Dielectric Characterization and Reference Materials

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Dielectric reference materials are analyzed with respect to fundamental requirements of linearity, homogeneity and isotropy. Generalized frequency- and temperature-dependent dispersion relations are presented which allow the prediction of broadband dielectric behavior from limited measurement data, determination of valid modal field structure in cavity or waveguide fixtures, and identification of discrepancies and errors in measurement data. An approach for examining the influence of deviations of sample homogeneity on a precisely specified electromagnetic field structure is outlined, and sufficient conditions for isotropic, uniaxial, or biaxial anisotropic dielectric behavior are reviewed in terms of a material's chemical lattice physics. These characteristics direct the choices of suitable reference materials useful for confirming or improving the accuracy of dielectric measurements.

Key words: anisotropy; Debye material; dielectric; dispersion; homogeneity; microwave complex permittivity; reference materials; relaxation.
1. INTRODUCTION

There is a need to know the dielectric properties of many different materials in order to design microwave and millimeter wave devices. There are additional needs for the validation and error analyses of dielectric measurement techniques and for the distribution of standard reference materials. Standard reference materials permit the confirmation and improvement of the accuracy of measuring procedures.

Materials, whether in the solid, liquid or gaseous states, may be electrically nonlinear, anisotropic, inhomogeneous, and dispersive both with respect to frequency and temperature. Because of these intrinsic complicating factors, it becomes difficult to ascertain the accuracy and precision with which dielectric measurements are made until reference materials are developed whose properties are sufficiently well-known so that they can be used as measurement standards.

The organization of this report is as follows. Section 2 contains a general overview of the national need for dielectric metrology and reference materials. Desired properties of ideal dielectric reference materials are described in section 3. Fundamental electrodynamic behavior of materials is reviewed in section 4.

Section 4 is critically important to the understanding of dielectric measurements and the physical qualification of suitable reference standards. Materials are described in terms of their complex constituent properties in an electric or magnetic field. Frequency-dependent polarization mechanisms are discussed, and generalized relaxation relations are derived that are applicable to the rf and microwave regions. These relations allow the predictive broadband characterization of any material, provided suitably sampled
dielectric property measurements are made as a function of frequency. For most materials the dielectric loss measurement error is much greater than the error in determination of real effective permittivity. Hilbert transform relations are derived for determination of the dielectric loss factor from discretely sampled real effective permittivity data. These relations, which are not limited to any portion of the frequency spectrum, are applied to frequency-sampled permittivity and dielectric loss factor data for an absorbent material having a single relaxation time.

The effect of temperature changes on the electrical properties of materials is next analyzed through basic concepts from statistical thermodynamics. Lastly, the dependence of important electrical properties of isotropy and uniaxial or biaxial anisotropy on fundamental molecular lattice symmetries is reviewed. Polymorphous phase changes can occur with temperature that alter the isotropic nature of materials, and it is important to recognize multi-phase lattice structure changes as well as coefficients of thermal expansion in the choice and use of dielectric reference or transfer standards.

Suitable low-loss dielectric reference materials that exhibit low to high polarizability are given in section 5 on the basis of measured data taken over a broad range in both frequency and temperature. The fundamental electromagnetic characteristics discussed in sections 3 and 4 are used as guidelines in this selection. Finally, section 6 summarizes the results of this study and makes recommendations for future work.

2. NATIONAL NEED FOR ENHANCED DIELECTRIC METROLOGY AND REFERENCE MATERIALS

It is appropriate to review the national need and necessity for improved dielectric materials characterization. In parallel with dielectric
characterization will evolve the use of reference materials whose properties are well-known and quantified parametrically with temperature, frequency, mechanical and chemical stress, aging, etc. that they serve as basis points for application and for measurement standards.

Components fabricated with dielectrics are critical to the performance of all electronic equipment used in communications, antennas and antenna housings, navigation, power generation and distribution systems, guidance and instrumentation control systems, radars, computers, sonars, frequency standards, and a large variety of rf, microwave and optical sensing devices. The continued migration to higher frequencies and the miniaturization of electronic equipment has meant that the normal operating temperature range over which dielectric component behavior must be known and perform satisfactorily has generally increased. There is a need both to know and to predict degradation and stability of dielectric materials over this range. Degradation of component dielectric materials leads to drastic losses in equipment reliability. In order to have increased reliability, all components must have more accurate ratings, improved design, and better quality control that stem from the development and more intelligent use of better dielectric materials. These goals can only be attained if the metrology for characterizing dielectric behavior concomitantly becomes more precise, with quantitative specification of procedure accuracies for the method(s) used.

The requirement of reliability for dielectric component devices necessitates a knowledge of measured performance under a wide range of qualifying conditions. Some of these are:
- **Frequency and Strength of Applied Field**
  Change in dielectric constant and absorption with frequency; linearity as a function of applied field strength.

- **Temperature**
  Change in dielectric characteristics due to thermal relaxation, volatilization, phase changes, and possible breakdown. Increasing miniaturization generally means new developments for dielectric components. It also necessitates more precise and enhanced dielectric metrology capabilities. How might dielectric components be designed and characterized that withstand higher temperatures due to increased numbers of dissipative elements in component electronics or more severe environments?

- **Relative Humidity from 0 to 100 Percent**
  Critical components must have high insulation resistance for high voltage and special circuit applications; they must have nonwetting surfaces and be arc resistant.

- **Resistance to Shock and Vibration**
  Fracturing of dielectric materials due to vibration can cause total loss of power generation for communication links, radar systems and sonar devices. Embrittlement of dielectrics as a result of exposure to corrosive environments leads to fracture followed by electrical failure. How can the sensitivity to shock and vibration be predicted or measured? Plasticized resins comprising some dielectric components volatilize as a result of heat and moisture. What dielectric
materials can be substituted that have similar electrical properties but that do not volatilize? How can these substitutes be measured and with what accuracy?

• **Resistance to Surface Contamination**
  Failures occur on insulating surfaces, printed circuit boards, and thin film dielectric components. How can these components be improved by glazing or surface treatments? What is the effect of various contaminants on the electrical behavior of dielectric surfaces and how might these effects best be measured so as to control degradational environmental factors?

• **Service Life**
  Ultra-low loss ceramic materials are often used in critical high-frequency circuits. What is the load life of ceramic capacitive elements? At what point does dielectric breakdown occur, particularly at microwave frequencies? What are the chemical and physical factors and mechanisms which control degradation of a dielectric under prolonged exposure to voltage stress and high temperature?

• **Resistance to Atomic Radiation**
  How does exposure to atomic radiation affect the properties of dielectric components? To what extent does radiation affect the impedance characteristics of field measurement probes?

This discussion is only a brief review of design requirements that of and by themselves justify an important need for standards in the form of dielectric reference materials and measurement methods. Many other requirements
could be made when specific applications are considered. For example, conductive elastomers are used for draining off electrostatic charge that collects on insulating surfaces (antennas, radomes). It is important to know what changes occur in the dielectric properties of these materials due to heat, aging, and weather exposure. In addition, dielectrics must retain stable and dependable properties when subjected to various processing and fabrication activities. Therefore research and development addressed to dielectric nondestructive evaluation are important and practical issues, particularly with regard to quality control.

It is often stated that specifications for thermal stability, exceptional dielectric strength, low dielectric loss, and high resistance to environmental conditions are unnecessarily stringent. However, these specifications are justified not only by safety factors, but also by a history of a dielectric materials failure in service. Specifications should become more conservative, and with this increase in material specifications will come a corresponding need for more precise dielectric measurements together with reference materials that are suited for both application and test procedures.

3. DESIRABLE PROPERTIES OF REFERENCE MATERIALS

Ideal reference materials usually have several characteristics; some are of primary importance and others of lesser or secondary value. The characteristics of an "ideal" dielectric reference material are given in table 1.
Table 1. Characteristics of an Ideal Dielectric Reference Material

<table>
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<tr>
<th>Primary Electrical Attributes</th>
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<tbody>
<tr>
<td>• Linearity</td>
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<td>• Homogeneity</td>
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<td>• Isotropy</td>
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<th>Secondary Nonelectrical Attributes</th>
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<td>• Availability</td>
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<tr>
<td>• Cost</td>
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The principal requirements for a dielectric reference material are that it behave linearly in an applied electric field, be homogeneous and isotropic over the frequency range of interest, and be insensitive to the environment in terms of temperature, chemical changes, or aging. A candidate reference material must then be understood well enough to avoid any problems with respect to these requirements. It is essential therefore that measurement techniques be analyzed in sufficient detail that bounds on measurement errors can be specified. In this way deviations from homogeneity, say, of a candidate material can be distinguished from measurement inaccuracies.

Several dielectric constant ranges are describable in terms of material application in the microwave region. A reference material for each of these ranges would be useful in metrology efforts. The general ranges are:
Low Dielectric Constant, Low Loss ($\varepsilon'_r \leq 4$, $\tan\delta < 0.001$)

This type of material is used to reduce distributed capacitance effects in all interconnecting, mounting, or packaging media. A dielectric reference material of this type would be very useful for calibrating measurement systems that are concerned with the dielectric characterization of radomes or antenna housings, substrates for millimeter-wave antenna systems, and packaging media used for enclosing solid explosives or propellants. Generally, it would be useful to have a low $\varepsilon'_r$, $\tan\delta$ reference material that is moldable or extrudable, that is stable over a wide range in temperature, and that has good working strength. For temperatures up to 250°C an organic reference material may be used; for applications above 250°C an inorganic material such as a low-density ceramic holds promise.

High Dielectric Constant, Low Loss ($\varepsilon'_r \geq 10$, $\tan\delta < 0.001$)

A reference material of this type is useful as a calibration standard for miniature capacitive elements or for substrate materials used in high frequency microstrip transmission lines. For these applications thermal stability and low temperature coefficient of $\varepsilon'_r$ are highly desirable. Materials for these uses must be capable of fabrication into thin flexible films on substrates. When dielectrics of this type are used for microstrip transmission lines, they should also have minimal surface defects, since the surface roughness of microstrip transmission lines at frequencies of 1 GHz and above strongly affects the attenuation of the line.
Very High Dielectric Constant, Ultra-Low Loss ($\varepsilon''_R \geq 100$, $\tan\delta < 0.0002$)

A reference material having this dielectric property would be useful in the characterization of capacitive elements in critical high-frequency circuit applications, where materials of high dielectric constant and ultra-low loss are needed. These materials typically must have $\varepsilon''_R \geq 100$ and have loss tangents $< 0.0005$ at 1 MHz and above, over a temperature range from $-40^\circ$ to $100^\circ$C. They also must have volume resistivities on the order of $10^{12}$ $\Omega$-m from $-40^\circ$ to $200^\circ$C and possess high dielectric strengths over the same temperature range.

Reference materials for the dielectric ranges above could be de jure standards for application. In all three cases, low-loss to ultra-low loss is important over a broad range in frequency. Depending on the temperature range of application, reference materials may or may not be organic (plastics) compositionally. The materials are generally of Cole-Cole type over the frequency range of interest, with negligible relaxation; such relaxation behavior is discussed on section 4.

Although the characteristics of an ideal dielectric reference material are divided into primary electrical versus secondary nonelectrical attributes, this distinction is artificial. In fact, all properties except availability and cost depend on the molecular (chemical) lattice physics of the material. Understanding the characteristics of ideal dielectric reference materials necessitates a general discussion of electromagnetic characteristics of all materials, polarization mechanisms intrinsic to materials, and temperature- and frequency-dependent relaxation processes. In addition, it is necessary to consider fundamental lattice structures in searching for reference materials.
that have preferred isotropic behavior, that are nonpolymorphic, and that have suitable hardness, tenacity, and wettability features.

4. ELECTROMAGNETIC CHARACTERISTICS OF MATERIALS

4.1 Physical Concepts Governing Electromagnetic Behavior

Any material is electromagnetically characterized by its permittivity $\varepsilon$ (F/m), magnetic permeability $\mu$ (H/m), and electrical conductivity $\sigma$ (S/m). Maxwell's equations, together with the constitutive equations relating field quantities in terms of material properties, completely govern electromagnetic wave propagation and behavior in that medium.

The constitutive equations for a linear, homogeneous and isotropic medium may be expressed in the frequency domain as

$$
\vec{B} = \mu \vec{H},
\vec{J} = \sigma \vec{E},
\vec{D} = \varepsilon \vec{E},
$$

where the magnetic induction $\vec{B}$ (Wb/m$^2$) is related to the magnetic field $\vec{H}$ (A/m) by the magnetic permeability; the current density $\vec{J}$ (A/m$^2$) is related to the electric field $\vec{E}$ (V/m) by the conductivity; and the dielectric displacement field $\vec{D}$ (C/m$^2$) is related to the electric field by the permittivity. Any deviation from linearity is usually included by making $\varepsilon$, $\mu$, or $\sigma$ field dependent. For anisotropic media, $\varepsilon$, $\mu$, or $\sigma$ is a second rank tensor as opposed to just a scalar function of frequency or simply a constant. For inhomogeneous media $\varepsilon$, $\mu$, or $\sigma$ is a function of spatial coordinates.
4.1.1 Anisotropy

When a dielectric is placed in an electric field \( \vec{E} \), the material becomes polarized, and the dielectric displacement field is often written

\[
\vec{D} = \epsilon_0 \vec{E} + \vec{P},
\]

(2)

where \( \vec{P} \) is defined as the electric polarization of the material (dipole moment per unit volume), or

\[
\vec{P} = \epsilon_0 \chi \vec{E};
\]

(3)

\( \chi \), the proportionality constant, is called the electric susceptibility, and the factor \( \epsilon_0 \) (free space permittivity equal to \( 8.854 \times 10^{-12} \text{ F/m} \)) is included in eq (3) to make \( \chi \) dimensionless. Then eq (2) becomes

\[
\vec{D} = \epsilon_0 (1 + \chi) \vec{E}
\]

(4)

or

\[
\vec{D} = \epsilon_0 \epsilon_r^* \vec{E},
\]

(5)

where \( \epsilon_r^* = 1 + \chi \) is called the dielectric coefficient or complex permittivity of the medium relative to a vacuum. The presence of a dielectric always affects the ratio of \( \vec{D} \) to \( \vec{E} \) by a factor of \( \epsilon_r^* \). For linear materials the dipole moment induced in a dielectric by an external field \( \vec{E} \) is directly proportional to \( \vec{E} \). As long as the electrical properties of the dielectric are independent of direction, it is isotropic; that is, \( \vec{P} \) and \( \vec{E} \) are collinear. For an anisotropic material, however, the polarization (or charge separation) obtained when an electric field is applied along one coordinate axis will be different than that produced by the same field applied along a different coordinate axis. Quantitatively, this can be expressed by writing
\[ \vec{P} = \epsilon_0 \vec{\chi} \cdot \vec{E}, \quad (6) \]

where \( \vec{\chi} = [x_x \underline{i}i + x_y \underline{j}j + x_z \underline{k}k] \) and \( x_x, x_y, x_z \) are the principal components of anisotropy of the electric susceptibility tensor expressed in dyadic form. For isotropic materials \( x_x = x_y = x_z \), and eq (6) reduces to eq (3). Equation (6) shows that \( \vec{P} \) and \( \vec{E} \) are not collinear when \( x_x \neq x_y = x_z \) or when \( x_x = x_y \neq x_z \) or when \( x_x \neq x_y \neq x_z \) (for two- or three-dimensional anisotropy), so that the electric susceptibility tensor may, in general, be viewed as an operation which takes a vector \( \vec{E} \) and converts it into a new vector \( \vec{P} \) which is not collinear with \( \vec{E} \).

4.1.2 Class A Dielectric Materials

If the nonpermeable dielectric material is not only linear and isotropic, but also spatially uniform (or homogeneous), we categorize it as a Class A dielectric. Spatial uniformity means simply that all spatial derivatives of the susceptibility tensor are zero. Class A dielectrics, whether in solid, liquid, or gaseous phases, make suitable primary reference materials provided the material characteristics possess long time stability (as a function of ambient conditions). However, material dielectrics that are linear, isotropic, and homogeneous when placed in an electric field at one frequency may not be isotropic or homogeneous at another frequency or under different temperature or pressure conditions. Similarly, dielectrics that behave linearly when placed in electric fields of low strength may not be linear in high strength fields (or at high temperature). Consequently, Class A dielectrics should be qualified as to their electrical characteristics with respect to frequency, polarization, and magnitude of applied field strength, as well as temperature and pressure.
4.1.3 Polar Versus Nonpolar Materials

Dielectric materials may also be divided into one of two categories: polar and nonpolar. A nonpolar material (such as inert or rare gases) is simply one that contains no (equivalent) dipoles (or separation of charge) when the material is not in an electric field. A polar material, on the other hand, possesses permanent polarization, even in the absence of an electric field, due to its molecular structure. Polar materials have permanent dipole moments at the microscopic or molecular level. A common polar material is the water molecule, which has the structure illustrated in figure 1a.

![Figure 1](image)

(a) (b)

Figure 1. The structure of the water molecule (a) and its equivalent dipolar representation (b).
Hydrogen has one valence electron and oxygen has six, so that there is a tendency for electrons to form a closed shell having effectively eight electrons around the oxygen. This results in covalent bonds similar to those in the hydrogen molecule. In addition, the atoms become charged because of this electron transferral, and two dipoles are established as portrayed in figure 1b. The permanent moment of the H$_2$O molecule is the vector indicated by $\vec{P}_{H_2O}$ in figure 1b. The H$_2$O molecule may be contrasted with the CO$_2$ molecule shown in figure 2. The individual moments of each CO pair cancel, yielding a zero permanent moment. In general, any distribution of charge may be described in terms of its multipole moments [1].

![Diagram](image)

(a) ![Diagram](image)

(b)

**Figure 2.** Structure of the CO$_2$ molecule (a). Net dipole moment is zero (b).

The relevance of this discussion to dielectric material properties is that the existence of permanent dipole moments on the molecular level gives rise to a type of polarization mechanism when an electric field is applied which is frequency dependent. Without an applied electric field in the case of the water molecule, the individual molecular dipole moments point in random directions, so that macroscopically their vector sum vanishes. In the presence of the applied electric field, $\vec{E}$, though, there is a pronounced
tendency of the dipoles to line up in the direction of $\vec{E}$, creating an 
orientational polarization whose magnitude can be computed [2].

4.1.4 Complex Material Constituent Properties

The solution of Maxwell's equations yields all of the quantities that 
describe the propagation of electromagnetic waves in terms of the propagation 
constant $jk$ where

$$k^2 = \omega \mu (\omega \epsilon - j\sigma) \quad (7)$$

for exp($+j\omega t$) time dependence for angular frequency $\omega$ and time $t$.

In general, the constituent electrical properties may be written as 
complex quantities; that is, for exp($+j\omega t$) time dependence,

$$\epsilon = \epsilon' - j\epsilon'' = [\epsilon_H' - j\epsilon_H''] \epsilon_0 = \epsilon_H^* \epsilon_0 ,$$
$$\sigma = \sigma' + j\sigma'' ,$$

and

$$\mu = \mu' - j\mu'' = [\mu_H' - j\mu_H''] \mu_0 = \mu_H^* \mu_0 .$$

(Note that for anisotropic materials each component of the $\epsilon$, $\sigma$, or $\mu$ tensor 
matrix is, in general, a complex quantity, depending on the nature of 
anisotropy.) The imaginary part of the propagation constant contains all 
necessary information about energy loss in a material medium during wave 
propagation. If magnetic properties are ignored, we may consider only the 
complex forms of $\epsilon$ and $\sigma$ in eq (7):

$$\omega \epsilon - j\sigma = \omega (\epsilon' - j\epsilon'') - j (\sigma' + j\sigma'') = (\sigma'' + \omega \epsilon') - j (\sigma' + \omega \epsilon'') . \quad (9)$$
Here \((\omega \varepsilon' + \sigma'')\) may be considered an effective permittivity and \((\sigma' + \omega \varepsilon'')\) as an effective conductivity. The term \((\sigma' + j\sigma'')\) physically represents carrier transport due to ohmic and Faradaic diffusion mechanisms, respectively, whereas \((\varepsilon' - j\varepsilon'')\) represents dielectric relaxation mechanisms. From eq (9), the loss tangent is simply defined as

\[
\tan \delta = \tan \left(\psi + \frac{\pi}{2}\right) = \frac{\sigma' + \omega \varepsilon''}{\sigma'' + \omega \varepsilon'},
\]

where \(\psi\) is the phase between \(\vec{E}\) and \(\vec{J}\). If there are no dielectric losses, \(\varepsilon'' \to 0\). Similarly, if there are no Faradaic losses, \(\sigma'' \to 0\); hence,

\[
\tan \delta = \frac{\sigma'}{\omega \varepsilon'},
\]

which describes losses physically due to ohmic conductivity.

4.1.5 Distinction Between Ohmic Conductivity (\(\sigma'\)) and Dielectric Loss Factor (\(\varepsilon''\)) or Between Faradaic Diffusion Transport (\(\sigma''\)) and In-Phase Polarization Phenomena (\(\varepsilon'\))

It is often stated that it is artificial to make distinctions between ohmic carrier transport phenomena and dielectric loss characteristic of a material when that material is placed in a time-varying electric field. Actual dielectric measurements are indifferent to the underlying physical processes. To the extent, however, that physical and chemical processes are understood, distinctions can be made and materials designed to have certain electromagnetic characteristics.

The lack of distinction between two loss mechanisms from only measurement data can be seen by inspection of eq (10). Another way to see the relation between conductivity and the imaginary part of the permittivity is to write Ampere's law,
\[ \nabla \times \vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t}, \]  
(12)

where \( \vec{J} \) is the conduction current in a material medium due to an applied electric field. For sinusoidal fields, eq (12) can be rewritten as

\[ \nabla \times \vec{H} = \sigma \vec{E} + \epsilon \frac{\partial \vec{E}}{\partial t} \]

\[ = [\sigma + j \omega \epsilon_0 \epsilon_n^s] \vec{E} \]

\[ = j\omega \left[ \epsilon_n' - j \left( \epsilon_n^n + \frac{\sigma}{\epsilon_0 \omega} \right) \right] \epsilon_0 \vec{E}. \]  
(13)

Hence, without other physical information it is evident that a conductivity \( \sigma \) is equivalent to an imaginary part of \( \epsilon \) given by

\[ \epsilon_n^n = \frac{\sigma}{\omega \epsilon_0}, \]  
(14)

so an equivalent form of eq (10) is

\[ \tan \delta = \frac{\epsilon_n^n}{\epsilon'} = \frac{\text{loss current}}{\text{charging current}}. \]  
(15)

4.1.6 Quality Factor of Dielectrics

The quality factor \( Q \) at a given frequency \( f \) of a dielectric is defined as the inverse of the loss tangent,

\[ Q = \frac{1}{\tan \delta} = \frac{\epsilon'}{\epsilon''} = \frac{\omega \epsilon' E_o^2}{\omega \epsilon'' E_o^2} \]

\[ = 2\pi f \frac{\frac{1}{2} \epsilon'}{\frac{1}{2} \sigma} \frac{E_o^2}{E_o^2}. \]
The quality factor $Q$ can be used as a descriptive characteristic of any dielectric material.

4.2. Polarization Mechanisms Intrinsic to Materials

The previous discussion shows that the relative permittivity of a material is the permittivity of the material normalized with respect to the permittivity of a vacuum. We can describe the electrical constituent properties of a material medium by the complex dielectric constant which, for isotropic material, may be written as $\varepsilon^*(x,y,z) = \varepsilon'(x,y,z) - j \varepsilon''(x,y,z)$, where $\varepsilon'$ is the effective permittivity and $\varepsilon''$ contains all of the information about energy loss (that due to both dielectric losses and ohmic conductivity) in the material during wave propagation.

As an aside, we recall that a pulse or "signal" of any specified initial form can be constructed by superposition of harmonic wave trains of infinite length and duration. The velocities with which the constant-phase surfaces of these component waves are propagated depend on the propagation constant, or on the parameters $\varepsilon$, $\mu$, and $\sigma$. If the medium is nonconducting and the quantities $\varepsilon$ and $\mu$ are independent of the frequency of the applied field, the phase velocity is constant and the signal is propagated without distortion. The presence of a loss mechanism, however, yields a functional relation between the frequency and phase velocity, as well as between frequency and attenuation. Hence in a lossy or absorptive medium the harmonic components suffer
relative displacements in phase in the direction of propagation, and the signal arrives at a distant point in a modified form. The signal is dispersed and attenuated, and a medium in which the phase velocity is a function of frequency $f$ (or in which the complex dielectric constant $\varepsilon'$ is a function of frequency) is said to be electrically dispersive.

The quantity $\varepsilon'(f;x,y,z)$ is a measure of the amount of polarization of the material. There can be a number of different polarizing mechanisms present, each having a characteristic relaxation frequency and dielectric dispersion centered around this relaxation frequency. At the relaxation frequency there is maximal absorption. Figure 3 illustrates the dispersions of $\varepsilon'$ (and $\sigma$) that may be observed in materials in the frequency range $10^3$ to $10^{15}$ Hz. At the highest frequencies, the polarizing species in a material are the electrons. Electronic polarization occurs when an applied electric field causes a net displacement of the electron cloud of an atom with respect to its nucleus. At frequencies below about $10^{13}$ Hz, there is also a contribution from atomic polarization. Atomic polarization occurs in structures (molecules, solutions, etc.) in which atoms do not share electrons equally and electric fields displace the electron clouds preferentially towards the stronger binding atoms. It also occurs when charged atoms are displaced with respect to each other. Dipolar polarization, that is, the orientation of polar molecules (molecules with asymmetric charge distributions), occurs at frequencies below about $10^{10}$ Hz.
Figure 3. Dielectric dispersion for various types of polarization.

At frequencies below about $10^9$ Hz, there are various types of charge polarization which may be collectively referred to as Maxwell-Wagner mechanisms [3,4]. One of these, interfacial (space-charge) polarization, occurs when migrating charge carriers are trapped or impeded in their motion by local chemical or electric potentials, causing local accumulations of charge and a macroscopic field distortion. Another low-frequency mechanism that can occur is due to mixtures of materials having differing electrical properties (such as conducting spheres imbedded in a dielectric). Several different equations are available to describe the resultant properties [5,6] for various geometries of the imbedded conductor: conducting spheres or rods in a dielectric, alternating layers of dielectrics and conductors, etc. The common cause of these effects is the distributions of charge that occur at
conductor-dielectric boundaries and the resultant action under applied
electric fields which can yield very large low-frequency dielectric constants.

Still another dispersion mechanism for dielectric behavior at low
frequencies, which is often distinguished from Maxwell-Wagner effects, is that
which occurs in colloidal suspensions [6]. Maxwell-Wagner effects occur when
the charge around conducting particles in a dielectric medium is a thin
coating which is much smaller than the particle dimensions [7]; the charge
responds to an applied electric field independently of the charge on nearby
particles. In colloidal suspensions, on the other hand, the charge layer is
on the same order of thickness or larger than the particle dimensions; hence
it is affected by the charge distributions of adjacent particles. The theory
of dispersion phenomena in colloidal suspensions is presently a fertile area
of research. Dukhin [7] has shown that colloidal responses result in far
higher low-frequency dielectric constants than those resulting from typical
Maxwell-Wagner mechanisms, with dielectric constants on the order of $10^5$ not
uncommon.

4.3 Dispersion and Relaxation Processes in Materials

Polarization processes occurring in material media as a result of
electromagnetic wave propagation are physically damped by either resonance or
relaxation. We recall that resonance is the state of a harmonic oscillator
when being driven at its preferred frequency. Relaxation, on the other hand,
is the state of a critically damped or overdamped oscillator. The effects on
$\varepsilon'$, $\varepsilon''$ of these two differing types of dispersion and absorption processes,
which occur in dielectric materials, are shown in figure 4.
At microwave frequencies, we are principally dealing with dipolar or orientation polarization phenomena. In this case, the frequency is sufficiently low so that the rotation of polar molecules has time to take place. At a frequency of $\omega = 1/\tau$, $\varepsilon'$ decreases because the individual dipoles can no longer keep in step with the applied field. The relaxation time $\tau$ represents the time required for the dipoles to revert to a random distribution. This is a diffusion process which is represented by figure 4(a).

Atomic and electronic polarization processes, on the other hand, take place in the infrared and optical portion of the spectrum (1 THz and above) and lead to the resonance-type dispersion and absorption phenomenon represented by figure 4(b). A given medium may display any or all of these four characteristic polarization phenomena, depending on its composition and molecular or atomic structure.
Relaxation processes are those observed in dielectric materials at microwave frequencies and below. Thus, it would be useful to consider some relaxation models. The relaxation models discussed here are based on the general equation of charge motion,

$$\ddot{q} + (\mu\sigma)^{-1} \dot{q} + (\mu\epsilon)^{-1} q = 0,$$

where $q$ is the charge and $\cdot$ represents differentiation with respect to time. All derivatives are with respect to time. Another relaxation model is based on the diffusion of charged ions whose concentration is spatially variable. In this case,

$$\frac{\partial^2}{\partial x^2} \bar{Q}(t;x,y,z) + \frac{\partial^2}{\partial y^2} \bar{Q}(t;x,y,z) + \frac{\partial^2}{\partial z^2} \bar{Q}(t;x,y,z) = \frac{1}{K} \frac{\partial}{\partial t} \bar{Q}(t;x,y,z) + \frac{\eta}{K} \bar{Q}(t;x,y,z),$$

where $\bar{Q}$, the concentration of charged ions, is a function of geometry and time. $K(t)$ is the diffusion coefficient and $\eta$ is a constant. For the latter case, spatial derivatives must be taken in determining diffusion relaxation which, in terms of electrical circuit analogues, lead to generalized distributed impedances (as opposed to lumped impedances) and nonlinear behavior [8].

4.3.1 Debye Relaxation

Materials having single relaxation time constants are called Debye materials. The complex permittivity in a Debye material is given by [9,10]
\[ \epsilon' - j\epsilon'' = \epsilon_\infty \left[ \frac{(\epsilon_s - \epsilon_\infty)/\epsilon_\infty}{1 + j\omega\tau} + 1 \right] \]

\[ = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2\tau^2} - j \frac{(\epsilon_s - \epsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} , \tag{19} \]

where \( \epsilon_s \) is the measured dielectric constant at zero frequency \((\epsilon_{d.c.} = \epsilon_s\epsilon_0)\), and \( \epsilon_\infty \) is the relative dielectric permittivity at infinite frequency \((\epsilon_{\text{infinite}} = \epsilon_\infty\epsilon_0)\). The derivation of the complex permittivity as a function of frequency in any dielectric material having only one relaxation time is given in the Appendix. In general, single relaxations are seldom observed. Multiple relaxations or distributions of relaxations are instead found, as we would expect from our discussion on polarization mechanisms.

4.3.2 Generalized Relaxation Distributions

Wyllie [11] has given an expression for material media in which multiple relaxations are found. In this case, the complex permittivity may be written

\[ \epsilon' - j\epsilon'' = \epsilon_\infty + (\epsilon_s - \epsilon_\infty) \int_0^\infty \frac{D(\tau)(1 - j\omega\tau)}{1 + \omega^2\tau^2} \, d\tau , \tag{20} \]

where \( D(\tau) \) is the time constant distribution function normalized such that

\[ \int_0^\infty D(\tau) \, d\tau = 1 . \]

One of the most commonly observed simple relaxation distributions in lossy media at microwave frequencies and below is the Cole-Cole distribution [10]. In the Cole-Cole distribution, eq (20) reduces to

\[ \epsilon' - j\epsilon'' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (j\omega T)^{-m}} , \tag{21} \]
where $0 \leq m \leq 1$. The loss tangent for the Cole-Cole distribution is

$$
\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\theta (\omega \tau)^{1-m} \sin[(1-m)\frac{\pi}{2}]}{1 + \theta + (2 + \theta)(\omega \tau)^{1-m} \cos [(1-m)\frac{\pi}{2}] + (\omega \tau)^{2(1-m)}},
$$

(22)

where $\theta = (\varepsilon_s - \varepsilon_\infty)/\varepsilon_\infty$. The $m = 0$ case corresponds to a Debye material (single relaxation). The $m = 1$ case corresponds to an infinitely broad continuous distribution (one having no relaxation). In the latter case the imaginary part of the complex permittivity disappears, and the real part becomes frequency independent.

The Cole-Cole distribution corresponds to a symmetric distribution of relaxation times of width $m$. Whereas a Debye material yields a plot of $\varepsilon''(\varepsilon')$ that is a semicircle whose center lies on the $\varepsilon'' = 0$ axis, a Cole-Cole $\varepsilon''(\varepsilon')$ plot is a semicircle whose center lies below the horizontal $\varepsilon'' = 0$ axis, on a line drawn from $(\varepsilon' = \varepsilon_\infty, \varepsilon'' = 0)$ that makes an angle of $m\pi/2$ with the horizontal axis. This is shown in figure 5.

![Debye and Cole-Cole plots](image)

**Figure 5.** $\varepsilon''$ versus $\varepsilon'$ plots for Debye and Cole-Cole materials.
In practice it is often difficult to access the actual form of the distribution function from dielectric data; however, its width, principal relaxation time $\tau_0$, and symmetry can be determined. Furthermore, the actual power-law frequency dependence of the complex permittivity can be found by suitably sampling the $\varepsilon'' (\varepsilon')$ function in frequency. A corollary to this statement is that a number of differing metrological techniques would be necessary to characterize completely an arbitrary dielectric material. Finally, fairly simple relations describing the functional relation of $\varepsilon^*$ with frequency arise from relatively complex distribution functions. For example, the relaxation time distribution function for a Cole-Cole material is

$$D(\tau) = \frac{\sin m \pi}{\tau [2\pi \cosh [(1-m) \ln \tau/\tau_0] - \cos m\pi]} \quad (23)$$

4.3.3 Universal Dielectric Response

In addition to the Cole-Cole expression, there are three other empirical relations commonly used to describe a non-Debye response. These are the Cole-Davidson [13], the combined Cole-Cole, and the Williams-Watkins [14] expressions. A characteristic feature of all the above empirical relations, besides being based on eq (17), is that at frequencies away from the relaxation frequency they reduce to expressions showing a power-law dependence on frequency for both $\varepsilon'$ and $\varepsilon''$. This common characteristic led Jonscher [15,16] to define this power-law dependence as the "universal dielectric response"; that is,

$$\varepsilon' = K \omega^{-c}, \quad (24)$$

where $K$ and $c$ are constants ($c \geq 0$) that depend on the material.
4.3.4 Relationships Between Real Effective Permittivity and Loss Tangent

4.3.4.1 Materials With Loss Factors That Are Constant With Frequency

The generalized relaxation given by eq (20) can be used to derive a relation between values of loss tangent and real effective permittivity. Equation (20) can be written

\[ \varepsilon'(\omega) - \varepsilon_\infty = \int_0^\infty \frac{F(\tau)}{1 + \omega^2 \tau^2} \, d\tau, \quad (25) \]

and

\[ \varepsilon''(\omega) = \int_0^\infty \frac{F(\tau) \omega \tau}{1 + \omega^2 \tau^2} \, d\tau. \quad (26) \]

The essential model posed by eq (25) and eq (26) is that a dielectric consists of dipoles which have a range or continuum of relaxation times. Over a restricted frequency range, measured values of the loss factor \( \varepsilon'' \) for some dielectrics are nearly constant, or approximately independent of frequency. One of the simplest relaxation distributions which can lead to this result is a simple inverse power law of the distribution function \( F(\tau) \) with relaxation, that is,

\[ F(\tau) = \frac{F_0}{\tau}, \quad \tau \neq 0, \quad (27) \]

where \( F_0 \) is constant.

Then

\[ \varepsilon'(\omega) - \varepsilon_\infty = F_0 \int_0^\infty \frac{d\tau}{\tau(1 + \omega^2 \tau^2)} \quad (28) \]

and

\[ \varepsilon''(\omega) = F_0 \int_0^\infty \frac{\omega}{1 + \omega^2 \tau^2} \, d\tau. \quad (29) \]
The integrals in eqs (28) and (29) are in standard form [17] and can be reduced to

\[ \varepsilon'(\omega) - \varepsilon_\infty = \frac{F_0}{2} \ln \frac{1}{\omega^2} \]  

(30)

and

\[ \varepsilon'' = F_0 \tan^{-1} \omega R \bigg|_0^\infty = F_0 \frac{\pi}{2}. \]  

(31)

For two values of \( \varepsilon' \), measured at \( \omega = \omega_1 \) and \( \omega = \omega_2 \), eq (30) gives

\[ \varepsilon'_1(\omega_1) - \varepsilon'_2(\omega_2) = \frac{F_0}{2} \left[ \ln \frac{1}{\omega_1^2} - \ln \frac{1}{\omega_2^2} \right] \]

or

\[ \Delta \varepsilon'(\omega) \equiv \varepsilon'_1(\omega_1) - \varepsilon'_2(\omega_2) = \frac{F_0}{2} \ln \frac{\omega_2^2}{\omega_1^2}. \]  

(32)

From eq (15) and eq (31),

\[ F_0 = \frac{2\varepsilon''}{\pi} = \frac{2}{\pi} \varepsilon' \tan \delta \]  

(33)

so that

\[ \Delta \varepsilon'(\omega) = \frac{2}{\pi} \varepsilon' \tan \delta \ln \frac{\omega_2}{\omega_1} \]  

(34)

or

\[ \frac{\Delta \varepsilon'}{\varepsilon'\tan \delta} = \frac{2}{\pi} \tan \delta \ln \frac{\omega_2}{\omega_1}. \]  

(35)

This result gives the change in real effective permittivity between two frequencies \( \omega_1 \) and \( \omega_2 \) and relates that change in real effective permittivity to the loss tangent of the dielectric material. Garton [18] first presented this result, although it does not seem to be well known and some published measurements are not consistent with it.
Equation (35) may be used in three ways:

(1) Check measured complex permittivity values for discrepancies (or predict one measurement from the other).

(2) Indicate where peak absorption frequencies occur.

(3) Determine which modal roots are valid in cavity or waveguide measurement fixtures.

4.3.4.2 Absorbent Materials Having Single Relaxation Times

Garton's work [18] may be extended for the Debye model of a dielectric, where tanδ is not constant with frequency. From eq (19) the charging and loss terms of a Debye dielectric may be written

\[
\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2\tau^2}, \tag{36}
\]

\[
\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2}, \tag{37}
\]

so that if we consider two measurement frequencies, \( \omega_1 = \omega_0 \pm \Delta\omega \) and \( \omega_2 = \omega_0 + \Delta\omega \), where \( \omega_0 \) is the arithmetic mean of \( \omega_1 \) and \( \omega_2 \), we can write

\[
\Delta\varepsilon' = \varepsilon'_1(\omega_1) - \varepsilon'_2(\omega_2)
\]

\[
= (\varepsilon_s - \varepsilon_\infty) \frac{[1 + \omega_0^2\tau^2(1 + \frac{\Delta\omega}{\omega_0})^2] - [1 + \omega_0^2\tau^2(1 - \frac{\Delta\omega}{\omega_0})^2]}{[1 + \omega_0^2\tau^2(1 + \frac{\Delta\omega}{\omega_0})^2] [1 + \omega_0^2\tau^2(1 - \frac{\Delta\omega}{\omega_0})^2]}. \]
If $\frac{\Delta \omega}{\omega_0} << 1$,

\[
(1 + \frac{\Delta \omega}{\omega_0})^2 \approx 1 + 2 \frac{\Delta \omega}{\omega_0}
\]

and

\[
(1 - \frac{\Delta \omega}{\omega_0})^2 \approx 1 - 2 \frac{\Delta \omega}{\omega_0},
\]

so that

\[
\Delta \varepsilon' = \frac{4(\varepsilon_s - \varepsilon_\infty) \omega_0^2 \tau^2}{(1 + \omega_0^2 \tau^2)^2} \frac{\Delta \omega}{\omega_0}
\]

or

\[
\Delta \varepsilon' = \frac{4 \overline{\varepsilon''} \omega_0 \tau}{1 + \omega_0^2 \tau^2} \frac{\Delta \omega}{\omega_0},
\]

where

\[
\overline{\varepsilon''} = \frac{(\varepsilon_s - \varepsilon_\infty) \omega_0 \tau}{1 + \omega_0^2 \tau^2}
\]

may be considered as the approximate mean value of the loss term between measurement frequencies $\omega_1$ and $\omega_2$. In this case,

\[
\ln \frac{\omega_2}{\omega_1} = \ln (1 + 2 \frac{\Delta \omega}{\omega_0})
\]

\[
= 2 \frac{\Delta \omega}{\omega_0}.
\]

Therefore

\[
\Delta \varepsilon' = \frac{2 \overline{\varepsilon''} \omega_0 \tau}{1 + \omega_0^2 \tau^2} \ln \frac{\omega_2}{\omega_1}
\]

or

\[
\Delta \varepsilon' = \frac{2 \varepsilon' \omega_0 \tau}{1 + \omega_0^2 \tau^2} \tan \delta \ln \frac{f_2}{f_1},
\]

so that

\[
\frac{\Delta \varepsilon'}{\varepsilon'} = \frac{2 \omega_0 \tau \ln 10}{1 + \omega_0^2 \tau^2} \tan \delta \log_{10} \frac{f_2}{f_1}.
\]
Lynch [19] has extended Garton's work for the Debye single relaxation model and has shown that

$$\frac{\Delta \epsilon'}{\epsilon'} = a \tan \delta \log_{10} \frac{f_2}{f_1}$$  (45)

where $1.0 \leq a \leq 2.3$ for $1 \leq \omega_0 \tau \leq 4$. The point is that eq (34) and/or eq (35) is generally valid, within a factor of 1.5, for a wide range of frequencies on both sides of a Debye absorption curve. Problems in applying either of the relations given by eq (35) or eq (45) arise because:

1. The assumption that the loss tangent of a dielectric is either constant or varies in a Debye fashion over a range in frequency is only approximately true.

2. Changes in measured real effective permittivity as a function of frequency are not often reported with sufficient precision to allow strict testing of the relations.

Despite the problems in applying real effective permittivity and loss tangent relations, Lynch [19] has compared reported measured values of loss tangent to calculated values of the loss tangent for several materials up to K-band. This comparison is given in table 2.

The validity of relations between real effective permittivity and loss tangent is worthy of further research, particularly for non-Debye relaxation mechanisms. Such relations might help identify discrepancies and errors in reported permittivity measurements.
Table 2. Comparison of Reported With Predicted Value of Loss Tangent (after reference [19])

<table>
<thead>
<tr>
<th>Material</th>
<th>Frequency</th>
<th>Relative Permittivity (Geometric Mean)</th>
<th>Loss Tangent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Reported</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>50 Hz</td>
<td>2.55</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>9 GHz</td>
<td>2.55</td>
<td>0.004</td>
</tr>
<tr>
<td>Polytetrafluoroethylene (Teflon)</td>
<td>50 GHz</td>
<td>2.12</td>
<td>0.000 05</td>
</tr>
<tr>
<td></td>
<td>24 GHz</td>
<td>2.10</td>
<td>0.000 25</td>
</tr>
<tr>
<td>Phenol-Formaldehyde Resin, containing 5.8% water</td>
<td>100 MHz</td>
<td>5.00</td>
<td>0.0068</td>
</tr>
<tr>
<td>Water at 0°C</td>
<td>3 GHz</td>
<td>79.8</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>9.3 GHz</td>
<td>45.4</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>24 GHz</td>
<td>16.3</td>
<td>1.70</td>
</tr>
<tr>
<td>Water at 75°C</td>
<td>3 GHz</td>
<td>61.9</td>
<td>0.055</td>
</tr>
<tr>
<td></td>
<td>9.3 GHz</td>
<td>60.4</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>24 GHz</td>
<td>51.7</td>
<td>0.43</td>
</tr>
</tbody>
</table>

4.3.4.3 Generalized Relationship for Any Dielectric Material Having an Arbitrary Number of Relaxation Times

A generalized relationship may be derived between real effective permittivity $\varepsilon'$ and loss factor $\varepsilon''$ for dielectric materials possessing an arbitrary number of relaxation times. In general, the permittivity can be regarded as a system function characterizing the electrical properties of a material with the applied electric field as input and the displacement field as output. In the time domain the material permittivity is simply the transient system response. Consider the (real) permittivity $\varepsilon(t)$ of any material that is impulsively excited at time $t = 0$ with an electric field.
The permittivity $\varepsilon(t)$ can always be decomposed into the sum of an even function $\varepsilon_e(t)$ and an odd function $\varepsilon_o(t)$; that is,

$$\varepsilon(t) = \varepsilon_e(t) + \varepsilon_o(t)$$  \hspace{1cm} (46)

where

$$\varepsilon_e(t) = \frac{[\varepsilon(t) + \varepsilon(-t)]}{2}$$ \hspace{1cm} (47)

and

$$\varepsilon_o(t) = \frac{[\varepsilon(t) - \varepsilon(-t)]}{2}.$$ \hspace{1cm} (48)

The decomposition process is shown schematically in figure 6 for a transient system response that contains no singularities at the origin.

Also,

$$\varepsilon_e(t) = \varepsilon_o(t), \ t > 0$$  \hspace{1cm} (49)

and

$$\varepsilon_e(t) = -\varepsilon_o(t), \ t < 0,$$  \hspace{1cm} (50)

so that

$$\varepsilon_o(t) = \varepsilon_e(t) \ sgn(t)$$  \hspace{1cm} (51)

and

$$\varepsilon_e(t) = \varepsilon_o(t) \ sgn(t).$$  \hspace{1cm} (52)

where

$$\text{sgn}(t) = \begin{cases} 1, & t \geq 0 \\ -1, & t < 0 \end{cases}.$$  \hspace{1cm} (53)

(See figure 7.)
Figure 6. Decomposition of permittivity \( \varepsilon(t) \) into even \( \varepsilon_e(t) \) and odd \( \varepsilon_0(t) \) parts.
Figure 7. The function $\text{sgn}(t)$.

The importance of eq (51) and eq (52) is that the even and odd decomposition functions of any material's permittivity in the time domain can be written as the product of two time functions. Taking the temporal Fourier transform $F$ of the material permittivity function yields,

$$F \{ \epsilon(t) \} \equiv \epsilon'(\omega) - j\epsilon''(\omega),$$

(54)

where

$$F \{ \epsilon_e(t) \} = \epsilon'(\omega)$$

(55)

and

$$F \{ \epsilon_o(t) \} = -j\epsilon''(\omega),$$

(56)

and where the Fourier transform $F(\omega)$ of an arbitrary function $f(t)$ is given by $F(\omega) = \int_{-\infty}^{\infty} f(t) e^{-j\omega t} \, dt$. The Fourier transform of the product of two time functions equals the convolution of their respective transforms divided by $2\pi$. Since

$$F \{ \text{sgn}(t) \} = \frac{2}{j\omega},$$

(57)
we may straightforwardly substitute eqs (55), (56), and (57) into (51) and (52) to obtain

\[ \epsilon''(\omega) = \frac{1}{\pi} \epsilon'(\omega) * \frac{1}{\omega} \]

and

\[ \epsilon'(\omega) = -\frac{1}{\pi} \epsilon''(\omega) * \frac{1}{\omega} \]

where * denotes convolution, or

\[ \epsilon''(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\epsilon'(u)}{\omega-u} \, du \tag{58} \]

and

\[ \epsilon'(\omega) = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\epsilon''(u)}{\omega-u} \, du \tag{59} \]

Equations (58) and (59) are valid when no singularities in \( \epsilon(t) \) exist at \( t = 0 \). The \( \int \) sign denotes Cauchy principal value. In other words, eqs (58) and (59) are exact expressions for obtaining the loss factor \( \epsilon'' \) or real effective permittivity \( \epsilon' \) from the real effective permittivity or loss factor, respectively, for any material provided \( \epsilon(t) \) contains no impulses at the origin. The restriction that \( \epsilon(t) \) contains no impulses at the origin means that \( \epsilon'(\omega) \to 0 \) as \( \omega \to \infty \). In fact, there is always an optical polarization that defines an optical dielectric constant \( \epsilon_{\infty} \), as given in eq (A-5):

\[ \epsilon_{\infty} = n^2 = 1 + \frac{\rho_{\infty}}{E} \tag{60} \]

where \( n \) is the refractive index of the material under the influence of the electric field \( E \). Therefore,

\[ \lim_{\omega \to \infty} \epsilon^*(\omega) = \lim_{\omega \to \infty} \epsilon'(\omega) \equiv \epsilon_{\infty} , \tag{61} \]
so that an impulse exists at the origin for $\varepsilon(t)$. This means that an even term $\varepsilon_\infty \delta(t)$ (Dirac delta function weighted by $\varepsilon_\infty$) is present in $\varepsilon(t)$ and $\varepsilon_e(t)$, but not in $\varepsilon_0(t)$. In other words, eq (58) is still valid, but $\varepsilon_\infty \delta(t)$ is lost in eq (59). We can then conclude that $\varepsilon''(\omega)$ is given by eq (58), but only the quantity $\varepsilon'(\omega) - \varepsilon_\infty$ is recovered from eq (59) ($\varepsilon'(\omega)$ can be determined from measurements of $\varepsilon''(\omega)$ only within the real optical limit $\varepsilon_\infty$). Hence eq (58) and (59) should be written

$$\varepsilon''(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\varepsilon'(u)}{\omega - u} \, du \quad (62)$$

and

$$\varepsilon'(\omega) = \varepsilon_\infty - \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\varepsilon''(u)}{\omega - u} \, du \quad (63)$$

The integral expressions on the right of eqs (62) and (63) are the Hilbert transforms of the permittivity and loss factor, respectively, and provide a means for computing the loss (or real effective permittivity) from observed real effective permittivity (or loss) measurements that are made over a range in frequency. The integration variable $u$ in eqs (62) and (63) is just a dummy variable, not necessarily the same as the angular frequency $\omega$ for which $\varepsilon''$ or $\varepsilon'$ is desired. Also, the relations given by eqs (62) and (63) are true for rf, microwave, mm, and IR frequency ranges. In other words, there are no frequency ranges restricting the validity of eqs (62) and (63). The only suppositions implicit in the derivation of these relations are

1. Dielectric material behaves linearly in presence of electric field.
2. Constitution of dielectric material does not change within analysis time.
(3) Dielectric is causal (does not polarize before stimulus of electric field).

These relations are quite useful for two reasons,

(1) Uncertainty in loss measurements for both low-loss standard reference materials and absorbent materials is usually much greater than the uncertainty in real effective permittivity measurements; that is,

\[
\frac{\Delta \varepsilon''}{\varepsilon''} \gg \frac{\Delta \varepsilon'}{\varepsilon'}. 
\]

Therefore precise measurements of real effective permittivity over a range in frequency can be used to determine the loss factor.

(2) Prediction of absorbent dielectric characteristics can be made from out-of-band measurements.

4.3.4.3.1 Example of Hilbert Transform Relationships in Prediction of Dielectric Properties for Absorbent (Dispersive) Materials

An example of the use of eq (62) for predicting the loss factor \( \varepsilon'' \) from discrete permittivity values \( \varepsilon' \) is shown in figures 8 and 9. The dielectric material shown in figure 8 has only a single relaxation time with \( \varepsilon_s = 6 \) and \( \varepsilon_\infty = 2 \). The predicted loss for this material is given in figure 9 and compares with the exact (discrete) loss shown in figure 10 by no more than 2% error over two decades in frequency. Similarly, the use of eq (63) for predicting the real effective permittivity \( \varepsilon' \) from discrete loss factor values, \( \varepsilon'' \) shown in figure 10, is presented in figure 11. The predicted real effective permittivity values in figure 11 can be seen to agree with actual permittivity values in figure 8 within 1.9%. 

39
Figure 8. Discrete relative permittivity, $\varepsilon_r$, for a simulated absorbent dielectric material as a function of $\omega T$. 

40
Figure 9. Predicted relative loss, $\varepsilon''_R$, for a simulated absorbent dielectric material as a function of $\omega \tau$, calculated from discrete relative $\varepsilon'_R$ (permittivity) data via Hilbert transform.
Figure 11. Predicted relative permittivity, $\varepsilon'_R$, for a simulated absorbent dielectric material as a function of $\omega \tau$, calculated from discrete $\varepsilon''_R$ (loss) data via Hilbert transform.
4.3.5 Effect of Temperature Changes

Polarization processes occurring in materials are generally strong functions of both angular frequency \( \omega \) and temperature \( T \). For this reason the complex permittivity tensor may be generally written as

\[
\mathbf{\varepsilon}^*(x,y,z; \omega,T) = \mathbf{\chi}^*(x,y,z; \omega,T) + \mathbf{I} ,
\]

(64)

where \( \mathbf{\varepsilon}^* \), \( \mathbf{\chi}^* \) are the complex frequency- and temperature-dependent permittivity and electrical susceptibility tensors, respectively, and \( \mathbf{I} \) is the identity matrix. In order to gain insight into temperature-dependent variations of the complex dielectric permittivity over the frequency range where dipolar or orientation phenomena occur, it is useful to consider concepts borrowed from statistical thermodynamics. The results will then be compared to those derived in the appendix for relaxation in dielectrics possessing one relaxation time.

If the polarizability of a material can be related to the known activation energy \( U \) of that material at a given temperature and under the influence of a time-varying electric field, then a means for predicting the dielectric behavior of that material as a function of temperature could be grasped. Of course, such predictive capability will be constrained by the assumptions implicit in the physical model and will need to be validated by measurements of the dielectric constant as a function of both frequency and temperature. Clearly, these types of measurements, combined with theoretical physical models, will not only enhance the means for predicting the dielectric constant, but can also aid in manufacturing (by inferring temperature fields through variable frequency dielectric metrology).
 Consider a bistable model of an elementary dipole within a dielectric whose molecular groupings can be characterized by well-defined, permanent dipole moments. In this type of model, we assume that a charge $q$ may be in one of two states that are separated by a distance $d$. These states are defined as minima of the potential energy $U$ and are portrayed in figure 12.

Figure 12. The potential energy of a bistable model as a function of distance has two minima, depicted by states 1 and 2. The depth of these minima are modified by an applied electric field, and charged particles can occupy either state [20].

In this model, an electric field acting on the dielectric causes movement of charge from the minimum of state 1 to the minimum of state 2. This charge movement is equivalent to a $180^\circ$ rotation of a dipole of moment

$$
|\vec{p}| = \frac{1}{2} qd .
$$

(65)
The potential difference due to the applied electric field \( \vec{E} \) is simply

\[
\psi_1 - \psi_2 = 2\vec{p} \cdot \vec{E} = qdE \cos \theta ,
\]

where \( \theta \) is the angle between the direction of the electric field and the dipole moment.

The interaction between individual dipoles within our dielectric can be neglected by assuming that the total number \( N \) of bistable dipoles per unit volume is small. For dipoles we may also generally assume that \( \theta = 0 \) and that equal potential energy exists for states 1 and 2 in the absence of an electric field. The visualization can be made in this microscopic assembly that the bistable dipoles are in a heat reservoir which consists of spontaneously active particles that exchange energy through thermal fluctuations with each other and the dipoles. Therefore the directions of the dipoles fluctuate. Occasionally thermal fluctuations allow a charge in the minimum of state 1 to acquire sufficient energy to go "over" the potential hill \( U \) and drop into the minimum of state 2. In state 2 the energy of the charge is returned to the heat reservoir and stays in state 2 until it acquires enough energy from the reservoir to return to state 1.

The probability of a jump by a charge in a double potential well (state) is derived and well known in classical statistical thermodynamics. Here it is sufficient to state that the number of dipoles jumping per unit of time from state 1 to state 2 is given in terms of the difference of potential energy between the two wells as

\[
u_{12} = A e^{-(U + pE)/kT} ,
\]
where \( U \) is the activation energy, \( k \) is Boltzmann’s constant \((1.37 \times 10^{-23} \text{ J/K})\) and \( T \) is absolute temperature \((\text{K})\). The constant \( A \) may or may not depend on temperature. Generally, for ionic solids it does not, whereas for organic polymers (plastics), \( A \) is inversely proportional to \( T \). The \( \pm \) signs within the exponential of eq (67) dictate whether the minimum in state 2 is lower or higher than that of state 1. Generally, \( U >> kT \).

For dipoles in normal dielectrics, \( p \) is of the order \( 10^{-29} \text{ C-m} \), whereas \( E \) for fields below breakdown strength is always less than \( 10^6 \text{ V/m} \). Therefore, in general,

\[
\frac{pE}{kT} << 1 .
\]  

(68)

Note that \( pE/kT \) is dimensionless and that, as \( T \rightarrow \infty \), thermal fluctuations dominate polarization, whereas when \( T \rightarrow 0 \), polarization \((pE)\) dominates.

Equation (67) may be approximately written

\[
u_{12} = u (1 - \frac{pE}{kT}) ,
\]  

(69)

where

\[
u = Ae^{-U/kT}
\]  

(70)

is the frequency of jumps in the absence of an applied electric field.

Similarly, the frequency of jumps from state 2 to state 1 can be written in linear form as

\[
u_{21} = u (1 + \frac{pE}{kT}) .
\]  

(71)

Provided the number of charges \( N \), jumping per unit of time from state 1 to state 2 is the same as that going from state 2 to state 1, \( N \), the average
population of charges in the wells of states 1 and 2 will not change with time. In other words at equilibrium

\[ N_1 u_{12} = N_2 u_{21} . \] (72)

The total number of bistable dipoles is constant or

\[ N_1 + N_2 = N . \] (73)

Equations (72) and (73) enable the calculation of \( N_1 \) and \( N_2 \) in equilibrium. Since the polarization per unit volume \( P \) is defined as that number of dipoles in one direction which is not compensated by dipoles in the opposite direction, or

\[ P = P_s = (N_1 - N_2) p , \] (74)

we have a basis from statistical thermodynamics to determine the variation of polarization with temperature when the dielectric material is in equilibrium; that is, from eq (72),

\[ N_1 u (1 - \frac{pE}{kT}) = N_2 u (1 + \frac{pE}{kT}) \]

or

\[ N_1 - N_2 = (N_1 + N_2) \frac{pE}{kT} = N \frac{pE}{kT} . \] (75)

Hence eq (74) may be written

\[ P_s = N \frac{p^2E}{kT} . \] (76)

We are now in a position to derive the frequency dependent properties of the model by noting that the change in number of dipoles in state 1 is equal to the outflow to state 2 less the inflow from state 2 or
\[
\frac{dN_1}{dt} = - N_1 u_{12} + N_2 u_{21}.
\] (77)

Since the total number of bistable dipoles is constant,

\[
\frac{dN_1}{dt} = - \frac{dN_2}{dt}
\]

or

\[
\frac{d(N_1 - N_2)}{dt} = 2 \frac{dN_1}{dt},
\] (78)

so that eq (77) becomes

\[
\frac{dN_1}{dt} = \frac{1}{2} \frac{d(N_1 - N_2)}{dt} = - N_1 u (1 - \frac{pE}{kT})
\]

\[+ N_2 u (1 + \frac{pE}{kT}).
\] (79)

Equation (79) can be simplified to read

\[
\frac{1}{2} \frac{d[N_1 - N_2]}{dt} = - u (N_1 - N_2) + u (N_1 + N_2) \frac{pE}{kT}
\] (80)

or

\[
\frac{1}{2} \frac{d[(N_1 - N_2)p]}{dt} = - u (N_1 - N_2) p + u N \frac{p^2E}{kT}.
\] (81)

We now have a differential equation for the dipolar polarization of a dielectric medium as a function of temperature; that is,

\[
\frac{1}{2u} \frac{dP}{dt} + P = \frac{Np^2E}{kT}.
\] (82)

Note the similarity between eq (82) and eq (A-7) in our derivation of relaxation in dielectrics with a single relaxation time; in other words, eq (82) is a relaxation equation with a relaxation time
\[ \tau = \frac{1}{2u} = \frac{1}{2A} e^{-u/kT}. \] (83)

We may generalize eq (82) to

\[ \tau \frac{dP_D}{dt} + P_D = \alpha_D E, \] (84)

where \( P_D \) is the dipolar polarization and \( \alpha_D \) is the dipolar polarizability of the dielectric material. Using simple Fourier transform methods we obtain

\[ \varepsilon^* (\omega, T) - \varepsilon_\infty (T) = \frac{\alpha_D}{1 + j\omega\tau} \] (85)

or

\[ \varepsilon' (\omega, T) = \varepsilon_\infty (T) + \frac{\alpha_D}{1 + \omega^2\tau^2}, \] (86)

and

\[ \varepsilon'' (\omega, T) = \frac{\alpha_D\omega\tau}{(1 + \omega^2\tau^2)} \] (87)

and

\[ \tan \delta (\omega, T) = \frac{\alpha_D\omega\tau}{\alpha_D + \varepsilon_\infty(T)(1 + \omega^2\tau^2)}. \] (88)

The permittivity and loss tangent are directly proportional in this model to the dipolar polarizability of the material, which is inversely proportional to temperature.

Equations (85), (86), (87), and (88) describe dispersive dielectric behavior for a bistable dielectric as a function of temperature and frequency. The temperature-dependent permittivity and loss tangent are given in terms of the dipolar polarizability, activation energy, and high-frequency (optical) permittivity at temperature \( T \). The derivation is limited to dielectric materials where interaction between individual dipoles can be neglected and for conditions where \( pE \ll kT \) (nonsuperconducting states).
An important area of further research would be to examine the temperature-dependent dispersive effects on dielectric behavior using the bistable model described above. Another fertile research area would be to examine equivalent dispersive effects in a dielectric material that result from either increased temperature or frequency. Still another would be to generalize the bistable model.

4.4 Other Sample Characteristics Important to the Search for Reference Materials

In a previous section the general electromagnetic characteristics of materials were discussed. The electrical properties were defined by constitutive equations in terms of fundamental physical processes occurring in a material in the presence of an electromagnetic field. It was further seen that a number of physical polarization mechanisms are responsible for the actual frequency-dependent behavior of a dielectric material. Provided the real and imaginary parts of the complex permittivity have been sufficiently sampled in frequency so as to characterize the relaxation distribution function, the dielectric behavior of an arbitrary material can be predicted, even at frequencies where measurement data are not taken. Since the differential equations describing the functional dependence of dielectric relaxation times with respect to temperature are similar to those describing dielectric relaxation times with respect to the time variations of an applied electric field, relations can be derived that allow the prediction of dielectric properties as a function of temperature and frequency. In practical application these relations permit the determination of temperature of a dielectric by measurement of its permittivity. Or, by changing the temperature of a
dielectric, we might control and predict its complex permittivity; this can be extremely useful in microstrip applications.

In other words, the same material dielectric value could be expected for different combinations of temperature and frequency. Provided the material has been adequately characterized with frequency, the dielectric behavior can be predicted for any temperature or excitation frequency (when the same physical relaxation processes occur). This would allow the prediction of dielectric properties at very high frequency from measured properties at lower frequencies and temperatures; this is a fundamental metrology problem. The applicability of temperature or frequency dispersion relations to any dielectric is a subject for further research. Measurement precision will undoubtedly need to be greater than that of many reported results.

This prologue is necessary for the understanding of dielectric sample measurements and the implications on physical processes occurring in the material under the influence of an applied electric field. These physical processes, which control the constituent properties, direct the choices of suitable reference materials. As we shall see later, they are also important in choosing the optimal metrology technique for any given physical dielectric.

4.4.1 Sample Homogeneity

In section 3, where desired properties of dielectric reference materials were discussed, it was stated that measurement techniques must be analyzed in sufficient detail that bounds on measurement errors can be specified. Measurement errors are both systematic and random and result from departures of the measurement system from assumptions used in an idealized theoretical model. Common fixtures used in dielectric metrology include sections of
transmission line (coax or rectangular waveguide), open or closed cavities, and various bridge circuits. In the first two cases, the modal structure of the applied electric field to the sample under test is very precisely specified so that corrections may be made to measurement data that are due to departures of the actual fixture from the idealized theoretical model of that fixture.

It is beyond the scope of this Technical Note to characterize any particular dielectric measurement fixture that can lead to inaccuracies in property determinations. However, it is within the scope of a standard reference material search to consider inhomogeneity within the actual sample. In this way deviations from homogeneity, say, of a candidate material can be distinguished from measurement inaccuracies. The influence of deviations from homogeneity on a very precisely specified electromagnetic field structure needs to be determined in order to quantify the homogeneity of a reference sample.

In the past, homogeneity of any reference sample was treated in a very practical, if not expedient, manner. Measurements were made on many samples of the same material produced by the same manufacturing process with fixture error bounds specified. These measurements were then compared, either nationally or internationally, with other laboratory measurements made with different fixtures.

While an inhomogeneous sample affects or even can destroy the expected modal field behavior within a precision fixture, the quantitative determination of when and how much a sample’s inhomogeneity affects field structure remain undetermined. How precisely dielectric measurements can define inhomogeneities within a sample also remains unknown and is probably fixture
dependent. In order to address the effects of sample dielectric inhomogeneity on the impressed electromagnetic field structure of a measurement fixture, it is necessary to reapply Maxwell's equations. The same analysis approach outlined below can also be used to quantify measurement errors that result from an eccentric waveguide or cavity fixture, nonuniform air gaps around a dielectric sample in a loaded transmission line or cavity, or nonorthogonality of endplates to the axis of a cylindrical cavity dielectric measurement device. All of the above lead to degenerate mode structures whose magnitude and ultimate effect on precision dielectric measurements can be ascertained.

4.4.1.1 Inhomogeneous Sample in Field of Arbitrary Dielectric Measurement Fixture

In this section a brief formulation in the frequency domain is given for examining the electromagnetic field interaction of any impressed source field on a dielectric that is three-dimensional, of arbitrary shape, and that possess any internal structure or loss characteristics. We start with Maxwell's equations where \( \exp(+j\omega t) \) time dependence is assumed. Ampere's and Faraday's laws may be written, respectively,

\[
\nabla \times \mathbf{H} - j\omega \varepsilon \mathbf{E} = (\sigma + j\omega \varepsilon) \mathbf{E} + \mathbf{J}_0 \quad (89)
\]

and

\[

\nabla \times \mathbf{E} + j\omega \mu \mathbf{H} = 0 . \quad (90)
\]

Here \( \mathbf{J} \) is the total current density, and for convenience we use eq (14) to distinguish the conductivity or loss factor from the permittivity of medium described by \( \varepsilon, \mu \) and \( \sigma \). \( \mathbf{J}_0 \) is an impressed current density. For now we will consider the physical situation of a sample dielectric and source contained in
freespace and a sample which may be inhomogeneous in conductivity and permittivity, but not in magnetic permeability.

The differential sample parameters may be defined as

\[ \sigma_s = \sigma_d - \sigma_0 = \sigma_d \]

and

\[ \epsilon_s = \epsilon_d - \epsilon_0 , \]

where \( \sigma_0, \epsilon_0 \) are the conductivity and permittivity of vacuum, respectively, and \( \sigma_d, \epsilon_d \) are the conductivity and permittivity of the dielectric sample, respectively. The differential sample parameters defined above are responsible for scattering incident electromagnetic energy. The effect of the sample is described by replacing the sample with an effective scattering current,

\[ \vec{J}_s = (\sigma_s + j\omega\epsilon_s) \vec{E} . \]

Ampere's law for our scattering lossy dielectric sample then becomes

\[ \nabla \times \vec{H} - j\omega\epsilon_0 \vec{E} = \vec{J}_s + \vec{J}_o . \quad (91) \]

In the customary development of the Helmholtz vector wave equation,

\[ \nabla \times \nabla \times \vec{E} = \nabla \nabla \cdot \vec{E} - \nabla^2 \vec{E} = -j\omega \mu \nabla \times \vec{H} = \omega^2 \mu \epsilon_0 \vec{E} - j\omega \mu (\vec{J}_s + \vec{J}_o) \]

or

\[ \nabla \times \nabla \times \vec{E} - k_o^2 \vec{E} = -j\omega \mu (\vec{J}_s + \vec{J}_o) , \quad (92) \]

where \( k_o^2 = \omega^2 \mu \epsilon_0 \).

As an aside, we know that free charge is absent from a uniformly lossy sample, so that \( \nabla \cdot \vec{E} = - \frac{\nabla \epsilon}{\epsilon} \cdot \vec{E} \). Provided the permittivity of the sample
under test remains spatially invariant, \( \nabla \cdot \mathbf{E} = 0 \), so the usual vector Helmholtz equation may be written,

\[
\nabla^2 \mathbf{E} + k_0^2 \mathbf{E} = j \omega \mu \left( \mathbf{J}_s + \mathbf{J}_o \right) .
\]  

(93)

In the case posed, the two equations to be solved are

\[
\nabla \times \nabla \times \mathbf{E}(\mathbf{r}, \omega) - k_0^2 \mathbf{E}(\mathbf{r}, \omega) = - j \omega \mu \mathbf{J}(\mathbf{r}, \omega)
\]  

(94)

and

\[
\nabla \times \nabla \times \mathbf{H}(\mathbf{r}, \omega) - k_0^2 \mathbf{H}(\mathbf{r}, \omega) = \nabla \times \mathbf{J}(\mathbf{r}, \omega),
\]  

(95)

where

\[
\mathbf{J}(\mathbf{r}, \omega) = \mathbf{J}_s(\mathbf{r}, \omega) + \mathbf{J}_o(\mathbf{r}, \omega).
\]  

(96)

From Gauss' law, \( \nabla \cdot \mathbf{B} = \nabla \cdot \mu \mathbf{H} = 0 \), so \( \nabla \cdot \mathbf{H} = 0 \) provided \( \mu \) is spatially invariant. Hence, since \( \nabla \cdot \nabla \times \mathbf{A} = 0 \),

\[
\mu \mathbf{H} = \nabla \times \mathbf{A}.
\]  

(97)

Similarly, since \( \nabla \times \nabla \psi = 0 \) for any scalar potential function \( \psi \) which is differentiable, we may write from eq (90),

\[
\mathbf{E} = - j \omega \mathbf{A} - \nabla \psi.
\]  

(98)

Substitution of eqs (97) and (98) into eq (89) yields

\[
\nabla \times \nabla \times \mathbf{A} = k^2 \mathbf{A} + \mu \mathbf{J}_o - \mu (\sigma + j \omega \epsilon) \nabla \psi
\]

or

\[
\nabla \nabla \cdot \mathbf{A} - \nabla^2 \mathbf{A} = k^2 \mathbf{A} + \mu \mathbf{J}_o - \mu (\sigma + j \omega \epsilon) \nabla \psi,
\]  

(99)

where \( k^2 = - j \omega \mu (\sigma + j \omega \epsilon) \).
If the Lorentz gauge condition is imposed

$$\nabla \cdot \vec{A} = -\mu (\sigma + j\omega)\psi ,$$  \hspace{1cm} (100)$$

then eq (99) is reduced to a vector differential equation containing the vector potential function $\vec{A}$ only; that is,

$$\nabla^2 \vec{A} + k^2 \vec{A} = -\mu \vec{J}_o ,$$  \hspace{1cm} (101)$$

which is the inhomogeneous vector Helmholtz equation. By taking the divergence of eq (99) and using the continuity equation, $\nabla \cdot \vec{J}_o = -j\omega \rho_0$, and the gauge condition (eq (100)), we may obtain the differential equation for $\psi$,

$$\nabla^2 \psi + k^2 \psi = -\frac{\omega^2}{k^2} \rho_0 ,$$  \hspace{1cm} (102)$$

where $\rho_0$ is the free charge density and eq (102) is the inhomogeneous scalar wave equation. Solutions for eqs (101) and (102) that correspond to outgoing waves from the source are given by

$$\vec{A}(\vec{r}) = \mu \iiint \vec{J}(\vec{r}_0) \ G_o(\vec{r};\vec{r}_0) \ dv$$  \hspace{1cm} (103)$$

and

$$\psi(\vec{r}) = \frac{\omega^2}{k^2} \iiint \rho_0(\vec{r}_0) \ G_o(\vec{r};\vec{r}_0) \ dv ,$$  \hspace{1cm} (104)$$

where

$$G_o(\vec{r};\vec{r}_0) = \frac{e^{-jk|\vec{r}-\vec{r}_0|}}{4\pi|\vec{r}-\vec{r}_0|} , \quad |\vec{r}-\vec{r}_0| = [(x-x_0)^2 + (y-y_0)^2 + (z-z_0)^2]^{\frac{1}{2}} .$$  \hspace{1cm} (105)$$

The function $G_o(\vec{r};\vec{r}_0)$ is the free-space Green's function pertaining to the three-dimensional scalar wave equation, where $\vec{r}$ denotes the position vector.
of a field observation point and \( \vec{r}_o \) denotes the position vector of a source point. From eqs (98) and (100) we can write

\[
\vec{E} (\vec{r}; \omega) = -j \omega \left[ \vec{A} (\vec{r}; \omega) + \frac{1}{k^2} \nabla \cdot \vec{A} (\vec{r}; \omega) \right]
\]

(106)

and

\[
\vec{H} = \frac{1}{\mu} \nabla \times \vec{A} .
\]

(107)

Hence, once we know the solution for \( \vec{A} (\vec{r}) \), the electromagnetic field vectors \( \vec{E} \) and \( \vec{H} \) can be found.

4.4.1.2 Coupling of Electromagnetic Field Components

The method of potentials in an infinite domain has been used to solve Maxwell's equations in terms of the free-space Green's function that is a solution to the three-dimensional scalar wave equation. The free-space vector Green's function for a source pointed in one coordinate direction may be derived in terms of this scalar Green's function. Since an arbitrary source field has components in all three coordinate directions, three vector Green's functions are generally needed. These can be compactly designated as the constituents of the free-space dyadic Green's function.

Consider an infinitesimal source located at \( \vec{r}_o \) with a current moment \(-1/(j \omega \mu)\) pointed in the x-direction. That is,

\[
\vec{J} (\vec{r}) = -\frac{1}{j \omega \mu} \delta(\vec{r} - \vec{r}_o) \hat{u}_x ,
\]

(108)

where \( \delta(\vec{r} - \vec{r}_o) \) is the Dirac delta function and \( \hat{u}_x \) is the unit vector pointed in the x-direction. Hence

\[
\oint \oint \oint \vec{J} (\vec{r}_o) \, dv = -\frac{1}{j \omega \mu} \hat{u}_x .
\]

(109)
Substitution of eq (108) into (103) gives

\[ \mathbf{A}(\mathbf{r}) = -\frac{1}{j\omega} G_o(\mathbf{r};\mathbf{r}_o) \hat{u}_x , \]

so that if we denote the electric field produced by this elementary source by

\[ \vec{G}_o^{(x)}(\mathbf{r};\mathbf{r}_o) \],

then

\[ \vec{G}_o^{(x)}(\mathbf{r};\mathbf{r}_o) = (1 + \frac{1}{k^2} \nabla \nabla \cdot \nabla) G_o(\mathbf{r};\mathbf{r}_o) \hat{u}_x , \quad (110) \]

which is a solution of the equation,

\[ \nabla \times \nabla \times \vec{G}^{(x)}(\mathbf{r};\mathbf{r}_o) - k^2 \vec{G}^{(x)}(\mathbf{r};\mathbf{r}_o) = -\delta(\mathbf{r} - \mathbf{r}_o) \hat{u}_x . \quad (111) \]

(Here we use the same notation as that of Tai [21].) It is straightforward to show that the function \( \vec{G}^{(x)}(\mathbf{r};\mathbf{r}_o) \) satisfies the radiation condition as \( |\mathbf{r}| \to \infty \), or

\[ \lim_{|\mathbf{r}| \to \infty} \left[ \nabla \times \nabla \times \vec{G}^{(x)}(\mathbf{r};\mathbf{r}_o) - jk \mathbf{r} \times \vec{G}^{(x)}(\mathbf{r};\mathbf{r}_o) \right] = 0 . \quad (112) \]

\( \vec{G}_o^{(x)}(\mathbf{r};\mathbf{r}_o) \) is designated in Tai’s [21] notation as a free-space vector Green’s function with a source pointed in the x-direction. Since a vector source can point in the y-direction or in the z-direction as well, we have two more free-space vector Green’s functions which we may denote by \( \vec{G}_o^{(y)}(\mathbf{r};\mathbf{r}_o) \) and \( \vec{G}_o^{(z)}(\mathbf{r};\mathbf{r}_o) \) which satisfy the following respective equations and whose respective solutions are given by

\[ \nabla \times \nabla \times \vec{G}_o^{(y)}(\mathbf{r};\mathbf{r}_o) - k^2 \vec{G}_o^{(y)}(\mathbf{r};\mathbf{r}_o) = -\delta(\mathbf{r} - \mathbf{r}_o) \hat{u}_y , \quad (113) \]

\[ \nabla \times \nabla \times \vec{G}_o^{(z)}(\mathbf{r};\mathbf{r}_o) - k^2 \vec{G}_o^{(z)}(\mathbf{r};\mathbf{r}_o) = -\delta(\mathbf{r} - \mathbf{r}_o) \hat{u}_z , \quad (114) \]
and

\[ \tilde{G}_o(x)(\mathbf{r}; \mathbf{r}_0) = (1 + \frac{1}{k^2} \nabla \cdot \nabla) \, G_o(\mathbf{r}; \mathbf{r}_0) \, \hat{u}_{x}, \quad (115) \]

\[ \tilde{G}_o(y)(\mathbf{r}; \mathbf{r}_0) = (1 + \frac{1}{k^2} \nabla \cdot \nabla) \, G_o(\mathbf{r}; \mathbf{r}_0) \, \hat{u}_{y}, \quad (116) \]

which also obey the same radiation condition as described in eq (112). The free-space dyadic Green's function is defined by

\[ \bar{G}_o(\mathbf{r}; \mathbf{r}_0) = G_{o}(x) \, \hat{u}_{x} + G_{o}(y) \, \hat{u}_{y} + G_{o}(z) \, \hat{u}_{z}. \quad (117) \]

Summarizing eqs (111), (113), and (114) yields

\[ \nabla \times \nabla \times \bar{G}_o(\mathbf{r}; \mathbf{r}_0) - k^2 \bar{G}_o(\mathbf{r}; \mathbf{r}_0) = - \vec{I} \, \delta(\mathbf{r} - \mathbf{r}_0), \quad (118) \]

where \( \vec{I} \) is the idem factor or unit dyad defined by \( \vec{I} = \hat{u}_{x} \hat{u}_{x} + \hat{u}_{y} \hat{u}_{y} + \hat{u}_{z} \hat{u}_{z} \) and \( \vec{A} \cdot \vec{I} = \vec{I} \cdot \vec{A} = \vec{A} \). Substitution of eqs (110), (115) and (116) into eq (117) gives

\[ \bar{G}_o(\mathbf{r}; \mathbf{r}_0) = (1 + \frac{1}{k^2} \nabla \cdot \nabla) \, G_o(\mathbf{r}; \mathbf{r}_0) \, \vec{I} \]

\[ = (\vec{I} + \frac{1}{k^2} \nabla \nabla) \, G_o(\mathbf{r}; \mathbf{r}_0). \quad (119) \]

Similarly, the three separate radiation conditions for the vector Green's functions can be combined to give

\[ \lim_{r \to \infty} [\nabla \times \bar{G}(\mathbf{r}; \mathbf{r}_0) - jkr \times \bar{G}_o(\mathbf{r}; \mathbf{r}_0)] = 0. \quad (120) \]
Recall Green's vector theorem,

\[ \iiint [\vec{W} \cdot \nabla \times \nabla \times \vec{Q} - \vec{Q} \cdot \nabla \times \nabla \times \vec{W}] \, dv = - \iiint [\vec{Q} \times \nabla \times \vec{W} - \vec{W} \times \nabla \times \vec{Q}] \cdot \vec{n} \, ds . \]  

(121)

Letting \( \vec{W} = \vec{E}(\vec{r}) \), \( \vec{Q} = \vec{G}_o(\vec{r};\vec{r}_o) \cdot \hat{a} \) where \( \hat{a} \) denotes a constant but arbitrary vector, we obtain

\[ \iiint (\vec{E}(\vec{r}) \cdot \nabla \times \nabla \times \vec{G}_o(\vec{r};\vec{r}_o) \cdot \hat{a} - [\vec{G}_o(\vec{r};\vec{r}_o) \cdot \hat{a}] \cdot \nabla \times \nabla \times \vec{E}(\vec{r})) \, dv \]

\[ - \iiint \left( [\nabla \times \vec{E}(\vec{r})] \times [\vec{G}_o(\vec{r};\vec{r}_o) \cdot \hat{a}] + \vec{E}(\vec{r}) \times \nabla \times \vec{G}_o(\vec{r};\vec{r}_o) \cdot \hat{a} \right) \cdot \vec{n} \, ds \]

\[ - \iiint \left( [\nabla \times \vec{G}_o(\vec{r};\vec{r}_o) \cdot \hat{a} + [\vec{E}(\vec{r}) \cdot \nabla \times \vec{G}_o(\vec{r};\vec{r}_o) \cdot \hat{a}] \right) \, ds , \]  

(122)

where \( \vec{n} \) is the outward unit vector normal to the surface \( S \). Substitution of eq (94) and eq (118) into eq (122) yields

\[ \iiint (\vec{E}(\vec{r}) \cdot k^2 \vec{G}_o(\vec{r};\vec{r}_o) \cdot \hat{a} - \vec{E}(\vec{r}) \cdot \vec{I} \delta(\vec{r}-\vec{r}_o) \cdot \hat{a} \]

\[ - \vec{G}_o(\vec{r};\vec{r}_o) \cdot \hat{a} \cdot k^2 \vec{E}(\vec{r}) + \vec{G}_o(\vec{r};\vec{r}_o) \cdot \hat{a} \cdot j \omega \mu \vec{J}(\vec{r})) \, dv \]

\[ = - \iiint \left( [\vec{n} \times \nabla \times \vec{E}(\vec{r})] \cdot \vec{G}_o(\vec{r};\vec{r}_o) \cdot \hat{a} + [\vec{n} \times \vec{E}(\vec{r})] \right) \]

\[ \cdot \nabla \times \vec{G}_o(\vec{r};\vec{r}_o) \cdot \hat{a} \right) \, ds . \]

Since \( \iiint \vec{E}(\vec{r}) \cdot \vec{I} \delta(\vec{r}-\vec{r}_o) \cdot \hat{a} \, dv = \vec{E}(\vec{r}_o) \cdot \hat{a} \), eq (122) may be rewritten (deleting \( \cdot \hat{a} \) since \( \hat{a} \) is a constant vector) as the Schwinger integral equation [22],
\[
\vec{E}(r) = j\omega \mu \iiint \vec{J}(\vec{r}_o) \cdot \vec{G}_o(\vec{r}_o;\vec{r}) \, dv
\]
\[
+ \iint_S \{ j\omega \mu [\vec{H}(\vec{r}_o) \times \vec{n}] \cdot \vec{G}_o(\vec{r}_o;\vec{r})
\]
\[
+ [\vec{n} \times \vec{E}(\vec{r}_o)] \cdot \nabla_o \times \vec{G}_o(\vec{r}_o;\vec{r}) \} \, dS ,
\]
where \( \nabla_o \) indicates differentiation with respect to the source point coordinates. From the radiation condition for an electromagnetic field in free-space we have

\[
\lim_{r \to \infty} \left[ \nabla \times \left( \frac{\vec{E}}{\vec{H}} \right) - jk\vec{r} \times \left( \frac{\vec{E}}{\vec{H}} \right) \right] = 0 \quad (124)
\]
or

\[
\lim_{r \to \infty} [-j\omega \mu \vec{H}(\vec{r}) - jkn \times \vec{E}(\vec{r})] = 0 . \quad (125)
\]

If we consider the volume to be of infinite extent, so that the enclosing surface \( S \) recedes to infinity, then eq (123) may be written in the following form using eq (125),

\[
\vec{E}(\vec{r}) = j\omega \mu \iiint \vec{J}(\vec{r}_o) \cdot \vec{G}_o(\vec{r}_o;\vec{r}) \, dv
\]
\[
+ \iint_S \{ \vec{n} \times \vec{E}(\vec{r}_o) \} \cdot [\nabla_o \times \vec{G}_o(\vec{r}_o;\vec{r}) - jkn \times \vec{G}_o(\vec{r}_o;\vec{r}) \} \, dS .
\]

Because of the radiation condition described by eq (112), the surface integral above goes to zero so that

\[
\vec{E}(\vec{r};\omega) = j\omega \mu \iint_v \vec{G}_o(\vec{r};\vec{r}_o) \cdot \vec{J}(\vec{r}_o) \, dv
\]
\[
= j\omega \mu \iint_v \vec{G}_o(\vec{r};\vec{r}_o) \cdot \{ \vec{J}_s(\vec{r}_o) + \vec{J}_o(\vec{r}_o) \} \, dv . \quad (126)
\]
The physical situation at hand consists of a primary current source and secondary source(s) in a homogeneous full space; because the surface boundary is at infinity, the surface integral in eq (123) vanishes. A further simplification can be made in eq (126) by directly calculating the incident field \( \vec{E}^{\text{inc}}(\vec{r}) \) due to the source current in the absence of the sample under test, so that

\[
\vec{E}(\vec{r};\omega) = \vec{E}^{\text{inc}}(\vec{r}) + j\omega \mu \iiint_{V} \vec{G}_{0}(\vec{r};\vec{r}_o) \cdot \vec{J}_s(\vec{r}_o) \, dv .
\]  

(127)

The induced secondary current density in eq (127) can be thought of as a superposition of point electric current dipole distributions. That is, the current density may be written as

\[
\vec{J}_s(\vec{r}) = \vec{I}d\vec{l} \delta(x) \delta(y) \delta(z) ,
\]

where \( \vec{I}d\vec{l} \) is a current dipole moment. The dyadic Green's function we need to look for is a solution to eq (118). In component form eq (118) becomes

\[
[\nabla \times \nabla \times - k^2] G^{mn}(\vec{r};\vec{r}_o) = - \delta(\vec{r}-\vec{r}_o) \delta^{mn} .
\]

(128)

Thus a component of the Green's tensor, say \( G^{yz}_0 \), can be interpreted as the \( y \)-component of the electric field due to a unit point dipole in the \( z \)-direction. Equation (127) may be written more explicitly as

\[
\vec{E}(\vec{r};\omega) = \vec{E}^{\text{inc}}(\vec{r};\omega) + j\omega \mu \iiint_{\text{sample volume}} [\sigma_s + j\omega \epsilon_s] \vec{G}_0(\vec{r};\vec{r}_o) \cdot \vec{E}(\vec{r}_o) \, dv ,
\]

(129)

where the volume integral is only over the sample volume since \( \sigma_s \) and \( \epsilon_s \) are identically zero outside the sample. Once the field is found in the interior
of the sample, the field at any exterior point can be found by using eq (129). The magnetic field may be found by use of eq (90),
\[
\vec{H}(\vec{r};\omega) = \vec{H}^{inc}(\vec{r};\omega) - \frac{1}{j\omega\mu} \iiint_{\text{sample volume}} \left[ \sigma_s + j\omega\varepsilon_s \right] \vec{F}(\vec{r};\vec{r}_o) \cdot \vec{E}(\vec{r}_o) \, dv ,
\]
where the tensor \( \vec{F}(\vec{r};\vec{r}_o) \sim F^{mn} \) whose elements are given by
\[
F^{xx} = \frac{\partial G^{xx}}{\partial y} - \frac{\partial G^{yx}}{\partial z} , \quad F^{xy} = \frac{\partial G^{xy}}{\partial y} - \frac{\partial G^{yy}}{\partial z} , \quad F^{xz} = \frac{\partial G^{xz}}{\partial y} - \frac{\partial G^{yz}}{\partial z} ,
\]
\[
F^{yx} = \frac{\partial G^{yx}}{\partial x} - \frac{\partial G^{xx}}{\partial y} , \quad F^{yy} = \frac{\partial G^{yy}}{\partial x} - \frac{\partial G^{xy}}{\partial y} , \quad F^{yz} = \frac{\partial G^{yz}}{\partial x} - \frac{\partial G^{zy}}{\partial y} ,
\]
\[
F^{zx} = \frac{\partial G^{zx}}{\partial x} - \frac{\partial G^{xz}}{\partial y} , \quad F^{zy} = \frac{\partial G^{zy}}{\partial x} - \frac{\partial G^{yz}}{\partial y} , \quad F^{zz} = \frac{\partial G^{zz}}{\partial x} - \frac{\partial G^{zx}}{\partial y} .
\]

The conductivity and permittivity may vary spatially within the target volume. The procedure would first be to solve for the electric field within the target so as to obtain the scattering current, after which the magnetic field may be determined.

Equation (129) may be used in straightforward fashion only after the field in the interior of the target has been calculated. A common technique is to divide the target into a number of cells where the electric field is constant in each. One then sets up a matrix equation of the form
\[
\vec{M} \cdot \vec{E} = \vec{E}^{inc}
\]
so that \( \vec{E} \) may be found by inverting \( \vec{M} \). However, the matrix \( \vec{M} \) is large and nonsparse so that inversion is not a trivial problem. Further, the
target must be divided into a relatively fine mesh for accurate field calculations when the fields are taken to be constant within each cell. For a three-dimensional problem in which the target is described by N points in each direction one is faced with inverting a \(3N^{3/2} \times 3N^{3/2}\) matrix for each frequency, since the three field components must be solved simultaneously due to the coupling implied by the Green's tensor. Thus, for a sample under test which is described by 100 points in each direction, the complex matrix to be inverted would be \(3000 \times 3000\). Another approach to the solution of eq (129) is to allow \(\hat{E}(r_o)\) within the sample to be approximately \(E^{inc}\) (Born approximation). This approach is valid for low-loss dielectric scatterers where contrasts in the imaginary part of the complex permittivity are close to zero such that very small phase changes are effected.

Equation (129) is an integral equation in the conductivity \(\sigma_s(x_o,y_o,z_o)\) and permittivity \(\varepsilon_s(x_o,y_o,z_o)\) of an inhomogeneous lossy dielectric sample under the influence of an applied electric field, \(\overrightarrow{E}(x,y,z;\omega)\), for an arbitrary fixture. Iterative Born techniques may be used to solve for the complex permittivity when losses are not low. It should also be noted that in modern laboratories scattering matrix parameters \(S_{pq}\) are generally measured with vector network analyzers or microwave n-ports. Therefore the vector components of the total electric field given in eq (129) must be related to scattering matrices [23].

Equation (129) may also be used to determine when dielectric samples are not axially centered in a cavity fixture. For example, in an ideal \(\text{TE}_{01n}\) cylindrical cavity there is no radial electric field unless either (1) the sample is azimuthally inhomogeneous or (2) the dielectric sample is
homogeneous, but a nonuniform air gap exists around the sample placed within the cavity (due to machining nonuniformities or eccentricity of the cylindrical waveguide). With the aid of eq (129) one may determine which of the above factors might be responsible for the presence of a nonzero radial electric field (or degenerate transverse magnetic resonant modes).

4.4.2 Isotropy

A sufficient condition for (microwave and optical) isotropy is that the material (1) have no long range order or lattice crystal structure (amorphous), (2) be cryptocrystalline (such as fused silica or glass), or (3) have a lattice crystal structure that belongs to the isometric system. In isometric and noncrystalline substances the dielectric constant is the same in all directions. Such substances are said to be electrically isotropic. In all other substances the velocity of an electromagnetic wave varies according to its direction of propagation in the crystal lattice structure; such substances are said to be electrically anisotropic. An electromagnetic wave entering a two-dimensionally anisotropic substance is split into two orthogonal waves traveling with different velocities. The substance thus has different dielectric indices. In optics this difference in dielectric or refractive indices is known as birefringence. Birefringence is usually quite small (for quartz it is 0.009) but for some materials, such as calcite, can be large (0.172).

The relationship between dielectric indices and crystal lattice structure can best be visualized by drawing in all directions from the center of a crystal lattice lines with length proportional to the dielectric constant for that wave propagation direction. The resulting figure is known as the
dielectric indicatrix (figure 13). For noncrystalline and isometric substances the indicatrix is a sphere, since the dielectric constant is the same in all directions. For substances whose lattice structure falls in the tetragonal and hexagonal systems, the indicatrix is a rotation ellipsoid in which all sections perpendicular to one axis are circular; this axis is always the axis of symmetry of the lattice structure. All electromagnetic waves traveling in the direction of this axis of symmetry have the same velocity, since the electric field variations are in the plane of the horizontal axes, which are equivalent in these systems. For this reason substances whose lattice structures are in the tetragonal and hexagonal systems are said to uniaxially anisotropic. For substances whose lattice structures fall within the orthorhombic, monoclinic, and triclinic systems, the dielectric indicatrix has lower symmetry. This is in agreement with lower lattice structure symmetry; the indicatrix is now a triaxial ellipsoid. A distinctive characteristic of such an ellipsoid is that it has only two circular sections, all others being ellipses. All electromagnetic wave propagation transverse to these circular sections will have the same velocity regardless of electric field behavior in these sections. The two directions at right angles to the circular sections of a dielectric triaxial ellipsoid have the same dielectric constant (in optics, these are termed the optic axes). Hence orthorhombic, monoclinic, and triclinic substances may be said to be dielectrically biaxial.

The orientation of the dielectric indicatrix is always related to the physical lattice symmetry. Only for triclinic substances can the position of the three principal axes of the dielectric indicatrix be independent of molecular lattice symmetry.
The dielectric properties of any substance are closely related to the molecular lattice symmetry. As one might expect, many other physical properties also show a similar dependence upon lattice direction, among which are thermal conductivity, compressibility, and thermal expansion. It is beyond the scope of this overview to discuss the theory and techniques of determining these physical properties relative to the (regular) molecular lattice structure of the material. The fundamental point here is that the simplest procedure by which one can obtain a dielectric reference material that is electrically isotropic is to use known materials that have amorphous molecular structures or that are cryptocrystalline (such as fused silica, fused titanium dioxide, etc. or glass). The reason why materials are in the noncrystalline isotropic state is that they are formed by rapid cooling or quenching from the molten state such that a regular lattice structure framework does not have time to develop on the molecular level. However, provided a crystalline material falls within the isometric lattice system it will also be electrically (and optically) isotropic. Hence one could pick materials which fall within the isometric system to ensure isotropy. In a similar way, uniaxial (two-dimensionally anisotropic) dielectric reference materials or biaxial (three-dimensionally anisotropic) dielectric materials can be taken from those substances whose molecular lattice structures fall into tetragonal and hexagonal or orthorhombic, monoclinic, and triclinic systems, respectively.

4.4.2.1 Isomorphism

Inorganic substances which have comparable lattice structure on the molecular level will have comparable dielectric property behavior. Substances with analogous formulas and in which the relative sizes of cations and anions
Figure 13. The dielectric indicatrix for (a) isotropic, (b) uniaxial, (c) biaxial substances. In (a) the indicatrix is a sphere, in (b) the indicatrix is a rotation ellipsoid and in (c) the indicatrix is a triaxial ellipsoid.
are similar usually have closely related molecular lattice structures. These lattice structures are then said to be isomorphous, and the phenomenon is known as isomorphism. As a result of similar internal structures such substances crystallize with similar external forms. A sufficient condition for isotropy is that the lattice structure belong to the isometric system. In this case, all principal diagonal components of the dielectric tensor are the same. An isomorph of a given material that falls within the isometric lattice structure system would then be expected to possess the same characteristics of isotropy that is requisite for a reference material or check standard. The same statement can be made for uniaxially of biaxially anisotropic reference materials.

Isomorphism is widespread among inorganic materials and naturally-occurring minerals and can be used as one basis of their classification. Many isomorphous groups are known such as the spinel group (AB$_2$X$_4$ double oxide structure, in which A is one or more divalent metals (Mg, Fe, Zn, Mn, Ni), B is one or more trivalent metals (Al, Fe, Cr, Mn or Ti$^{+4}$) and X is oxygen.), the garnet group (X$_3$Y$_2$ (SiO$_4$)$_3$ in which X may be Ca, Mg, Fe$^{+2}$, or Mn$^{+2}$ and Y may be Al, Fe$^{+3}$, or Mn$^{+3}$), and the hematite group (X$_2$O$_3$ in which X may be Al, Fe$^{+3}$ or Fe$^{+2}$ and Ti$^{+4}$). See tables 3, 4 and 5 for various isomorphs of these groups together with chemical composition.

Note that all isomorphs of the spinel and garnet groups are electrically isotropic. Similarly, corundum (or alumina), which is an isomorph of the hematite group and which is widely used as a substrate material for high frequency applications (due to its high permittivity, low dielectric loss, and inert behavior when subjected to chemical, vacuum or thermal processing), has a lattice structure which is inherently uniaxially anisotropic. Of course,
Table 3. Naturally occurring isomorphs of the isometric garnet group

<table>
<thead>
<tr>
<th>ISOMORPH</th>
<th>FORMULA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Almandite</td>
<td>$\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$</td>
</tr>
<tr>
<td>Pyrope</td>
<td>$\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$</td>
</tr>
<tr>
<td>Spessartite</td>
<td>$\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$</td>
</tr>
<tr>
<td>Grossularite</td>
<td>$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$</td>
</tr>
<tr>
<td>Andradite</td>
<td>$\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$</td>
</tr>
<tr>
<td>Uvarovite</td>
<td>$\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$</td>
</tr>
</tbody>
</table>

Table 4. Naturally occurring isomorphs of the isometric spinel group

<table>
<thead>
<tr>
<th>ISOMORPH</th>
<th>FORMULA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinel</td>
<td>$\text{MgAl}_2\text{O}_4$</td>
</tr>
<tr>
<td>Magnetite</td>
<td>$\text{Fe}_3\text{O}_4$</td>
</tr>
<tr>
<td>Chromite</td>
<td>$(\text{Mg,Fe})\text{Cr}_2\text{O}_4$</td>
</tr>
<tr>
<td>Franklinite</td>
<td>$(\text{Zn,Mn,Fe})(\text{Fe,Mn})_2\text{O}_4$</td>
</tr>
<tr>
<td>Hausmanite</td>
<td>$\text{MnMn}_2\text{O}_4$</td>
</tr>
<tr>
<td>Chrysoberyl</td>
<td>$\text{BeAl}_2\text{O}_4$</td>
</tr>
</tbody>
</table>

Table 5. Naturally occurring isomorphs of the hexagonal hematite group

<table>
<thead>
<tr>
<th>ISOMORPH</th>
<th>FORMULA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corundum (Alumina)</td>
<td>$\text{Al}_2\text{O}_3$</td>
</tr>
<tr>
<td>Hematite</td>
<td>$\text{Fe}_2\text{O}_3$</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>$\text{FeTiO}_3$</td>
</tr>
</tbody>
</table>
one way to create a type of "pseudo-isotropy" in a material such as alumina is to take very fine particles of corundum and sinter them under high pressure and high temperature so that microcrystalline anisotropy is "averaged" out in the finished ceramic substrate. However, this is done at the expense of surface finish (or roughness) of the microstrip transmission line product, and surface finish is a major contributor to attenuation. In fact, a lack of smoothness and flatness in an alumina ceramic controls the accuracy of photolithography and ease with which components can be bonded to a completed circuit on a microwave transmission line.

Many other isomorphous groups are of practical importance in any study of dielectrics. Some of these are the silica group, the rutile group or the olivine-forsterite group. See tables 6 and 7.

Table 6. Isomorphs of the uniaxially anisotropic tetragonal rutile group

<table>
<thead>
<tr>
<th>ISOMORPH</th>
<th>FORMULA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutile</td>
<td>TiO$_2$</td>
</tr>
<tr>
<td>Pyrolusite</td>
<td>MnO$_2$</td>
</tr>
<tr>
<td>Cassiterite</td>
<td>SnO$_2$</td>
</tr>
<tr>
<td>Plattnerite</td>
<td>PbO$_2$</td>
</tr>
<tr>
<td>Tapiolite</td>
<td>FeTa$_2$O$_6$</td>
</tr>
</tbody>
</table>
Table 7. Isomorphs of biaxially anisotropic orthorhombic olivine group

<table>
<thead>
<tr>
<th>ISOMORPH</th>
<th>FORMULA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forsterite (steatite)</td>
<td>Mg$_2$SiO$_4$</td>
</tr>
<tr>
<td>Fayalite</td>
<td>Fe$_2$SiO$_4$</td>
</tr>
<tr>
<td>Olivine</td>
<td>MgFeSiO$_4$</td>
</tr>
<tr>
<td>Monticellite</td>
<td>CaMgSiO$_4$</td>
</tr>
</tbody>
</table>

As we shall see later, titanium dioxide (rutile) in fused form has ultra-low dielectric loss characteristics over a broad band in frequency, with a high relative dielectric constant of 100. The olivine group, on the other hand, is an example of a continuous solid solution primarily of forsterite and fayalite. In sintered form as a ceramic, this isomorph presents itself as a candidate dielectric reference material of very low loss (0.003 at 25°C) and of constant dielectric constant (5.80) from 100 Hz to 10 GHz.

Of course, many of the sintered or fused forms of the above dielectric materials (which are inherently electrically anisotropic on the basis of their molecular lattice structures) can be used as "isotropic" dielectric reference materials that are relatively dispersionless with respect to frequency and temperature (from 100 Hz to 30 GHz, say). However, the electrical characteristics of these fused or sintered forms then become dependent on proprietary manufacturing processes which are subject to change (and availability), and the dielectric characteristics, including homogeneity and isotropy, of the manufactured products are subject to validation and continuous quality control.
Isomorphism occurs because anions and cations of the same relative size (that is, showing the same coordination) and in the same numbers usually crystallize with the same lattice structure. Until the development of X-ray diffraction techniques for the determination of crystal lattice structures, it was somewhat of an enigma why materials that behaved dissimilarly chemically could show complete similarity in crystalline structure. At first sight some isomorphous pairs do not even have analogous formulas. Consider, for example, the aluminum phosphate (AlPO₄) mineral, also known as berlinite. Berlinite is isomorphous with quartz; the true analogy is seen when the formula of quartz is written SiSiO₄. Both Al and P are similar in ionic size to Si and thus can exist in a crystal structure in fourfold coordination with oxygen. Consequently, AlPO₄ can crystallize with the same structure as quartz. Similarly, tantalite, FeTa₂O₆, is isomorphous with rutile, TiO₂ (TiTi₂O₆); the metallic ions are similar in size, and all show sixfold coordination with oxygen.

In summary, materials belonging to the same isomorphous groups have the same characteristic isotropy. Because the atomic weights and induced dipole moments for differing isomorphous compounds are not the same, however, isomorphous materials do not display the same complex polarizability on the molecular (or macroscopic) level. A fertile area for future applied research would be to measure the dispersive frequency- and temperature-dependent characteristics of dielectric isomorphs and to relate the macroscopically measured dielectric behavior to calculable atomic or molecular polarizability.
4.4.2.2 Polymorphism

Any discussion of dielectric isotropy or anisotropy in a search for reference materials would be incomplete without mention of polymorphism. Almost all elements or compounds can exist in more than one crystal form; this phenomenon is known as polymorphism. Each form has different physical properties and a distinct crystal structure. In other words, the atoms or ions are arranged differently in different polymorphs of the same substance. It is therefore not surprising that polymorphs of the same substance have differing directional optical and electrical properties. A polymorphic substance can be described as dimorphic, trimorphic, etc., according to the number of distinct crystalline forms. Polymorphism is an expression of the fact that molecular crystal structure is not determined exclusively by chemical composition, and there is often more than one structure into which the same atom or ions in the same proportions may be built up. One example is the relationship between diamond and graphite. In diamond each carbon atom is linked to four other carbon atoms by homopolar bonds, all the linkages being of equal strength and the crystal as a whole being a giant molecule (as in most organic materials). In graphite each carbon atom is linked to three other carbon atoms by homopolar or covalent bonds, which results in the formation of planar sheets of carbon atoms. These sheets are joined by weak residual van der Waals forces. Diamond (C) falls in the isometric lattice system, whereas graphite (C) falls in the hexagonal system. Diamond is therefore electrically isotropic and would make an excellent dielectric reference material were it not for its extreme hardness. This example presents the greatest known contrast in structure and properties to be found in any pair of polymorphous substances. Other physical properties of materials such as hardness and mechanical strength
are generally determined by the weakest atomic bonds, which are the first to suffer disruption under increasing mechanical or thermal strain.

Different polymorphs of the same substance are formed under different conditions of pressure and temperature. The diamond-graphite equilibrium curve, for example, is given in figure 14. Another example of the stability relations between four polymorphs of quartz is shown in figure 15.

Whether or not a change from one polymorph to another is reversible and takes place at a definite temperature and pressure is a basis for the recognition of two types of polymorphism. When the change from one polymorph to another is reversible, the polymorphism is known as enantiotropic; when the change is irreversible, the polymorphism is monotropic. The polymorphism of quartz is enantiotropic; hence, at a pressure of 101 325 Pa,

\[
\begin{align*}
867{}^\circ C & \quad \Rightarrow \quad 1470{}^\circ C \\
quartz & \quad \rightarrow \quad \text{tridymite} & \quad \rightarrow \quad \text{cristobalite}
\end{align*}
\]

However, the reaction rates for the quartz polymorphs are exceedingly slow. Cristobalite is a common naturally occurring substance; because of its isotropy (isometric system), mechanical stability and hardness, it would make a good dielectric reference material in sufficiently pure form. Generally, high-low polymorphs are characterized by the fact that the high-temperature forms have higher symmetry (implying greater electrical isotropy) than the corresponding low-temperature forms. In addition, high-temperature polymorphs of a substance usually have more open lattice structures than low-temperature forms and therefore have lower density. As an aside, if the various polymorphs of rare earth oxides are understood in terms of their lattice structures and molecular
Figure 14. Diamond-graphite polymorphous equilibrium curve.

Figure 15. Stability relations for polymorphs of dry SiO₂ (silica).
polarization properties, it may be possible to predict high-temperature superconducting properties from macroscopic dielectric measurements.

4.4.3 Hardness

Machinability of a reference material depends on both its hardness and tenacity. The hardness of a material (or mechanical stability) is generally defined as its resistance to scratching, and relative hardness as a useful diagnostic property has its origin (and reference materials) in systematic mineralogy. It was given qualitative precision by the Austrian mineralogist Mohs, who in 1822 proposed the relative hardness scale given in table 8. Each of these minerals will scratch those minerals lower in the scale.

Table 8. Mohs' relative hardness scale

<table>
<thead>
<tr>
<th>Increasing Hardness</th>
<th>Decreasing Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>10. Diamond, C</td>
<td>1. Talc, Mg₃Si₄O₁₀(OH)₂</td>
</tr>
<tr>
<td>9. Corundum, Al₂O₃</td>
<td>2. Gypsum, CaSO₄ · 2H₂O</td>
</tr>
<tr>
<td>8. Topaz, Al₂SiO₄(OH,F)₂</td>
<td>3. Calcite, CaCO₃</td>
</tr>
<tr>
<td>7. Quartz, SiO₂</td>
<td>4. Fluorite, CaF₂</td>
</tr>
<tr>
<td>6. Orthoclase, KAlSi₃O₈</td>
<td>5. Apatite, Ca₅(PO₄)₃(F,Cl,OH)</td>
</tr>
<tr>
<td>5. Importanter, Ca₅(PO₄)₃(F,Cl,OH)</td>
<td>6. Orthoclase, KAlSi₃O₈</td>
</tr>
<tr>
<td>4. Fluorite, CaF₂</td>
<td>7. Quartz, SiO₂</td>
</tr>
<tr>
<td>3. Calcite, CaCO₃</td>
<td>8. Topaz, Al₂SiO₄(OH,F)₂</td>
</tr>
<tr>
<td>2. Gypsum, CaSO₄ · 2H₂O</td>
<td>9. Corundum, Al₂O₃</td>
</tr>
<tr>
<td>1. Talc, Mg₃Si₄O₁₀(OH)₂</td>
<td>10. Diamond, C</td>
</tr>
</tbody>
</table>

The scale that Mohs established is still used today in unaltered form and is a tribute to his perspicacity. In his original description Mohs endeavored
to make the intervals on the scale as nearly equivalent as possible while at the same time to select common minerals for the individual units. The interval between corundum and diamond is greater than that between other units on the scale, but minerals of intermediate hardness were (and still are) unknown. Hardness varies somewhat with crystallographic direction, many minerals being softer on cleavage surfaces than in other directions; therefore finely crystalline specimens of inorganic materials are better used as standards than coarsely crystalline minerals.

Quantitative procedures for hardness determination have shown that the intervals on Mohs' scale are approximately equal, except between 9 and 10. Thus, although it is qualitative, Mohs' scale is well suited for comparing relative hardness in minerals and other materials and is unlikely to be superseded. The fingernail has a hardness equal to 2 1/2 while a pocket knife has hardness 5 1/2. Minerals or materials of hardness 1 generally have a greasy feel; those of hardness 2 can be scratched with the fingernail. Materials of hardness 3 can be cut by a knife; those of hardness 6 and over are not scratchable by a knife and, moreover, will scratch silica glass. A set of small pieces of hardness points or conical pieces of standard minerals set in brass rods are useful for determining material hardness.

With respect to the lattice crystal structure, hardness is the resistance of the structure to mechanical deformation. The following relations hold between hardness and lattice crystal structure:

(1) The greater the valency or charge of atoms or ions, the greater the hardness.

(2) The smaller the atoms or ions, the greater the hardness.
(3) The greater the packing density of atoms or ions, the greater the hardness.

The effect of ionic size on hardness can be clearly seen by examination of *isomorphous* groups, where the lattice structure is the same for all members of that group. The hematite group (see table 5) comprises oxides of trivalent metals ranging in ionic size (see figure 17) from $\text{Fe}^{3+}$ (0.064 nm) to $\text{Al}^{3+}$ (0.051 nm); hardness increases with decreasing ionic size, from 6 for hematite to 9 for corundum (alumina). Another example is in the calcite group which comprises carbonates of divalent metals ranging in ionic size from $\text{Ca}^{2+}$ (0.099 nm) to $\text{Mg}^{2+}$ (0.066 nm). In this case calcite (CaCO$_3$) has a hardness of 3, whereas magnesite (MgCO$_3$) has a hardness of 4 1/2.

Figure 16 illustrates the periodic table and gives both the charge and atomic radius (in nanometers) of the common ions. From figure 16 we see that for an element which can exist in several valence states (form ions of different charge), the ionic radius decreases with increasing positive charge; e.g., $\text{V}^{3+}$: 0.074 nm; $\text{V}^{5+}$: 0.059 nm). Intuitively, this might be expected since as electrons are lost the nucleus exerts a greater pull on those remaining, decreasing the effective radius of the ion. This same rule is observed in going across a horizontal row in the periodic table; the radius of the ions, in general, decreases.

The effect of valency or charge on hardness can be seen by comparing compounds with the same structure and similar ionic sizes. Soda niter (NaNO$_3$) and calcite (CaCO$_3$) have the same structure, and the ionic sizes of Ca (0.099 nm) and Na (0.097 nm) are similar. However, the hardness of soda niter is 2 and that of calcite is 3 [24]. The difference in hardness is due to differences in valence states.
Lastly, the effect of packing density has already been alluded to in symmetry considerations of different polymorphs. For example, low- or high-quartz has a greater packing density (2.65 g/cm³) than does tridymite (2.26 g/cm³), even through tridymite has greater lattice symmetry (less electrical anisotropy). Quartz has a hardness of 7, whereas tridymite has a hardness of 6½.

<table>
<thead>
<tr>
<th>H</th>
<th>He</th>
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<tbody>
<tr>
<td>Li⁺</td>
<td>N⁺</td>
</tr>
<tr>
<td>0.68</td>
<td>0.13</td>
</tr>
<tr>
<td>Br⁻</td>
<td>O²⁻</td>
</tr>
<tr>
<td>0.35</td>
<td>1.40</td>
</tr>
<tr>
<td>I⁻</td>
<td>F⁻</td>
</tr>
<tr>
<td>0.23</td>
<td>1.36</td>
</tr>
<tr>
<td>C ⁴</td>
<td>Ne</td>
</tr>
<tr>
<td>0.16</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Na⁺</th>
<th>Mg²</th>
<th>Al³</th>
<th>Si⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.97</td>
<td>0.66</td>
<td>0.51</td>
<td>0.42</td>
</tr>
<tr>
<td>P⁺</td>
<td>S⁶</td>
<td>Cl⁻</td>
<td>A</td>
</tr>
<tr>
<td>0.35</td>
<td>0.30</td>
<td>1.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.84</td>
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<table>
<thead>
<tr>
<th>K¹</th>
<th>Ca²</th>
<th>Sc²</th>
<th>Ti⁴</th>
<th>V²⁺</th>
<th>Cr³⁺</th>
<th>Mn⁴⁺</th>
<th>Fe³⁺</th>
<th>Co³⁺</th>
<th>Ni²⁺</th>
<th>Cu²⁺</th>
<th>Zn²⁺</th>
<th>Ga³⁺</th>
<th>Ge⁴⁺</th>
<th>As³⁺</th>
<th>Se³⁺</th>
<th>Br⁻</th>
<th>Kr</th>
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<tbody>
<tr>
<td>1.33</td>
<td>0.99</td>
<td>0.81</td>
<td>0.68</td>
<td>0.59</td>
<td>0.52</td>
<td>0.60</td>
<td>0.64</td>
<td>0.63</td>
<td>0.63</td>
<td>0.69</td>
<td>0.74</td>
<td>0.62</td>
<td>0.46</td>
<td>0.42</td>
<td>0.42</td>
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<td>0.74</td>
<td>0.63</td>
<td>0.80</td>
<td>0.74</td>
<td>0.72</td>
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<table>
<thead>
<tr>
<th>Rb⁺</th>
<th>Sr²</th>
<th>Y³</th>
<th>Zr⁴</th>
<th>Nb⁵</th>
<th>Mo⁶</th>
<th>Ru⁷</th>
<th>Rh⁸</th>
<th>Pd²⁺</th>
<th>Ag⁺</th>
<th>Cd²⁺</th>
<th>In³</th>
<th>Sn⁴⁺</th>
<th>Sb⁴⁺</th>
<th>Te⁶⁺</th>
<th>I⁻</th>
<th>Ne</th>
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<tbody>
<tr>
<td>1.47</td>
<td>1.12</td>
<td>0.79</td>
<td>0.69</td>
<td>0.62</td>
<td>0.57</td>
<td>0.68</td>
<td>0.80</td>
<td>1.26</td>
<td>0.97</td>
<td>0.81</td>
<td>0.71</td>
<td>0.62</td>
<td>0.76</td>
<td>0.56</td>
<td>2.16</td>
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<table>
<thead>
<tr>
<th>Cs¹</th>
<th>Ba²</th>
<th>La²⁺</th>
<th>Ce³⁺</th>
<th>Pr³⁺</th>
<th>Nd⁴⁺</th>
<th>Sm⁵⁺</th>
<th>Eu⁶⁺</th>
<th>Gd⁷⁺</th>
<th>Tb⁸⁺</th>
<th>Dy⁹⁺</th>
<th>Ho¹⁰⁺</th>
<th>Er¹¹⁺</th>
<th>Tm¹²⁺</th>
<th>Yb¹³⁺</th>
<th>Lu¹⁴⁺</th>
<th>Tl⁶⁺</th>
<th>Bi³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.67</td>
<td>1.34</td>
<td>1.14</td>
<td>1.03</td>
<td>0.85</td>
<td>0.78</td>
<td>0.68</td>
<td>0.62</td>
<td>0.72</td>
<td>0.69</td>
<td>0.80</td>
<td>1.37</td>
<td>1.10</td>
<td>1.47</td>
<td>0.84</td>
<td>1.20</td>
<td>0.96</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Th⁶⁺</th>
<th>U⁴⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.02</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Figure 16. The periodic table, giving the charge and radius (in 10⁻¹⁰ m) of the common ions.

Since the bonding within the lattice structure of a material can be different in different directions, the hardness of a material may be expected to vary with direction. Such variations, though, are usually quite small.
Some degree of correlation exists between hardness and chemical composition [24] as is given in table 9.

Table 9. Correlation between mechanical hardness and chemical composition for inorganic compounds

<table>
<thead>
<tr>
<th>HARDNESS</th>
<th>CHEMICAL COMPOSITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>≤ 3</td>
<td>Heavy metals (silver, copper, mercury, lead)</td>
</tr>
<tr>
<td>≤ 5</td>
<td>Sulfides (except those of nickel and iron)</td>
</tr>
<tr>
<td>≤ 5</td>
<td>Hydrates</td>
</tr>
<tr>
<td>&gt;5½</td>
<td>Anhydrous oxides and silicates</td>
</tr>
<tr>
<td>≤ 5½</td>
<td>Carbonates, sulfates, phosphates</td>
</tr>
</tbody>
</table>

The relevance of this discussion to the search for dielectric reference materials is that materials are desired that not only are linear, homogeneous and isotropic, but that have a hardness of at least 5½ on the Mohs Scale.

4.4.4 Tenacity

Tenacity of a material is defined as the resistance that material offers to breaking, crushing, bending, or cutting. Most inorganic compounds or minerals are brittle. In other words, they can be crushed to a fine powder. This allows some degree of fusibility (e.g., fused quartz, alumina, rutile), but at the expense of machinability. A few inorganics (native metals) are malleable, which simply means their shape can be readily changed without breaking; hammering or grinding causes the grains to be rolled out into plates. A material is called elastic if after bending it springs back into
its original form. Reference materials will probably necessarily have a tenacity which is brittle, albeit remain elastic.

4.4.5 Wettability

Both inorganic and organic materials exhibit marked differences in the properties of their surfaces. One such property of great technical significance for a dielectric reference material is called the "wettability," that is, the relative ease with which a surface of that material can be coated with water. Lyophile materials are those which are easily wetted, and lyophobe materials are those not easily wetted. The differences in surface wettability have been applied for many years in the minerals extraction industries (e.g., for separation of lyophobe minerals such as diamonds from accompanying lyophile minerals).

All degrees of wettability between extremely lyophile and extremely lyophobe materials exist. Generally, materials with ionic bonding are lyophile. Those with metallic or covalent bonding (such as sulfides or plastics) are lyophobe. Diamond is an example of covalent bonding within an isometric lattice structure and is lyophobe. Quartz, on the other hand, has ionic bonding in silicon and oxygen tetrahedra and is lyophile. Most ceramics also have ionic bonding and are lyophobe. Ideally, a dielectric reference material is a substance which is lyophobe, since a wettable material can affect electrical property measurements (and performance in practice). Because of these factors one might place priority on some organic materials such as polytetrafluoroethylene (Teflon) or cross-linked polystyrene (Rexolite) which exhibit covalent bonding structures. The problem here then becomes one of thermal expansion over the temperature range of application;
however, these are problems of significance in application, and provided the
temperature is kept constant (and specified), some of the organic materials
will be seen to be useful dielectric check standards.

4.4.6 Piezoelectric Versus Pyroelectric

Two other properties can be significant in a search for low-loss dielectric reference materials. One of these, pyroelectricity, results from the fact that polarization changes can be induced by changes in temperature. Pyroelectric materials, such as lithium sulfate, barium nitrite, and tourmaline, are commonly used in infrared sensing devices; these types of low-loss materials, whose dielectric properties are strong functions of temperature, usually occur in substances whose lattice structures have polar symmetry axes.

The other common phenomenon, piezoelectricity, results from the fact that polarization charges can be created by directed pressure. The application of piezoelectricity to radio with the use of quartz is well-known; here an alternating electric field generated by the circuit is applied across a quartz plate, properly cut and mounted and dimensioned so that one of its natural frequencies of mechanical vibration coincides with the resonant frequency of the circuit. The frequency of transmission or reception is therefore stabilized and precisely controlled. In general, any material lacking a center of lattice symmetry will be piezoelectric, although the effect may be very weak. In dielectric metrology, samples are rarely placed under directive stresses, although measurements may be taken at widely variant temperatures. Therefore, as long as the candidate dielectric reference material is homogeneous, linear and isotropic, has suitably low loss over a broad range
in frequency and temperature, and has adequate machinability, it may be piezoelectric, but be minimally pyroelectric. The material must also not undergo molecular polymorphism over small temperature ranges.

5. SUITABLE DIELECTRIC REFERENCE MATERIALS

Thus far, basic principles of dielectrics and requirements for reference materials in terms of spatial homogeneity, isotropy, long-term stability, and wettability (moisture absorption) have been reviewed. In addition, the desirability of a dielectrically nondispersive, non-Debye material, both with respect to frequency and temperature variations, has been indicated or, at least, if the material is dispersive, that it be predictable in terms of ambient conditions and frequency of the applied field. These concepts have been looked at in the context of the chemical physics of materials.

Generally, the constitutive electrical parameters of materials are measured by replacing vacuum or air with a specimen of known dimensions in an electrical circuit and measuring appropriate changes in the circuit. The sample holder is usually a lumped parameter circuit reactance or a section of transmission line or cavity (open or closed), and the observation may be of resonance or of impedance. Actual measurements characteristically involve three steps [25], namely, the solution of an electromagnetic boundary value problem, the dimensional gauging of the system used, and the electrical measurements on the system such as the complex impedance or the complex resonant frequency of the system. It is beyond the scope of this Technical Note to describe the standard configurations that are widely used in dielectric and magnetic measurements except to say that these measurements depend on the state of development of basic rf and microwave measurements --
impedance, attenuation, etc. Usually the dimensional gauging of the system and small departures of the system from the form assumed in the initial ideal boundary value problem are the limiting factors, as opposed to electrical observations.

As stated earlier, standard dielectric samples (or those whose dielectric properties are characterized by well-known and precise limits of error) are useful in a laboratory in order to improve or confirm the accuracy of the measuring procedures and equipment used. Standardization of the permittivity of a material and, concomitantly, the comparison of the measuring accuracy at separate laboratories have the feature that the standard for the work is assumed identical for all laboratories, being $\varepsilon_0$ for the dielectric constant of the vacuum [26].

Numerous dielectric measurements of various solid insulating materials have been made by the National Institute of Standards and Technology and Von Hippel [27]. These measurements were made with parallel-plate capacitors, short-circuited transmission lines, and cavity resonators. Some of the results of these dielectric measurements are shown in figure 17 on materials that might prove to be useful low-loss reference standards over a broad range in frequency and temperature. Data are summarized showing the material composition, temperature, dielectric constant, loss tangent, frequency, dielectric strength and dc volume resistivity (at 25°C), thermal linear expansion (when known), softening point, and moisture absorption. Note that these dielectric measurements for fused quartz, various ceramics and plastics are given parametrically as a function of frequency at one temperature, 25°C. All materials are low-loss and display no relaxation over the frequency range of measurement, with the exception of barium titanate.
<table>
<thead>
<tr>
<th>Material Composition</th>
<th>T (°C)</th>
<th>Dielectric Constant (Frequency in Hertz)</th>
<th>Loss Tangent (Frequency in Hertz)</th>
<th>Dielectric Strength in Volts/μm (25 °C)</th>
<th>DC Volume Resistivity in Ohm-m (25°C)</th>
<th>Thermal Expansion (linear) in Parts/°C</th>
<th>Softening Point in °C</th>
<th>Moisture Absorption in Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glasses</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>100% Silicon Dioxide (fused quartz)</td>
<td>25</td>
<td>3.82 3.82 3.82 3.82 0.0001 0.00004 0.00006 0.00025</td>
<td>410 &gt;10^{16} 5.7×10^{-7} 1667</td>
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<tr>
<td>Ceramics</td>
<td></td>
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</tr>
<tr>
<td>Aluminum Oxide (99.5%) (corundum)</td>
<td>25</td>
<td>9.48 9.44 9.37 0.00026 0.00025 0.00037</td>
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<td></td>
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<tr>
<td>Barium Titanate</td>
<td>25</td>
<td>1143 600 100 0.0105 0.30 0.60 3</td>
<td>10^{10} - 10^{11} 1400-1430 0.1</td>
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<td>9.65 9.65 9.65 0.0003 &lt;0.0003</td>
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<tr>
<td>Magnesium Oxide</td>
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</tr>
<tr>
<td>Magnesium Silicate (forsterite)</td>
<td>25</td>
<td>13.9 13.9 13.8 13.7 0.0004 0.0005 0.0017 0.0065</td>
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<tr>
<td>Magnesium Titanate</td>
<td>25</td>
<td>5.77 5.77 5.77 0.0007 0.0006 0.00089</td>
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<td>Steatite 410 (fayalite)</td>
<td>25</td>
<td>100 100 100 0.003 0.00025</td>
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<td>Plastics (Organics)</td>
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<tr>
<td>Cross-linked Polystyrene (Recolite)</td>
<td>25</td>
<td>2.55 2.55 2.54 0.00011 0.00013 0.00048</td>
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<td></td>
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</tr>
<tr>
<td>Polytetrafluoroethylene (Teflon)</td>
<td>25</td>
<td>2.1 2.1 2.1 2.08 &lt;0.0002 &lt;0.0002 0.00015 0.0006</td>
<td>39-79 10^{15} 9.0×10^{-5} 66 0.00</td>
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<td>Polyethylene</td>
<td>25</td>
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<td>Polymethyl Methacrylate</td>
<td>27</td>
<td>3.12 2.76 2.60 0.0140 0.0057</td>
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</table>

Figure 17. Dielectric characteristics of some glasses, ceramics, and organics (solids) as a function of frequency.
On first examination, it seems that polytetrafluoroethylene (Teflon) would make an ideal dielectric reference material for low-loss, low permittivity applications. Teflon has a dielectric constant close to 2.0 from 10 kHz to 25 GHz, a loss tangent \(< 0.0006\) over the same frequency range and no wettability. It is also nonflammable, completely inert to most chemicals, and inexpensive. However, it has a relatively low softening point or glass transition temperature [28] (~66°C). Furthermore, it has a high coefficient of expansion (see figure 18), low fusibility, and exhibits strong degradation in dielectric properties when exposed to ionizing radiation.

![Figure 18. Thermal expansion of polytetrafluoroethylene as a function of temperature [27].](image)

In fact, the deterioration of the insulating characteristics of plastics (or most organic materials) in the presence of ionizing radiation is well known. Only the polymer polystyrene (Rexolite), which is a high-molecular-weight derivative of vinyl benzene \([C_6H_5CH\text{--CH}_2]_n\) (where \(n\) is normally
greater than 500), shows no permanent dielectric degradation after suffering irradiation dosages as high as 300 C·kg⁻¹ and dosage rates as high as 40 C·kg⁻¹ per hour [27]. Polystyrene also can absorb some water, which accounts, at least partly, for its loss tangent being an order of magnitude greater than polytetrafluoroethylene and polyethylene. Polyethylene exhibits good low permittivity, low loss dielectric reference material characteristics. The problem with polyethylene, though, is not only its low melting point of 105°C, but also the fact that it oxidizes at temperatures less than 80°C, becomes brittle, and therefore loses its dielectric characteristics. Even when stabilized against degradation by heat, polyethylene still deteriorates when exposed to ultraviolet light [27] with consequent embrittlement and loss of electrical characteristics.

Figure 19. Temperature dispersive characteristics of cross-linked polystyrene (Rexolite) at 10 GHz.
Of the organic solids shown, cross-linked polystyrene appears to have the best characteristics for a low-loss, low permittivity dielectric reference material (and check standard). The temperature dispersive dielectric characteristics of cross-linked polystyrene are shown in figure 19.

The dispersive dielectric characteristics of fused silica, alumina, steatite, and titanium dioxide as a function of temperature [27] are shown in figures 20, 21, 22, and 23, respectively.

![Fused Silica Dispersion Characteristics](image)

**Figure 20.** Temperature dispersive characteristics of fused silica at 10 GHz [25,26].

Fused silica displays very low loss ($\tan \delta < 0.002$) from 0°C to 500°C while at the same time exhibiting a constant dielectric constant of 3.82 over the same temperature range. Apart from its tenacity (brittleness) fused silica (in pure form) satisfies the preferred characteristics of a low permittivity, low-loss dielectric reference material.
For a high dielectric permittivity and low-loss material, either alumina with $\epsilon = 9.48$ ($\geq 99.5\%$ pure) or steatite (fayalite) with $\epsilon' = 5.77$ exhibits notable characteristics. Alumina, however, has lower loss at temperatures less than 150°C than does fayalite, although at 10 GHz fayalite's permittivity and loss tangent are approximately independent of temperature (from 0°C to 500°C). At much lower frequencies ($< 10$ kHz) fayalite becomes strongly dispersive with temperature; therefore alumina is probably the better choice for both a reference material and check standard.

For very high dielectric constant ($\sim 100$), fused rutile or titanium dioxide behaves well as a reference material, as long as the temperature does not exceed 250°C. Barium titanate also possesses a very high dielectric constant ($\epsilon' = 100$ at 25 GHz); however, it also possesses a loss tangent of 0.60 at 25 GHz, has a ferroelectric perovskite lattice structure, and exhibits nonlinearity and dielectric hysteresis. For a dielectric reference material of very high permittivity and low loss, titanium dioxide would be the better choice.
Figure 21. Temperature dispersive characteristics of alumina (99.5% pure) at 1 MHz [26,27].
Figure 22. Temperature dispersive characteristics of steatite (fayalite) at 10 GHz [27].
Figure 23. Temperature dispersive characteristics of fused titanium dioxide (rutile) at 1 MHz.
6. CONCLUSIONS

Because dielectric components are critical to the performance of all electronic equipment, a national need exists for improved dielectric materials and precision measurement methods. Reference materials serve as basis points for measurement accuracy standards. Ideal dielectric reference materials should be electrically and magnetically linear, homogeneous, and isotropic. It is best that they also have low thermal expansion coefficients, high softening temperatures, and both chemical and mechanical stability, while still being machinable and readily available.

To characterize properly the electromagnetic nature of any material, it is necessary to understand and determine the fundamental physical processes that govern electromagnetic behavior and that define the constituent electric and magnetic properties. Materials polarize in an applied electric field. The principal polarization mechanism depends on the frequency of the applied field and may be electronic, atomic, dipolar, or interfacial in nature. The electric polarizability of a material defines that material's complex dielectric constant which is, in general, expressed in complex form as the sum of the real effective permittivity and loss factor. For uniaxially or biaxially anisotropic materials, the dielectric constant is a 3 x 3 complex tensor. If the material attenuates electromagnetic waves propagating through them, both the real effective permittivity and loss factor become functions of frequency, or are dispersive. It is important to understand frequency-dependent behavior of a dielectric if it is to be used as a standard reference material.

Polarization, or charge separation in material media, is physically damped in the rf and microwave regions by relaxation processes. Analogous to
a R-C ladder lumped parameter circuit, the time-constant distribution function quantifies a material's intrinsic relaxation and allows the derivation of analytic relations between permittivity and loss tangent as a function of frequency. These dispersion relations were derived for a Debye material (single relaxation) and for a material that has an infinitely broad, continuous distribution function (no relaxation). It was shown that suitably sampled measurements of \( \epsilon' \) and \( \epsilon'' \) may be fruitfully used to indicate whether a single or multiple distribution of relaxation times exist in a dielectric material and, if a distribution exists, the symmetry of that distribution. Once a material has been classified as a Debye material, for example, only the low- and high-frequency complex permittivity measurements are needed to completely characterize that material over all frequencies.

The derived dispersion relations in section 4.3 reveal a change in real effective permittivity that varies linearly with the loss tangent and that varies logarithmically with change in measurement frequency for either a material characterized by single relaxation or no relaxation. These effective permittivity-loss tangent relations are very useful for determining the broadband dispersion characteristics of a dielectric reference material from limited measurement data or, for that matter, predicting the dielectric behavior of any material, even at frequencies where measurement data are not taken. They are also useful for determining which modal roots are valid in dielectric cavity or waveguide measurement fixtures, identifying discrepancies and errors in reported dielectric measurements, and indicating where peak absorption frequencies occur in lossy materials.
Generalized relationships between the real effective permittivity, ε'(ω), and loss factor, ε"(ω), for any dielectric material possessing an arbitrary number of relaxation times of any distribution asymmetry were derived. The loss factor as a function of frequency can be determined by the Hilbert transform of discretely sampled permittivity values. Similarly, the real effective permittivity as a function of frequency is equal to the Hilbert transform of the loss factor plus the high-frequency (optical) limit, ε∞. Numerical Hilbert transform results indicate that measurements taken over three decades in frequency suffice to predict either the real effective permittivity from the loss factor or the loss factor from the real effective permittivity in the dipolar relaxation regime, with an error bound less than two percent. This was true as long as discretized data are obtained over the range 0.1 ≤ ωτ ≤ 10, where τ is the principal relaxation time of the dielectric. The Hilbert transform relationships are valid for rf, microwave, mm, and IR frequency ranges. The only presuppositions are that the dielectric material behave linearly in the presence of an electric field, the dielectric is causal (does not polarization before stimulus of the electric field), and the constitution of the dielectric does not change within the time of observation (as, for example, some polymorphic materials do change with variations in temperature). The Hilbert transform relations are quite useful in the characterization of reference materials in the following two ways. First, uncertainty in loss measurements (for both low-loss standard reference materials and absorbent materials) is usually much greater than the uncertainty in real effective permittivity measurements. Therefore precise measurements of real effective permittivity over a range in frequency can be
used to determine the loss factor as a function of frequency. Second, prediction of absorbent dielectric characteristics can be made from out-of-band measurement data. In the search for dielectric reference materials, the effects of temperature variations are quite important in the determination of softening points that can lead to volumetric creep phenomena or in the determination of expansion and contraction characteristics of the material under study. Expansion or contraction of a dielectric reference material can lead to serious air gap errors in precision dielectric measurement fixtures if not accounted for. Hence (linear) thermal expansion coefficients less than 10⁻⁸/K are preferred. In addition, fundamental changes in a material's polarizability or loss occur as a result of differing temperature-dictated energy states of the material. It is vital to know the fundamental behavior of the complex dielectric constant as a function of temperature, particularly if that material is a reference standard. Stated differently, if the polarizability of a material can be related to the known activation energy of that material at a given temperature and under the influence of a time-varying electric field, then a means for predicting the dielectric behavior of that material as a function of temperature can be gained. In order to accomplish this, a bistable model of an elementary dipole within a dielectric whose molecular groupings could be characterized by well-defined, permanent dipole moments was considered. Consideration of the probability of a jump by a charge in a double potential well led to a relation which describes the dispersive behavior of a dielectric as a function of absolute temperature, frequency, activation energy, and the dipolar polarizability of the material. The temperature-dependent relaxation time follows Boltzmann's law, and a marked similarity was noted in the differential equation for the dipolar
polarization of a dielectric medium as a function of temperature with that derived for Debye dielectrics, as a function of frequency of the applied electric field. The derivation given in section 4.3.5 for the effect of temperature on dielectric properties is limited to dielectric materials where the interaction between individual dipoles can be neglected and for conditions where \( pE << kT \) (nonsuperconducting states), where \( p \) is the dipole moment, \( E \) is the applied electric field, \( k \) is Boltzmann's constant and \( T \) is absolute temperature.

The temperature-dependent dispersive effects on dielectric behavior using the bistable model are an important area for further research and laboratory examination. The same material dielectric property measurement made at a given temperature and frequency could be expected for a different combination of temperature and frequency. The limitations of the bistable model, noninteraction of individual molecular dipoles, and temperature domain (particularly near critical superconducting states) remain to be determined.

In the past, homogeneity of any dielectric reference sample was determined by making many measurements on samples of the same material produced by the same manufacturing process. These measurements were then compared with those made at other laboratories where different fixtures were used. Generally, corrections that are due to departures of the actual fixture from the idealized theoretical model of that fixture are made to dielectric measurement data. It is important to be able to distinguish deviations from homogeneity in a candidate reference material from fixture measurement inaccuracies. Therefore an approach for examining the influence of deviations from homogeneity on a precisely specified electromagnetic field structure was
outlined. This approach replaces the sample with an effective scattering current. Sample geometry, impressed field structure of the measurement fixture, and frequency of excitation are all arbitrary. The dielectric sample under test can be considered as a superposition of electric dipole distributions, and the total electric field at any point exterior to the sample may be written as sum of the impressed field in the sample plus a convolution integral of the tensor Green function with the scattering current that defines the sample. The convolution integral reduces to only an integration over the sample volume, where the spatial distribution of $\epsilon'$, $\epsilon''$ is arbitrary. The equation for determination of the complex dielectric constant at any frequency and for any sample point is a Fredholm integral equation of the second kind. If the dielectric sample under test displays low loss, it may be possible to determine the permittivity distribution independently of how the sample was machined by making use of the Born approximation (field within sample approximately equal to incident field). Iterative Born techniques may be used to solve for the complex permittivity when sample losses are not low. The same analysis can provide corrections to measurement data when an otherwise homogeneous sample is not axially centered in a cavity or waveguide fixture, or when a nonuniform air gap exists around the sample within either of the above fixtures. Similarly, the effects of eccentricity of a cylindrical waveguide or axially nonorthogonal endplates on a resonating fixture can be determined by the same equations.

One of the last primary characteristics of an ideal dielectric reference material is that the complex permittivity be the same in all directions, or that the reference material be electrically isotropic. A sufficient condition for isotropy is that the material have no lattice structure (or be amorphous),
be cryptocrystalline (such as fused silica), or have a lattice crystal structure that belongs to the isometric system. Similarly, materials whose lattice structures are in the tetragonal and hexagonal systems are intrinsically uniaxially anisotropic, and those whose lattice structures fall within the orthorhombic, monoclinic, and triclinic systems are biaxially anisotropic. Knowledge of the molecular lattice structure allows the choice of a reference material which, in terms of its directional electrical properties, is intrinsically isotropic or has well-defined anisotropy. This is an important point since inorganic substances which have the same lattice structure on the molecular level will have the same directional dielectric property behavior. Substances with analogous formulas and in which the relative sizes of cations and anions are similar usually have closely related lattice structures and are said to be isomorphous. An isomorph of a material that falls within the isometric lattice structure system would be expected to possess the same characteristics of isotropy that is requisite for a reference material or check standard. Because the atomic weights and induced dipole moments of differing isomorphous compounds are not the same, however, isomorphous materials are not expected to display the same complex polarizability.

Any discussion of dielectric isotropy or anisotropy in a search for reference materials would be incomplete without mention of polymorphism. Polymorphism is an expression of the fact that molecular crystal structure is not exclusively determined by chemical composition, and there is often more than one structure into which the same atom or ions in the same proportions may be built up. The change from one polymorph to another is largely dependent on temperature and pressure conditions and may be reversible or irreversible. Dry quartz, for example, has lattice structures that may be isometric,
hexagonal, or trigonal, depending on the temperature and pressure conditions. The important point here is that it is desirable not to have a reference material which is polymorphic over small temperature ranges.

At present a type of "pseudo-isotropy" is enforced on many dielectrics used in application that are otherwise intrinsically anisotropic. For example, alumina (corundum), which is an isomorph of the hematite group, is widely used as a substrate material for high frequency applications (due to its high real effective permittivity, low dielectric loss, and inert behavior when subjected to chemical, vacuum or thermal processing), and has a lattice structure which is inherently uniaxially anisotropic. By taking very fine particles of corundum and sintering them under high pressure and high temperature, the microcrystalline anisotropy is "averaged" out in the finished ceramic substrate. However, this is done at the expense of surface finish of microstrip transmission line product, a major contributor to attenuation.

Secondary characteristics of a reference material, such as its machinability, chemical inertness, and moisture absorption, are also important considerations. The machinability of a material depends on both its hardness and tenacity. Several relations hold between hardness and lattice crystal structure. First, the greater the valency or charge of atoms or ions, the greater the hardness. Second, the smaller the atoms or ions, the greater the hardness. Third, the greater the packing density of atoms or ions, the greater the hardness. Dielectric reference materials should have a hardness of at least 5½ on the Moh scale. Correlations between mechanical hardness and chemical composition for inorganic compounds quite naturally lead to the choice of anhydrous oxides and silicates as candidate reference materials.
(as opposed to carbonates, sulfates, phosphates, or sulfides). Most inorganic compounds, on the other hand, are brittle. This allows some degree of fusibility, but at the expense of machinability. Reference materials will probably have a tenacity which is brittle yet be elastic. A final characteristic of an ideal dielectric reference material is that it be a substance which is lyophobe, since a wettable material can affect electrical property measurements. Solids with covalent bonding (such as diamond) are lyophobe and generally chemically inert, as are many organic materials such as polytetrafluoroethylene or polystyrene. Generally, however, materials with ionic bonding are lyophilic (wettable), and the problem with most organics is their temperature coefficient of expansion, as well as deterioration in the presence of ionizing radiation. Hence compromises must be made in the secondary characteristics of machinability, wettability, and possibly dispersion to give proper emphasis on electrical linearity, homogeneity, and isotropy.

Numerous dielectric measurements on solid insulating materials have been made. These measurements were made with parallel-plate capacitors, transmission-reflection and short-circuit lines, and cavity resonators. Data indicating the material composition, temperature, real effective permittivity, loss tangent, thermal linear expansion, softening point, and moisture absorption were compiled. All materials studied were low-loss and displayed negligible relaxation over the frequency range of measurement, with the exception of barium titanate.

On first examination, it appeared that polytetrafluoroethylene would make an ideal dielectric reference material for low-loss, low permittivity applications. Polytetrafluoroethylene has a dielectric constant close to 2.0 from
10 kHz to 35 GHz, a loss tangent $\leq 0.001$ over the same frequency range and no wettability. It is also nonflammable, completely inert to most chemicals and of low cost. However, it does have a relatively low softening point, high temperature coefficient of expansion, low fusibility and exhibits strong degradation in dielectric properties when exposed to ionizing radiation. The deterioration of the insulating characteristics of plastics (or most organic materials) in the presence of ionizing radiation is well known [27]. Only the polymer polystyrene shows no dielectric degradation after being exposed to high radiation. Thus, of the organic solids studied, cross-linked polystyrene appears to have the optimal characteristics for a low-loss, low effective permittivity dielectric reference material (and check standard).

Of the inorganic materials studied, fused silica exhibits very low loss ($\tan \delta < 0.002$) from $0^\circ C$ to $500^\circ C$ while at the same time displaying a constant dielectric constant of 3.82 over the same temperature range. Apart from its brittleness, fused silica (in pure form) satisfies the characteristics of a low real effective permittivity, low-loss dielectric reference material. For a high dielectric constant and low-loss material, alumina (99.5 percent pure, with $\epsilon' = 9.48$) exhibits notable characteristics and, because of its lower loss at temperatures less than $150^\circ C$, is probably a better choice for a reference material than are the steatite ceramics. Lastly, fused rutile or titanium dioxide behaves well as a reference material for very high dielectric constant (~100), as long as the temperature range does not exceed $250^\circ C$.

In summary, this technical report has addressed itself to the national need for enhanced dielectric metrology and reference materials, as well as to desired properties of reference materials. Fundamental electromagnetic
characteristics of all materials that relate to polarization mechanisms and both frequency- and temperature-dependent relaxation processes were reviewed. Since inhomogeneous materials result in a complex coupling of all electromagnetic field components upon which the constituent dielectric properties are defined, an approach for analyzing the effects of inhomogeneities in an arbitrary measurement fixture was presented, with suggestions for the determination of the complex permittivity of a sample which has spatial variance. Fundamental electromagnetic concepts of isotropy and uniaxial or biaxial anisotropy were also reviewed with a special emphasis on the chemical lattice physics. All of these considerations together with measurement data could be used to choose suitable dielectric reference materials to be chosen.

In addition, a number of fundamental areas that deserve further investigative effort, both for the advancement of broadband dielectric metrology and for understanding dielectric behavior of materials in electromagnetic fields, became evident. These are summarized below and given as recommendations for future work in applied dielectric metrology.

(1) Measure dispersive frequency- and temperature-dependent characteristics of dielectric isomorphs and relate macroscopically measured dielectric behavior to calculable atomic or molecular polarizability.

(2) Determine validity of relations between real effective permittivity and loss tangent for lossy dielectric materials which exhibit Debye and non-Debye relaxation mechanisms. From these relations examine the predictability of dielectric properties at high frequency (non-transition state) from measured properties at lower frequencies, a
classical metrology problem. Clearly, broadband techniques of
dielectric metrology would be part of this effort.

(3) Examine dielectric equivalence of frequency-dependent dispersion and
temperature-dependent dispersion for ionically bonded solid mater-
ials. If possible, relate these properties to lattice structures of
high-temperature superconductors.

(4) Most international comparisons of dielectric measurements involve a
prior check on the homogeneity of the subject reference material by
taking a number of individual sample measurements. However, future
assumptions about dielectric homogeneity are always subject to the
nonchangeability of proprietary manufacturing processes. This is
undesirable both from a point of view of future availability as well
as quality control of a proprietary manufacturing process. In
addition, most metrology techniques involve the solution of
electromagnetic boundary value problems where the sample geometry
must be precisely machined so as to fall within the idealized
surfaces of an orthogonal coordinate system. This ensures
separability of the electromagnetic field components in subsequent
computation of complex permittivity, as well as independence of
components of the polarization field from each other. In this case,
dielectric material characterization is subject to the precision
with which the geometry of the measuring fixture and sample are
known (as opposed to actual measurements of attenuation, impedance,
etc.), which again is undesirable. It should be possible, in
principle, to characterize the spatial homogeneity of a dielectric
material independently of that material's geometry, as long as the
field of the exciting source and system characteristics of receiving probe(s) are known (measured). A fundamental dielectric metrology problem would be to examine the precision with which the dielectric properties of an inhomogeneous dielectric can be measured in a specified source field, over a broad range in frequency.

(5) Intrinsically anisotropic dielectric materials are commonly fused or sintered [29] under high temperature to form a macroscopic "pseudo-isotropy" that is subject to proprietary manufacturing processes, where quality control is uncertain. The metrology problem of general electromagnetic field interaction with either a uniaxially anisotropic or biaxially anisotropic material needs to be examined, so as to ascertain when principal directions of anisotropy can be determined, what the nature of dielectric anisotropy under carefully controlled conditions is on electromagnetic field behavior, and how best to implement laboratory measurements.

(6) Error budgets for all existing dielectric metrology techniques need to be developed over broad ranges in temperature and frequency. Dielectric substrates used in printed circuit patch antennas must have real effective permittivities uniform to ±0.01 over 3 to 30 GHz bandwidths in order not to suffer phasing errors greater than 2° (phasing errors of multi-element antenna arrays can routinely be measured to 0.1°). This implies dielectric measurements should be made that are accurate to ±0.5 percent -- an accuracy which is very difficult to attain [22] and which must necessarily be demonstrated by proper quantification of the error budget for the particular measurement technique.
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APPENDIX
RELAXATION IN DIELECTRICS WITH A SINGLE RELAXATION TIME

In this appendix the polarization response of matter on a molecular scale is considered. From eq (3) we have a definition for the static dielectric constant in terms of the static value of the polarization $P_s$, where

$$\epsilon_s - 1 = \frac{P_s}{E} \tag{A-1}$$

and $\epsilon_s$ is the static permittivity of a material in a static electric field $E$. If we consider a parallel plate capacitor (whose plates have area $A$ that are separated by distance $d$) which is filled with dielectric material, then the polarization $P_s$ implies a dipole moment of the dielectric in the whole of the capacitor that is

$$M_s = P_s Ad \tag{A-2}$$

Hence $P_s$ can also be defined as a dipole moment per unit volume. Dipole moment signifies the product of charge and distance and is a concept that will prove important for the interpretation of dielectric properties on a microscopic scale.

From a perspective of macroscopic properties, eq (A-1) gives a relationship between $P_s$ and the electric field $E$ in equilibrium. If $E$ changes with time, $P$ at any given moment will generally differ from $P_s(E)$. A trend toward equilibrium, however, implies that $P$ will approach $P_s$, and an assumption about the rate of $P$ as a function of time will yield a differential equation for $P(t)$. The simplest assumption is to take the time rate of approach to equilibrium proportional to the distance from equilibrium, that is,

$$\tau \frac{dP(t)}{dt} = P_s - P(t) \tag{A-3}$$
where the relaxation time $\tau$ is constant.

A small modification may now be made in eq (A-1). As discussed earlier, several mechanisms of polarization operate in a dielectric. One of these is electronic polarization, which involves resonance phenomena and is responsible for the optical refractive index. This polarization responds to a changing electric field in negligible time at all frequencies used for electrical measurements. In order to separate this polarization out of eq (A-1) we write

$$\epsilon_s - 1 = \frac{P_D + P_\infty}{E}, \quad (A-4)$$

where $P_0$ refers to the static orientation or "dipolar" polarization and $P_\infty$ is the optical polarization that defines an optical dielectric constant $\epsilon_\infty$ by the simple relation,

$$\epsilon_\infty - 1 = n^2 - 1 = \frac{P_\infty}{E}, \quad (A-5)$$

where $n$ is the refractive index of the material. As an aside, there is some ambiguity with regard to the frequency at which $n$ should be measured, since frequencies generated by microwave oscillators can be as high as 100 GHz, where resonance phenomena just begin to appear. Generally, the optical refractive index is measured for frequencies of 100 - 1000 THz. For practical purposes, however, it is usually, satisfactory to consider $\epsilon_\infty$ as the square of the refractive index measured at frequencies from 10 GHz to 1 THz.

From eqs (A-4) and (A-5),

$$(\epsilon_s - \epsilon_\infty) E(t) = P_D, \quad (A-6)$$

and we may rewrite eq (A-3) as

$$\tau \frac{d(P_D + P_\infty)}{dt} = P_s - (P_D + P_\infty)$$
The right side of eq (A-7) is the equilibrium value of $P_0$ corresponding to $E(t)$, and eq (A-7) is analogous to a simple lumped parameter network computation of the charge on a capacitor in series with a resistor. For a periodic electric field $E(t) = E_0 e^{j\omega t}$, the solution to eq (A-7) may be written immediately for the dipolar polarization,

$$P_0^*(t) = \frac{(\epsilon_s - \epsilon_\infty)}{1 + j\omega\tau} E_0 e^{j\omega t} \quad \text{(NO INITIAL POLARIZATION)}, \quad (A-8)$$

as long as the dielectric has no polarization as a result of its previous history. Here the asterisk * represents a complex quantity. When the dielectric in question is polarized at $t = 0$ as a result of its previous history, the general solution for dipolar polarization may be written,

$$P_0^*(t) = P_0 e^{-t/\tau} + \frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau} E_0 e^{j\omega t} \quad \text{(DIELECTRIC HAVING INITIAL POLARIZATION VALUE $P_0$)}, \quad (A-9)$$

For time-varying field measurements the first term of eq (A-9) can be neglected in comparison to the second. Ignoring the first term yields from basic principles the complex dielectric constant

$$\epsilon^*(\omega) - \epsilon_\infty = \frac{P_0^*(\omega)}{E(\omega)} . \quad (A-10)$$

For $P_0 = 0$,

$$\epsilon^*(\omega) - \epsilon_\infty = \frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau} \quad (A-11)$$
or
\[ \varepsilon''(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau} \quad (A-12) \]

which is identical with the Debye relaxation eq (19), where
\[ \varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2\tau^2} \quad (A-13) \]
and
\[ \varepsilon''(\omega) = (\varepsilon_s - \varepsilon_\infty)\omega\tau/(1 + \omega^2\tau^2) \quad . \quad (A-14) \]

Equations (A-13) and (A-14) are called the Debye equations since they were first derived by Debye [9].

Generally, one measures the permittivity \( \varepsilon'(\omega) \) and the loss tangent \( \tan\delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} \), so that
\[ \tan\delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{\varepsilon_s + \varepsilon_\infty \omega^2\tau^2} \quad (A-15) \]

It is instructive to plot \( \varepsilon'(\omega\tau) \), \( \varepsilon''(\omega\tau) \), and \( \tan\delta(\omega\tau) \) for a dielectric which behaves in a Debye fashion. Consider, for example, a dielectric with \( \varepsilon_s \) and \( \varepsilon_\infty \) measured at 6 and 2, respectively. If the dielectric behaves in a Debye manner, figures A-1 and A-2 show how \( \varepsilon'_R \) and \( \varepsilon''_R \) behave as a function of \( \omega\tau \). It is not difficult to show that the maximum of \( \varepsilon'_R(\omega\tau) \) occurs at \( \omega\tau = 1 \) and has a magnitude of \( (\varepsilon_s - \varepsilon_\infty)/2 \). The inflection point of \( \varepsilon'_R(\omega\tau) \) also occurs at \( \omega\tau = 1 \) and for a Debye dielectric always has a magnitude at this inflection point equal to the arithmetic average of \( \varepsilon_s \) and \( \varepsilon_\infty \). The maximum loss tangent, however, does not coincide with the maximum of \( \varepsilon''_R(\omega\tau) \) as indicated in figure A-3. Instead, the maximum value of \( \tan\delta \) for a Debye dielectric occurs at \( \omega\tau = \sqrt{\varepsilon_s/\varepsilon_\infty} \) (always at a radian frequency greater than the reciprocal of the relaxation time) and has a predictable magnitude of \( (\varepsilon_s - \varepsilon_\infty)/2\bar{\varepsilon} \), where \( \bar{\varepsilon} \) is the geometric mean of \( \varepsilon_s \) and \( \varepsilon_\infty \).
Figure A-1. Behavior of real part of $\varepsilon'$ as a function of $\omega \tau$ for a dielectric with $\varepsilon_s = 6$, $\varepsilon_\infty = 2$. 

\[ \frac{\varepsilon_s + \varepsilon_\infty}{2} \]
Figure A-2. Behavior of imaginary part of $\varepsilon^*$ as a function of $\omega \tau$ for a dielectric with $\varepsilon_s = 6, \varepsilon_\infty = 2$. 
Figure A-3. Loss tangent as a function of $\omega \tau$ for a dielectric with $\varepsilon_s = 6$, $\varepsilon_\infty = 2$. 

The equation shown in the graph is:

$$\bar{\varepsilon} = \text{G.M.}(\varepsilon_s, \varepsilon_\infty)$$

And the expression:

$$\frac{\varepsilon_s - \varepsilon_\infty}{2 \varepsilon}$$

where $\varepsilon_s$ is the initial relative dielectric constant, $\varepsilon_\infty$ is the final relative dielectric constant, and $\varepsilon$ is the relative dielectric constant at some intermediate point.
Dielectric reference materials are analyzed with respect to fundamental requirements of linearity, homogeneity, and isotropy. Generalized frequency- and temperature-dependent dispersion relations are presented which allow the prediction of broadband dielectric behavior from limited measurement data, determination of valid modal field structure in cavity or waveguide fixtures, and identification of discrepancies and errors in measurement data. An approach for examining the influence of deviations of sample homogeneity on a precisely specified electromagnetic field structure is outlined, and sufficient conditions for isotropic, uniaxial, or biaxial anisotropic dielectric behavior are reviewed in terms of a material's chemical lattice physics. These characteristics direct the choices of suitable reference materials useful for confirming or improving the accuracy of dielectric measurements.
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