Chapter 8

Electrical Properties of Porous Alumina Ceramics Fabricated using Rice Husk and Sucrose

8.1. Introduction

Alumina (Al_2O_3) has been recognized as one of the most common and important ceramic materials for both low and high temperature structural as well as functional applications. High refractoriness, good thermal properties, high temperature mechanical strength, good corrosion, erosion, abrasion and oxidation resistance, chemical inertness, dimensional stability, superior hardness, low density etc. make alumina ceramics suitable for various structural and functional applications.[159] Alumina possesses strong ionic inter atomic bonding giving rise to its desirable characteristics. Apart from this, despite its low dielectric constant ($\varepsilon' = 8-10$),[160] at high frequencies (around GHz) the dielectric properties of alumina are attractive for various applications because of its low dielectric loss. Values of loss tangent (tan δ) as low as $2x10^{-5}$ have been reported.[161] Various electrical and electronic applications of alumina includes substrate in electronic packaging, in sensors, high temperature electrical insulators, gas laser tubes, high voltage insulators, dielectric resonators, patch antennas, spark plugs for high compression automobile and air craft engines etc.[162] Dielectric properties of alumina are of interest, considering its wide range of electrical and electronic applications. Various authors have studied dielectric properties of alumina. Farag et al. have studied the effect of doping on dielectric properties of alumina.[163] Huang et al. have studied microwave dielectric properties of nano alpha-alumina.[164] In addition to dense alumina, porous alumina also finds importance in various electrical applications particularly in fields like sensors, substrates, high temperature radome applications, etc. These applications require porous alumina with controlled porosity, microstructure and dielectric properties. Incorporation of various sizes of pores in a ceramic material provides a wide range of dielectric constant mainly for high frequency applications. Using various levels of porosity in order to alter the effective dielectric constant in the same material allows patterning different dielectric constants in a single unit. Therefore, controlling the porosity and

microstructure of pores can yield a wide range of dielectric constant in a single material.[165] The requirement for the ceramic matrix and porous microstructure may vary depending on the end use and type of the application area.

A few studies based on dielectric properties of porous alumina have been found in the literature. Penn. et al. studied effect of porosity and grain size on microwave dielectric properties of sintered alumina.[166] Brouers et al. have reported a dielectric anomaly in electrolyte-saturated porous alumina ceramics.[167] Pawlowski et al. reported the relationship between structure and dielectric properties in plasma sprayed alumina coatings. They studied the effect of porosity on dielectric constant and loss tangent of the porous alumina coatings.[168]

Considering the wide range of applications of alumina in electrical devices and importance of influence of porosity and pore microstructure on dielectric properties of porous alumina, the present study is aimed at fabrication of porous alumina with wide range of tailored dielectric properties through tailoring of porosity and pore microstructure. Porous samples were fabricated using low cost additives such as rice husk (RH), an agricultural waste as pore former and sucrose as binder as well as a pore former taking into account the cost effectiveness of the product. Microstructure of prepared samples was controlled by varying the volume fraction and size of RH pore former in the composition. Dielectric properties of the developed samples were measured and co-related with their porous microstructure. Also, effect of frequency and temperature on the measured dielectric properties has been investigated. A reference sample of dense alumina (2% porosity) was also fabricated intentionally through the same process without using RH pore former. The microstructure and corresponding dielectric properties of the reference dense alumina sample were also studied.

In the present investigation we also tried to compare our experimental results with the predicted values obtained using theoretical models equations from literature for a porous material system. Although the present study is focused on porous alumina ceramics, we would like to emphasize that the results of this study should also be valid for tailoring of dielectric properties through control of pores' microstructure for other materials also.

8.2. Sample Preparation and Characterization

The procedure for making ceramic mixtures for different compositions have been discussed in chapter 5. Specifically to make samples for electrical property measurement, the ceramic mixture of different compositions were dry pressed into circular disk shaped pellets (15 mm x 5 mm thick approximately). The samples were then processed as per the schedule given in chapter 5.

Dielectric properties of samples were measured at room temperature as well as at successive higher temperatures up to 500˚C using a Novo Control Alpha-A High Performance Frequency Analyzer in the frequency range 1 Hz to 1 MHz at an applied AC voltage of 1V. For dielectric measurements, the sintered porous alumina samples were polished using fine emery papers to make the surfaces smooth and parallel for better contact with the electrodes. After polishing, the samples were dried at 150˚C for 4 h to remove moisture (if any) and then cooled to room temperature before inserting between the electrodes. Dielectric constant, ε' and loss tangent, $\tan \delta$ measurements were made on disk shaped samples (13 mm x 4 mm thick). Two probe electrical measurements were carried out on each sample pellet coated with silver paint on both the surfaces. Before making measurements, the surfaces were checked for good contact. The sample was located between two cell electrodes and then inserted into non-inductive furnace used for heating the samples at constant rate of heating. Temperature of the sample was measured using a thermocouple. Dielectric constant and loss tangent of samples were measured at different temperatures (room temperature to 500˚C) as a function of frequency (10^0-10^6 Hz). The real part, ε', of dielectric constant was calculated using the relation:

$$\varepsilon' = \frac{LC_s}{A\varepsilon_0} \quad ....(8.1)$$

where L is the thickness in m, A is the sample area in m^2, C$_s$ is the capacitance in F and ε_0, the permittivity of free space= 8.85x10^{-12} C^2/Nm^2. Loss tangent, $\tan \delta$ was calculated from the relation:

$$\tan \delta = \frac{4\pi\sigma_{ac}}{\omega\varepsilon'} \quad ....(8.2)$$

ω is the angular frequency, σ_{ac} is the electrical conductivity of the sample.

Microstructure of the obtained porous samples for various composition was studied using SEM. The dielectric properties such as dielectric constant (ε´) and loss tangent, tan δ, of same porous alumina sample was measured as a function of frequency in the range 10^0-10^6 Hz at various temperatures between room temperature to 500˚C. Data obtained from dielectric measurements were co-related with the porosity and pore size of the porous compacts.

8.3. Theory

Dielectric properties of ceramic materials are of immense technological as well as scientific interest. One of the important parameters for any dielectric material is its dielectric constant or dielectric permittivity (ε) which is its ability to store charge in a capacitor. It represents the level of energy distribution inside the material.[161] In the presence of sinusoidal electric field, across a capacitor with lossy dielectric, the complex permittivity can be expressed as:

$$\varepsilon = \varepsilon´ - i\varepsilon´´ \quad ....(8.3)$$

where ε´ represents the real part of the permittivity (i.e., the dielectric constant) and characterizes the material's ability to store charge. ε´´ is the imaginary part of the permittivity which is a measure of the energy dissipation in the material. It is an indicator of the energy absorbing capability. Dielectric loss is generally described by loss tangent:

$$\tan \delta = \frac{\varepsilon´´}{\varepsilon´} \quad ....(8.4)$$

Dielectric constant in a crystalline solid results from electronic, ionic, dipole orientation and space charge contributions to the polarizability. Electronic contribution is always present and is the main contributor in the optical range of frequencies. About one third of the polarizability usually corresponds to electronic processes for ceramic materials. For materials with high refractive index, the electronic polarizability is more. For high dielectric constant oxide ceramics, ionic contributions overshadow the electronic part. In contrast, co-valent ceramics have no contribution from ionic polarizability. In ionic oxide ceramics, ionic polarizability arises from the displacement of ions of opposite sign from their regular lattice sites under the influence of an applied field and also from the

deformation of the electronic shells resulting from the relative displacement of the ions. For ions which are highly polarizable there is an additional contribution to the dielectric constant resulting from the deformation of electronic shells following the displacements of the ions. Orientational or ion jump polarization effects are normally not observed at room temperature but can be used as a sensitive tool for investigating relaxation phenomena. Space charge polarization for poly crystalline and poly phase materials occurs at high temperature. It is due to the interruption of the charge carriers at the phase boundary and buildup of charges at the interface. In this case, the grain boundaries or a grain boundary phase puts high resistance to the mobility of charge carriers. This increases the polarization and gives high dielectric constant.

Power dissipation in an insulator or capacitor is directly proportional to the dielectric loss factor, tan δ. The main advantage of ceramic materials as dielectrics is that this loss factor is small as compared to other materials. Energy loss in dielectrics results from three primary processes:

1. Ions migration losses

    a. DC conductivity losses

    b. Ions jump and dipoles relaxation losses

2. Ions vibration and deformation losses

3. Electronic polarization losses

The major factor affecting the use of ceramic materials is the ion migration losses which tend to increase at low frequencies and high temperature. Loss factor is directly correlated with the electrical conductivity. Conduction losses are small at frequencies greater than 10^0 Hz at room temperature, but these are important at low frequencies and high temperatures. In general ion jump relaxation between two equivalent ion positions is responsible for the largest part of the dielectric loss factor for crystals. Ions vibration and deformation losses become important at room temperature only at frequencies in the infrared region corresponding to 10^{12} to 10^{14} Hz but are not of a major concern for frequencies below about 10^{10} Hz. This is beyond the range of frequencies that are normally of concern for electronic

applications. These electron polarization losses give rise to absorption and colour in the visible spectrum.

At lower frequencies, conduction losses become important. At moderate frequencies, ions jump and dipole losses are most important. At intermediate frequencies dielectric losses are small and at sufficiently high frequencies ions polarization effects give energy absorption. For reasonably good insulators, the conductivity increases exponentially with temperature. Consequently, one can expect, that tan δ increases exponentially with temperature. Dielectric losses fall into two categories, intrinsic and extrinsic. Intrinsic losses are dependent on the crystal structure and can be described by the interaction of the phonons system with the ac electric field. AC electric field alters the equilibrium of the phonons system and the subsequent relaxation is associated with energy dissipation.[169] Fundamental review of the theory of intrinsic losses is presented by Gurevich.[170] These intrinsic losses set the lower limit of losses found in pure "defect –free" single crystals. Extrinsic losses are associated with imperfections in the crystal structure, e.g., porosity, impurities, microstructural defects, grain boundaries, microcracks, and random crystallites orientation etc. It is evident from the earlier studies[161] that the losses in sintered polycrystalline ceramics are strongly affected by these extrinsic factors. One of the most important extrinsic defect is the porosity and pore morphology such as pore size, connectivity, orientation, shape etc. which influences the loss in ceramics. Effect of these extrinsic factors on the dielectric properties of porous ceramics is investigated in the present work choosing porous alumina in terms of variation in porosity and pore microstructure.

8.3.1. Effect of porosity on dielectric constant (ε')

In porous materials, the porosity and pore microstructure introduces in homogeneities in the bulk sample. This alters the mechanisms of leakage and breakdown exhibited by the dense analog. The presence of pores in solid dielectrics significantly degrades the electrical characteristics. Porous ceramics can be visualized as a two-phase heterogeneous system where the pore phase is randomly distributed in a connected ceramic matrix phase.[171] The presence of pores yields local changes in the dielectric properties. At macroscopic scale of dimensions, the

measured value of dielectric constant can be denoted strictly as the equivalent dielectric constant. Since porous materials can be considered as a special case of composites (pore phase dispersed in alumina matrix phase), the equivalent dielectric properties depend on the type of porous microstructure such as volume fraction of pores, their size, shape, connectivity, orientation etc. The effect of these elements on dielectric constant (ε) could be characterized by mixture law using the following expression:[172]

$$\lg = \sum \varphi_i \lg \varepsilon_i \quad\text{...(8.5)}$$

where ϕ_i is the volume fraction of i phase, ε_i is the dielectric constant of i phase. Many effective models have been proposed in the literature to take the various situations into account for calculating the equivalent dielectric constant of porous crystalline ceramics. The models consider the dielectrics as a composite system of two dielectrics with different dielectric constants.[173] All these models are based on five basic structural models: specifically the series, parallel, Maxwell, Heidinger, etc.[174] These models are applicable to predict the dielectric properties of porous samples having nearly spherical pores. Another model commonly known as Maxwell-Garnet model which is appropriate for ellipsoidal shaped insulating inclusionss,[167] can be more suitable to predict the equivalent dielectric constant of RH based porous alumina samples having elongated (nearly elliptical) pores. The model shows two mechanisms to explain the dielectric anomaly in rocks. The first is due to presence of small plate like insulating inclusions (clay or other foreign particles) in the conducting rock. The argument is as follows: One starts from the Maxwell-Garnett formula giving the effective dielectric constant ε_{MG} of an ellipsoid made of material B coated by an ellipsoidal shell made of material A[167,175]

$$\varepsilon_{MG} = \varepsilon_A \frac{(1-g)\varepsilon_A + g\varepsilon_B + q(1-g)(\varepsilon_B - \varepsilon_A)}{(1-g)\varepsilon_A + g\varepsilon_B - qg(\varepsilon_B - \varepsilon_A)} \quad\text{.........................(8.6)}$$

where ε_A and ε_B are the dielectric constant of materials A and B respectively, q is the volume fraction of material B (porosity in this case) and g is the depolarization factor in the direction of the field.

The two effects have to be considered together. If one considers two types of ellipsoids: a concentration x_1 of prolate spheroids ($g\rightarrow0$), and a concentration x_2 of oblate spheroids ($g\rightarrow1$) the Maxwell-Garnet approximation can be generalized as:

$$\varepsilon_{MG}=\varepsilon_A \frac{1+(1-g_1)x_1\alpha_1+(1-g_2)x_2\alpha_2}{1-g_1x_1\alpha_1-g_2x_2\alpha_2} \quad\text{................................(8.7)}$$

with

$$\alpha_i=\varepsilon_A \frac{\varepsilon_B-\varepsilon_A}{\varepsilon_A+g_i(\varepsilon_B-\varepsilon_A)}; \; \alpha_i=1,2\text{.....................................(8.8)}$$

In fact, in porous ceramics there is a distribution of g values because there is a distribution of aspect ratio and therefore one has to average over ellipsoid orientations and depolarization factors, g.

8.3.2. Effect of porosity on loss tangent (tan δ)

Since loss tangent is affected by presence of pores, the porosity adds an additional term to loss. An initial plot of tan δ against porosity on a log-log plot suggested a straight line which would give a dependence of the form[160]

$$\tan \delta = AP^n \text{..(8.9)}$$

However, this form is not realistic as tan δ would become zero when the material is fully dense. A simple modification that was made to the above equation was to add a term for tan δ at zero porosity. This is more realistic, as it considered that the loss due to porosity is an additional term to the loss. Thus, the modified equation becomes

$$\tan \delta = \tan \delta_0 + AP^n \text{......................................(8.10)}$$

where $\tan \delta_0$ is the loss tangent of the fully dense material. A fit using this model gives $\tan \delta_0= 1.322 \times10^{-5}$, $A= 1.298\times10^{-2}$ and $n= 1.73$. A further refinement to this model would be to consider that since $\tan \delta_0$ is due to the fully dense material, this term should depend on the amount of material present, i.e., it should depend on the porosity, so that

$$\tan \delta = (1-P) \tan \delta_0 + AP^n \text{.............................. (8.11)}$$

Eqn. 8.11 can be rearranged to put it into the form of mixture law

$$\tan \delta = (1\text{-}P) \tan \delta_0 + P\left(AP^{(n\text{-}1)}\right) \ldots \ldots \ldots \ldots \ldots (8.12)$$

It can be seen that there is very little difference between Eqn. 8.11 and Eqn. 8.12. The data were fitted to this model Eqn. 8.12 which gives $\tan \delta_0 = 1.336 \times 10^{-5}$, $A = 1.298 \times 10^{-2}$ and $n = 1.73$. Eqn. 8.12 is a good fit to the data which gives $\tan \delta$ of a 100% dense ceramic which is more as compared to that of a single crystal ceramic. This is expected as even in a fully dense ceramic there will be sources of loss e.g., random grain orientation and grain boundaries which are not present in a single crystal. It is not unreasonable to consider that the loss may be related to the surface area of the porosity as the structure of the alumina at the surface of a pore is different from that of the alumina in the bulk matrix.

8.4. Results and Discussion

Dielectric properties (ε') and $\tan \delta$ of RH based porous alumina compacts have been examined as a function of two parameters such as frequency and temperature and two microstructural parameters such as porosity and pore size. The experimental results have been compared with the predicted values of ε' and $\tan \delta$ using appropriate models and theories.

8.4.1. Dielectric constant

A. Effect of frequency and temperature

Variation of dielectric constant (ε') with frequency as a function of temperature (room temperature to 500°C) for the reference alumina sample and other porous samples with varying porosity and microstructure is shown in Fig. 8.1 (a)-(c). It is seen that ε' value decreases with increase in frequency at all temperatures irrespective of the sample composition and microstructure. Such a behavior is a general trend for most dielectric ceramic materials. With increase in frequency, fast variation of the electric field takes place which is responsible for scattering of charge carriers at high frequencies. This process leads to random orientation of dipole moments and accordingly decreases value of ε'. According to Koop's model[176] the dielectric constant at low frequency comes from the grains as well as pore boundaries which have a high dielectric constant. At high frequency, ε' results from the grains which have a small dielectric constant.
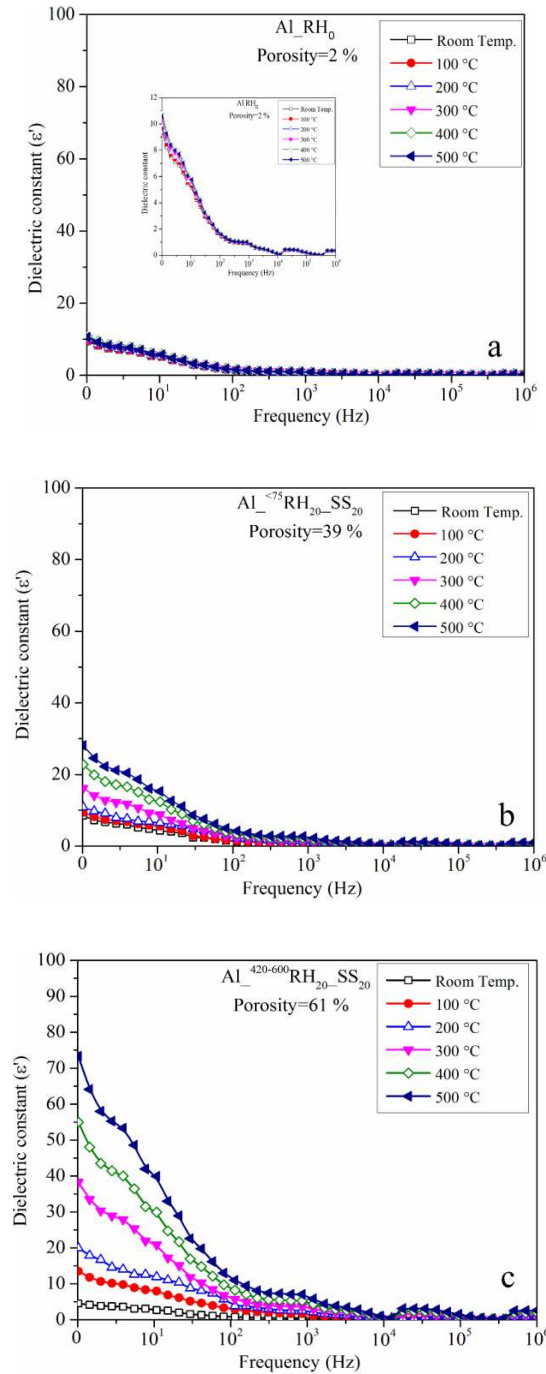
Fig. 8.1 Variation of dielectric constant of porous alumina samples as a function of frequency at different temperatures with porosities (a) 2% (b) 39% (c) 61%.

The general feature of the curves in Fig. 8.1 (a)-(c) is that these consist of three regions according to the rate of decrease of dielectric constant. The first region, defined by the frequency range (10^0-10^2 Hz), shows a sharp decrease in dielectric constant with frequency. The second region which is in the intermediate

frequency range (10^2-10^4 Hz), is characterized by a comparatively slow decrease in the ε value. In the high frequency region (10^4-10^6 Hz), the dielectric constant is almost constant and nearly temperature and frequency independent. The decrease in ε´ in the high frequency region is mainly because of the conduction losses and Maxwell Wagner effect.[177] In general, the frequency dependence of ε´ can be explained due to the mixed contribution of ions jump, conduction losses and interfacial effects.

Decrease in dielectric constant can be explained on the basis of decrease in polarization with the increase in frequency. It is well known that polarization of a dielectric material is the sum of the contributions of electronic, ionic, dipolar and interfacial polarizations. At low frequencies, all the polarizations respond easily to the time varying electric field. As the frequency of the electric field increases, different polarization contributions filter out, as a result, the net polarization of the material decreases which leads to the decrease in the value of ε´. Little fluctuations in the ε´ value in the high frequency regions may be because of the polarization effects at the electrodes.

Fig. 8.1 (a)-(c) also shows the dependence of the dielectric constant (ε´) of the investigated porous alumina samples with temperature as a function of frequency. As expected, ε´, increases with increase in temperature at each frequency level. This can be attributed to contribution of more than one type of polarization at high temperature. At very low temperature, electronic polarization contributes to the overall dielectric constant. With increase in temperature, other polarizations such as ionic and dipolar polarizations also add to the overall dielectric constant. At high temperature, orientational and space charge polarization may start leading to much higher value of dielectric constant. At higher temperature, however, there is an increasing contribution resulting from ion mobility and crystal imperfections mobility. Also, at higher temperature, dc conductivity effects which increase exponentially with temperature become important. The combined effect of all these processes is to give a sharp rise in the dielectric constant with increasing temperature, corresponding to both ion jump orientation effects and space charge effects resulting from the increased concentration of charge carriers.

Rise of dielectric constant with increase in temperature can be divided into two ranges. The first range (from room temperature up to 200˚C), magnitude of dielectric constant is small. In this temperature range the electronic polarization may be the most predominant one where it needs very small thermal energy and small electric field for the polarization process. Obviously, the electronic polarization is nearly field independent in this temperature region except for small electric field. Such a behavior is general in ionic solids. In the second range (200-500˚C), the magnitude of dielectiric constant increases at a faster rate with temperature. This can be attributed to contribution of other types of polarizations which include Maxwell-Wagner polarization, orientational polarization etc. This appears in the intergranular regions. The space charge contribution, which depends on the purity and imperfections, may also start to play a role in the polarization process at high temperature. At higher temperatures, the charge carriers are free to move through the sample causing different types of polarization and hence ε' increases. Table 8.1 shows the data of dielectric constant for various samples with temperature at 1Hz. The reference alumina sample (2% porosity) shows ε value of 9.42 to 10.9 in the temperature range (room temperature to 500˚C). In comparison Govindaet al.[178] reported ε value of 9.4 of Al_2O_3 at 30˚C which is frequency dependent.

B. Effect of pore microstructure

In addition to examining the changes in ε' as a function of frequency and temperature, we also examined dependence of dielectric constant at various temperatures for all samples on the microstructure (porosity and pore size). Fig. 8.2 (a)-(c) shows the variation of dielectric constant of porous alumina samples with increase in porosity as a function of frequency at room temperature, 200˚C and 500˚C, respectively.

Table 8.1 Variation of dielectric constant of porous alumina samples as a function of porosity and pore size at different temperatures.

| $Al\_^xRH_y\_SS_{20}$	Microstructure		Dielectric constant (ε')					
	Porosity(%)	Avg. Pore size (µm)	Room Temp.	100°C	200°C	300°C	400°C	500°C
$Al\_RH_0\_SS_{05}$ (Reference sample)	2	4	9.42	9.6	10.1	10.3	10.6	10.9
$Al\_^{<75}RH_{10}\_SS_{20}$	22	52	6.3	8.5	9.7	12.8	13.6	18.7
$Al\_^{75-180}RH_{10}\_SS_{20}$	24	145	6.2	8.7	10.0	13.2	20.7	27.9
$Al\_^{<75}RH_{20}\_SS_{20}$	39	64	5.8	9	10.9	16.2	16.2	28.1
$Al\_^{75-180}RH_{20}\_SS_{20}$	43	165.7	5.6	10.9	11.78	17.5	23.3	32.8
$Al\_^{180-355}RH_{20}\_SS_{20}$	45	320.5	5.4	11.1	14.5	26.2	32.0	45
$Al\_^{355-420}RH_{20}\_SS_{20}$	54	480	5.0	12.4	18.2	35.4	45.9	56.2
$Al\_^{420-600}RH_{20}\_SS_{20}$	61	510	4.5	13.5	19.9	38.3	55.0	73.3
$Al\_^{75-180}RH_{30}\_SS_{20}$	59	170	4.1	13.2	15.4	27.6	46.7	69.4
$Al\_^{<75}RH_{40}\_SS_{20}$	62	66	5.2	10.5	12.3	19.7	31.1	46.4
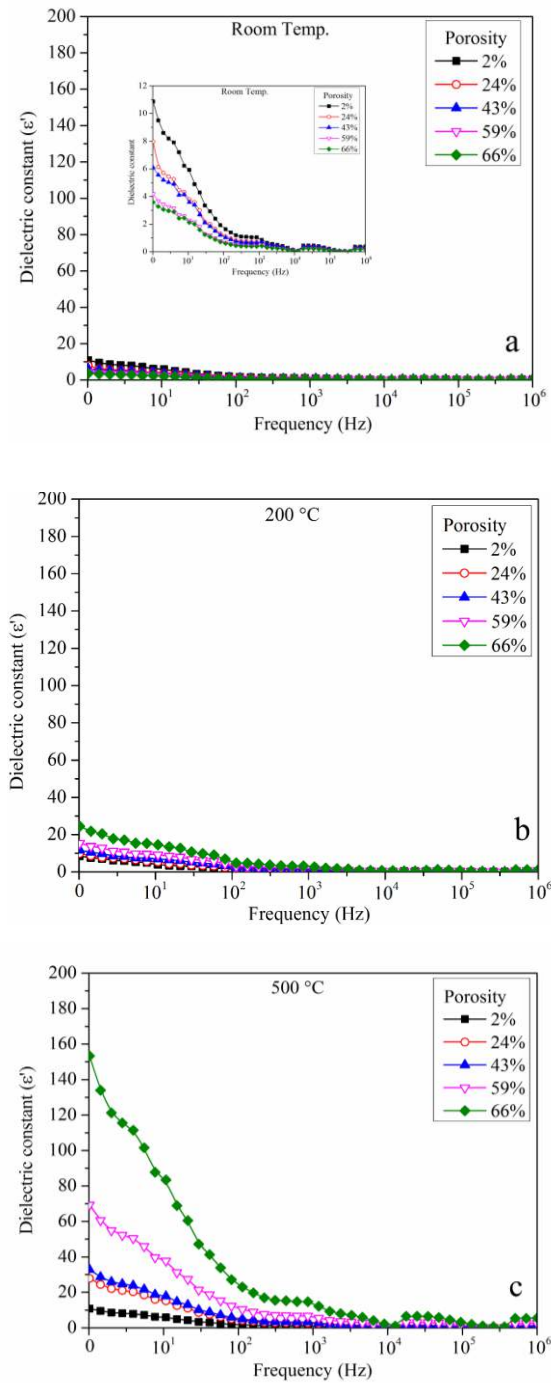
Fig. 8.2 Variation of dielectric constant of porous alumina samples as a function of frequency with increasing in porosity at (a) Room temperature (b) 200˚C and (c) 500˚C

The result shows that dielectric constant decreases dramatically with the increase in porosity at room temperature. This observation has been reported by other researchers also.[172] Similarly, the ε value also decreases with increase in pore size (Fig. 8.3 (a)-(c)) of samples when measured under similar conditions. This

observation can be attributed to the rule of mixture as expected, which has already been mentioned in Eqn. 5.[179] As the porous specimen contains air inside the pores and the ε value of air is comparatively less than that of the matrix (alumina in this case), as per the mixture rule, the dielectric constant of the resultant porous ceramics will be proportionately less depending on the volume fraction of porosity and pore size. Also, even presence of a small amount of moisture (if present) in the pores will decrease the dielectric constant of samples at room temperature. In the presence of moisture, polar water molecules increase the bonding strength with the other molecules present on the pore surfaces. These limit the freedom of movement of charge carriers inducing a reduced effect on the dielectric constant. In highly porous samples, the solid material content is less than the dense analog. This again reduces the total charge carried by the sample which reduces ε.
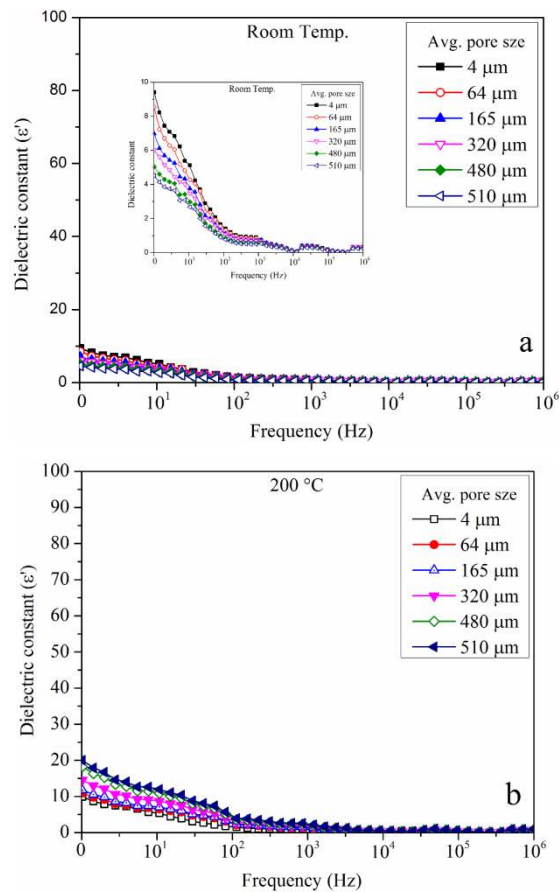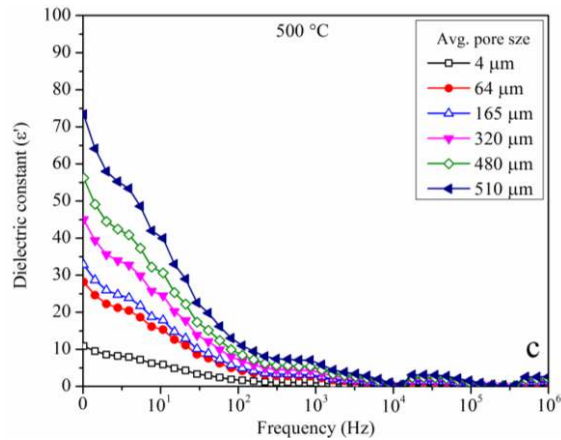
Fig. 8.3 Variation of dielectric constant of porous alumina samples as a function of frequency for different pore size at (a) Room temperature (b) 200˚C and (c) 500˚C

In contrast to the response of dielectric properties with increase in porosity and pore size at room temperature, at higher temperatures the value of ε and tan δ increases with increase in porosity and pore size. This observation can be attributed to rigorous multiple scattering of the charge carriers taking place at the pore surfaces[180] at higher temperatures. This decreases the effective dielectric constant of samples. With increase in porosity and pore size, the total pore surface area increases which leads to higher conductivity at high temperature and thus tan δ also increases. Also, with increase in porosity and pore size, the interfacial effects are more pronounced. This is responsible for significant increments in dielectric properties.

The sample $Al\_^{<75}RH_{10}\_SS_{20}$ having 22 % porosity and 52 μm avg. pore size exhibited maximum room temperature dielectric constant of 6.3. Similarly minimum dielectric constant of 3.6 was obtained for the sample $Al\_^{75-180}RH_{40}\_SS_{20}$ having 66 % porosity and 175 μm avg. size at room temperature. The corresponding dielectric constant of the samples at 500˚C was 18.7 and 153.3 respectively.

8.4.2. Loss tangent

A. Effect of temperature and frequency

Fig. 8.4 (a)-(c) shows the variation of tan δ with temperature as a function of frequency for the developed porous alumina samples.
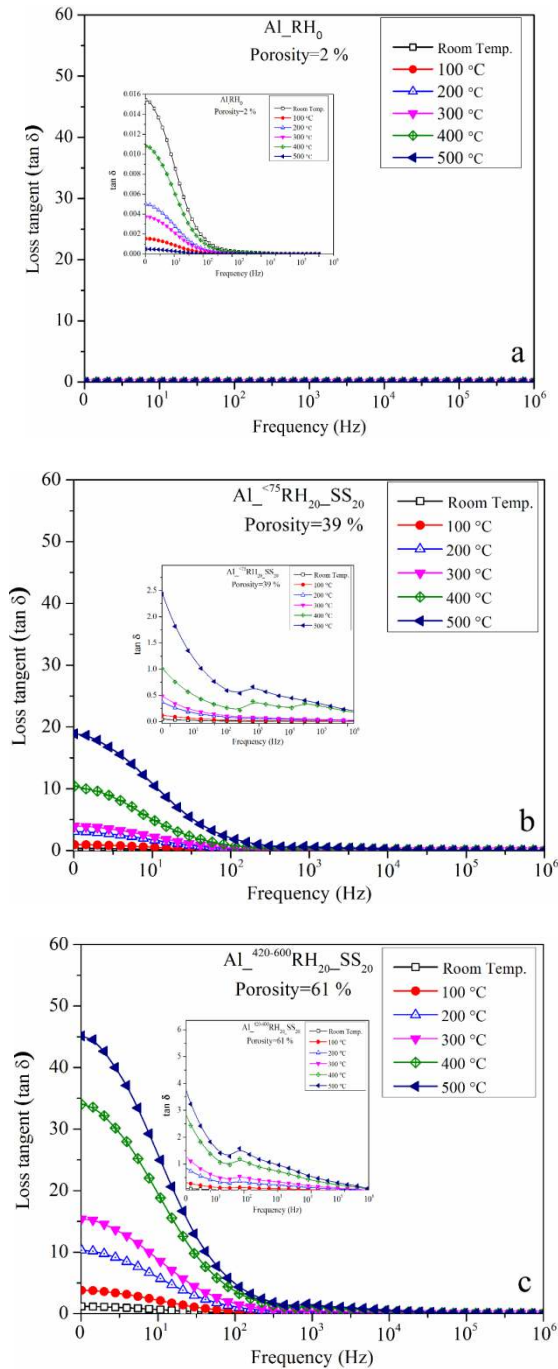
Fig. 8.4 Variation of loss tangent of porous alumina samples as a function of frequency at different temperatures with porosities (a) 2% (b) 39% (c) 61%.

Tan δ also decreases with increasing frequency at various temperatures similar to the response of dielectric constant with frequency. The decrease of tan δ with frequency could be accounted for using Koop's model.[179] In the low frequency region which corresponds to high resistivity (due to grains and pore boundaries)

more energy is required for mobility of charge carriers. Thus, the energy loss is high. In the high frequency range which corresponds to low resistivity (due to the grains and bulk of the sample), a small energy is needed for displacement of charge carriers in the grains and hence the energy loss is small. In the low frequency zone, fast decrease of tan δ is due to high loss. Only pores and free surface take part in the conduction and polarization process. In the intermediate frequency zone, relaxation takes place which leads to slow decrease in loss tangent value. It seems that tan δ value is in general small.

Unlike the trend of dielectric constant, tan δ versus frequency curve showed a maxima (hump) for all the samples. For the reference sample, the peak was not clearly visible due to extremely low values of loss tangent. Unlike normal Debye relaxation process, where the loss tangent shows a pronounced peak, in the present case, the same increases slowly and an anomalous non-Debye type relaxation process manifests. The effects of ion jump losses are visible here and manifested by the hump. For samples with low porosity, the effect of conduction loss is more pronounced over that of ion jump effects at very low frequencies. This is due to the fact that, for less porous samples, the structure is comparatively more compact and hence the probability of migration and conduction is more than that of the sample with higher porosity. Conduction losses dominate at very low frequencies compared to the ion-jump losses because of the lower porosity level, i.e., the more compact structure which allows relatively easy conduction. Also, the formation of maxima can be attributed to the possibility of formation of an ion pair due to the replacement of an aluminium ion with a divalent cation in the crystal lattice and the corresponding formation of a vacancy.[180] For the sample $Al\_^{<75}RH_{20}\_SS_{20}$ (porosity= 39%), the peak was observed at a frequency of approximately 10^3 Hz whereas for sample $Al\_^{420-600}RH_{20}\_SS_{20}$ (porosity= 61%) the obtained peak occurs at approximately 10^2 Hz. Shifting of the frequency of the peak with porosity of samples can be again related to the larger surface area and conduction losses for the sample having more porosity. It can be noted that the peak position (frequency) was independent of the temperature though the magnitude of loss tangent was more at high temperature.

The porous solid is assumed to be composed of pores, pore boundary, grains and grain boundaries. While the grains have low resistivity and large thickness, the grain boundaries and pore boundaries have high resistivity and small thickness. The observed peak in tan δ may be attributed to the contribution from the grain boundaries and pore boundaries, where the impurities and defects reside. These take part in the conduction in the low frequency range. The role of grains and bulk solid may appear at higher temperature.

Fig. 8.4 also shows increase in tan δ value with temperature. The reason is similar to that already described for dielectric constant. At low temperature, as the contribution to polarization is less, the conductivity also becomes small due to which the loss tangent is small. At high temperature, more than one type of polarization occurs which leads to high conductivity and hence high loss.

Another possible explanation for this can be that at room temperature, the interfacial polarization is negligible even at low frequencies. As the temperature is raised, the interfacial polarization increases. At the same time, the conduction losses and ion jump losses also increase. These can in one sense be considered local space charge polarization resulting from mobility barriers. The combined result is that, the conductivity increases at high temperature. The dielectric losses increase even more rapidly and hence high loss at higher temperature.

B. Effect of pore microstructure

The dependence of loss tangent on porosity and pore size as a function of frequency has been shown separately in Fig. 8.5 (a)-(c) and Fig. 8.6 (a)-(c).
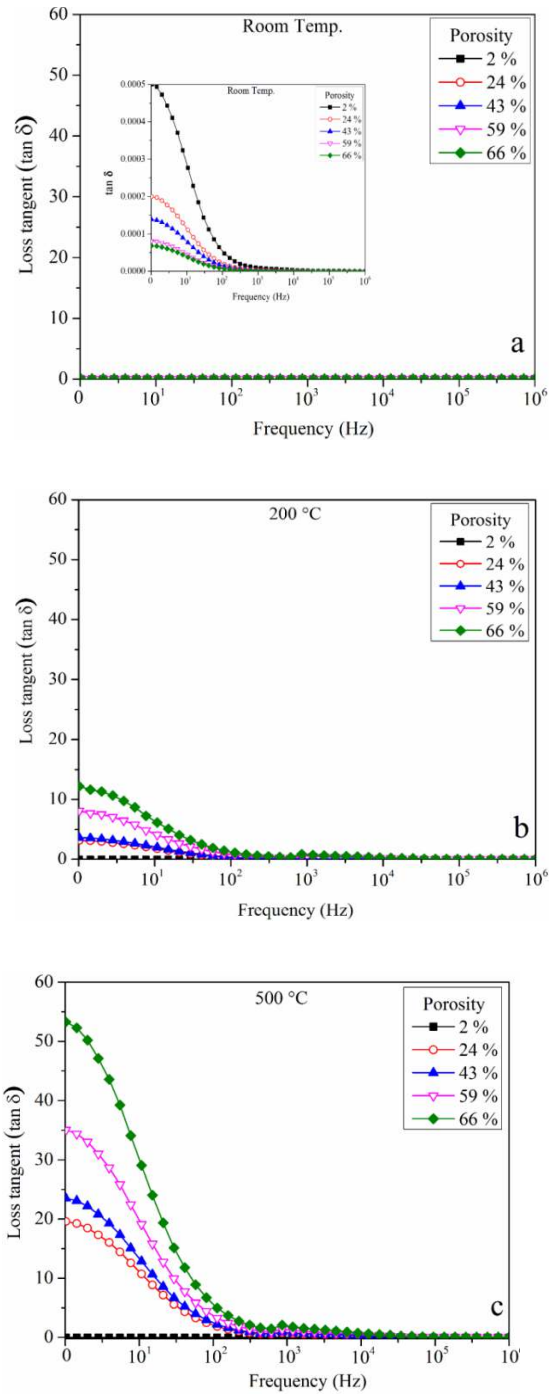
Fig. 8.5 Variataion of loss tangent of porous alumina samples as a function of frequency with increasing in porosity at (a) room temperature (b) 200˚C and (c) 500˚C
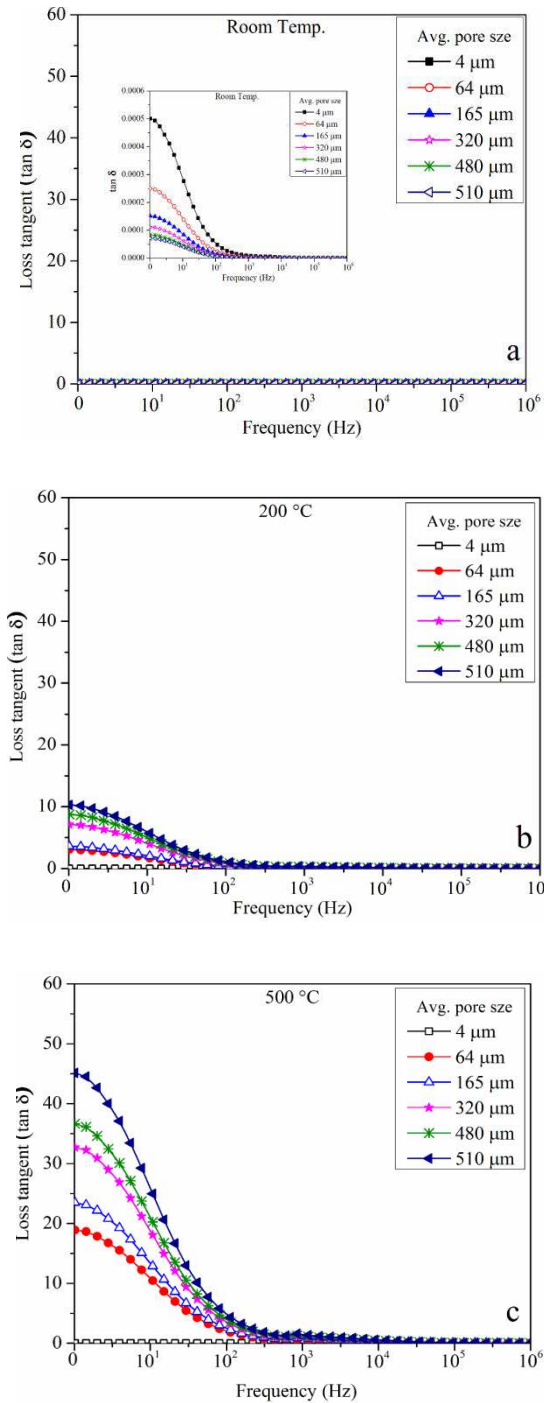
Fig. 8.6 Variation of loss tangent of porous alumina samples as a function of frequency for different pore size at (a) Room temperature (b) 200°C and (c) 500°C

Loss factor decreases with both increases in porosity and pore size. As already discussed for dielectric constant, the decrease in tan δ can be explained by mixture rule. Large number of pores and bigger pores add to increase in free surfaces and

interfaces in to the porous ceramics. Highly energetic free surfaces absorb electrical energy and lead to high conductivity and high loss at high temperatures.[181]

The sample $Al\_^{<75}RH_{10}\_SS_{20}$ having 22% porosity and 52 μm avg. pore size exhibited maximum room temperature loss tangent of 0.4×10^{-3}. Similarly minimum room temperature tan loss of 0.03×10^{-3} was obtained for the sample $Al\_^{75-180}RH_{40}\_SS_{20}$ having 66 % porosity and 175 μm avg. size. The corresponding tan δ values of the samples at 500˚C were 14.69 and 53.27 respectively. Table 8.2 lists the tan δ values for porous alumina samples as a function of porosity and pores size at different temperatures against each sample composition.

Table 8.2 Variation of loss tangent of porous alumina samples as a function of porosity and pore size at different Temperatures.

$Al\_^{x}RH_{y}\_SS_{20}$	Microstructure		Loss tangent (Tan δ)					
	Porosity (%)	Avg. Pore size (μm)	Room Temp.	100˚C	200˚C	300˚C	400˚C	500˚C
Al_RH$_0$ (Reference sample)	2	4	0.0005	.00 86	0.001	0.005	0.011	0.016
$Al\_^{<75}RH_{10}\_SS_{20}$	22	52	0.00044	0.6734	2.122	3.064	9.0718	14.68
$Al\_^{75-180}RH_{10}\_SS_{20}$	24	145	0.0004	0.9449	3.037	3.968	10.422	18.9
$Al\_^{<75}RH_{20}\_SS_{20}$	39	64	0.0003	1.0862	3.121	4.086	12.959	19.58
$Al\_^{75-180}RH_{20}\_SS_{20}$	43	165.7	0.0003	1.2306	3.592	4.76	13.902	23.49
$Al\_^{180-355}RH_{20}\_SS_{20}$	45	320.5	0.00034	2.3677	7.110	10.93	17.016	32.71
$Al\_^{355-420}RH_{20}\_SS_{20}$	54	480	0.0003	2.9833	8.745	14.22	31.115	36.63
$Al\_^{420-600}RH_{20}SS_{20}$	61	510	0.00027	3.812	10.30	15.42	34.032	45.14
$Al\_^{75-180}RH_{30}\_SS_{20}$	59	170	0.00002	3.236	8.050	14.69	19.276	35.04
$Al\_^{<75}RH_{40}\_SS_{20}$	62	66	0.00002	4.844	27.95	21.3	12.16	53.27
$Al\_^{75-180}RH_{40}\_SS_{20}$	66	175	0.00002	4.8441	12.16	21.3	27.95	53.27

8.4.3. Comparison of results

A. Prediction of dielectric constant at room temperature

Prediction of the equivalent dielectric constant of porous alumina with increase in porosity by analytical calculations requires knowledge of the ε´ values

of each phase. The dielectric constant of air and fully dense alumina were taken as[166] 1 and 9.42 (reference), respectively.[163] Fig. 8.7 shows the influence of porosity on room temperature dielectric constant of porous alumina ceramics, compared with the predicted values based on Maxwell-Garnet model equation for ellipsoidal shaped dispersed phase.
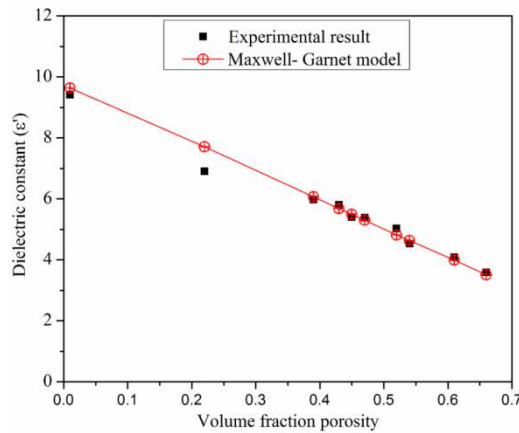

Fig. 8.7 Comparison of dielectric constant between the experimental results and Maxwell-Garnet model of the porous alumina ceramics with different amount and pore size of rice husk at room temperatures

The dielectric constant of a polycrystalline poly phase ceramics (in this case alumina phase and pore phase) depends on the individual ε values of the phases present. In this type of situations a "mixing theory" proposed by Maxwell-Garnet model is often applied to predict the effective dielectric constant of the two phase porous system,[167] as already described in the theory section (Eqn. 7).

From the Fig. 8.7, it can be observed that the experimental results are in close agreement with the Maxwell-Garnet equation. It is interesting to note that effective values of dielectric constant of most of samples within the porosity range 22 to 66 % are almost overlapping with the predicted values except for a few data points where there is a little deviation from the predicted graph. This may be due to the fact that other factors like pore size, distribution of pores, pore orientation pore connectivity etc. has not been considered in the predicted graph.

B. Prediction of loss tangent at room temperature

The experimental data were fitted to the model Eqn. 8.12 to give $\tan \delta_0 =$ 1.40×10^{-5} and A= 1.298×10^{-2} and n= 1.73. From the Fig. 8.8, it is observed that the results fit well to the graph of predicted results. Though a few experimental data points are almost tallying to the predicted ones, some of the data points show a considerable deviation from the predicted values. This deviation may be due to the following two reasons: first, the model equation for loss tangent has been derived considering the spherical pores in the dense matrix whereas the majority of the pores in the present work are ellipsoidal shaped pores. Secondly, various other microstructural factors related to pores such as distribution and orientation of pores, pore connectivity etc. has not been considered here during calculation.
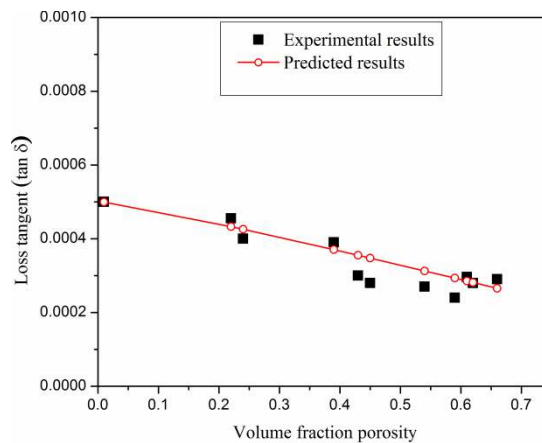

Fig. 8.8 .Experimental results for individual samples and fits to the models discussed in Section 8.2.2 (Eqn. 8.12).

Comparison of experimental results obtained for dielectric constant (ϵ') and loss tangent ($\tan \delta$) with the respective predicted values shows some variation between these two sets of data points. The reasons for the deviations have already been discussed separately. Apart from those, other factors such as presence of impurity, grain size, shape, orientation etc. have not been considered in the present study.

Also, the crystal structure defects in the surfaces and interfaces such as grains and pore boundaries also contribute to some extent to the effective dielectric

constant and loss tangent in the porous ceramics, which may be the reason for deviation of the experimental results.

8.5. Summary

1. The dielectric properties such as dielectric constant, ε' and loss tangent, tan δ of the samples were characterized by frequency analyzer at room temperature as well as at successive higher temperatures as a function frequency. The observed dielectric properties have been co-related with the microstructure of the samples such as porosity and pore size.

2. The dielectric constant and loss tangent of the porous alumina decreased with porosity and pore size at room temperature while it increased at successive higher temperatures. At room temperature, the mixture rule helps in decreasing the dielectric constant and loss tangent. In contradiction, at high temperature multiple scattering of charge carriers was due to large pore surfaces and interfaces with samples of high porosity.

3. Similarly, both ε' and tan δ decrease with increase in frequency and increases with increase in temperature. The decreasing trend of the loss part of the dielectric constant is primarily due to the conduction and the interfacial effects and is strongly influenced by the pore characteristics.

4. The hump in the ε' spectrum for the specimens especially with more porosity is because of the loss due to the ion-jump mechanism. However for specimens with low porosity, the hump is not pronounced.

5. The room temperature dielectric constant ranged from 6.3 (for sample $Al\_^{<75}RH_{10}\_SS_{20}$ having porosity 22 % and avg. pore size 52 µm) to 3.6 (for sample $Al\_^{75-180}RH_{40}\_SS_{20}$ having porosity 66 % and avg. pore size 175 µm.).

6. The measured experimental values of dielectric constant fitted well with the predicted model obtained from Maxwell-Garnet theory.

7. The tan δ values ranges between 0.0005 to 53.27.

8. Similarly the experimental data points of the tan δ values were close to the power law model.

9. A little deviation in the predicted results in comparison to the experimental results can be explained in terms of the fact that the effects of various other parameters such as distribution and orientation of grains and grain boundaries, distribution and orientation of pores etc. have not been considered.