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Low frequency dielectric relaxation from complex impedance and complex electric 'modulus'

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The low frequency dielectric characteristics of many materials are often difficult to obtain accurately because of the d.c. conductivity contribution, which is the major portion of the loss, and which has to be subtracted from the total dielectric loss. This is particularly true for small dielectric relaxation peaks which tend to be overwhelmed by the d.c. conduction loss. An equation was derived which enables one to calculate the dielectric characteristics at low frequency, for specimens with small dielectric relaxation peaks, without subtracting the d.c. conductivity, from the complex impedance plot and complex electric "modulus" plot.

1. Introduction

In many dielectrics, a d.c. conductivity-related dielectric relaxation is observed at low frequencies [1–6]. In ionic conductors such as glasses and β-Al_2O_3, this conductivity-related dielectric relaxation is often called the migration loss [2, 6, 7], since it is related to the ionic migration in these materials. An identical dielectric relaxation is observed in electronic conducting glasses [4, 8] also. In the evaluation of the low frequency dielectric relaxation of these materials, it is customary to subtract the d.c. conductivity contribution from the dielectric loss. Because of this subtraction procedure, it is often difficult to obtain an accurate value of the permittivity at low frequency. Partly because of this reason, alternate quantities such as admittance [9], impedance [5, 10], and electric "modulus" [5, 11] are used, without subtraction of the d.c. conductivity contribution to evaluate the low frequency dielectric characteristics. Since these quantities are related to the permittivity, it should be possible to obtain the permittivity from impedance and electric "modulus". It is the purpose of this paper to show a method to do this for specimens with small dielectric relaxation.

2. Theory

The complex impedance Z^* is given by [5, 10]

$$Z^* = \frac{M^*}{j\omega C_0} = Z' - jZ'' \tag{1}$$

where M^* is the complex electric "modulus"; ω is the angular frequency; C_0 is the capacitance with vacuum and is given by the product of the vacuum permittivity ϵ_0 and area A divided by the distance apart d of plates.

$$C_0 = \frac{\epsilon_0 A}{d} \tag{2}$$

Z' and Z'' are real and imaginary parts of complex impedance, respectively.

The complex electric "modulus" M^* is expressed by [5, 11]

$$M^* = \frac{1}{\epsilon^*} = M' + jM'' \tag{3}$$

where ϵ^* is the complex relative permittivity. M' and M'' are real and imaginary parts of complex electric "modulus", respectively.

The complex relative permittivity is given by

$$\epsilon^* = \epsilon' - j\left(\epsilon'' + \frac{\sigma}{\omega\epsilon_0}\right) \tag{4}$$

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where σ is the d.c. conductivity; ϵ' and ϵ'' are the real and imaginary parts of the relative permittivity, respectively, after subtraction of the d.c. conductivity contribution.

When the relative permittivities ϵ', ϵ'' are plotted on a complex plane, they often are approximated by a part of a circle as is shown schematically in Fig. 1a [12]. The corresponding equation is given by

$$\epsilon' - j\epsilon'' = \frac{\Delta\epsilon}{1 + (j\omega\tau)^{1-\alpha}} + \epsilon_\infty, \quad 0 > \alpha > 1 \tag{5}$$

where τ is the relaxation time, α is a parameter indicating the broadness of the frequency dependency of the imaginary component ($\alpha = 0$ corresponds to Debye's equation). ϵ_∞ is the relative permittivity at high frequency; $\Delta\epsilon$ is the dielectric strength given by the difference between the static relative permittivity ϵ_s and the high frequency value ϵ_∞. The maximum of the dielectric loss is observed at $\omega\tau = 1$. In many materials τ is approximately given by [1, 3, 5, 8]

$$\tau \simeq \frac{\epsilon_0\epsilon_\infty}{\sigma} \tag{6}$$

Alternatively, the experimental data are often analysed [5, 10, 11] in terms of the complex impedance Z^* or the complex electric "modulus". Similarly to the relative permittivity, when these complex quantities, Z', Z'', M', M'' are plotted on a complex plane, they also are approximated by a part of a circle as is shown schematically in Figs. 1b and c. The corresponding equations are given by

$$Z^* = Z' - jZ'' = \frac{R}{1 + (j\omega\tau_z)^{1-\alpha_z}}, \quad 0 > \alpha_z > 1 \tag{7}$$

$$M^* = M' + jM'' = \frac{1/\epsilon_\infty}{1 - (j\omega\tau_m)^{1+\alpha_m}}, \quad 0 > \alpha_m > 1 \tag{8}$$

where τ_z, τ_m are the relaxation times, α_z, α_m are parameters indicating the broadness of the frequency dependency of the imaginary components. R is the d.c. resistance.

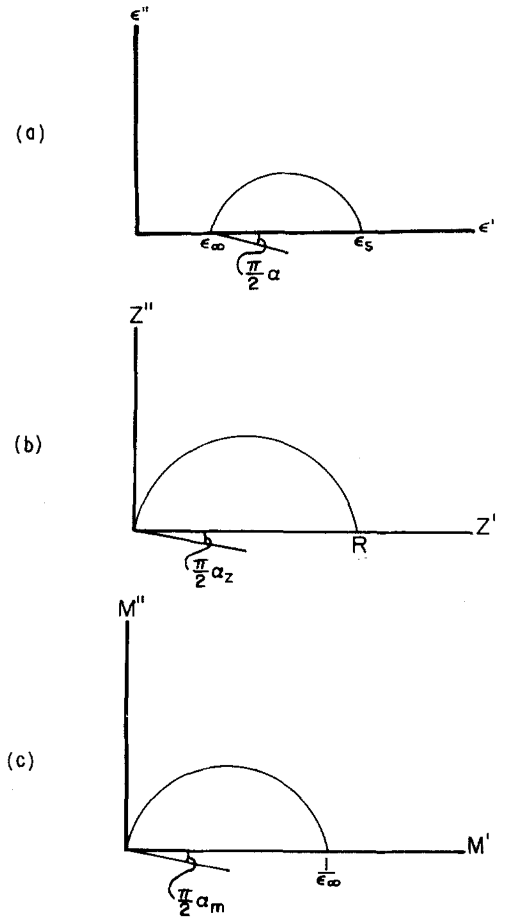

Figure 1 Schematic representation of (a) complex dielectric constant, (b) complex impedance and (c) complex electric "modulus".

Equation 7 can be expanded as

$$Z^* = \frac{R}{1 + \sin\frac{\pi}{2}\alpha_z(\omega\tau_z)^{1-\alpha_z} + j\cos\frac{\pi}{2}\alpha_z(\omega\tau_z)^{1-\alpha_z}}. \tag{9}$$

On the other hand, the substitution of Equations 3, 4 and 5 into Equation 1 gives

$$Z^* = \left[R \quad 1 + \omega(\epsilon_0\epsilon_\infty/\sigma)(\Delta\epsilon/\epsilon_\infty)\cos\frac{\pi}{2}\alpha(\omega\tau)^{1-\alpha} \quad \left\{\left[1 + \sin\frac{\pi}{2}\alpha(\omega\tau)^{1-\alpha}\right]^2 + \left[\cos\frac{\pi}{2}\alpha(\omega\tau)^{1-\alpha}\right]^2\right\}^{-1}\right. \tag{10}$$

$$\left. + j\left(\omega\frac{\epsilon_0\epsilon_\infty}{\sigma} + \omega(\epsilon_0\epsilon_\infty/\sigma)(\Delta\epsilon/\epsilon_\infty)\left[1 + \sin\frac{\pi}{2}\alpha(\omega\tau)^{1-\alpha}\right]\left(\left\{\left[1 + \sin\frac{\pi}{2}\alpha(\omega\tau)^{1-\alpha}\right]^2 + \left[\cos\frac{\pi}{2}\alpha(\omega\tau)^{1-\alpha}\right]^2\right\}^{-1}\right)\right)\right]^{-1}$$

When $\Delta\epsilon/\epsilon_\infty$ is zero, Equation 10 becomes

$$Z^* = \frac{R}{1 + j\omega(\epsilon_0\epsilon_\infty/\sigma)} \qquad (10a)$$

thus Z'' has the maximum at $\omega\tau_z = 1$, and $\tau_z = \epsilon_0\epsilon_\infty/\sigma$, which is identical with Equation 6. Therefore, for specimens with small $\Delta\epsilon/\epsilon_\infty$, Z'' maximum is expected near $\omega\tau_z = \omega\tau = 1$. At Z'' maximum, i.e. at $\omega\tau = 1$, Equation 10 becomes

$$Z^* = R\left\{1 + \frac{(\Delta\epsilon/\epsilon_\infty)\cos\frac{\pi}{2}\alpha}{2\left(1+\sin\frac{\pi}{2}\alpha\right)} + j\left(1 + \frac{(\Delta\epsilon/\epsilon_\infty)}{2}\right)\right\}^{-1}. \qquad (11)$$

Thus, in order to make Z^* given by Equation 9 approximate to that given by Equation 10, for small $\Delta\epsilon/\epsilon_\infty$, α_z must be given by the following equation:

$$\tan\frac{\pi}{2}\alpha_z = \frac{(\Delta\epsilon/2\epsilon_\infty)\left[\cos\frac{\pi}{2}\alpha\Big/\left(1+\sin\frac{\pi}{2}\alpha\right)\right]}{1 + (\Delta\epsilon/2\epsilon_\infty)} \qquad (12)$$

This is shown in Fig. 2 using $(\pi/2)\alpha$ as a parameter.

The extent of approximation employed is shown in Fig. 3, where the impedance is plotted on a complex plane for $\Delta\epsilon/\epsilon_\infty = 0$ (solid line) and for $\Delta\epsilon/\epsilon_\infty = 0.1$, $(\pi/2)\alpha = 40°$ (broken line). Here, data points were calculated using Equation 10 and $\tan(\pi/2)\alpha_z$ was calculated using Equation 12.

Similarly, equations for M^* are

$$M^* = \frac{1/\epsilon_\infty}{1 + \sin\frac{\pi}{2}\alpha_m(\omega\tau_m)^{1+\alpha_m} - j\cos\frac{\pi}{2}\alpha_m(\omega\tau_m)^{1+\alpha_m}} \qquad (13)$$

and

$$M^* = \frac{1}{\epsilon_\infty}\left[1 + (\Delta\epsilon/\epsilon_\infty)\left[1+\sin\frac{\pi}{2}\alpha(\omega\tau)^{1-\alpha}\right]\left\{\left[1+\sin\frac{\pi}{2}\alpha(\omega\tau)^{1-\alpha}\right]^2 + \left[\cos\frac{\pi}{2}\alpha(\omega\tau)^{1-\alpha}\right]^2\right\}^{-1}\right.$$
$$\left. -j\left(\frac{\sigma}{\omega\epsilon_0\epsilon_\infty} + (\Delta\epsilon/\epsilon_\infty)\cos\frac{\pi}{2}\alpha(\omega\tau)^{1-\alpha}\left\{\left[1+\sin\frac{\pi}{2}\alpha(\omega\tau)^{1-\alpha}\right]^2 + \left[\cos\frac{\pi}{2}\alpha(\omega\tau)^{1-\alpha}\right]^2\right\}^{-1}\right)\right]^{-1} \qquad (14)$$

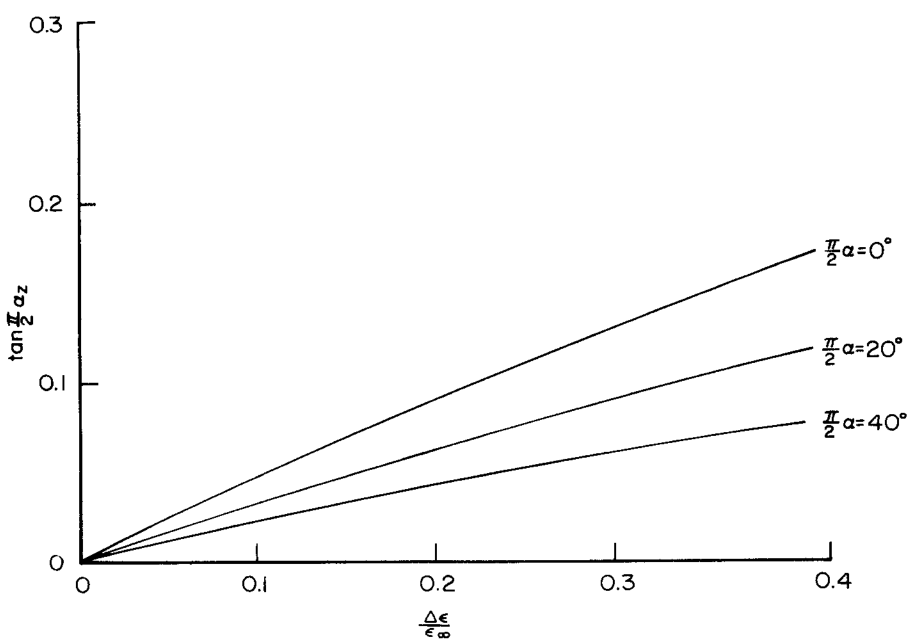

Figure 2 Relationship between $\tan(\pi/2)\alpha_z$ and $\Delta\epsilon/\epsilon_\infty$ as it varies with the $(\pi/2)\alpha$ parameter.

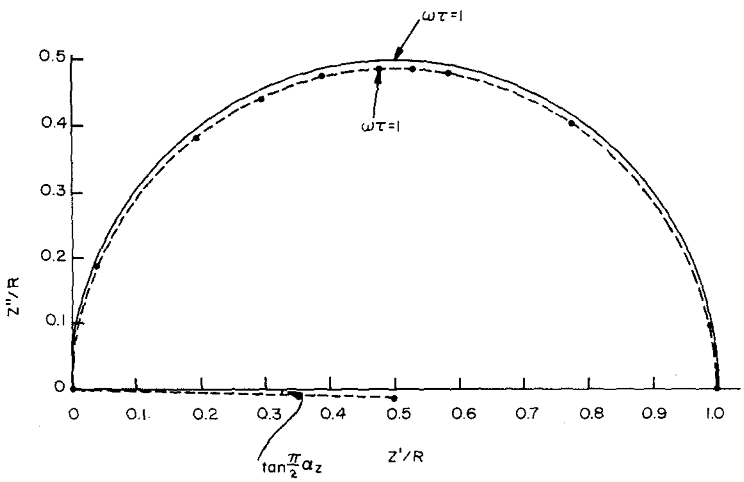

Figure 3 Complex impedance according to Equation 10 for $\Delta\epsilon/\epsilon_\infty = 0$ (solid line) and for $\Delta\epsilon/\epsilon_\infty = 0.1$, $(\pi/2)\alpha = 40°$ (broken line).

Similarly to Z'', for specimens with small $\Delta\epsilon/\epsilon_\infty$, the M'' maximum is expected near $\omega\tau_m = \omega\tau = 1$.

At M'' maximum, i.e., at $\omega\tau = 1$, Equation 14 becomes

$$M^* = \frac{1}{\epsilon_\infty}\left\{1 + \frac{\Delta\epsilon}{2\epsilon_\infty} - j\left[1 + \frac{\dfrac{\Delta\epsilon}{\epsilon_\infty}\cos\dfrac{\pi}{2}\alpha}{2\left(1+\sin\dfrac{\pi}{2}\alpha\right)}\right]\right\}^{-1} \tag{15}$$

Thus, in order to make M^* given by Equation 13 approximate to that given by Equation 14, for small $\Delta\epsilon/\epsilon_\infty$, α_m must be given by the following equation.

$$\tan\frac{\pi}{2}\alpha_m = \frac{\Delta\epsilon/2\epsilon_\infty}{1 + (\Delta\epsilon/2\epsilon_\infty)\left[\cos\dfrac{\pi}{2}\alpha \Big/ \left(1+\sin\dfrac{\pi}{2}\alpha\right)\right]}. \tag{16}$$

This is shown in Fig. 4 using $(\pi/2)\alpha$ as a parameter.

The extent of approximation employed is shown in Fig. 4, where the electric "modulus" is plotted on a complex plane, for $\Delta\epsilon/\epsilon_\infty = 0$ (solid line) and for $\Delta\epsilon/\epsilon_\infty = 0.1$, $(\pi/2)\alpha = 40°$ (broken line). Here data points were calculated using Equation 14 and tan $(\pi/2)\alpha_m$ was calculated using Equation 16.

Combining Equations 12 and 16,

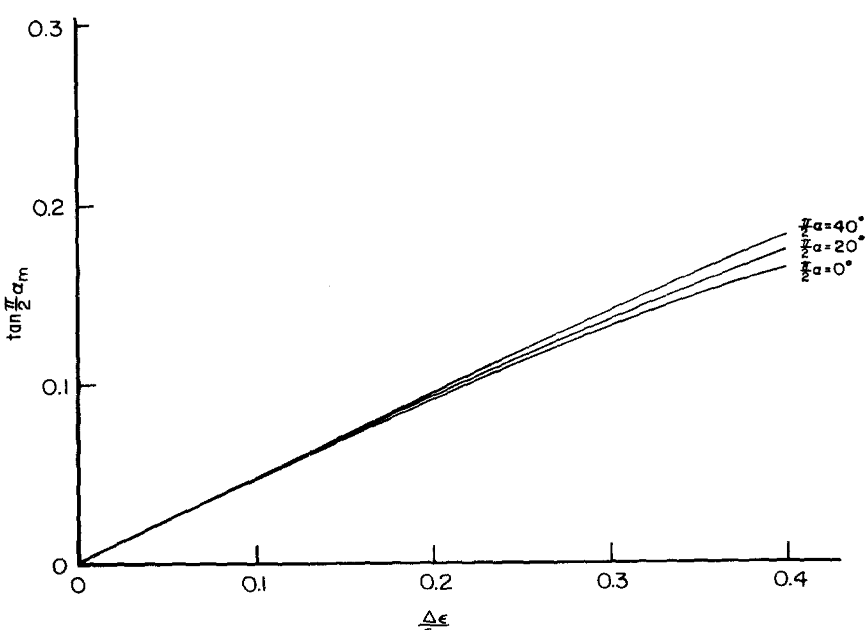

Figure 4 Relationships between tan $(\pi/2)\alpha_m$ and $\Delta\epsilon/\epsilon_\infty$ as $(\pi/2)\alpha$ parameter.

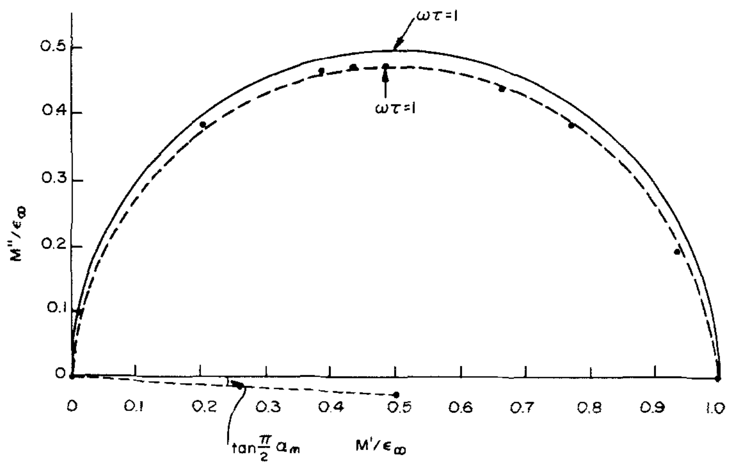

Figure 5 Complex electric "modulus" by Equation 14 for $\Delta\epsilon/\epsilon_\infty = 0$ (solid line) and for $\Delta\epsilon/\epsilon_\infty = 0.1$, $(\pi/2)\alpha = 40°$ (broken line).

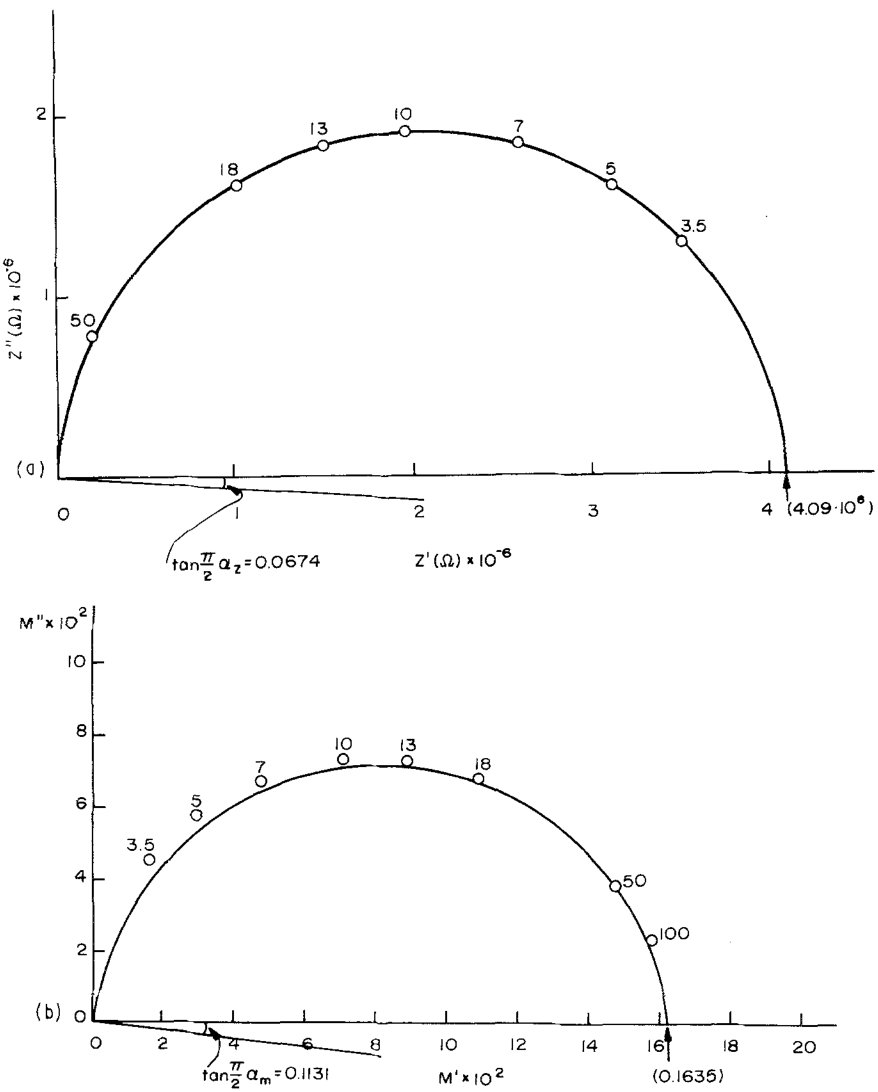

Figure 6 An example of experimental data for 1120 p.p.m. $Na_2O–GeO_2$ glass at 375° C. (Numbers in the figures are frequency in kHz.) (a) Complex impedance, (b) complex electric "modulus".

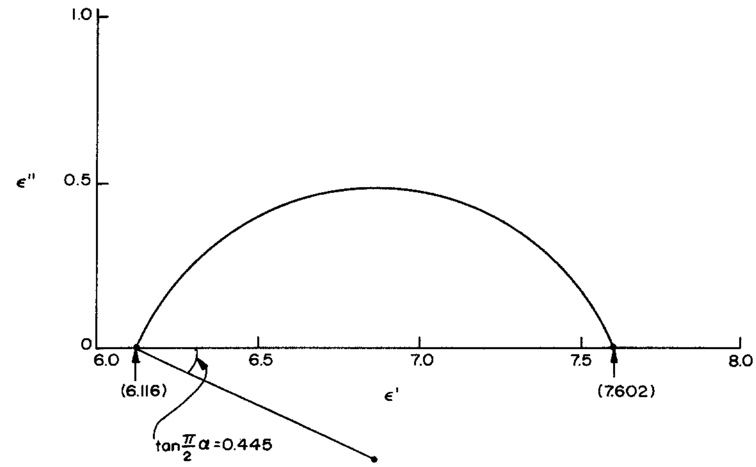

Figure 7 Complex dielectric constant for 1120 p.p.m. Na_2O-GeO_2 glass at 375° C, obtained by the present method.

$$\frac{\Delta\epsilon}{\epsilon_\infty} = \frac{2\tan\frac{\pi}{2}\alpha_m\left(\tan\frac{\pi}{2}\alpha_z + 1\right)}{1 - \tan\frac{\pi}{2}\alpha_z \cdot \tan\frac{\pi}{2}\alpha_m}. \qquad (17)$$

Equation 17 shows that the small dielectric strength $\Delta\epsilon/\epsilon_\infty$ can be evaluated from α_m and α_z without the usual d.c. conductivity subtraction procedure. Once $\Delta\epsilon/\epsilon_\infty$ is obtained, the parameter α can be determined either from Fig. 3 (or Equation 12) or Fig. 5 (or Equation 16). Thus, the complete low frequency dielectric characteristics can be determined from the complex impedance plot and complex electric "modulus" plot.

3. Application to the experimental data

To demonstrate the use of Equations 12, 16 and 17, experimental data of high purity GeO_2 glass with 1120 p.p.m. Na_2O was used. Dissipation factor $\tan\delta$ and capacitance were determined as a function of frequency and temperature, using a GenRad capacitance bridge type 1615. Complex impedance and complex electric "modulus" were calculated and are shown in Figs. 6a and b respectively. Experimental data on $\tan(\pi/2)\alpha_z$ and $\tan(\pi/2)\alpha_m$ from Fig. 6 were used to calculate $\Delta\epsilon/\epsilon_\infty$ from Equation 17. The value of 0.243 was obtained for $\Delta\epsilon/\epsilon_\infty$ at 375° C for this specimen. Using this value and $\tan(\pi/2)\alpha_z$, $(\pi/2)\alpha = 24°$ $(\tan(\pi/2)\alpha = 0.445)$ was obtained from Fig. 3, (or Equation 12). These results are shown in Fig. 7, using the value of $\epsilon_\infty = 6.116$, obtained from the complex electric "modulus" plot (M' maximum corresponds to $1/\epsilon_\infty$, cf. Fig. 1c).

4. Conclusion

Equations 12, 16 and 17 were derived using assumptions $\tau_z \simeq \tau_m \simeq \tau \simeq \epsilon_0\epsilon_\infty/\sigma$. The relation, $\tau \simeq \epsilon_0\epsilon_\infty/\sigma$, has been found approximately true for a number of materials [1, 3, 5, 8] including conventional ionic conducting glasses, electronic conducting glasses and single as well as polycrystalline ceramics. The relation $\tau_m = \tau_z = \epsilon_0\epsilon_\infty/\sigma$ holds for any material with a small value of $\Delta\epsilon/\epsilon_\infty$. Therefore, the results in this paper are expected to be applicable to a variety of materials with low concentrations of charge carriers. Since the d.c. conductivity subtraction procedure which causes a large error can be circumvented, the low frequency dielectric relaxation characteristics such as the relative dielectric strength $\Delta\epsilon/\epsilon_\infty$ and the parameter describing the broadness of the dielectric loss peak α can be obtained with reasonable accuracy.

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