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DIELECTRIC CHARACTERIZATION OF POWDERY SUBSTANCES USING AN INDIRECTLY COUPLED OPEN-ENDED COAXIAL CAVITY RESONATOR
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DIELECTRIC CHARACTERIZATION OF POWDERY SUBSTANCES USING AN INDIRECTLY COUPLED OPEN-ENDED COAXIAL CAVITY RESONATOR

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University of Oulu Graduate School; University of Oulu, Faculty of Information Technology and Electrical Engineering

Abstract

The main objective of this thesis was to research and develop a sensitive characterization method for dielectric powdery substances which could be utilized in various industrial and research fields.

With modern electromagnetic simulation tools and the presented experimental measurements, the characterization of dielectric powders using an indirectly coupled open-ended coaxial cavity resonator operating in TEM mode at 4.5 GHz was found to have potential. The modelling and the experimental measurement results of commonly used dielectric powders revealed that, from the nine classical mixing rules, it was possible to derive reliable inclusion permittivity values when using the properties of the perturbed resonator and the Bruggeman symmetric and the Looyenga mixing theories. In addition, the determination accuracy of the inclusion permittivity was found to be greatly improved with the correction factor included into the previously presented permittivity equation of the quarter wave coaxial resonator. Determination of the dielectric losses was found to be reliable when using the differences between the perturbed and unperturbed resonator and the general mixing model equation.

The sensitivity of the characterization method was researched with both humidity exposed and surfactant treated modified SiO$_2$, Al$_2$O$_3$ and ZrO$_2$ powders. Experimental results showed that the effect of adsorbed water on the particles was most pronounced when measuring the dielectric losses of the inclusions. Furthermore, a clear correlation with the theory of the general mixing model was found. Thus, in addition to the changed dielectric properties between dry and humidity exposed powders, it was also possible to determine the moisture content with reasonable accuracy. This correlated well with the traditional, mass based, determination. Stearic acid coating of the particles induced only a small change in inclusion permittivity but a notable change in dielectric losses. Unlike the cases with the larger particle sized SiO$_2$ and Al$_2$O$_3$, the dielectric loss of ZrO$_2$ inclusions, with stearic acid coating, was decreased significantly from 6.2 × 10$^{-3}$ to 3.8 × 10$^{-3}$.

When characterizing magnesium and calcium titanate composite powders, with CaTiO$_3$ molar ratios of 0.0, 0.02, 0.05 and 0.1, the method was found to have good sensitivity and accuracy. Additions of CaTiO$_3$ exhibited a clear increase in net inclusion permittivities from 13.4 up to 14.9 and in dielectric loss tangents from 7.1 × 10$^{-3}$ up to 8.5 × 10$^{-3}$. In addition, a good correlation was found in the theoretical determination of the CaTiO$_3$ molar ratios using the resonator measurement results and the general mixing model.

The characterization method was proved to be capable of measuring the dielectric properties and detecting even very slight changes in the powders. Thus, the method could be utilized in various types of powdery material characterization, for example, in the analysis and quality control of different composite powders.

Keywords: dielectric characterization, loss tangent, moisture content, permittivity, powder, stearic acid, surfactant treatment, titanate composite
Tuhkala, Marko, Epäsuorasti kytketyn avoimen koaksialioresonaattorin käyttö jauhemaisten aineiden dielektristen ominaisuuksien karakterisoinnissa. 
Oulun yliopiston tutkijakoulu; Oulun yliopisto, Tieto- ja sähköteknikan tiedekunta 
Oulun yliopisto, PL 8000, 900014 Oulun yliopisto

Tiivistelmä

Väitöstyön päätavoitteena oli tutkia ja kehittää herkkä jauhemaisten eristemateriaalien karakterisointimenetelmä, jota voitaisiin hyödyntää usealla teollisuuden ja tutkimuksen alueella. 


Karakterisointimenetelmän osoitettiin soveltuvan eristemateriaalien mittaustaan sekä havaitsemaan jauhemaisten aineiden eristemateriaalien ominaisuuksissa. Menetelmää voitaisiin hyödyntää useaamassa eristemateriaalien mittaamisissa, kuten esimerkiksi erilaisten kompositiaineiden analysoinnissa ja laaduntarkkailussa.
“To reach a port we must sail, sometimes with the wind, and sometimes against it. But we must not drift or lie at anchor.”

Oliver Wendell Holmes
Acknowledgements

This work was undertaken at the Microelectronics and Materials Physics Laboratories of the University of Oulu and was part of projects funded by the European Research Council. The work also received funding from the Riitta and Jorma J. Takanen foundation.

I would like to thank my supervisor Professor Heli Jantunen for the opportunity and facilities to carry out my research effectively. Her competence and experience in research guided me through the planning of the experimental and writing processes. I also owe my deepest thanks to Docent Jari Juuti who has an excellent ability to review and give constructive comments on the scientific reporting. Furthermore, I want to acknowledge Docent Antti Uusimäki for his improvement comments on publication writing, Professor Arthur Hill for help that was very much more than revision of the language and Professor Sergio Sombra and Professor Eung Soo Kim for the detailed review of the manuscript.

Also, I am grateful to the personnel and colleagues of the laboratory with whom I had very valuable conversations regarding research experiments and who were without reserve ready to share their knowledge. In addition, I want to thank the Center of Microscopy and Nanotechnology for technical assistance in the experimental work.

The most beloved thanks go to my family; my wife Sanna and our daughter Emma who encouraged me and showed interest about the research details as they were frequently discussed during breakfast, lunch and dinner.

Oulu, July 2014

Marko Tuhkala
**List of abbreviations and symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Ampere</td>
</tr>
<tr>
<td>a.c.</td>
<td>Alternating current</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Aluminum oxide</td>
</tr>
<tr>
<td>A_r</td>
<td>Electric field ratio</td>
</tr>
<tr>
<td>A_s</td>
<td>Area occupied by stearic acid molecule</td>
</tr>
<tr>
<td>B-3dB</td>
<td>Bandwidth at -3 dB</td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>Barium titanate</td>
</tr>
<tr>
<td>BET</td>
<td>Branauer-Emmet-Teller theory for SSA</td>
</tr>
<tr>
<td>c</td>
<td>Speed of light (299792458 m/s)</td>
</tr>
<tr>
<td>CaTiO₃</td>
<td>Calcium titanate</td>
</tr>
<tr>
<td>CF</td>
<td>Correction factor</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>D</td>
<td>Electric flux density</td>
</tr>
<tr>
<td>d.c.</td>
<td>Direct current</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>Δεᵣ</td>
<td>Difference in relative permittivity</td>
</tr>
<tr>
<td>ΔL</td>
<td>Length increase due to fringing field</td>
</tr>
<tr>
<td>E</td>
<td>Electric field</td>
</tr>
<tr>
<td>Eₑ</td>
<td>External electric field</td>
</tr>
<tr>
<td>Eᵢ</td>
<td>Internal electric field</td>
</tr>
<tr>
<td>ε₀</td>
<td>Vacuum permittivity (8.854 × 10⁻¹² Fm⁻¹)</td>
</tr>
<tr>
<td>ε_air</td>
<td>Permittivity of pure air</td>
</tr>
<tr>
<td>εₑ</td>
<td>Matrix permittivity</td>
</tr>
<tr>
<td>ε_eff</td>
<td>Effective permittivity</td>
</tr>
<tr>
<td>EFTEM</td>
<td>Energy filtered transmission electron microscope</td>
</tr>
<tr>
<td>εᵢ</td>
<td>Inclusion permittivity</td>
</tr>
<tr>
<td>ε_MUT</td>
<td>Permittivity of material under test</td>
</tr>
<tr>
<td>EPMA</td>
<td>Electron Probe Microanalyzer</td>
</tr>
<tr>
<td>εᵣ</td>
<td>Relative permittivity</td>
</tr>
<tr>
<td>f</td>
<td>Volume fraction</td>
</tr>
<tr>
<td>fₐ</td>
<td>Volume fraction of air</td>
</tr>
<tr>
<td>f_d</td>
<td>Volume fraction of dielectric material</td>
</tr>
<tr>
<td>f₃d</td>
<td>Volume fraction of dielectric material component 1</td>
</tr>
<tr>
<td>f₄d</td>
<td>Volume fraction of dielectric material component 2</td>
</tr>
<tr>
<td>f₅</td>
<td>Volume fraction of stearic acid</td>
</tr>
</tbody>
</table>
\( f_w \) Volume fraction of water
\( f_r \) Resonance frequency
\( \text{H}_2\text{O} \) Water
\( L \) Length of the resonator sample cavity
\( \text{La}_2\text{O}_3 \) Lanthanum oxide
\( \lambda \) Electromagnetic signal wavelength
\( \text{LTCC} \) Low temperature co-fired ceramic
\( m \) Mass
\( m_s \) Mass of stearic acid
\( m_p \) Mass of powder
\( M \) Molar mass
\( M_s \) Molar mass of stearic acid
\( \text{MC} \) Moisture content
\( \text{MgTiO}_3 \) Magnesium titanate
\( \text{MS} \) Mass spectrometry
\( \text{MUT} \) Material under test
\( N_A \) Avogadro constant \((6.022 \times 10^{23} \text{ mol}^{-1})\)
\( Q \) Quality factor \((f_r / B_{3\text{dB}})\)
\( Q_d \) Dielectric material quality factor
\( Q_{\text{ext}} \) External quality factor, e.g., coupling
\( Q_l \) Loaded quality factor
\( Q_m \) Metal quality factor
\( Q_{\text{rad}} \) Radiation quality factor
\( \rho \) Density of the material
\( \rho_{\text{MUT}} \) Density of the material under test
\( \text{R.H.} \) Relative humidity
\( \text{RF} \) Radio frequency
\( \text{SA} \) Stearic acid
\( S_{21} \) Forward transmission coefficient S-parameter
\( \text{SiO}_2 \) Silicon dioxide
\( \text{SSA} \) Specific surface area
\( \text{STA} \) Simultaneous thermal analysis
\( \tan \delta_e \) Loss tangent of matrix, e.g., air
\( \tan \delta_{\text{eff}} \) Effective loss tangent
\( \tan \delta_d \) Dielectric loss tangent
\( \tan \delta_{d1} \) Dielectric loss tangent of material component 1
\( \tan \delta_{d2} \) Dielectric loss tangent of material component 2
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>tan $\delta_w$</td>
<td>Dielectric loss tangent of water (0.157 at 3 GHz)</td>
</tr>
<tr>
<td>TG</td>
<td>Thermogravimetry</td>
</tr>
<tr>
<td>$V_{cavity}$</td>
<td>Volume of the sample cavity</td>
</tr>
<tr>
<td>VNA</td>
<td>Vector network analyzer</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>Zirconium dioxide</td>
</tr>
</tbody>
</table>
List of original papers

This thesis is based on the following four refereed publications, which are cited in the text by their corresponding Roman numerals.


Journal Paper I introduces a novel method to characterize dielectric properties of powder materials using an indirectly coupled open-ended coaxial cavity resonator and classical mixing rules and a general mixing model. In the paper the method is modelled using modern electromagnetic simulation tools and the measurement results of commonly used dielectric powders are analyzed.

In Paper II and Paper III the sensitivity of the characterization method is compared to theoretically calculated values using powders that are exposed to humidity or modified with stearic acid surfactant, respectively. In addition, the effect of stearic acid coating and water adsorption on the dielectric properties of micrometre sized particles is presented.

The applicability of the characterization method in composite powder measurements is researched and analyzed in Paper IV using magnesium and calcium titanate powder composites as sample materials. Furthermore, the capability to quantify the amounts of adsorbed water, surfactant and the molar ratios of composite powders is covered in Papers II-IV.

All the planning of the experiments described in the thesis was done by the author with contributions from Docent and Academy Research Fellow J. Juuti and Professor H. Jantunen. All the modellings, experiment setups, measurements and analyses were designed and done by the author and discussed together with the co-authors. Original papers were written by the author with the contribution of co-authors.
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1 Introduction

The dielectric properties of materials are among the most substantial factors in electronics and optoelectronics product manufacturing. These dielectrics are mostly utilized as solid components but there are certain applications which require the material to be used in powder format. Examples of these can be found in composite technology, coating, plasma sintering, printed electronics and low temperature co-firing ceramic raw material processes [1-6]. In addition to the electronics industry, several other industrial areas, such as the pharmaceutical and food industries, also utilize powdery ingredients. Common to all of these is the fact that the properties of the powdery substances can affect only the manufacturing process or have an additional direct effect on the properties of the final product, e.g., changes in flowability, shelf life, mechanical, chemical or electrical properties [7-14]. These changes in the critical properties can occur during different production phases, for example, in coating processes or after storage where humidity or impurities of the air can affect the material properties. This creates an urgent need for a sensitive and applicable method to monitor and characterize the properties of powdery substances.

1.1 Current state in powder characterization

Several different methods and theories have been presented for the characterization of dielectric material. The great majority of them concern the characterization of bulk material and only a few cover the characterization of powders. The earliest methods were presented some decades ago, such as the microwave cavity method of Conger and Tung in 1967 [15]. Their method was based on resonator perturbation, where the powdery sample is introduced into a resonator cavity using a quartz tube. The derivation of the dielectric properties of the particles was performed using the mixing rules of Lorenz, Bruggeman and Böttcher (also known as the Bruggeman symmetric mixing rule [16]). Later, in 1998 Nelson et al. presented an open-ended coaxial line method, which utilized the Looyenga mixing rule in the determination of the complex permittivity of coal and limestone [17]. Nelson et al. concluded that the method gave reasonable accuracy in the determination of permittivity but was inaccurate for low-loss dielectric materials. In 2006 Ebara et al. reported a waveguide based method that was found to correlate with the Lichtenecker mixing equation in the estimation of the dielectric properties of silica and ferrite powders [18]. Kitaitsev et al.
presented a waveguide based method for high-lossy powdery materials in 2007 [19]. They found correlation between the measurement results of composite powders containing hexagonal ferrites and the Maxwell-Garnet mixing rule. However, Maxwell-Garnet was overestimating the permittivity of Al₂O₃ when using the brass electrode characterization method reported by Bounga et al. in 2011 [20]. One of the recent methods, which has been presented by Austin et al. in 2013, utilizes an open-reflection microwave resonance sensor in the determination of the moisture content of microcrystalline cellulose and α-lactose monohydrate [21]. In this thesis the benefits of the presented method are also compared to these earlier techniques.

1.2 Objectives and outline of the thesis

The main objective of this thesis was to develop a method to characterize dielectric properties of powdery substances. The objective covered the question of whether a determination of dielectric properties of particles could be stable and easily implementable, and also whether the sensitivity to detect changes and the accuracy of the method was adequate when using modified powders. Furthermore, the applicability of the characterization method was one of the key priorities.

Chapter 2 introduces the theories behind the characterization method and the experimental methods used in the research phases. The theory section illustrates the basic functionality of the resonator used in the characterization and how classical mixing theories are utilized with the response of the resonator in the derivation of the inclusion permittivity. In the experimental sections detailed descriptions are given of electromagnetic simulations and resonator characterizations of commonly used dielectric powders, modified powders and powder composites.

Chapter 3 presents the results of the simulation modellings and the resonator measurements of commonly used dielectric powders below a permittivity of 30. The results cover the correlation of the method with the classical mixing models and the importance of the correction factor in the determination of the inclusion permittivity. Furthermore, the determined dielectric losses, by using the differences between a perturbed and an unperturbed resonator and the general mixing model, are presented and results are compared to the literature.

Chapter 4 presents the resonator measurement results of humidity exposed and stearic acid surfactant modified powders. Determined changes in the
dielectric properties are reported, including new and valuable information about
the effect of modification of the powders. In addition, the quantification accuracy
of the characterization method is compared to mass-based determination.

In Chapter 5 the method is utilized in a composite powder application. The
materials characterized are the very commonly used magnesium titanate and
calcium titanate. The sensitivity of the method is discussed and the resonator
measurement results of determined molar masses are compared to the mass-based
method.

The final section, Chapter 6, summarizes the main findings of the research
including the applicability of the characterization method.
2 Theories and experimental methods

This chapter describes the principles of the open-ended quarter wave resonator, the mixing equations and how they are utilized in the research experiments when determining dielectric properties of powdery substances. The descriptions of the experiments (sections 2.3 - 2.6), based on Papers I-IV, are cumulative and only relevant changes are added compared to previous sections.

2.1 Open-ended coaxial cavity resonator

The operating frequency of a quarter-wave resonator in TEM mode is inversely dependent on the length of the cavity. With an open-ended resonator the length of the cavity is close to the one quarter of the signal wave length. In addition to dimensions, the resonance frequency also depends on the permittivity of the material filling the resonator. This can be described by (Eq. 1). [22]

\[ \varepsilon_r = \varepsilon_{eff} = \left( \frac{c}{4Lf_r} \right)^2, \]  

(1)

where \( \varepsilon_r, \varepsilon_{eff}, c, L \) and \( f_r \) are relative and effective permittivities, speed of light in vacuum, length and resonance frequency of the resonator, respectively. Because of the open-ended structure, the expanding electric field, i.e., the fringing field affects the length and dielectric calculations. This has been demonstrated and is discussed further in section 3.1.1, based on results of Paper I.

How lossy the resonator is and how closely the resonator operates to the resonance frequency can be expressed with a quality factor, \( Q \). Generally, the resonator restores and dissipates energy that is excited via external coupling. The definition for the quality factor can be written as follows (Eq. 2):

\[ Q = \frac{\text{energy stored in the resonator during cycle}}{\text{energy dissipated during cycle}} \]  

(2)

The relation between stored energy and dissipation depends on the materials used, the cavity surface quality and the isolation material between inner and outer conductors, i.e., its permittivity and the relation between the conductor radii, \( r_a \) and \( r_b \) (Fig. 1). It has been experimentally demonstrated that with a dimension relation \( r_c: r_a \approx 3.6 \) the quality factor achieves the highest value [22, 23]. Physical structure related critical dimensions and directions of the electric and magnetic fields are shown in Fig. 1.
Total losses of the whole resonator are made up of dielectric losses, metal losses in the resonator body, radiation losses and external coupling losses, referring to subscripts $d$, $m$, $rad$ and $ext$ of (Eq. 3) [24]. Dielectric losses of the material between the inner and outer conductors are frequency dependent and affected by both intrinsic and extrinsic loss factors, i.e., interaction of an a.c. electric field with phonons and interfaces between particles, and their size and shape, respectively [25, 26].

$$\frac{1}{Q_t} = \frac{1}{Q_d} + \frac{1}{Q_m} + \frac{1}{Q_{rad}} + \frac{1}{Q_{ext}}$$  \hspace{1cm} (3)

At low frequencies a d.c. conductivity, which is temperature and ion content dependent, has a notable role when measuring the dielectric properties of materials. At microwave frequencies the effect of the d.c. conductivity often becomes irrelevant [24].

In the research presented in this thesis, the determination of the effective loss of the dielectric particle (inclusion) material was based on the relative loss difference between a perturbed and an unperturbed resonator at the same coupling strength (Fig. 2), i.e., the $Q$ values ($Q = f_r / B_{3dB}$) of an empty and a filled resonator (Eq. 4) [27, 28]. As all other variables remain the same it can be concluded that other loss factors have a much smaller effect on the $Q$ factor than the dielectric air-particle material filling the cavity. This was also demonstrated in Papers I-IV. Thus, the effective loss tangent is given in (Eq. 4):

$$\tan \delta_{eff} = \frac{1}{Q_{filled}} - \frac{1}{Q_{empty}}$$  \hspace{1cm} (4)
The relations of the dielectric loss tangents of composites can be described by the general mixing model (Eq. 5), which can be used to define the loss tangent of the dielectric material.

\[(\tan \delta_{\text{eff}})^\alpha = \sum f_i (\tan \delta_i)^\alpha\]

where \(\tan \delta_{\text{eff}}\) is the loss tangent of the composite and \(f_i\) and \(\tan \delta_i\) are the volume fraction and the loss tangent of the \(i^{th}\) dielectric material, respectively. With a component of dry powder, the composite consists of dielectric material particles and air. Parameter \(\alpha\) determines the mixing model where values -1, 0 and 1 refer to serial, logarithmic and parallel mixing, respectively [29-31].

### 2.2 Determination of dielectric properties of powder particles with mixing rules

As described, the dielectric properties of the material filling the coaxial resonator affect the frequency response of the resonator. When the material is in powdery format, it can be thought to be as a composite that consists of particles that form the powder and the air between the particles, i.e., an air-particle mixture (Fig. 3).
Thus, the measured parameter, either resonance frequency or the difference between quality factors of an empty and a filled resonator, is an effective value ($\varepsilon_{\text{eff}}$ and $\tan \delta_{\text{eff}}$) that includes both the properties of the particles and the air. To be able to determine dielectric properties of the particles, mixing rules can be utilized to derive the approximated values from the measured effective values. However, it is also known that the frequency dependence of inclusions can differ from the values of the solid materials due to electromagnetic dispersion caused by the inclusions [16] (p. 11, 22, 178, 196, 215) [32].

### 2.2.1 Electromagnetic theory behind the mixing rules

The principles behind the mixing rules do not just result from experiments but have a solid electrostatic foundation [16] (p. 41). Based on Maxwell’s equations the average flux density can be defined by the average electric field through the homogenous dielectric material of the air-particle mixture (Eq. 6).

$$\overline{D} = \varepsilon_{\text{eff}} \overline{E}$$  \hspace{1cm} (6)

Because the inclusions ($\varepsilon_i$ and $\tan \delta_i$) are only partly filling the space of the environment ($\varepsilon_e$ and $\tan \delta_e$), the average flux density and average electric field can be weighted by the volume fractions of inclusion ($f$) and environment ($1 - f$), (Eq. 7 and 8)

$$\overline{D} = f \varepsilon_i E_i + (1 - f) \varepsilon_e E_e$$  \hspace{1cm} (7)

$$\overline{E} = f E_i + (1 - f) E_e$$  \hspace{1cm} (8)

---

**Fig. 3.** Powdery material from dielectric properties point of view. Darker areas represent inclusions and lighter area matrix, e.g., air.
As the electric fields are assumed to be constants, the effective permittivity can be written by the equation (Eq. 9).

\[ \varepsilon_{\text{eff}} = \frac{\overline{E}}{E} = \frac{\varepsilon_i A_r + \varepsilon_e (1-f)}{f A_r + (1-f)} \]  

where the electric field ratio between internal and external field is described by \( A_r = E_i/E_e = 3\varepsilon_e/(2\varepsilon_e + \varepsilon_i) \), which leads to the Maxwell-Garnett mixing equation (Eq. 10). [16] (p. 40, 41) [32] (p. 116, 118), [33] (p. 159)

\[ \varepsilon_{\text{eff}} = \varepsilon_e + 3f \varepsilon_e \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e - f(\varepsilon_i - \varepsilon_e)} \]  

It is worth noting that in real applications there are uncertainties that are difficult to cover by a simple model, e.g., interactions between particles in dense materials and inclusion shapes and sizes. [16] (p. 39, 147, 150)

### 2.2.2 Mixing rule correlation

The purpose of the research was not to bring yet another mixing equation into a large number of existing ones that have proliferated since the Maxwell-Garnett equation was proposed [34], but to find a satisfactory correlation with the existing mixing models and the measurement method. Therefore, several classical mixing models were taken into consideration for modelling and resonator measurements [Paper I]. All the models were well known and they estimated the effective permittivity of the mixture in a three-dimensional environment with spherical inclusions and two material components in relation to the volume fractions. In addition to the Maxwell-Garnet (Eq. 10) mixing equation, Bruggeman-nonsymmetric (Eq. 11), Bruggeman-symmetric (Eq. 12), Coherent potential formula (Eq. 13), Differential (Eq. 14), Lichtenecker (Eq. 15), modified-Lichtenecker (Eq. 16), Looyenga (Eq. 17) and Sen-Scala-Cohen (Eq. 18) generalized mixing models were analysed. [16] (p. 162, 163, 167, 168, 174) [35]

\[ \frac{\varepsilon_i - \varepsilon_{\text{eff}}}{\varepsilon_i - \varepsilon_e} = (1-f) \left( \frac{\varepsilon_{\text{eff}}}{\varepsilon_e} \right)^{1/3} \]  

\[ \frac{\varepsilon_i - \varepsilon_{\text{eff}}}{\varepsilon_i + 2\varepsilon_{\text{eff}}} f + \frac{\varepsilon_e - \varepsilon_{\text{eff}}}{\varepsilon_e + 2\varepsilon_{\text{eff}}} (1-f) = 0 \]  

\[ \varepsilon_{\text{eff}} = \varepsilon_e + f(\varepsilon_i - \varepsilon_e) \frac{3\varepsilon_{\text{eff}}}{3\varepsilon_{\text{eff}} + (1-f)(\varepsilon_i - \varepsilon_e)} \]
$$\frac{d\varepsilon_{\text{eff}}}{df} = \frac{3\varepsilon_i (\varepsilon_i - \varepsilon_{\text{eff}})}{\varepsilon_i + 2\varepsilon_{\text{eff}} - 3f\varepsilon_i}$$

$$\Rightarrow f = 1 - \frac{1}{3} \frac{\varepsilon_i - \varepsilon_{\text{eff}}}{\varepsilon_i - \varepsilon_e} \left( 2 + \left( \frac{\varepsilon_i - \varepsilon_{\text{eff}}}{\varepsilon_i - \varepsilon_e} \right)^{\frac{1}{3} - 1} \right)$$  \hspace{1cm} (14)

\[
\log \varepsilon_{\text{eff}} = f \log \varepsilon_i + (1-f) \log \varepsilon_e \hspace{1cm} (15)
\]

\[
\log \varepsilon_{\text{eff}} = (1-k) f \log \varepsilon_i + (1-f) \log \varepsilon_e \hspace{1cm} (16)
\]

\[
\varepsilon_{\text{eff}}^{1/3} = (1-f) \varepsilon_e^{1/3} + f \varepsilon_i^{1/3} \hspace{1cm} (17)
\]

\[
\frac{\varepsilon_{\text{eff}} - \varepsilon_e}{\varepsilon_i - \varepsilon_e} = f \left( \frac{\varepsilon_{\text{eff}}}{\varepsilon_i} \right)^{1/3} \hspace{1cm} (18)
\]

where $\varepsilon_{\text{eff}}, \varepsilon_i, \varepsilon_e$ are the permittivity of composite, matrix (e.g., air) and inclusion, respectively and $f$ is the volume fraction of inclusions (dielectric material).

**Principles of the mixing rules**

The classical mixing rules are based on the assumption that in a determination of the effective permittivity, inhomogeneities of the material are much smaller in size than the signal wavelength in the material [35]. Bruggeman-symmetric treats both environment and inclusion symmetrically. This means that the effective permittivity is the same in both cases as $\varepsilon_i \rightarrow \varepsilon_e, \varepsilon_e \rightarrow \varepsilon_i$ and $f \rightarrow 1-f$, unlike the Maxwell-Garnet mixing rule, which is nonsymmetric. With dilute mixtures, where the $f \ll 1$, Bruggeman-symmetric, Maxwell-Garnet and Coherent potential define the same effective permittivity [16] (p. 162). The Looyenga mixing model, also known as Landau-Lifshitz-Looyenga, is based on a power law approximation $\varepsilon_{\text{eff}} = (1-f) \varepsilon_i^\beta + f \varepsilon_i^\beta$, which averages the permittivity to the certain power of $\beta$ by a volume fraction. Also, the Looyenga equation ($\beta = 1/3$) treats the permittivities of a two component mixture symmetrically. In addition to the Looyenga mixing rule, both the Bruggeman-non-symmetric and the Sen-Scala-Cohen mixing rules are also based on the differential analysis, i.e., the equations have been commonly written with a power of $1/3$ [16] (p. 167). Furthermore, the Lichtenecker mixing rule, which averages the logarithms of permittivities can also be thought to be part of the power law mixing laws when written as $\varepsilon_{\text{eff}} = \varepsilon_i / \varepsilon_e^{1/3}$ [16] (p. 167) [36]. The differential equation (Eq. 14) presented by Jylhä and Sihvola [35], combines the properties of Maxwell-Garnett for low- and Bruggeman-symmetric for high-volume fractions, which is most notable with
high contrast between inclusion and environment. The main advantage is that low volume fractions can be modelled with better accuracy [35]. In the present research the inclusion concentrations were targeted above the volume fraction 0.25, which has also been reported to give comparable and reliable results elsewhere [18, 37, 38].

It should be noticed from the presented equations that all other but the modified-Lichtenecker, due to correction factor 1-k, closely define the same effective permittivity with very low and very high volume fractions, i.e., \( f \ll 1 \) or \( f \gg 0 \). [16]. In some cases, due to the physical limitation of different powdery material, e.g., uniform particle size distribution, high volume fractions are difficult to obtain.

2.3 Electromagnetic simulation modelling

A modern simulation tool (CST Microwave Studio®) was used in the research to model the electromagnetic response of the open-ended coaxial resonator with different permittivity powders filling the sample cavity [Paper I]. The relative permittivity range of the samples, below \( \varepsilon_r = 30 \), was chosen to correlate with commonly used, easily available and stable dielectric materials. For the correlation between simulated and measured results and the mixing rules, the varying volume fractions were modelled by adding vertical air pipes into the modelled sample (Fig. 4). The diameter variations of the air pipes, from 0.21 mm to 0.50 mm, were much smaller than the signal wavelength in the simulations with different permittivity samples, i.e., from 66.8 mm to 332.2 mm. Volume fractions of 0.34, 0.44, 0.54, 0.64, 0.84 and 1 were achieved by changing the volume of the air pipes. An excitation signal coupling was done by using two probes and forward transmission coefficients between the probes were simulated, i.e., \( S_{21} \)-parameters for resonance frequency and quality factor. The coupling strength was defined to be low, below -30 dB. All the material characteristics of the modelled resonator and the environment were set to meet the properties of the real characteristics of the experiments using lossy materials in component definitions.
2.4 Resonator measurements of wide permittivity range

The resonator prototype was manufactured from oxygen-free copper to achieve the highest possible quality factor by minimizing metal losses [Paper I]. The dimensions, length and radii of the centre rod and the sample cavity, were selected to obtain the best resonance at 4.5 GHz operating frequency. The centre rod was secured tightly with a solder paste onto the bottom of the cavity. Several different resonators were manufactured and the highest quality factor was achieved with dimensions of: \( L = 15.1 \text{ mm}, \ r_a = 1.375 \text{ mm} \) and \( r_b = 4.95 \text{ mm} \). This correlated also with the statement of obtaining the highest quality factor by using \( r_b/r_a = 3.6 \), reported elsewhere [22, 23]. Due to the construction method tolerances, the actual volume of the cavity, \( V_{cavity} \), was 1.092 cm\(^3\) instead of 1.072 cm\(^3\) calculated directly from the measured dimensions. The measured value was used in calculations.
2.4.1 Powder characterization

In the experimental measurement of dielectric powders, the frequency responses of the resonator were measured using a vector network analyzer (VNA) (Rohde & Swartz ZVB 20 GHz). Differences between an empty (f_r = 4.55 GHz and Q = 1200 at -35 dB) and sample filled resonators were measured as a function of volume fraction using either five or six different compaction levels of powdery samples filling the sample cavity. The volume fraction of the sample, f, was defined by the density of the inclusion and the volume of the cavity. This can be written as f = (m_{filled_resonator} - m_{empty_resonator}) / (\rho_{MUT} \times V_{cavity}), where the divider defines the maximum theoretical mass of the solid sample. Because the open end of the resonator has the strongest electric field it is most sensitive to the dielectric properties of the sample material. Thus, a homogenous composition of the powder sample was aimed for along the whole of the sample cavity. Powder particle densities were measured at room temperature by the Archimedes method with a 10.115 cm³ pycnometer (Gay-Lussac BlauBrand®, Brand GmbH + Co KG, Germany) and clean de-ionized water. In the measurement of the varying permittivity the powders used were storage dry and dielectric characterization was performed under laboratory conditions without special control of the room temperature and ambient moisture [Paper I]. Coupling and ground strength between RF probes and the resonator was kept at -35 dB in all the measurements. Thus, the external effect on the resonance and quality factor could be minimized and the results were comparable. In addition, tuning of the coupling was performed in order to obtain the best possible symmetry of the forward transmission coefficient in the vicinity of the resonance frequency, i.e., symmetric S_{21} in -3 dB bandwidth.

2.4.2 Analysed powdery materials

Resonator measurement correlation with the theory of the simulation model and the values reported in the literature was confirmed by measuring different commonly used dielectric powders having a reported permittivity below 30 [Paper I]. The powders selected were SiO₂ (Strem Chemicals, 99.8%, 100 mesh), sintered and ground LTCC CT 2000 (Heraeus Holding GmbH), α-Al₂O₃ (Teknofokus, 30 µm), α-Al₂O₃ (Teknofokus, 6 µm), ZrO₂ (Sigma-Aldrich, 99%, < 5 µm) and La₂O₃ (Alfa Aesar, REacton®, 99%). Particle sizes were in the
micrometre range. The dielectric properties and material densities of the powders reported in literature are listed in Table 2.

Table 2. Dielectric properties and inclusion densities of measured powders given in literature for comparison.

<table>
<thead>
<tr>
<th>Dielectric powder</th>
<th>εr</th>
<th>tan δ</th>
<th>ρ_MUT [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ [39, 40]</td>
<td>3.8 – 5.4</td>
<td>3.8 × 10⁻⁴ – 1 × 10⁻³</td>
<td>2.65</td>
</tr>
<tr>
<td>Heraeus CT 2000 [41]</td>
<td>9.1</td>
<td>2.6 × 10⁻³</td>
<td>&gt; 3.05</td>
</tr>
<tr>
<td>Al₂O₃ 30 µm [40, 42]</td>
<td>9 – 11.5</td>
<td>1 × 10⁻⁴ – 1 × 10⁻²</td>
<td>3.96 – 4.1</td>
</tr>
<tr>
<td>Al₂O₃ 6 µm [40, 42]</td>
<td>9 – 11.5</td>
<td>1 × 10⁻⁴ – 1 × 10⁻²</td>
<td>3.95 – 4.1</td>
</tr>
<tr>
<td>ZrO₂ [39, 40, 42-44]</td>
<td>12.5 – 25</td>
<td>7 × 10⁻⁴ – 1 × 10⁻²</td>
<td>5.89</td>
</tr>
<tr>
<td>La₂O₃ [42, 45-47]</td>
<td>16 – 30</td>
<td>...*</td>
<td>6.51</td>
</tr>
</tbody>
</table>

* Not available in literature

2.5 Characterization of modified powders

As described in the introduction section, there are various processes and applications which are sensitive to mechanical or chemical variations of the powdery materials that are used in the manufacturing of the products. Therefore, the sensitivity and the applicability of the characterization method were researched with powders that had been modified either by an adsorbed ambient moisture or by a surfactant treatment [Paper II, Paper III]. The following chapters 2.5.1 and 2.5.2 describe the relevant differences in the characterization and how the modifications were done.

2.5.1 Humidity exposure

In the experiment described in Paper II, the characterization was performed for SiO₂, α-Al₂O₃ and ZrO₂ powders that were exposed to 5% R.H. and 100% R.H. ambient humidity at room temperature (+ 21 °C). For estimating the relationship of hygroscopicity with particle size, the specific surface areas, SSA, of the powders were BET analysed (ASAP™ 2020, Micromeritics Instrument Corporation, U.S.A.) based on gas adsorption on the particles. The SSA values are listed later in Table 4 together with the dielectric characterization results. In order to achieve an equal exposure, all master samples of the powders (~ 30 g) were spread in wide bowls and dried in a desiccator having 3% – 5% measured relative humidity (Testo 608-H2). After one week of drying the master samples were halved, reweighed and exposed to 100% relative humidity for a week. Water
adsorption on the particles was measured by a traditional mass based method (Precisa XB 620M).

**Characterization and theoretical values**

All the dielectric characterizations were done in a room humidity of 15% R.H. – 20% R.H.. In order to minimize the drying effect of sample on the measured parameters, the samples were characterized immediately after sample loadings. Effective permittivities of dry and moist powders were compared and inclusion permittivities were determined using Bruggeman symmetric and Looyenga mixing equations. A general mixing model was used both in the determination of the dielectric loss tangent of the dry and moist inclusions and in theoretical calculations of the effective loss tangents because water is known to be a dominant factor in dielectric losses in the microwave frequency range [48]. Based on the theory of the general mixing model the effective loss tangent can be written as

\[
\tan \delta_{\text{eff}} = f_d \tan \delta_d + f_w \tan \delta_w + f_a \tan \delta_a
\]

where subscripts \(d\), \(w\) and \(a\) refer to dielectric material, water and air. In the theoretical effective loss tangent calculations of moist powder, a dielectric loss tangent of water at 3 GHz (\(\tan \delta_w = 0.157 [49]\)) was used with the calculated loss tangent of dry dielectric material, \(\tan \delta_d\). In addition, an assumption was made that water is adsorbed on particles and has taken space from the air.

**Response as a function of time**

To validate the effect of moisture adsorption and the sensitivity of the characterization method, the effect of desorption was measured as a function of time. Dense samples of moist SiO₂ and Al₂O₃ powders were measured for three hours while the samples were drying in room humidity (20% R.H.) after 100% R.H. exposure. The probes were adjusted to maintain -35 dB coupling strength while the resonator was left untouched. Thus, desorption was the only factor that was affecting the frequency response of the resonator.

**2.5.2 Surfactant treatment**

The sensitivity of the method to detect the effect of surface modified particles was verified with stearic acid treated oxide powder particles [Paper III]. In addition, the extent to which stearic acid surface modification affected the dielectric
properties was analysed. Earlier presented SiO$_2$, Al$_2$O$_3$ and ZrO$_2$ powders were treated with stearic acid solution where the stearic acid amount was theoretically specified to be able to cover the particles with a single monolayer. The amount of stearic acid required to form one monolayer on the particles was based on the measured surface specific areas of the powder and the area of the stearic acid molecule (0.21 nm$^2$) (Eq. 19) [50].

$$m_s = \left( \frac{M_s}{N_A \cdot A_s} \right) \cdot m_p,$$

where subscripts $s$ and $p$ refer to stearic acid and powder and $m$, $M$, $N_A$ and $A$ represent mass, molar mass, Avogadro constant ($6.022 \times 10^{23}$ mol$^{-1}$) and the area occupied by a molecule forming one monolayer on the particle, respectively.

**Particle coating**

Half of the desiccator dried master samples were treated with stearic acid (Fluka, $\geq 97\%$, boiling point 361 °C, 284.49 g / mol) solution with a concentration of 2 mg/ml. The solvent was prepared by dissolving stearic acid into ethanol (Altia Plc., ETAX, Aa, 99.5 wt. %) and dosed to form master samples. The stearic acid amount per master sample was 3.6 mg / 5.5g, 8 mg / 8g and 120 mg / 10.5 g for SiO$_2$, Al$_2$O$_3$ and ZrO$_2$ powders, respectively. The adsorption on the particles was assisted by ball mixing the oxide powder and the stearic acid – ethanol solution for six hours. After mixing the coated particles were separated from the solution with a centrifuge and dried in a desiccator for one week before coating coverage inspections and dielectric characterization.

**Coating inspections**

Stearic acid coating coverage inspections were done using an energy filtered transmission electron microscope (EFTEM, LEO 912 Omega, Carl Zeiss AG, Germany). For the theoretical comparison between the theoretical maximum amount and the realized adsorbed amount of surfactant, the particles (50 mg powder sample) were measured by the simultaneous thermal analysis method using thermogravimetry, differential scanning calorimetry and mass spectrometry (STA-TG-DSC-MS, Netzsch QMS 403 C + STA 449 F3 Jupiter®), Germany). The determined water and stearic acid contents in the powders were based on mass
difference and \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) ion currents after reaching temperatures of 250 °C and 600 °C, respectively.

**Characterization and theoretical values**

The dielectric characterization of untreated and surfactant treated powders was performed at room temperature and humidity (15-20% R.H.) using samples having six different volume fractions. In addition, the dielectric characteristics of stearic acid were measured to enable a theoretical comparison. The inclusion permittivities were determined by using Bruggeman symmetric and Looyenga mixing equations.

In the theoretical comparison, a general mixing model was used with the measured dielectric loss tangents of stearic acid and dry oxide inclusion at 3.5 GHz. Furthermore, residues of water were included as one parameter. The stearic acid volume fractions were calculated using the theoretical maximum amount, i.e., the added amount of surfactant to form one monolayer on the particles, and the amount measured with the thermo-gravimetric instrument. The changed density was recalculated and used with the volume fraction based mixing models in the determination of the dielectric properties of the treated powder.

### 2.6 Characterization of \( \text{MgTiO}_3-\text{CaTiO}_3 \) composite powders

The applicability of the characterization method to composite powder measurements was researched using commonly used calcium and magnesium titanates [Paper IV]. The molar ratio determination accuracy was also analyzed.

#### 2.6.1 Sample material preparations

In the experiments the \( \text{CaTiO}_3 \) molar ratios (x) of the \((1-x)\text{MgTiO}_3-x\text{CaTiO}_3\) powder composite were 0, 0.02, 0.05 and 0.1. Of these the 0.95\( \text{MgTiO}_3 \)-0.05\( \text{CaTiO}_3 \) is the most commonly used composite molar ratio due to its neutral temperature coefficient [51, 52]. The titanates used were commercial \( \text{MgTiO}_3 \) (Alfa Aesar, 99%, +325 mesh, formula weight 135.98 g/mol., metals basis) and \( \text{CaTiO}_3 \) (Alfa Aesar, 99%+, +325 mesh, formula weight 120.21 g/mol., metals basis). Densities were measured and recalculated based on the molar ratios when mixed into composites. The adsorbed humidity effect was minimized by drying in a silica desiccator before and after mixing. 10 g master samples were prepared for
each composite powder, which had CaTiO$_3$ contents of 225.7 mg, 562.0 mg and 1116.6 mg, respectively. To enable homogenous powder composites, the calcium and magnesium titanate components were thoroughly dry mixed in geometric series. The homogeneities of the composite samples were inspected with an Electron Probe Microanalyzer, EPMA (JEOL JXA-8200 WD/ED, Jeol Inc. U.S.A). Before the dielectric characterization, agglomerates were decreased and uniform compositions along the resonator sample cavity were achieved by using a stainless steel mesh with 200 µm openings.

2.6.2 Dielectric characterization

The calcium titanate and magnesium titanate base powders and the composites were characterized by the previously described method at room temperature and 50% relative humidity. The inclusion permittivity determinations of the composite powders were based on the combination of the relative permittivities of the magnesium and calcium titanate inclusions and air. The determined dielectric loss tangent of calcium titanate was used in the comparison between measured and calculated theoretical effective loss tangents of the composite powders.
3    Powders with different dielectric properties

In this chapter the determination of the dielectric properties of the inclusions and correlation with classical mixing rules and a general mixing model are demonstrated with modelling and measurement results based on the experiments described in sections 2.3 and 2.4. The effect of the correction factor on the determination accuracy of the inclusion permittivity is presented. Furthermore, the applicability of the mixing theories in complex permittivity determination is discussed. Results were originally reported in journal Papers I and II.

3.1    Modelling results

3.1.1 Varying permittivity and the effect of correction factor in permittivity determination

In the modelling of the resonance frequency dependence on the permittivity of the material, the resonance frequency was found to be stable and the quality factor saturated below -30 dB coupling strength. Thus, the -35 dB strength was used, which enabled the most accurate measurement of the frequency response and the determination of dielectric properties. The comparison with the set properties of $\varepsilon_{\text{MUT}}$, i.e., $\varepsilon_i$, and equation (Eq. 1) showed the calculated $\varepsilon_{\text{eff}}$ values to be remarkably higher. The difference, $\Delta\varepsilon_i$, was most relevant with materials having low permittivity, including also the well-known permittivity of air, and became negligible with higher permittivity materials. The differences in permittivities remained nearly a constant over the modelled permittivity range, resulting in $\Delta\varepsilon_i$ to be between 0.22 and 0.25 when the inclusion permittivity was $1.0059 \leq \varepsilon_i \leq 30$. This corresponded to a determined inclusion permittivity error of 22.0 - 0.83%, as shown in Fig. 5.
Fig. 5. Correction factor magnitude relation to sample permittivity in numerical values and percentages when sample volume fraction is 1. Correction factor is most relevant with samples having low permittivity [Paper I]. (Paper I, reprinted with permission from Journal of Applied Physics. Copyright 2013, AIP publishing LLC)

The main reason for the difference is the electrical length of the open-ended resonator, which is due to the expanded electromagnetic waves, i.e., the fringing field. Thus, the actual $\lambda/4$ length of the resonator is the electrical length $L_{\text{electrical}} = L + \Delta L$, where the $L$ is the length of the cavity and $\Delta L$ is the length increase due to the fringing field. With the samples having $\varepsilon_i >> 1 \rightarrow \Delta L \approx 0 \rightarrow L_{\text{electrical}} = L = \lambda/4$. [53-56] The equation (Eq. 1) then results in (Eq. 20):

$$\varepsilon_{\text{eff}} = \left(\frac{c}{\sqrt{4(L+\Delta L)f_r}}\right)^2,$$

Correction factor

It was found with the modelling that although the $\Delta L$ decreased when the permittivity of the material filling the cavity increased, the error in the calculated permittivity, $\Delta \varepsilon_t = \varepsilon_t - \varepsilon_{\text{MUT}}$, remained approximately constant. This difference, determined with an unperturbed empty cavity and the known permittivity of air, was used as a correction factor (CF) resulting in equation (Eq. 21).

$$\varepsilon_{\text{eff}} = \left(\frac{c}{4Lf_r}\right)^2 - \left(\varepsilon_{\text{empty}} - \varepsilon_{\text{air}}\right) = \left(\frac{c}{4Lf_r}\right)^2 - CF$$

(21)
It was demonstrated that by using the constant correction factor, based on an empty cavity and the known permittivity of air, the error due to the fringing field in the calculated value was reduced significantly (Fig. 5). As a result the error in determined permittivity was reduced to less than 0.5%.

3.1.2 Simulation model correlation with the mixing rules

The effective permittivities determined from of the mixing rules, presented in section 2.2.2, were compared to simulation results with different sample permittivity and varying volume fractions. From the analysed equations, the Bruggeman-symmetric (Eq. 12) and the Looyenga (Eq. 17) mixing rules were found to have the best effective permittivity correlation with the calculated values (Eq. 21) using the frequency response of the resonator and the set dielectric parameters of the MUT. Fig. 6 shows the modelled effective permittivity correlation with Bruggeman symmetric and Looyenga mixing rules with inclusion permittivities 2.1, 9.9 and 30. Furthermore, it was noted that volume fraction point ~ 0.43 can be used in the determination of very small changes in inclusion permittivity. At this particular point these two mixing rules closely define the same effective permittivity when $\varepsilon_e = \varepsilon_{\text{air}}$ and sample permittivity $\varepsilon_{\text{MUT}} \leq 50$. The difference in effective permittivity increases on both sides of the volume fraction 0.43 (Fig. 7).
Fig. 6. Effective permittivities of Bruggeman symmetric, Looyenga and modelled samples as a function of volume fraction. Determined inclusion permittivities and modelled sample permittivities were 2.1, 9 and 30. Without the correction factor the determined inclusion permittivity would have been noticeably higher with the low permittivity sample. This would have resulted in a determined value of 2.5 instead of a sample permittivity of 2.1. With ε_i = 2.1 sample the effective permittivity curves of Bruggeman symmetric and Looyenga mixing rules are overlapping [Paper I]. (Paper I, reprinted with permission from Journal of Applied Physics. Copyright 2013, AIP publishing LLC).
Fig. 7. Bruggeman symmetric and Looyenga mixing rule effective permittivity comparison when inclusion permittivity is between 1 and 50 and volume fractions are 0.33, 0.43 and 0.53. The difference in effective permittivities of the mixing rules is smallest when the volume fraction is close to 0.43 [Paper I]. (Paper I, reprinted with permission from Journal of Applied Physics. Copyright 2013, AIP publishing LLC).

It was found from the modelling results that reasonable accuracy could be obtained using the measured effective permittivities and the Bruggeman symmetric and the Looyenga mixing rules when the volume fraction was close to 0.43. This point, where both mixing rules define the same effective permittivity and cross each other, reduces the variation in the determination of inclusion permittivity. Thus, when selecting the volume fractions within the vicinity of 0.43, a better accuracy can be achieved [Paper I].

### 3.1.3 Determined material losses

#### Effective loss tangents

In the determination of the sample material losses it was found both with simulations and experimental measurements that the effective loss tangent increased systematically with the amount of dielectric material particles filling the cavity (Fig. 8) [Paper I]. This conclusion correlated also in experiments when very small changes in dielectric material were applied [Paper II, Paper IV].
Measurements with SiO₂ and ZrO₂, shown in Fig. 9, illustrate the same systematic increase in effective loss tangents when the amount of sample material was increased. Thus, it can be concluded that the dielectric properties of a sample dominate the changes in quality factor. In addition to the frequency dependence of the dielectric losses of the sample material, there are also other frequency dependent loss factors that affect the resonator losses. These are the surface roughness and any sharp corners of the sample cavity and the skin depth. With the particular oxygen-free full copper resonator and the frequency ranges used these effects were found to be negligible and reliable effective loss tangents were achieved by using the differences between a perturbed and an unperturbed resonator (Eq. 4).

Fig. 8. Dielectric loss tangents and effective loss tangents as a function of volume fraction. Loss tangent of the modelled sample was $2 \times 10^{-4}$. (Paper I, reprinted with permission from Journal of Applied Physics. Copyright 2013, AIP publishing LLC).
Fig. 9. Effective permittivities and effective loss tangents of SiO₂ and ZrO₂ powders as a function of volume fraction. Frequency ranges were 3.22 - 3.49 GHz and 2.3 - 3.80 GHz for SiO₂ and ZrO₂ powder samples, respectively. These results were published originally in Paper II. (Paper II, reprinted with permission from Applied Physics Letters. Copyright 2013, AIP publishing LLC).

**Dielectric loss tangents**

For dry particles the effective loss tangent, based on the general mixing model, can be written as \( \tan \delta_{\text{eff}} = f_d \tan \delta_d + f_a \tan \delta_a \), where \( f \) is the volume fraction of the material and subscripts \( d \) and \( a \) refer to the dielectric material and air. Because the loss tangent of air can be approximated closely to zero the equation for dielectric loss results in (Eq. 22),

\[
\tan \delta_d = \frac{\tan \delta_{\text{eff}}}{f_d}
\]

Based on the effective loss tangent and the volume fractions of dielectric material it was demonstrated with the modelling that reasonable accuracy could be obtained using the general mixing model with parallel mixing. In the present research, as shown in Fig. 8, the calculated dielectric loss tangent (\( \tan \delta_d \)) was reasonably close to the set dielectric loss tangent of the sample. This correlation with the principles of the general mixing model equation in parallel mode has also been reported by Fukuda et al. and Huang et al. [29, 57]. Regarding the present modelling results, the slight difference between the set loss tangent and the calculated value can be influenced by the loss tangent definition frequency of the modelled sample and the accuracy of the simulation model.
3.2 Resonator measurements of dielectric powders

3.2.1 Varying permittivity

The measured effective permittivities were found to have a good correspondence with the effective permittivities of the Bruggeman symmetric and Looyenga mixing rules when using inclusion permittivities that correlated with the values in the literature [Paper I]. With SiO$_2$ powder (Fig. 10 a) the best correlation was achieved with an inclusion permittivity value of 3.9 that was close to the reported values measured from a solid material in the gigahertz range [39, 40]. It is important to note that with a low permittivity sample both mixing rules correlate well with the measured values. As illustrated by the simulation in Fig. 7, the difference between Bruggeman symmetric and Looyenga mixing rules increases as the permittivity of the sample increases. This highlights the importance of the 0.43 volume fraction in the permittivity measurements. Furthermore, in order to enable comparable measurement results, a particular volume fraction, i.e., compaction level, should be defined, as has also been reported by Macutkevic et al. and Sheen et al. [38, 37]. With the presented method, the volume fraction of 0.43 can be defined to be the targeted compaction level. In the measurement of LTCC Heraus CT 2000 powder the results of effective permittivity were found to match with the mixing rules when the determined inclusion permittivity was 8.8 (Fig. 10 b). This was very close to the reported value in the datasheet [41]. With aluminium oxides (Fig. 10 c and d) the different particle sizes (30 µm and 6 µm) did not significantly affect the measured effective permittivities in this particular case and thus both results correlated with the mixing rules with an inclusion permittivity of 9.8. However, when the particle size approached the nanometre range, the effect could be more pronounced and notable due to electromagnetic dispersion caused by the small dielectric particles [16] (p. 11, 22, 178, 196, 215) [32]. With zirconium and lanthanum oxides the determined inclusion permittivities of 13.9 and 18.2, respectively, were found to have the best correlation with the effective permittivities of the Bruggeman symmetric and the Looyenga mixing rules (Fig. 10 e and f). With lanthanum oxide the volume fraction of 0.43 could not be achieved due to the particle size and the shape and dimensions of the sample cavity. Thus, the extrapolation from the graphs was performed to achieve the point of 0.43 volume fraction. It should also be noticed that lanthanum oxide is a rare earth oxide and has a very strong hygroscopic
nature (moisture absorption), which can influence the dielectric properties [45, 58].

3.2.2 Determined dielectric losses

In the resonator measurements of the effective loss tangents, the calculated dielectric loss tangent values correlated with the reported values in the literature (Table 2). The general mixing model with parallel mixing ($\alpha = 1$) was revealed to be a reasonably accurate method to determine the dielectric loss tangents of the dielectric powdery materials based on the measured effective loss tangent and the volume fractions used. The experimental results exhibited the same behaviour as was found with the simulations. The same good correlation and applicability of the general mixing model was also found with the modified and composite powders, as presented in later sections [Paper II, Paper IV]. The measured effective loss tangents (Eq. 4) and the calculated dielectric loss tangents (Eq. 22) are plotted as a function of volume fraction in Fig. 10 and listed in Table 3.
Fig. 10. Measured effective permittivities, effective loss tangents and calculated dielectric loss tangents of dielectric powders used in the resonator measurements. Theoretical effective permittivities due to Bruggeman symmetric and Looyenga mixing rules are plotted with the inclusion permittivities listed in Table 3.

<table>
<thead>
<tr>
<th>Dielectric powder</th>
<th>$\varepsilon_i$</th>
<th>$\tan \delta_i$ (averaged)</th>
<th>$\rho_{\text{MUT}}$ [g/cm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>3.9</td>
<td>$3 \times 10^{-4}$</td>
<td>2.29</td>
</tr>
<tr>
<td>Heraeus CT 2000</td>
<td>8.8</td>
<td>$4 \times 10^{-3}$</td>
<td>3.43</td>
</tr>
<tr>
<td>Al$_2$O$_3$ 30 µm</td>
<td>9.8</td>
<td>$5.8 \times 10^{-3}$</td>
<td>4.06</td>
</tr>
<tr>
<td>Al$_2$O$_3$ 6 µm</td>
<td>9.8</td>
<td>$1.2 \times 10^{-2}$</td>
<td>3.84</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>13.9</td>
<td>$5.6 \times 10^{-3}$</td>
<td>5.93</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>18.2</td>
<td>$2.9 \times 10^{-3}$</td>
<td>6.5</td>
</tr>
</tbody>
</table>

3.3 Discussions of the results

When comparing the results with previous researches, similar conclusions can be found. Conger et al. and Nelson et al. have also reported consistent correlation with the measured effective permittivity values when determining inclusion permittivity using the Bruggeman symmetric (often mentioned in literature as Böttcher formula [16]) and the Looyenga mixing rules [15, 17]. However, Nelson et al. reported their open-ended coaxial cable technique to be inaccurate to measure low-loss dielectric samples [17]. The measured effective permittivity correlation with the Lichtenecker mixing rule and derived inclusion permittivity were not as good as that reported by Ebara et al. [18]. Furthermore, good curve correlation between the measured effective graph and the graph of the mixing rule is not adequate to detect a credible inclusion permittivity. This finding has also been reported by Sheen et al. [37]. Thus, the use of the Bruggeman symmetric and the Looyenga mixing rules with the defined volume fraction ($f_d = 0.43$) gives better accuracy when detecting small changes in permittivity with the particular characterization method as was found with modified particles [Paper II – Paper IV]. Regarding the previous researches the permittivity range used in this research was significantly wider and the Bruggeman symmetric and the Looyenga mixing equations exhibited the best correlation with the simulated and the measured results. Although the model was not strictly three dimensional due to the air pipes, the modelling results correlated well with the measurement results. Furthermore, increasing the complexity of the model did not notably change the response of the modelled resonator within the used permittivity range.

Although it is possible to measure very accurately the resonance frequency and quality factor with modern VNAs and calculate the effective permittivity, the
determination of the inclusion permittivity by using the mixing rules also depends on the density determination. The maximum theoretical filling factor is determined by the inclusion density and the volume of the sample cavity. As can be seen from the equations of the mixing rules, the error in volume fraction becomes significant as the contrast between inclusion permittivity and environment increases. Hence, increased accuracy in density measurements results in better accuracy in inclusion permittivity determination.
4 Characterization of modified powders

The scope of this chapter is to demonstrate the detection sensitivity of the resonator when characterized powdery materials were modified, either by adsorbed water due to humidity exposure or by surfactant coating treatment. In addition to the effect of the changed dielectric properties of the modified particles, the quantification accuracy to detect moisture and surfactant content is covered. Results have originally been reported in journal Papers II and III.

4.1 Humidity effect on complex permittivity and moisture content quantification

*Weak adsorption*

Dielectric powders that had been exposed to humidity induced noticeable changes in the electrical properties of the resonator. Resonance frequencies and quality factors changed compared to when dry powders were used, even though the moisture adsorption was weak. With silicon dioxide the moisture adsorption was very low, only 0.1 vol. %, and it caused only minor changes to the effective permittivities of the measured samples. Although the permittivity of the water (~80 [49]) is much higher than that of silicon dioxide it is also reported that water adsorbed on particles has a permittivity that is different from that of a plain water sphere [16] (p. 236). Correlation with the Bruggeman symmetric and the Looyenga mixing rules was achieved with an inclusion permittivity of 3.92 that was close to the value determined with dry SiO₂ powder, i.e., 3.88. However, the moisture effect was clearly noted in the effective loss tangents as a significantly decreased quality factor. In Fig. 11 the theoretical effective loss tangent is plotted with the moisture content (mc) traditionally measured with a precision balance (0.045 wt. %, 0.1 vol. %). When determining moisture content based on the differences in quality factors between dry and moist powder samples, a match with the theoretical effective loss tangents was obtained with 0.085 vol. % of water. This correlates reasonable well with the traditionally determined value. When comparing the presented method to that of Austin et al., calibration data are not needed to achieve good accuracy with determined moisture content [21].
Fig. 11. Measured effective permittivities and loss tangents of SiO$_2$ powder after 5% and 100% relative humidity exposures. Theoretical moisture contents are plotted both with 0 and mass based volume percentages. The resonance frequencies of the resonator perturbed by the sample were within the range of 3.53-3.22 GHz [Paper II]. (Paper II, reprinted with permission from Applied Physics Letters. Copyright 2013, AIP publishing LLC).

**Strong adsorption**

Measurements with aluminium and zirconium oxide powders exhibited much higher moisture adsorption than was found with the fairly hydrophilic SiO$_2$ powder. Despite the smallest particle size, ZrO$_2$ did not adsorb as much moisture as Al$_2$O$_3$. This was also evident in changes in the physical composition of the aluminium oxide powder, i.e., increased agglomeration and decreased flowability. However, the stronger adsorption and increased water layers on oxide inclusions did not cause any significant effect on the measured effective permittivity. Thus, the determined inclusion permittivities in both cases were close to the values measured with dry samples (Table 4). However, the effect of the stronger adsorption was clearly seen in the measurements of the effective losses, which in the case of Al$_2$O$_3$ increased the calculated dielectric loss tangent from $5 \times 10^{-3}$ to $1.1 \times 10^{-2}$. In both cases, the calculated moisture content, based on the measured effective loss tangents and the general mixing model with the dielectric loss
tangent of water [49], correlated reasonably well with the traditional mass based moisture content determination.


<table>
<thead>
<tr>
<th>Powder</th>
<th>ρ_{MUT} [g/cm³]</th>
<th>SSA [m²/g]</th>
<th>ε_dry</th>
<th>ε_moist</th>
<th>tan δ_dry</th>
<th>tan δ_moist</th>
<th>MC_a [vol.%]</th>
<th>MC_b [vol.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>2.29</td>
<td>0.3</td>
<td>3.88</td>
<td>3.92</td>
<td>2×10⁻⁴</td>
<td>3×10⁻⁴</td>
<td>0.1</td>
<td>0.085</td>
</tr>
<tr>
<td>Al₂O₃</td>
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<td>0.45</td>
<td>9.6</td>
<td>9.9</td>
<td>5×10⁻³</td>
<td>1.1×10⁻²</td>
<td>2.5</td>
<td>3.5</td>
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<tr>
<td>ZrO₂</td>
<td>5.93</td>
<td>5.05</td>
<td>13.5</td>
<td>13.6</td>
<td>6×10⁻³</td>
<td>9×10⁻⁵</td>
<td>1.0</td>
<td>1.09</td>
</tr>
</tbody>
</table>

^ Mass based

Based on measured loss tangents

4.1.1 Detecting the effect of desorption

Since the open end of the coaxial cavity resonator has the strongest electric field, it is the most sensitive to changes in dielectric properties. Thus, the effect of moisture desorption was clearly detected. The effective permittivities and the loss tangents of silicon dioxide and aluminium oxide are shown as a function of time in Fig. 12. In the case of silicon dioxide, desorption caused similar but opposite changes in the dielectric properties to those that were detected when measuring several samples with different volume fractions. The effective permittivity, and thus the inclusion permittivity, remained the same during the measurement period. Despite the hydrophilic nature of the particular silicon dioxide, the changes in the effective loss tangents were noticeable during drying. [Paper II]

In the case of aluminium oxide, the stronger ability to adsorb water [59, 60] caused a more pronounced effect and changes could also be noted in inclusion permittivity with the particular sample during the desorption period, i.e., 10.3 > ε_i > 9.8. Even though, the inclusion permittivity of the dry powder was eventually also reached with Al₂O₃ sample, the drying however was uneven along the sample and can also be found as higher loss tangents at the end. Thus, to enable an accurate determination of the dielectric properties and the moisture content, the homogeneity of the sample should be maintained. In addition, frequency and the temperature dependence of the dielectric loss tangent of water can affect the accuracy when determining moisture content by using the general mixing model and the measured dielectric properties [49, 61].
Fig. 12. Effective permittivities and effective loss tangents of Al₂O₃ and SiO₂ as a function of time when powders dried for 3 hours at room humidity (20% R.H.) after 100% R.H. exposure. (Paper II, reprinted with permission from Applied Physics Letters. Copyright 2013, AIP publishing LLC).

4.2 Detection of surfactant treatment effect

4.2.1 Coating effect on permittivity

Surfactant treatment with stearic acid induced only a minor change in inclusion permittivity in the cases of treated SiO₂, Al₂O₃ and ZrO₂ particles (Fig. 13). With
SiO$_2$ powder, the inclusion permittivity remained virtually the same as that of untreated particles, i.e., 3.9. However, stearic acid coating on Al$_2$O$_3$ and ZrO$_2$ particles had a slightly stronger effect in that it decreased the permittivity from 9.8 to 9.7 and from 13.6 to 13.2, respectively. STA-TG-DSC-MS measured stearic acid volume percentages in SiO$_2$ (0.05 vol. %) and Al$_2$O$_3$ (0.52 vol. %) powders were much lower than in the case of ZrO$_2$ (1.36 vol. %) as illustrated in Fig. 14. Thus, the stearic acid coating, having a permittivity of 2.3 at 3.5 GHz [Paper III], had a much greater effect on the inclusion permittivity of coated ZrO$_2$. However, it should be noted that residues of adsorbed water, following the coating process, can attenuate this permittivity decrease because of the high permittivity of water in the gigahertz range [Paper II]. STA-TG-DSC-MS measured residues of water after surfactant treatment were 0.02 vol. %, 0.92 vol. % and 0.69 vol. % for SiO$_2$, Al$_2$O$_3$ and ZrO$_2$, respectively.

![Fig. 13. Measured effective permittivities and loss tangents of surfactant treated and untreated oxide powders as a function of volume fraction. Theoretical effective loss tangents are plotted with dosed amount of surfactant and with measured amounts of H$_2$O and surfactant. The resonance frequencies of the resonator perturbed by sample were within the range of 3.53 – 3.21 GHz, 3.03 – 2.65 GHz and 3.79 – 2.17 GHz for SiO$_2$, Al$_2$O$_3$ and ZrO$_2$, respectively [Paper III]. (Paper III, reprinted with permission from Powder Technology. Copyright 2014, Elsevier LTD).](image-url)
4.2.2 Coating effect on losses and theoretical correlation

The stearic acid coating had a pronounced impact on dielectric losses when the dielectric properties of untreated and surfactant treated particles were compared. As the amount of adsorbed water was included into the theoretical calculations using the general mixing model, the total loss tangent of treated powder resulted in

$$\tan \delta_{\text{eff}} = f_d \tan \delta_d + f_s \tan \delta_s + f_w \tan \delta_w + f_a \tan \delta_a = f_d \tan \delta_d + f_a \tan \delta_a.$$  

In the equation the subscripts \(d\), \(s\), \(w\), \(a\) and \(d\) refer to untreated dielectric material, stearic acid, water, air and treated dielectric material, respectively. Theoretical calculations of \(\text{SiO}_2\) with a dosed, and optimally adsorbed, amount of stearic acid did not differ notably from the untreated \(\text{SiO}_2\) inclusions (Fig. 13). This was due to the fact that the measured dielectric loss tangent of stearic acid (\(\tan \delta_s = 6 \times 10^{-4}\)) was close to that of the untreated and dry silicon dioxide inclusion (\(\tan \delta_d = 2 \times 10^{-3}\)). Furthermore, the volume ratio of the stearic acid was low (Table 5). However, the resonator measured loss tangent of the treated powder was clearly higher than that of the untreated powder, i.e. \(4 \times 10^{-4}\). With the STA-TG-DSC-MS measured amounts of stearic acid and \(\text{H}_2\text{O}\), which has a high dielectric loss tangent at 3 GHz (\(157 \times 10^{-3}\)) [49], the recalculated theoretical loss tangent came closer to the measured loss tangent of the treated \(\text{SiO}_2\) powder. The amounts of stearic acid and water were very low, which made it difficult for the thermogravimetry and mass spectrometry to determine exact values for the theoretical comparison. Because of low dielectric loss tangent of untreated \(\text{SiO}_2\),
only a very small amount of H2O can affect the calculated theoretical loss tangent of the treated powder [Paper II].

With aluminium oxide the theoretically calculated loss tangent with optimally coated surfactant also remained ($5 \times 10^{-3}$) because of low amount of stearic acid. In contrast, the measured effective loss tangents increased and a significantly higher dielectric loss tangent ($6.1 \times 10^{-3}$) was detected. With the recalculated amounts of surfactant and H2O, the theoretical value had a better correlation (Fig. 13). Despite the increased hydrophobicity due to the stearic acid coating on aluminium oxide particles, the hydrophilic nature of Al2O3 caused water adsorption during the coating process. This could be the reason for the increased dielectric losses [49-60].

In a case of coated ZrO2, the composition of the powder clearly changed compared to that of untreated powder in that it became more fluid and dispersed. Also EFTEM micrographs, inspected from several sides of the particles, indicated a more extensive coating with 5 nm thickness compared to SiO2 and Al2O3 particles (Fig. 15). Because of this, even the lowest volume fraction was dense, i.e., minimum $f_d > 0.3$. The theoretical amount of stearic acid was notable higher, due to the highest SSA value, than with silicon dioxide and aluminium oxide powders. This clearly decreased the theoretical effective loss tangents of treated ZrO2 powder. However, the measured effective loss tangents were significantly below the theoretical values and even more so when the amount of adsorbed water was included in the recalculations of theoretical effective loss tangent values. The measured dielectric loss tangent of coated ZrO2 inclusions decreased from that of untreated inclusions, i.e., from $6.2 \times 10^{-3}$ to $3.8 \times 10^{-3}$. This indicated that due to the stearic acid coating the extrinsic factors, e.g., particle morphologies and boundaries that affect the electric field inside the resonator, had a more pronounced impact on dielectric losses than even the theoretical amount of low loss stearic acid [62]. Similar findings regarding decreased dielectric losses were also reported in a case of surfactant ($n$-hexylphosphonic acid) treated BaTiO3 nanoparticles, and organic molecules coated and self-passivated nano- and micro-particles, respectively [63-65].
Fig. 15. EFTEM images of stearic acid coated oxide particles [Paper III]. (Paper III, reprinted with permission from Powder Technology. Copyright 2014, Elsevier LTD).
Table 5. Measured densities and SSA values of dry untreated powders, calculated densities of treated powders and dielectric properties of untreated and surface coating processed inclusions at room temperature in the 2.17 - 3.79 GHz frequency range. Stearic acid density and dielectric loss tangent at 3.5 GHz were used in calculations of theoretical effective loss tangents. [Paper III]. (Paper III, reprinted with permission from Powder Technology. Copyright 2014, Elsevier LTD).

<table>
<thead>
<tr>
<th>Powder</th>
<th>$\rho$ [g/cm$^3$]</th>
<th>$\rho$ [g/cm$^3$]</th>
<th>SSA [m$^2$/g]</th>
<th>$\varepsilon_i$ untreated</th>
<th>$\varepsilon_i$ treated</th>
<th>$\tan\delta_d$ untreated</th>
<th>$\tan\delta_d$ treated</th>
<th>vol.% a</th>
<th>vol.% b</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>2.29</td>
<td>2.28</td>
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<td>3.9</td>
<td>3.9</td>
<td>$2 \times 10^{-4}$</td>
<td>$4 \times 10^{-4}$</td>
<td>0.15</td>
<td>0.05</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>4.06</td>
<td>4.01</td>
<td>0.45</td>
<td>9.8</td>
<td>9.7</td>
<td>$5 \times 10^{-3}$</td>
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<td>0.41</td>
<td>0.52</td>
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<td>ZrO$_2$</td>
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<td>5.82</td>
<td>5.05</td>
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<td>13.2</td>
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<td>$3.8 \times 10^{-3}$</td>
<td>6.39</td>
<td>1.36</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>0.98</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$6 \times 10^{-4}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Theoretical amount of adsorbed surfactant
b Measured amount of adsorbed surfactant
c Based on the measured amounts of adsorbed surfactant and water
5 MgTiO$_3$-CaTiO$_3$ composite powder characterization

In this chapter the applicability of the characterization method in the composite applications with two materials, MgTiO$_3$ and CaTiO$_3$, is described. In addition to the ability to detect changes in the dielectric properties when increasing the content of CaTiO$_3$, the quantification accuracy of the determination of molar ratios of composite powders is analysed. Results have originally been reported in journal Paper IV.

5.1 Permittivity changes due to varying molar ratio

An increase in calcium titanate content was clearly observable when measuring the dielectric properties of composite magnesium calcium titanate powders. As expected, the effective permittivities and the loss tangents were most affected with the highest volume fractions of CaTiO$_3$ inclusions but the differences were also detectable with the lowest volume fractions investigated (Fig. 16). The resonator measurement results showing steadily changing effective dielectric properties indicated homogenous MgTiO$_3$-CaTiO$_3$ mixtures with CaTiO$_3$ content of 0, 2, 5 and 10 mol. %. Homogeneous calcium distribution in the composite powders was also visible in EPMA analysis (inserts in Fig. 17). Thus, it was reasonable to assume that the changes in the measured resonance frequencies and the increase in the calculated effective permittivities were caused by the increased amount of calcium titanate inclusions.

When determining inclusion permittivities of the composite powder using Bruggeman symmetric and Looyenga mixing rules, a clear increase was found. Inclusion permittivities changed from that of MgTiO$_3$ (13.4) to 13.5, 14.0 and 14.9 with CaTiO$_3$ amount of 2, 5 and 10 mol. %, respectively (Fig. 17).
Fig. 16. Measured effective permittivities and loss tangents of \((1-x)\text{MgTiO}_3-x\text{CaTiO}_3\) as a function of volume fraction where molar ratios \((x)\) of \text{CaTiO}_3\) are 0, 0.02, 0.05, and 0.1. The resonance frequencies of the resonator perturbed by the powder samples were within the range of 2.12 - 3.66 GHz. [Paper IV]. (Paper IV, reprinted with permission from Journal of Applied Physics. Copyright 2014, AIP publishing LLC).

Fig. 17. Measured effective permittivities of \((1-x)\text{MgTiO}_3-x\text{CaTiO}_3\) composite powders with \text{CaTiO}_3\) molar ratios \((x)\) of 0.02 (a), 0.05 (b) and 0.1 (c) and effective permittivities of Bruggeman symmetric and Looyenga mixing models with inclusion permittivities of 13.5 (a), 14.0 (b) and 14.9 (c). Measured effective loss tangents of MgTiO3 and composite powders and theoretical effective loss tangents calculated by the general mixing model. The resonance frequencies of the resonator perturbed by the powder samples were within the range 2.12 – 3.66 GHz. EPMA figures of calcium distribution (light dots in 100 µm × 100 µm analysis areas) in composite powders as inserts. [Paper IV]. (Paper IV, reprinted with permission from Journal of Applied Physics. Copyright 2014, AIP publishing LLC).
5.2 Determined dielectric losses and theoretical quantification

The effect of increasing the amount of calcium titanate was more pronounced when measuring the effective loss tangents of the composite powders (Fig. 16). The measured dielectric loss tangent of CaTiO$_3$ ($2.1 \times 10^{-3}$) was much higher than that of MgTiO$_3$ ($7.1 \times 10^{-3}$). This was also clearly observed with the measured composite powder samples as systematically increasing dielectric losses. When comparing the measured values of composite samples and the theoretically calculated values with the added amount of CaTiO$_3$, a clear correlation was found (Fig. 17). With two dielectric powder components, the general mixing model equation results in $\tan \delta_{\text{eff}} = f_{d1} \tan \delta_{d1} + f_{d2} \tan \delta_{d2} + f_a \tan \delta_a = f_d \tan \delta_d + f_a \tan \delta_a$, where the subscripts $d1$, $d2$, $d$ and $a$ refer to titanate components, composite inclusions and air, respectively. With 0.98MgTiO$_3$-0.02CaTiO$_3$ samples (Fig. 17 a) the calculated dielectric loss tangent was $7.4 \times 10^{-3}$. Also the composite samples with 5 mol. % of CaTiO$_3$ had a good theoretical correlation (Fig. 17 b). In this commonly used molar ratio case the dielectric loss tangent was $7.9 \times 10^{-3}$, which also correlated with the reported value in the 3 GHz range [66]. With the 0.9MgTiO$_3$-0.1CaTiO$_3$ samples (Fig. 17 c) a slight difference was found between the measured and the theoretical effective loss tangents. The calculated dielectric loss tangent was $8.5 \times 10^{-3}$, whilst the theoretical value, based on the 10 mol. % of CaTiO$_3$, was $8.7 \times 10^{-3}$. An exact correlation between the measured and theoretical effective loss tangents was achieved with 9.5 mol. % CaTiO$_3$ amount.

Measurement results of dielectric properties with mass based and theoretical CaTiO$_3$ weight percentages are listed in Table 6. The measurement results in the range 2.12-3.66 GHz correlated with the values reported elsewhere [66-69]. However, it should be noticed that electromagnetic dispersion due to small particles can cause differences in the frequency dependence when compared with the bulk material [16] (p. 11, 22, 178, 196, 215) [32].

<table>
<thead>
<tr>
<th>Powder</th>
<th>$\rho$ [g/cm³]</th>
<th>$\varepsilon_i$</th>
<th>$\tan \delta_\text{meas.}$</th>
<th>$\tan \delta_\text{meas.}$</th>
<th>$\tan \delta_\text{theor.}$</th>
<th>wt. % b</th>
<th>wt. % c</th>
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<tbody>
<tr>
<td>MgTiO₃</td>
<td>3.953</td>
<td>13.4</td>
<td>$7.1 \times 10^{-3}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.98MgTiO₃-0.02CaTiO₃</td>
<td>3.955 a</td>
<td>13.5</td>
<td>$7.4 \times 10^{-3}$</td>
<td>$7.4 \times 10^{-3}$</td>
<td>2.26</td>
<td>2.26</td>
<td>-</td>
</tr>
<tr>
<td>0.95MgTiO₃-0.05CaTiO₃</td>
<td>3.956 a</td>
<td>14.0</td>
<td>$7.9 \times 10^{-3}$</td>
<td>$7.9 \times 10^{-3}$</td>
<td>5.62</td>
<td>5.62</td>
<td>-</td>
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<td>11.17</td>
<td>10.61</td>
<td>-</td>
</tr>
<tr>
<td>CaTiO₃</td>
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<td>-</td>
<td>$2.1 \times 10^{-2}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

- Calculated density based on the volume percentages of MgTiO₃ and CaTiO₃ powders.
- CaTiO₃ weight percent of 10 g master samples based on the measured masses of MgTiO₃ and CaTiO₃.
- CaTiO₃ weight percent of the measured samples determined by the general mixing model.
6 Conclusion

The purpose of the thesis was to research and develop a characterization method for powders that is sensitive to small changes in dielectric properties and that could be utilized in the vast field of powdery material applications. The presented indirectly coupled open-ended quarter wave coaxial cavity resonator method was researched using electromagnetic simulations and measurements of untreated and modified dielectric powders.

The electromagnetic simulation and the measurement results of commonly used dielectric powders followed the relation between the mixing rules of Bruggeman symmetric and Looyenga and the response of the resonator. It can be concluded that, together with the measured effective permittivity and the mixing rules, an inclusion permittivity can be determined and that it gives good correspondence with the electromagnetic model. Determination of dielectric loss tangents of inclusions, based on the measured effective loss tangents in proportion to volume fractions, gives credible results.

Moisture adsorption was found to affect the dielectric properties of powders by increasing the permittivity and the effect was even more pronounced in the increased dielectric losses. The characterization method was shown to be sufficiently sensitive to detect small changes in dielectric properties due to adsorbed water. This was demonstrated by the comparison between dry and humidity exposed powders. The effect was greater with very hygroscopic materials, e.g., aluminium oxide, which showed a dielectric loss increase from $5 \times 10^{-3}$ to $1.1 \times 10^{-2}$. In addition, the sensitivity was demonstrated clearly with the measurements of humidity desorption as a function of time and with surfactant coated powder particles. The stearic acid surfactant coating decreased the permittivity of the inclusions. This effect was found to be the greatest with zirconium oxide which had the smallest particle size. Thus, the permittivity decreased from 13.6 to 13.2. The coating significantly increased the dielectric losses of silicon dioxide and aluminium oxide, i.e., from $2 \times 10^{-4}$ to $4 \times 10^{-4}$ and from $5 \times 10^{-3}$ to $6.1 \times 10^{-3}$, respectively. However, with zirconium oxide, the changed extrinsic loss factors such as particle morphologies and boundaries had a greater effect on the dielectric losses. These decreased the dielectric loss of ZrO$_2$ inclusions notably from $6.2 \times 10^{-3}$ to $3.8 \times 10^{-3}$.

Applicability for ceramics applications was researched with magnesium and calcium titanate powder composites. The characterization method was demonstrated to be capable of detecting changes in MgTiO$_3$ when the CaTiO$_3$
content was changed from 0 mol. % up to 10 mol. %. In such cases the inclusion permittivity increased systematically from that of pure MgTiO$_3$, i.e., 13.4, to 14.9. The change was even clearer with the dielectric loss tangent which increased from $7.1 \times 10^{-3}$ to $8.5 \times 10^{-3}$.

Material quantification by using a general mixing model and the measured effective loss tangents, i.e., changes in the quality factors of the resonator, were found to have good accuracy and correlation with traditional mass based quantification. When detecting the moisture content of humidity exposed powders, the mass based moisture contents of SiO$_2$, Al$_2$O$_3$ and ZrO$_2$ were 0.1, 2.5 and 1.0, respectively. The corresponding values based on measured quality factors and general mixing model were 0.085, 3.5 and 1.09, respectively. The accuracy was even greater when detecting molar ratios of composite powders MgTiO$_3$ and CaTiO$_3$. Exact correlation with mass based determination was found with 2 mol. % and 5 mol. % calcium titanate content. A slight difference existed with the 0.9MgTiO$_3$-0.1CaTiO$_3$ composite, which was determined to have a CaTiO$_3$ content of 9.5 mol. % by the resonator measurements of quality factor and the general mixing model.

The researched novel powder characterization method was shown to be a useful method for measuring dielectric properties of powders and detecting changes due to powder modifications. The research provides solutions and gives valuable additions to knowledge in the field of the dielectric properties of powders. This area is still only weakly understood and there is very limited information in the literature. In addition, the theoretical determination of the moisture content and the molar ratios, without the need for calibration data, was shown to be accurate when compared to traditional mass based methods. Thus, the method is suitable for utilization in various applications, for example, in quality monitoring including purity, phase transitions and the homogeneity of master samples. Furthermore, the techniques described in this thesis, together with the simulation and the measurement results, give a significant overview of this novel sensitive method which may be developed further into a commercial device. This further development could include the use of nanometre sized particles and core-shells that also are currently the subject of enhanced scientific interest.
# References

Original papers


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Original publications are not included in the electronic version of the dissertation.
486. Liu, Meirong (2014) Efficient super-peer-based coordinated service provision
490. Aapaoja, Aki (2014) Enhancing value creation of construction projects through early stakeholder involvement and integration
492. Sliz, Rafal (2014) Analysis of wetting and optical properties of materials developed for novel printed solar cells
495. Mehtonen, Saara (2014) The behavior of stabilized high-chromium ferritic stainless steels in hot deformation
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497. Myllylä, Teemu (2014) Multimodal biomedical measurement methods to study brain functions simultaneously with functional magnetic resonance imaging
498. Tamminen, Satu (2014) Modelling the rejection probability of a quality test consisting of multiple measurements
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DIELECTRIC CHARACTERIZATION OF POWDERY SUBSTANCES USING AN INDIRECTLY COUPLED OPEN-ENDED COAXIAL CAVITY RESONATOR