified to

$$\frac{dP_{hopping}(t)}{dt} + \frac{1}{\tau} P_{hopping}(t) = \frac{1}{\tau}(\varepsilon'_s - \varepsilon'_\infty)\varepsilon_0 E_0 \exp(j\omega t). \tag{2.96}$$

By comparing equation (2.96) to the first order linear equation,

$$\frac{dy}{dx} + p(x)y = q(x), \tag{2.97}$$

the solution of equation (2.96) can be obtained and it is in a complex form as (Moulson, Herbert, 2003),

$$P^*{}_{hopping}(t) = C\exp\left(-\frac{t}{\tau}\right) + \frac{\varepsilon'_s - \varepsilon'_\infty}{1 + j\omega t}\varepsilon_0 E^*, \tag{2.98}$$

where C is constant. The first term on the right hand side of equation (2.98) ascribes the time-dependent decay of the dc charge on the capacitor. The second term describes the ac behavior of the polarization due to the hopping of charge carrier between wells (Hence, West, 1990).

According to equation (2.21), it can be shown that

$$\varepsilon^* - 1 = \frac{P^*_{total}}{\varepsilon_0 E^*}, \tag{2.99}$$

where $P^*_{total} = P^*_s + P^*_\infty$. Therefore, it can be shown that

$$\varepsilon^* = 1 + \frac{P^*_s}{\varepsilon_0 E^*} + \frac{P^*_\infty}{\varepsilon_0 E^*}, \tag{2.100}$$

According to equation (2.34), we can demonstrate that

$$\varepsilon^* = 1 + \frac{P^*_s}{\varepsilon_0 E^*} + \frac{(\varepsilon'_\infty - 1)\varepsilon_0 E^*}{\varepsilon_0 E^*} = \varepsilon'_\infty + \frac{P^*_s}{\varepsilon_0 E^*}, \tag{2.101}$$

where $P^*_{hopping} = P^*_s$. Hence,

$$P^*_{hopping} = (\varepsilon^* - \varepsilon'_\infty)\varepsilon_0 E^*. \tag{2.102}$$

If the term of $C\exp(-t/\tau)$ in equation (2.98) is neglected, we can use equations (2.98) and (2.102) to show that

$$\varepsilon^* - \varepsilon'_\infty = \frac{\varepsilon'_s - \varepsilon'_\infty}{1 + j\omega\tau}. \tag{2.103}$$

It is worth noting that equation (2.103) is the same as equation (2.57) and they are called to be '*Debye relaxation equation*'. This implies that both of orientational polarization resulting from the permanent dipole moments and hopping polarization resulting from the localized charges between wells can exhibit the same dielectric relaxation behavior. As a result, the dielectric spectra induced by these two polarizations should be similar. Moreover, these polarizations in materials are frequency and temperature dependent corresponding to a relaxation time of a system and the energy required for the relaxation process, respectively. Indeed, both polarizations are equivalent to the polarization resulting from dipole moments, but the dipole moments of both polarizations are produced by different ways.

2.8 Cole-Cole and other relaxation models

The Debye relaxation model as equations (2.57) and (2.103) is based on a single relaxation time; all of dipoles in a system have the same relaxation time. This system can only be found in an ideally dielectric material; thus, the model is not sufficient to describe the dielectric relaxation phenomena for most practical dielectric materials such as ceramics and glasses. In these materials, a distribution of relaxation times is important to interpret the experimental results. KS Cole, RH Cole (1941) have adapted the Debye relaxation model to obtain the suitable model for ascribe the relaxation behavior of real dielectric materials. Cole-Cole relaxation model, the empirical relation, is

$$\varepsilon^* = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{1+(j\omega\tau)^\alpha}, \tag{2.104}$$

where α is constant parameter with $0 < \alpha \leq 1$. When $\alpha = 1$, the Cole-Cole relaxation model is transformed to the Debye relaxation model. If α<1, it implies that the relaxation has a distribution of relaxation times, leading to a broader peak shape than a Debye peak, as displayed in figure 2.9. The slope of a step decrease in dielectric constant and the peak height of dielectric loss decrease with decreasing the α value.

Nowadays, several models have proposed to modify the Cole-Cole relaxation model; some of the models are listed below for comparison purpose:

Debye relaxation model, $$\varepsilon^* = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{1 + j\omega\tau},$$

Cole-Cole relaxation model, $$\varepsilon^* = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{1 + (j\omega\tau)^\alpha},$$

Davison-Cole relaxation model, $$\varepsilon^* = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{(1 + j\omega\tau)^\beta}, \tag{2.105}$$

Havriliak-Negami relaxation model, $$\varepsilon^* = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{[1 + (j\omega\tau)^\alpha]^\beta}. \tag{2.106}$$

All of these models depend on the value of α and β chosen within the ranges of $0 < \alpha \leq 1$ and $0 < \beta \leq 1$. It is clear that the Davison-Cole model will reduce to the Debye model for $\beta = 1$. It has been found that some materials such as glycerol triacetate and Pyralene obey the Davison-Cole model (Kao, 2004). For Havriliak-Negami relaxation model, the parameters α and β are not based on the physics of the dielectric polarization, although the modification of the original Cole-Cole model empirically may take the equation better fit experimental data. The modification does not lead to a better understanding of the physics behind the distribution of relaxation times.

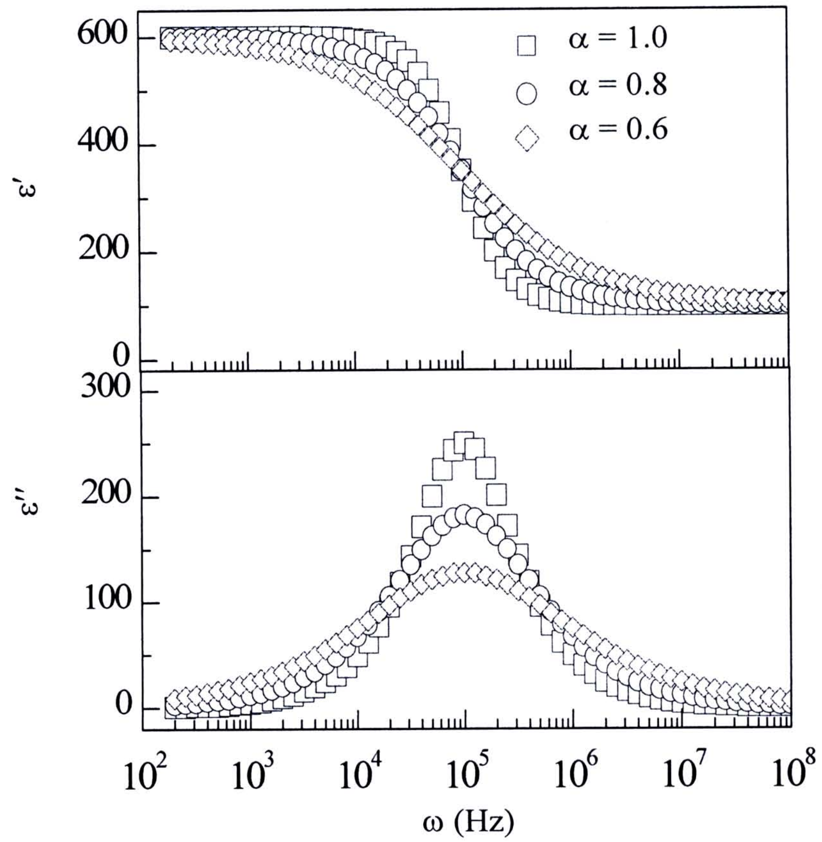

Figure 2.9 Frequency dependence of dielectric properties of dielectric materials with different distributions of relaxation times obtained from Debye and Cole-Cole relaxation models (plotted using equation (2.104)).

2.9 The effect of dc conductivity on dielectric properties

If an alternating electric field is applied across a parallel-plate capacitor with the plate area of one unit and two plates are separated by dielectric layer, the total current density will be given by

$$J_{total} = J + \frac{dD}{dt} = J + \varepsilon^{*}_{permit}\frac{dE}{dt}, \tag{2.107}$$

where J is the conduction current or current density. ε^{*}_{permit} allows for dielectric losses due to the friction accompanying polarization and orientation of electric dipoles.

If $E^* = E_0 \exp(j\omega\tau)$, equation (2.107) can be expressed as

$$J^*_{total} = \sigma_{dc}E^* + j\omega\varepsilon_0(\varepsilon' - j\varepsilon'')E^* = (\sigma_{dc} + \omega\varepsilon_0\varepsilon'')E^* + j\omega\varepsilon_0\varepsilon'E^*, \qquad (2.108)$$

where σ_{dc} is the electrical conductivity of the dielectric material inserted between the plates. The first term on the right-hand side represents a loss component due to the inelastic scattering of conducting charge carriers with scatters during their migration, which is present at all frequencies (Kao, 2004). The second term represents the loss component due to the friction in the polarization processes, which increases with increasing frequency and disappears if $\omega = 0$. The third term is a lossless component, it is the displacement current (Hence, West, 1990).

In some dielectric materials, the dc conductivity σ_{dc} is not small and thus can not be negligible; as a result, σ_{dc} will contribute to the dielectric loss of the dielectric materials. The total complex dielectric constant can be demonstrated as

$$\varepsilon^* = \varepsilon' - j\left(\varepsilon'' + \frac{\sigma_{dc}}{\omega\varepsilon_0}\right). \qquad (2.109)$$

Taking the dc conductivity into account, the Debye relaxation model as equation (2.103) is transformed to

$$\varepsilon^* = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{1 + j\omega\tau} - j\frac{\sigma_{dc}}{\omega\varepsilon_0}. \qquad (2.110)$$

The dielectric loss ε'' is expressed as

$$\varepsilon'' = \frac{\varepsilon'_s - \varepsilon'_\infty}{1 + (\omega\tau)^2}\omega\tau + \frac{\sigma_{dc}}{\omega\varepsilon_0}, \qquad (2.111)$$

$$\tan\delta = \frac{(\varepsilon_s' - \varepsilon_\infty')\omega^2\varepsilon_0\tau + (1+\omega^2\tau^2)\sigma_{dc}}{\omega\varepsilon_0(\varepsilon_s' + \varepsilon_\infty'\omega^2\tau^2)}. \tag{2.112}$$

When $\omega\tau << 1$, equations (2.111) and (2.112) reduce to

$$\varepsilon'' = \frac{\sigma_{dc}}{\omega\varepsilon_0}, \tag{2.113}$$

$$\tan\delta = \frac{\sigma_{dc}}{\omega\varepsilon_0\varepsilon_s'}. \tag{2.114}$$

When $\omega\tau \approx 1$, equations (2.111) and (2.112) reduce to

$$\varepsilon'' = \frac{\varepsilon_s' - \varepsilon_\infty'}{2} + \frac{\tau\sigma_{dc}}{\varepsilon_0}, \tag{2.115}$$

$$\tan\delta = \frac{(\varepsilon_s' - \varepsilon_\infty')\varepsilon_0 + 2\tau\sigma_{dc}}{\varepsilon_0(\varepsilon_s' + \varepsilon_\infty')}. \tag{2.116}$$

When $\omega\tau >> 1$, equations (2.111) and (2.112) reduce to

$$\varepsilon'' = \frac{\varepsilon_s' - \varepsilon_\infty'}{\omega\tau} + \frac{\sigma_{dc}}{\omega\varepsilon_0}, \tag{2.117}$$

$$\tan\delta = \frac{(\varepsilon_s' - \varepsilon_\infty')\varepsilon_0 + \tau\sigma_{dc}}{\omega\tau\varepsilon_0\varepsilon_\infty'}. \tag{2.118}$$

The frequency dependence of dielectric loss ε'' including the effect of dc conductivity is revealed in figure 2.10. It is clear that both of the dc conductivity and relaxation process have a remarkable influence on the dielectric properties of materials. For some lossy dielectric materials (Maensiri et al., 2007; Manna et al., 2008), the dc conductivity dominates highly; consequently, the loss due to the relaxation process can not be observed. The evolution of dc conductivity effect on the dielectric loss behavior is revealed in figure 2.11. The loss component related to the relaxation process will be concealed when the dc conductivity of the dielectric materials increases; as a result, it is difficult to study the relaxation behavior of these dielectric materials. This loss component related to dc conductivity is the serious problem and major obstacle for the use of these materials to fabricate electronic devices.

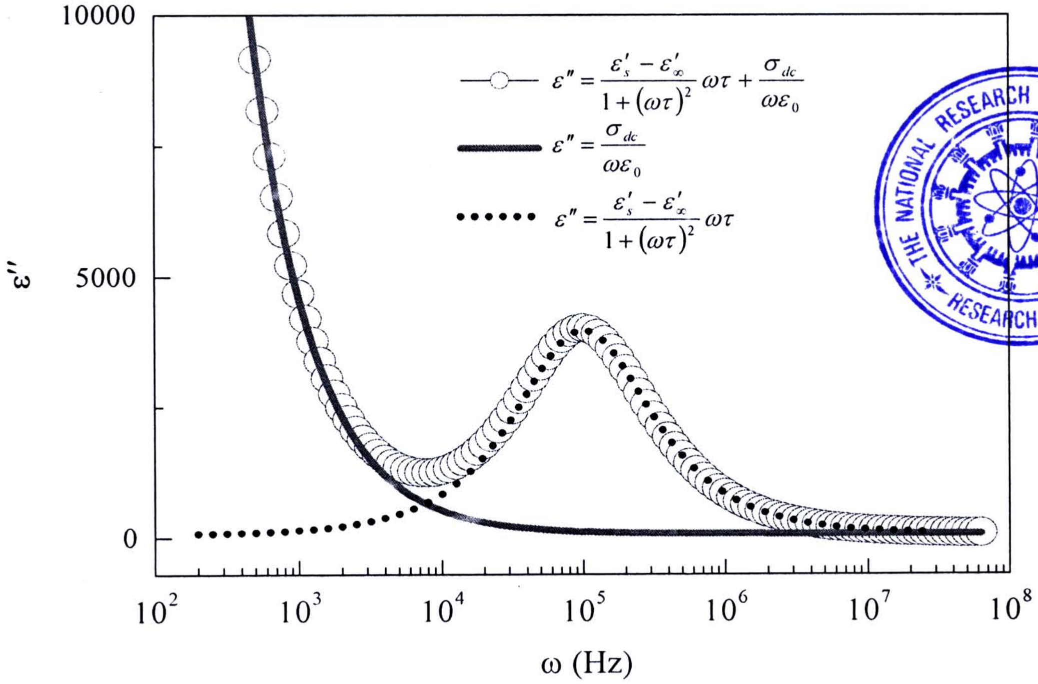

Figure 2.10 Frequency dependence of dielectric loss ε'' represented by the Debye relaxation model, including the effect of dc conductivity. This figure shows the evolution of the relaxation process and dc conductivity contributing to the dielectric loss.

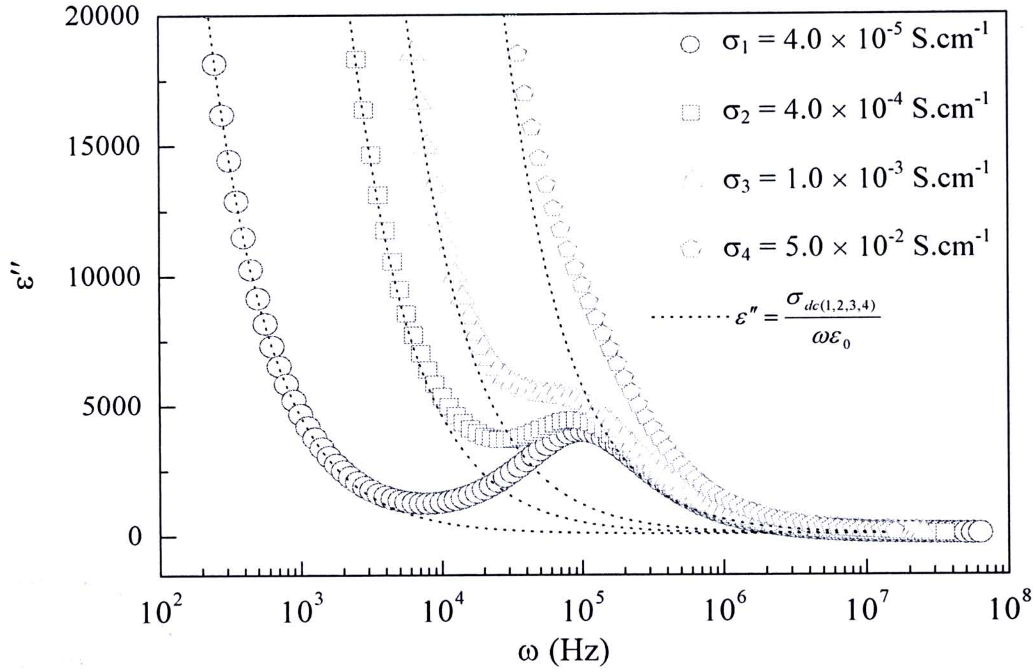

Figure 2.11 Effect of dc conductivity σ_{dc} on dielectric relaxation behavior of dielectric materials. The dot lines represent only the loss component due to the effect of dc conductivity in order to compare with the total dielectric loss, which consists of the loss components due to the relaxation process and dc conductivity.

2.10 Interfacial polarization

As well known, under an influence of an external applied electric field, mobile charge carriers in a material can move freely in the direction with respect to the direction of the field, depending on the kinds of charge, i.e., positive or negative charges. In some materials, however, these free charges cannot move through the bulk materials because they are restricted by some barriers existing in these materials. The accumulation of the charges at the interface between the barriers and conducting parts will produce space charge polarization. The space polarization occurred at these interfaces is usually called '*interfacial polarization*'. In some cases, the interfacial polarization can occur at the interface between different materials, which have a difference in conductivity. To study the mechanism of the interfacial polarization, it is firstly assumed that there is a system consisting of two parallel sheets of different materials, and these two materials are inserted into the space between two parallel metallic plates of unit area, as displayed in figure 2.12.

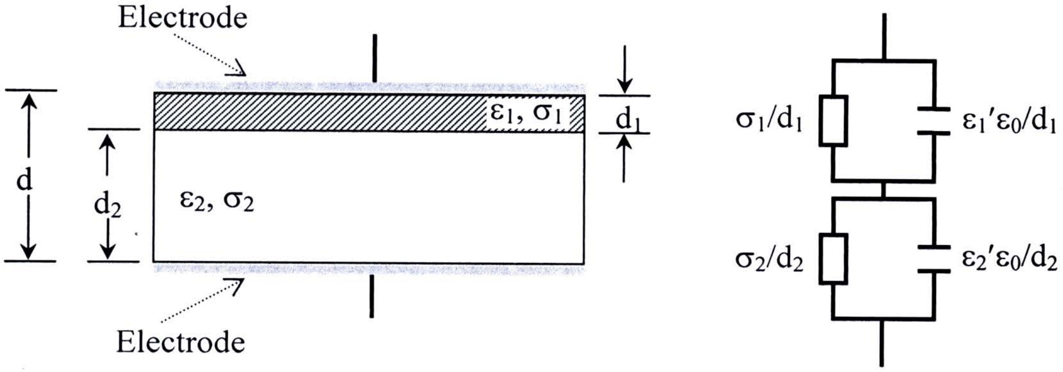

Figure 2.12 Schematic two-layer dielectric model comprising two materials, which have differences in electrical conductivity, thickness, and dielectric constant.

As shown in figure 2.12, when an alternating electric field is applied to the system, the admittance of the system is

$$Y^* = \frac{Y_1^* Y_2^*}{Y_1^* + Y_2^*} . \tag{2.119}$$

Y_1^* and Y_2^* of the materials are

$$Y_1^* = \frac{1}{d_1}(\sigma_1 + j\omega\varepsilon_0\varepsilon_1') \tag{2.120}$$

$$Y_2^* = \frac{1}{d_2}(\sigma_2 + j\omega\varepsilon_0\varepsilon_2') \tag{2.121}$$

where $\varepsilon_1'(\varepsilon_2')$, $\sigma_1(\sigma_2)$, and $d_1(d_2)$ are the dielectric constant, the electrical conductivity, and the thickness of the upper material (lower material), respectively. By substitution equations (2.120) and (2.121) into equation (2.119), we obtain

$$Y^* = \frac{\sigma_1\sigma_2}{\sigma_1 d_2 + \sigma_2 d_1}\left[\frac{\begin{pmatrix}1-\omega^2\tau_1\tau_2 \\ +\omega^2\tau_1\tau + \omega^2\tau_2\tau\end{pmatrix} + j\begin{pmatrix}\omega\tau_1 + \omega\tau_2 \\ +\omega^3\tau_1\tau_2\tau - \omega\tau\end{pmatrix}}{1+\omega^2\tau^2}\right], \tag{2.122}$$

where

$$\tau_1 = \frac{\varepsilon_1'\varepsilon_0}{\sigma_1}, \tag{2.123}$$

$$\tau_2 = \frac{\varepsilon_2'\varepsilon_0}{\sigma_2}, \tag{2.124}$$

$$\tau = \varepsilon_0\frac{(\varepsilon_1' d_2 + \varepsilon_2' d_1)}{(\sigma_1 d_2 + \sigma_2 d_1)}. \tag{2.125}$$

The total complex admittance can be expressed as

$$Y^* = \frac{1}{d}(\sigma + j\omega\varepsilon'\varepsilon_0). \tag{2.126}$$

By comparing equations (2.122) and (2.126), the dielectric constant and electrical conductivity of the system can be obtained

$$\varepsilon' = \frac{1}{\varepsilon_0}\left(\frac{\sigma_1\sigma_2 d}{\sigma_1 d_2 + \sigma_2 d_1}\right)\frac{(\tau_1 + \tau_2 - \tau) + \omega^2\tau_1\tau_2\tau}{1+\omega^2\tau^2}, \tag{2.127}$$

$$\sigma = \left(\frac{\sigma_1\sigma_2 d}{\sigma_1 d_2 + \sigma_2 d_1}\right)\frac{1-\omega^2(\tau_1\tau_2 + \tau_1\tau + \tau_2\tau)}{1+\omega^2\tau^2}. \tag{2.128}$$

Under static dc electric field, $\omega \to 0$, the static dielectric constant ε'_s reduce to

$$\varepsilon'_s = \frac{1}{\varepsilon_0}\left(\frac{\sigma_1\sigma_2 d}{\sigma_1 d_2 + \sigma_2 d_1}\right)(\tau_1 + \tau_2 - \tau), \tag{2.129}$$

and the static conductivity or dc conductivity reduce to

$$\sigma_s = \left(\frac{\sigma_1\sigma_2 d}{\sigma_1 d_2 + \sigma_2 d_1}\right). \tag{2.130}$$

Considering the dielectric constant and conductivity at high frequency, the space charges cannot follow the alternating electric field; therefore, the interfacial polarization can not be produced. In this case, $\omega \to \infty$, the dielectric constant and conductivity are expressed as

$$\varepsilon'_\infty = \left(\frac{\varepsilon'_1\varepsilon'_2 d}{\varepsilon'_1 d_2 + \varepsilon'_2 d_1}\right), \tag{2.131}$$

$$\sigma_\infty = \sigma_s\left(\frac{\tau_1\tau_2 + \tau_1\tau + \tau_2\tau}{\tau_2}\right). \tag{2.132}$$

As shown in figure 2.12, the dielectric loss of the system can be calculated by considering the total current of the system. From equation (2.126), the total current of the system is

$$I^* = Y^* V^* = \frac{1}{d}(\sigma + j\omega\varepsilon'\varepsilon_0)V^*, \tag{2.133}$$

where $V^* = V\exp(j\omega t)$. By comparing equation (2.133) with equation (2.14), we obtain

$$\sigma = d(\omega C_0 \varepsilon''), \tag{2.134}$$

where $C_0 = \varepsilon_0 / d$; therefore, the dielectric loss ε'' of the system can be expressed as

$$\varepsilon'' = \frac{\sigma}{\varepsilon_0 \omega} = \left(\frac{1}{\varepsilon_0 \omega}\right)\left(\frac{\sigma_1 \sigma_2 d}{\sigma_1 d_2 + \sigma_2 d_1}\right)\frac{1-\omega^2(\tau_1\tau_2 + \tau_1\tau + \tau_2\tau)}{1+\omega^2\tau^2}. \tag{2.135}$$

From the system displayed in figure 2.12, we assume that $d_2 > d_1$, $\varepsilon_1' > \varepsilon_2'$, and $\sigma_2 > \sigma_1$. Indeed, these assuming conditions are really occurred in materials, which consist of conducting grain (material-layer 2) and insulating grain boundary (material-layer 1). The frequency dependence of the dielectric constant calculated from equation (2.127) for the system displayed in figure 2.12 with different values of σ_1, σ_2, ε_1', ε_2', d_1, and d_2 is revealed in figure 2.13. Considering figure 2.13(a), a static dielectric constant ε_s' and a high-frequency dielectric constant ε_∞' do not change with the variation of σ_2 (conductivity of grain). However, the step decrease in the dielectric constant shifts to low frequency range with decreasing σ_2, indicating that the relaxation time of the system (τ) depends on σ_2. Based on this model, the relaxation behavior of materials is controlled by the conductivity of the grain. Figure 2.13(b), both ε_s' and ε_∞' change with the variation of σ_1, while the frequency at the step decrease remains constant. It is concluded that ε_s' and ε_∞' are depended on the conductivity of the grain boundary of materials. Figures 2.13(c), with varying the dielectric constant of the grain boundary (ε_1'), both ε_s' and τ change, while ε_∞' is constant. It is interesting that ε_s' does not change with the variation of the dielectric constant of the grain (ε_2'); in contrast, ε_2' has only an effect on ε_∞' as demonstrated in figure 2.13(d). These results can be explained that the concentration of trapped charges at the grain boundaries can control the value of ε_s' and τ of the materials, while ε_∞' is controlled by the dielectric response of the bulk grains, which can usually be produced by the electronic and atomic polarization. This model of the interfacial polarization can be used to ascribe the effect of microstructure on the dielectric properties of ceramic materials. As shown in figures 2.13(e) and 2.13(f), ε_s' of the materials depends strongly on the grain size (d_2) and the thickness of the grain boundary (d_1), it increases with increasing d_2 and d_1. Moreover, τ of the system is also depended on d_2.

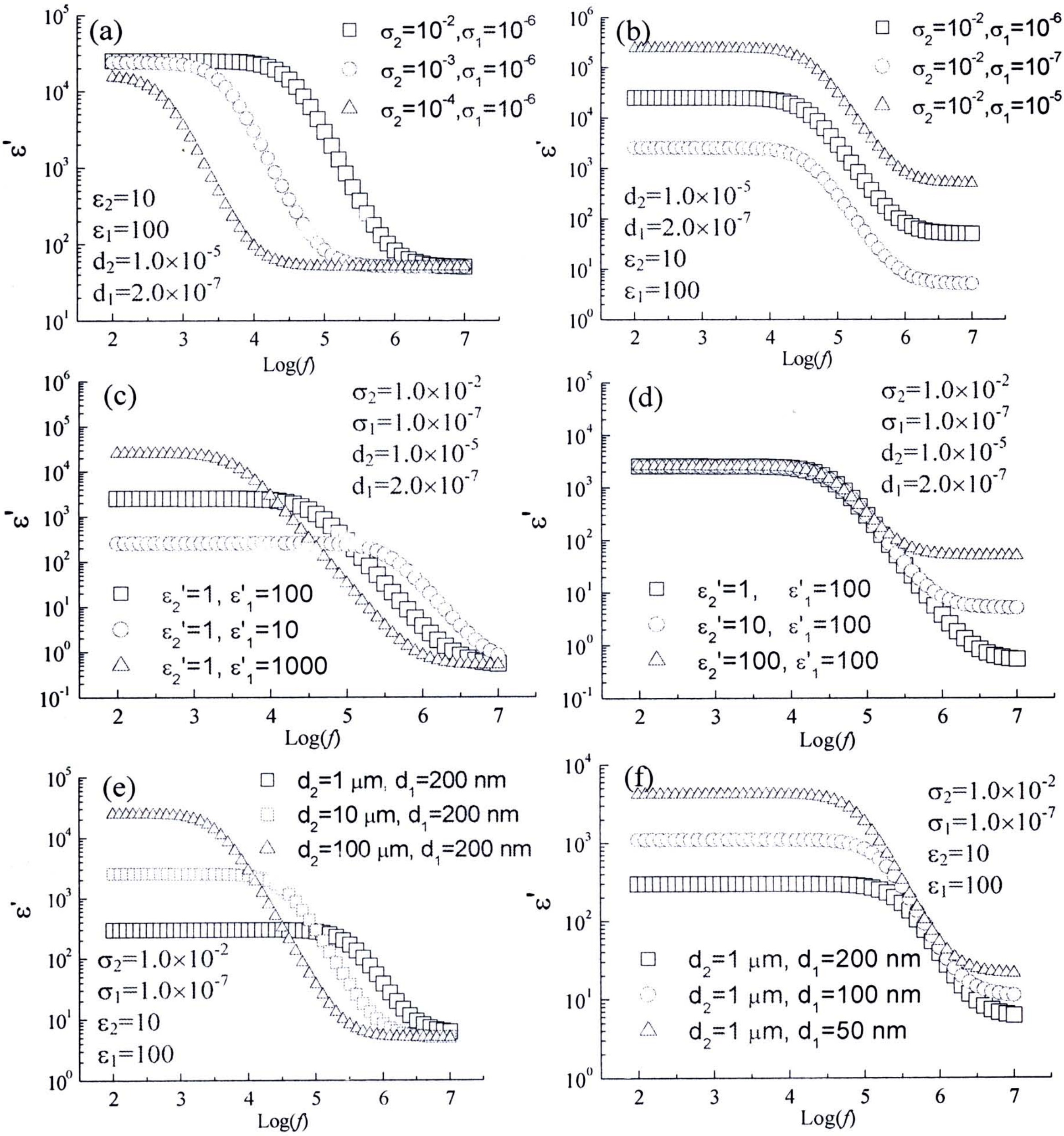

Figure 2.13 Frequency dependence of dielectric constant calculated from equation (2.127) for the system, as displayed in figure 2.12, with different values of σ_1, σ_2, ε_1', ε_2', d_1, and d_2.

2.11 Temperature dependence of polarization

As previous section, the frequency dependence of the orientational and hopping polarizations was discussed. The development of theses dipole models also provided a basis for understanding the temperature dependence of the dielectric properties of a material. As expressed in equation (2.70), the probability of a jump of ion in wells in terms of Boltzmann statistics can be expressed as $P = A\exp(-Q/k_BT)$. Moreover, it can be revealed from equations (2.92) and (2.93) that P was a function of temperature, which is inversely proportional to the average relaxation time of dipoles in the material, $\tau \equiv 1/2P$. As a result, the relaxation time can be proved to be exponentially temperature dependent as the following,

$$\tau = \frac{1}{2A}\exp\left(+\frac{E_a}{k_BT}\right), \tag{2.136}$$

where E_a is the activation energy for the relaxation process in unit of Joule per mole (J/mole) or electron volt (eV). The constant $1/2A$ is defined as the relaxation time at the limited high-temperature of the material that can maintain the insulating properties:

$$\tau_0 \equiv \frac{1}{2A}, \tag{2.137}$$

hence,

$$\tau = \tau_0 \exp\left(+\frac{E_a}{k_BT}\right). \tag{2.138}$$

Equation (2.138) is well known to be as 'Arrhenius law'. By considering equation (2.136) and the Debye relaxation model, the temperature dependence of polarization can be introduced through the temperature dependence of dielectric loss (ε'') and the loss tangent ($\tan\delta$). To describe the effect of temperature on the dielectric properties, the variation of the ε'' peak and $\tan\delta$ peak positions due to the variation of temperature is considered. According to the relation in equation (2.136), equations (2.63) and (2.64) can be derived as

$$\omega_{p(\varepsilon'')} = \frac{1}{\tau} = \tau_0^{-1}\exp\left(-\frac{E_a}{k_B T}\right), \tag{2.139}$$

$$\omega_{p(\delta)} = \frac{\sqrt{\varepsilon_s' / \varepsilon_\infty'}}{\tau} = \frac{\sqrt{\varepsilon_s' / \varepsilon_\infty'}}{\tau_0}\exp\left(-\frac{E_a}{k_B T}\right), \tag{2.140}$$

where $\omega_{p(\varepsilon'')} = 2\pi f_{p(\varepsilon'')}$ and $\omega_{p(\delta)} = 2\pi f_{p(\delta)}$. $f_{p(\varepsilon'')}$ and $f_{p(\delta)}$ are the frequencies at the peak of ε'' and $\tan\delta$, respectively. Therefore, it can be shown that

$$f_{p(\varepsilon'')} = \frac{1}{2\pi\tau_0}\exp\left(-\frac{E_a}{k_B T}\right) = f_0\exp\left(-\frac{E_a}{k_B T}\right), \tag{2.141}$$

$$f_{p(\delta)} = \frac{\sqrt{\varepsilon_s' / \varepsilon_\infty'}}{2\pi\tau_0}\exp\left(-\frac{E_a}{k_B T}\right) = f_0\sqrt{\frac{\varepsilon_s'}{\varepsilon_\infty'}}\exp\left(-\frac{E_a}{k_B T}\right), \tag{2.142}$$

where $f_0 = 1/2\pi\tau_0$. When the temperature dependence of the dielectric relaxation behavior has been observed in the experimental results, the frequency at the peaks of ε'' and $\tan\delta$ can easily be obtained. Then, the activation energy required for the observed relaxation is able to calculate from the slope of the $\ln[f_{p(\varepsilon'')}]$ vs. 1/T (K^{-1}) plot. Taking natural logarithm to equation (2.141), it can be expressed as

$$\ln f_{p(\varepsilon'')} = -\frac{E_a}{k_B}\left(\frac{1}{T}\right) + \ln f_0 . \tag{2.143}$$

This equation is the linear relation between $\ln[f_{p(\varepsilon'')}]$ vs. 1/T (K^{-1}) with slope $-E_a / k_B$. It is worth noting that there are several important data that can be obtained from the temperature dependence of the dielectric relaxation behavior. The estimated τ_0 from the experimental data is used to suggest that the relaxation process is either ionic or electronic polarization in origin (Hence, West, 1990). In general, if τ_0 is in the range of 10^{-13} to 10^{-14} s, the relaxation process originates from the ionic polarization. If τ_0 is very low values, this relaxation process should originate from the electronic polarization. The investigation of the relaxation behavior may face a problem when the measuring temperature increases, ε'' peak may be swamped by the large magnitude of dc conductivity as clearly seen in figure 2.11. Thus, the peak can not be observed.

2.12 Impedance spectroscopy

Impedance spectroscopy is a powerful tool to study the electrical properties of inhomogeneous materials, which exhibit electrically inhomogeneous structure in these materials (Macdonald, 2005; Sinclair et al., 2002; West et al., 2004; Liu et al., 2004, 2005; Morrison et al., 2001). It can be used to separate the electrical responses of a conducting part and an insulating part of the inhomogeneous materials. For example, the electrical responses of semiconducting grains and insulating grain boundaries of $CaCu_3Ti_4O_{12}$ ceramics can be excluded by this technique (Sinclair et al., 2002). Generally, the complex impedance Z^* of a polycrystalline material can be obtained in the usual way, i.e.,

$$Z^* = \frac{V^*}{I^*}, \tag{2.144}$$

where V^* and I^* are the applied voltage and the measuring current, respectively. On the other hand, Z^* can be obtained from the complex dielectric constant ε^*:

$$Z^* = \frac{1}{j\omega C_0 \varepsilon^*}, \tag{2.145}$$

where $\varepsilon^* = \varepsilon' - j\varepsilon''$, $\omega = 2\pi f$, and $C_0 = \varepsilon_0 A/d$, where A is the electrode area and d is the sample thickness.

Complex impedance data Z^* of the polycrystalline material can usually be modeled by an ideal equivalent circuit that consists of resistors R and capacitors C. Generally, there is more than one electrical response in the heterogeneous material. Since the polycrystalline ceramic displays grain-boundary impedance in addition to grain (bulk) effect (Liu et al., 2005), it can be represented by the equivalent circuit shown in figure 2.14.

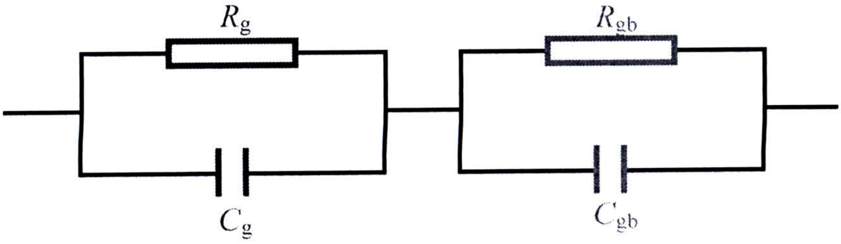

Figure 2.14 Equivalent circuit used to represent the electrical properties of a polycrystalline ceramic material that exhibits grain (R_g ,C_g) and grain-boundary (R_{gb} ,C_{gb}) effects.

As shown in figure 2.14, the circuit consists of a series array of two sub-circuits–one representing grain effects and the other representing grain boundaries. Each sub-circuit is composed of a resistor and capacitor joined in parallel. Normally, the electrical response from the grain boundary should be associated with larger resistance and capacitance than those of grains (Macdonald, 2005; Sinclair et al., 2002). Grain boundary's response frequency is therefore much lower than that of grain, and it gives rise to a relatively strong peak in the impedance. For the materials that show grain and grain-boundary responses and are represented by the equivalent circuit in figure 2.14, the complex impedance Z^* can be expressed as (Sinclair, West, 1989)

$$Z^{*} = Z' - jZ'' = \frac{1}{R_g^{-1} + j\omega C_g} + \frac{1}{R_{gb}^{-1} + j\omega C_{gb}}. \tag{2.146}$$

With excluding the real part Z' and imaginary part Z'' of Z^{*}, it can be shown that

$$Z' = \frac{R_g}{1 + (\omega R_g C_g)^2} + \frac{R_{gb}}{1 + (\omega R_{gb} C_{gb})^2}, \tag{2.147}$$

$$Z'' = R_g\left[\frac{\omega R_g C_g}{1 + (\omega R_g C_g)^2}\right] + R_{gb}\left[\frac{\omega R_{gb} C_{gb}}{1 + (\omega R_{gb} C_{gb})^2}\right], \tag{2.148}$$

where (R_g, R_{gb}) and (C_g, C_{gb}) are the resistances and capacitances of grains and grain boundaries, respectively.

From equations (2.147) and (2.148), the electrical responses from the grains and grain boundaries are located at $1/2\pi R_g C_g$ and $1/2\pi R_{gb} C_{gb}$, respectively. The peak values of Z'' are proportional to the associated resistances, $R_{g,gb} = 2Z''_{\max}$ (Li M et al., 2009). To brief the dielectric properties of the material from its impedance, ε^{*} of the equivalent circuit in figure 2.14 can be derived from equation (2.145) combined with equation (2.146). The result can be expressed as

$$\varepsilon^{*}(\omega) = \varepsilon'_{\infty} + \frac{\varepsilon'_{s} - \varepsilon'_{\infty}}{1 + j\omega\tau} - j\frac{\sigma_{dc}}{\omega\varepsilon_0}, \tag{2.149}$$

where

$$\varepsilon'_{\infty} = \frac{1}{C_0}\left[\frac{1}{C_g^{-1} + C_{gb}^{-1}}\right], \tag{2.150}$$

$$\varepsilon'_{s} = \frac{R_g^2 C_g + R_{gb}^2 C_{gb}}{C_0 (R_g + R_{gb})^2}, \tag{2.151}$$

$$\sigma_{dc} = \frac{1}{C_0(R_g + R_{gb})}, \qquad (2.152)$$

$$\tau = \frac{R_g R_{gb}(C_g + C_{gb})}{R_g + R_{gb}}. \qquad (2.153)$$

If we assume that $R_{gb} \geq R_g$ and $C_{gb} \geq C_g$, equations (2.150) to (2.150) can be reduced to

$$\varepsilon'_\infty = \frac{C_g}{C_0}, \qquad (2.154)$$

$$\varepsilon'_s = \frac{C_{gb}}{C_0}, \qquad (2.155)$$

$$\sigma_{dc} = \frac{1}{C_0 R_{gb}}, \qquad (2.156)$$

$$\tau = R_g C_{gb}. \qquad (2.157)$$

Assuming that grains and grain boundaries form a two-layer capacitor, as shown in figure 2.12, with thickness $(d_1 + d_2)$, where d_1 and d_2 are the thickness of the grain (grain size) and grain boundary, respectively. Equation (2.155) can therefore be shown as

$$\varepsilon'_s = \frac{\varepsilon_1(d_1 + d_2)}{d_1}, \qquad (2.158)$$

where ε_1 is the dielectric constant of the grain boundary layer. This equation also explains the influence of microstructure of materials on their dielectric constant. The dielectric constant can be increased by increasing the grain size of the materials and reducing the thickness of the grain boundary. These results are very consistent with the expected results as revealed in figure 2.13.

2.13 Internal barrier layer capacitor model

An internal barrier layer capacitor model is a simplified model and usually used to explain the origin of giant dielectric properties in bulk polycrystalline materials. It can ideally be constructed as figure 2.15 with the thickness of the bulk d, the microstructure of this constructed model comprises cubic grains and grain boundaries with the thickness d_g (grain size) and d_{gb}, respectively. The total capacitance (C) of this bulk model can be calculated by assuming that $d_g \geq d_{gb}$; therefore, the capacitance of an individual element C_i can be given by

$$C_i = \frac{\varepsilon'_{gb}\varepsilon_0 d_g^2}{d_{gb}}, \tag{2.159}$$

where ε'_{gb} is the dielectric constant of the grain boundary. The capacitance of an individual element per number of element in column is

$$C_{i(column)} = \frac{\varepsilon'_{gb}\varepsilon_0 d_g^2 / d_{gb}}{d / d_g}. \tag{2.160}$$

The capacitance per unit area is

$$C_{i(area)} = \frac{\varepsilon'_{gb}\varepsilon_0 d_g}{d d_{gb}}. \tag{2.161}$$

sine there are $1/d_g^2$ columns per unit area. The dielectric constant of the bulk model can be expressed as

$$\varepsilon' = \frac{\varepsilon'_{gb} d_g}{d_{gb}}. \tag{2.162}$$

It is important to note that the dielectric constant derived from the construction of the internal barrier layer capacitor model depends on the dielectric constant of the grain boundary (ε'_{gb}), the grain size (d_g), and the grain boundary thickness (d_{gb}). This model is similar to that model obtained from the interfacial polarization model as equation (2.158).

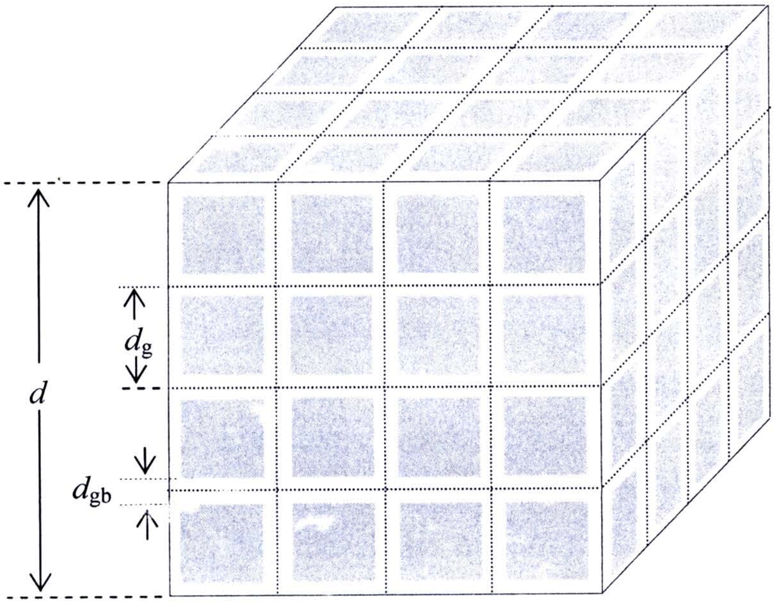

Figure 2.15 Construction of internal barrier layer capacitor model (Adapted from Moulson, Herbert, 2004).