A NOVEL LOW TEMPERATURE CO-FIRING CERAMIC (LTCC) MATERIAL FOR TELECOMMUNICATION DEVICES

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OULU 2001

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Academic Dissertation to be presented with the assent of the Faculty of Technology, University of Oulu, for public discussion in Kajaaninsali (Auditorium L 6), Linnanmaa, on December 7th, 2001, at 12 noon.

OULUN YLIOPISTO, OULU 2001

Manuscript received 31 October 2001
Manuscript accepted 7 November 2001

Communicated by
Professor Heiko Thust
Doctor Esa Kemppinen

ISBN 951-42-6553-X (URL: http://herkules.oulu.fi/isbn951426553X/)

ALSO AVAILABLE IN PRINTED FORMAT
ISBN 951-42-6552-1
ISSN 0355-3213 (URL: http://herkules.oulu.fi/issn03553213/)

OULU UNIVERSITY PRESS
OULU 2001

Jantunen, Heli, A novel Low Temperature Co-firing Ceramic (LTCC) material for telecommunication devices
Department of Electrical Engineering and Infotech Oulu, University of Oulu, P.O.Box 4500, FIN-90014 University of Oulu, Finland
2001
Oulu, Finland
(Manuscript received 31 October 2001)

Abstract

The thesis describes the development of a novel LTCC material system for RF and microwave telecommunication purposes.

The work has been divided into three parts. In the first section, the compositional and firing properties of this novel LTCC dielectric have been studied as well as its thermomechanical and dielectric properties. The second section describes the multilayer component preparation procedure for the ceramic material including tape casting and lamination parameters and the selection of the conductor paste. In the last section, the novel LTCC material system has been used to demonstrate its properties in RF multilayer resonators and a bandpass filter.

The dielectric material for the novel LTCC system was prepared using magnesium calcium titanate ceramic, the firing temperature of which was decreased to 900°C by the addition of a mixture of zinc oxide, silicon oxide and boron oxide. The powder was made without any prior glass preparation, which is an important process advantage of this composition. The fired microstructure was totally crystalline with high density (3.7 Mg m^{-3}) and low porosity (0.5 %). The mechanical properties were virtually identical to the values of the commercial LTCCs, but the higher thermal expansivity makes it most compatible with alumina substrates. The dielectric values were also good. The permittivity was 8.5 and the dissipation factor ($0.9 \cdot 10^{-3}$ at 8 GHz) less than that of the commercial LTCCs. Furthermore, the temperature coefficient of the resonance frequency was demonstrated to be adjustable between the range of +8.8 ... -62 ppm/K with a simple compositional variation of titanium oxide.

The slurry for the tape casting was prepared using poly(vinyl butyral) -base organic additives and the 110 µm thick tapes had a smooth surface (RA < 0.5 µm). The multilayer components were prepared using 20 MPa lamination pressure, 90°C temperature and 1 h dwell time. The most suitable conductor paste for this composition was found to be commercial silver paste (duPont 6160), which produced satisfactory inner and outer conductor patterns for multilayer components. Finally, resonators with a resonant frequency range of 1.7 ... 3.7 GHz were prepared together with a bandpass filter suitable for the next generation of telecommunication devices. This demonstration showed the potential of the developed novel LTCC material system at high RF frequencies.

Keywords: ceramic materials, LTCC materials, microwave properties, telecommunication devices

Aikaa myöten
ajan tajun aistimilla,
alkaa ympäristö yllättää,
aivot ymmärtää
erilaista elomuotoa
ekologista elinkaarta,
tulee tutuksi tulevaisuus
ja haluaa hallita
hiukkasen

Omistettu hyvälle ystävälleni Helille
väitöspäivänä,
kiitoksena lukuisista ja monimuotoisista keskusteluista
matkan varrella

Kaisa Kerätär

Acknowledgements

First of all, I wish to thank my supervisor Professor Seppo Leppävuori, who arranged the opportunity to do this research with circumstances I was never able to dream. I am also most grateful to Dr. Antti Uusimäki, the mental tutor of this work, for his encouraging and endless support from the very first beginning. The valuable advice from Professor Risto Rautioaho is also appreciated. The role of Mr. Aimo Turunen was also important especially in the electromagnetic simulations. I am also grateful to everyone in the Microelectronics and Materials Physics Laboratory for the unreserved working atmosphere and especially Mr. Timo Vahera for his tireless help in many ways. The staff of the Institute of Electron Optics, University of Oulu, and especially Ms. Raija Peura and Mr. Olli Taikina-aho have supported my work with excellent professional skills and a helpful attitude. Many people from Materials Engineering Laboratory have also helped with practical work. I am very grateful to Dr. A. E. Hill for revising the English language of the manuscript.

This work was financially supported by the Academy of Finland, Tauno Tönning Foundation, Nokia Foundation and Electronic Materials, Packaging and Reliability Group of Infotech Oulu, all of which are gratefully acknowledged.

Special thanks are to be expressed to my long lasting friend, Ms. Kaisa Kerätär, who wrote the poem for this thesis, to all my friends, who have been patient with this one topic in my recent life and to my former colleagues and supervisors, who have taught me so much. I also thank my little sister, Ms. Marjaana Kymäläinen and her family.

Finally, my deepest gratitude is dedicated to my husband and better half, Mr. Juhani Asunmaa, who has shared with me many varying stages of life.

I thank you all!

Oulu, October 2001 Heli Jantunen

List of abbreviations and symbols

ε_r	permittivity
λ	wavelength
ρ	bulk density
σ_f	fracture strength
τ_e	temperature coefficient of dielectric constant
τ_f	temperature coefficient of resonance frequency
a	half length of indent diagonal
BE	back scattering mode in SEM
C	capacitance
c	radial crack length
DF	Dissipation Factor
E	Young’s modulus (elastic modulus)
EDS	Energy Dispersive Spectrometer
FESEM	Field Emission Scanning Electron Microscope
GPS	Global Positioning System
HTCC	High Temperature Co-fired Ceramic
H_v	Vickers hardness
JCPDS	Joint Committee of Powder Diffraction Standard
K_{IC}	fracture toughness
L	inductance
LTE	Linear Thermal Expansivity
LTCC	Low Temperature Co-fired Ceramic
MCM	Multi-Chip Module
PCB	Printed Circuit Board
PEG	Polyethylene glycol
PVA	Polyvinyl alcohol
PVB	Poly(vinyl butyral)
R	resonator
RA	arithmetic average roughness
RF	Radio Frequency

SAM	Scanning Acoustic Microscope
SEM	Scanning Electron Microscope
SSA	Specific Surface Area
TE	Transverse Electric field
TEM	Transverse ElectroMagnetic field
TM	Transverse Magnetic field
v_c	compressional velocity of acoustic wave
v_s	shear velocity of acoustic wave
XRD	x-ray diffraction

List of original papers

Original papers, presented at the end of the thesis, are referred to throughout the text by their roman numbers.

I Jantunen H, Rautioaho R, Uusimäki A & Leppävuori S (2000) Compositions of $MgTiO_3$- $CaTiO_3$ ceramic with two borosilicate glasses for LTCC technology. The Journal of European Ceramic Society, No. 20, pp. 2331-2336.

II Jantunen H, Rautioaho R, Uusimäki A & Leppävuori S (2000) Preparing low loss LTCC material without glass addition. The Journal of American Ceramic Society, Vol. 83, No. 11, pp. 2855-2857.

III Jantunen H, Uusimäki A, Rautioaho R & Leppävuori S. The effect of processing route on the thermomechanical properties of a low temperature firing ceramic for electronic packaging. Accepted to the British Ceramic Transactions, 2001.

IV Jantunen H, Uusimäki A, Rautioaho R & Leppävuori S. The temperature coefficient of microwave resonance frequency of a LTCC system. Accepted to the Journal of American Ceramic Society, 2001.

V Jantunen H, Turunen A, Leppävuori S & Uusimäki A. Meshed and uniform ground planes on LTCC strip line resonators and bandstop filters. Submitted to the IEEE Transactions on Components and Packaging Technologies, 2001.

VI Jantunen H, Leppävuori S, Turunen A & Uusimäki A. Multilayer resonators and a bandpass filter fabricated from a novel Low Temperature Co-fired Ceramic (LTCC). Accepted to the Journal of Electronic Materials, 2001.

The object of paper I was to introduce a novel dielectric ceramic for the LTCC process. It presents compositional studies and basic methods used for microstructure and firing investigations. As a result, the sintering temperature of the well-known dielectric ceramic ($MgTiO_3$-$CaTiO_3$) was decreased from 1360°C to 900°C, suitable for the LTCC process.

Paper II describes a straightforward method of making this novel LTCC material without any prior glass preparation route. The results showed that this method produced a composition with improved firing properties more suitable for the LTCC process without impairment of the microstructural and dielectric properties.

In papers III and IV, the main purpose was to determine the thermomechanical properties of this low firing ceramic and to demonstrate the possibility of optimising the temperature coefficient of the resonance frequency. The achieved results were compared with the properties of commercial LTCC materials. The thermomechanical properties of this novel LTCC dielectric with the straightforward preparation route were good, the essential dielectric dissipation factor was low and the temperature stability of the resonance frequency was shown to be adjustable through compositional variation.

Papers V and VI describe structures, modeling and preparation methods and also measured values of designed multilayer RF resonators and filters. In paper V, a commercial LTCC material system was used and the effects of meshed and uniform ground planes on the Q-factor of the resonators were studied. According to these results, paper VI describes the preparation of multilayer resonators and a bandpass filter from the novel LTCC dielectric using uniform ground planes. This paper also describes tape casting and lamination parameters of the novel low firing dielectric ceramic and the selection of a suitable conductor paste. Thus, paper VI is an applicational demonstration of performance of the whole novel LTCC material system. It was shown that it is suitable for multilayer RF and microwave components and the achieved values of resonators and filter were excellent.

The experimental tests of papers I-IV were the contribution of the author. In papers V and VI, the experiments and simulations were done in association with the co-authors and staff and basic ideas were the contribution of the author. The manuscripts for publications were written by the author with the kind help of the co-authors.

Contents

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Original papers

1 Introduction

1.1 The LTCC material system for RF and microwave components

Telecommunication technology industry today requires high volume and low cost circuit fabrication, while at the same time demanding excellent electrical performance, reliability, circuit miniaturisation and surface mounting techniques. [Barnwell *et al*. 2000, Miyake *et al*. 1999]. Recently, Low Temperature Co-fired Ceramics (LTCCs) have been intensively studied for these applications. Although ceramic materials have been used for RF filters, resonators and antennas for several decades [Wakino *et al*. 1987, Fujishima 2000, Alford *et al*. 1997, Mizoe *et al*. 1999, Shutler *et al*. 1997, Huang & Lin 2000 Dakeya *et al*. 2000], LTCC technology has now attained the level of a real combination of dielectric ceramic layers with embedded electrodes made of high conductivity metals such as silver or copper. [Barnwell *et al*. 2000, Tummala 1991, Sheen 1999] LTCC technology provides a promising way to realise high quality multi-chip modules (MCM) which have huge market prospects. [Scrantom & Gravier 1999] The major RF opportunities are in the fields of mobile telecommunication devices (0.9–2 GHz), wireless local networks such as Bluetooth (2.4 GHz), geographical positioning such as GPS (1.6 GHz) and in broad band access connection systems (5.8–40 GHz). [Barnwell *et al*. 2000]

LTCC technology possesses several advantages making it suitable for mass market telecommunication applications. The process itself enables high yield, fast turnaround and reduced cost of devices with three dimensional microwave structures. This combination, together with the possibility of fabricating fine conductive lines and spaces, small interconnect vias and high dielectric layer counts leading to high density packaging, has recently resulted in intensive research into LTCC technology. [Barnwell *et al*. 2000] Additionally, using computer aided component design and simulation systems, LTCC filters have been produced with 100% yield up to tolerances in materials and manufacturing processes. [Bailey *et al*. 1997]

The key areas for LTCC technology are the development of the material and the process, and component design and reliability, which all form their own field of research requiring a wide understanding of the subject. On the other hand, a real functional LTCC system cannot be developed if any of these areas are neglected.

In the development of a novel dielectric material for the LTCC system, the electrical and thermomechanical demands are obvious for enabling the production and usage of reliable components. In the special case of RF applications, the dielectric properties such as low dissipation factor (DF), appropriate permittivity (ε_r) and near zero temperature coefficient of the resonance frequency (τ_f) are important. These three values enable the construction of RF filters with convenient size, low insertion loss, a steep cut-off and operational stability of the performance curve at ambient temperatures. [Penn *et al.* 1997]

After successful development of the novel dielectric material, it should be employed in a multilayer process. This first requires the preparation of a green dielectric tape, which is itself at the state of the art. Tape suitable for multilayer manufacturing needs to withstand handling and via punching and produce, after lamination and low temperature co-firing, a solid material with the desired properties. [Cahn *et al.* 1996, chap. 7] A good surface smoothness and compatibility with embedded conductive lines are also essential properties. [Sheen 1999, Barnwell *et al.* 2000]

The last decade has seen the appearance of many commercial LTCC material systems including ceramic tapes and suitable conductor and resistor pastes (duPont 951 and 943, Ferro A6-5-M-13, Heraeus CT700) and their electrical and thermomechanical properties have been well reported. [Barnwell *et al.* 2000, Jones *et al.* 2000, Amey *et al.* 2000, Scrantom & Gravier 1999] This development has accelerated their utilisation, but although microwave components have already been constructed [Sheen 1999, Liang *et al.* 1999, Miyake *et al.* 2000], improved ceramics are still needed. In particular, only a few LTCC materials for RF applications, with the combination of low DF and optimised temperature coefficient of the resonance frequency, have been introduced. [Barnwell *et al.* 2000, Kagata *et al.* 1992]

After these two stages of development, the novel LTCC material system can be tested in a real multilayer RF and microwave component. In the case of commercial LTCC material systems, the material and tape preparations do not need to be arranged. Information from commercial material manufacturers also guides users through the process steps giving the necessary material parameters for component design and preparation.

1.2 Objective and outline of this thesis

The main target of this thesis has been to develop a novel LTCC dielectric for RF and microwave components. The basics of the already existing low temperature fired dielectrics were first studied and the special demands of the multilayer preparation procedure and microwave components were taken into account. The stages of development shown in Fig. 1.1 were used to consider the requirements of the whole process. This means that the requirements set by RF components and the multilayer process could be taken into account in material development. Similarly, a most suitable tape from the component design standpoint could be prepared. The stages of the development were also able to give valuable feedback to each other.

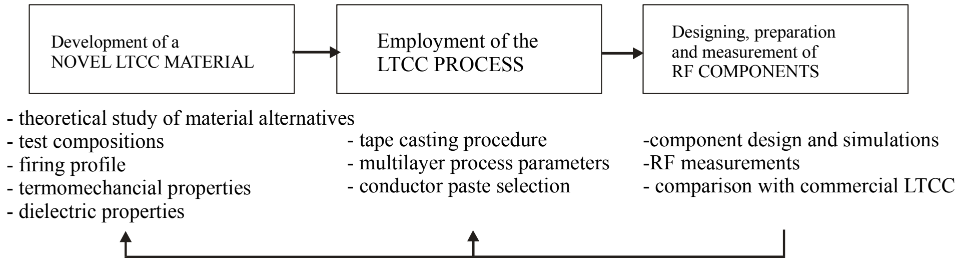


Fig. 1.1. The stages of development used for a novel LTCC material system.

This thesis describes the literature studies and empirical work done to develop a novel LTCC material system and the content of the summary is as follows:

In Chapter 2, the background and the specifications for the novel dielectric LTCC are laid down and the straightforward preparation method is presented. Furthermore, it introduces the measurements and results of the most important thermomechanical properties of this ceramic material. The possibility of optimising its dielectric values is also discussed.

The Chapter 3 describes the multilayer component preparation route for this dielectric material including the parameters needed for tape casting, laminating and firing. The microstructural properties of the fired tapes were required to be the same as those achieved in the stage of the material development in the Chapter 2. This method was used to ensure that the process had no effects on the final, fired dielectric material and thus on its properties. The selection of a suitable co-firing conductor material is also presented.

The design and structure of the multilayer resonators and filter chosen to demonstrate the abilities of this novel LTCC material system are outlined in Chapter 4 as well as their measured properties at RF frequencies.

The objectives of this thesis is thus to introduce a novel LTCC material system starting from the compositional studies of the dielectric ceramic and its dielectric, firing and thermomechanical properties. Furthermore, the multilayer component preparation procedure for this novel LTCC material system will be also presented. The author also hopes that the thesis is able to give guidance when the same types of dielectric materials are further developed.

2 Development of a LTCC dielectric material

2.1 Basis of the dielectric materials for the LTCC process

Dielectric materials used for LTCC components have to have proper firing, dielectric and thermomechanical properties so that mechanically reliable multilayer structures with the desired electrical performance can be produced.

“Proper” firing properties means that the dielectric material has to achieve a dense, non-porous microstructure below 950°C that it can be co-fired with low resistive conductor materials such as silver or copper. This is a fundamental demand and cannot be neglected in any circumstances. Additionally, any densification or crystallisation of the composition should not start at too low a temperature because this can prevent the evaporation of the organics and solvents used in conductive pastes and dielectric and thus cause residual carbon traces in the microstructure. [Tummala 1991]

For commercial LTCCs, the firing profile is specified accurately in the information given by the manufacturers and for new dielectric materials this is an essential part of their development. Fig. 2.1 shows a typical firing profile for LTCCs. The steps 1, 3 and 5 are heating and cooling periods, step 2 is for burning out the organic additives and step 4 is the actual sintering period.

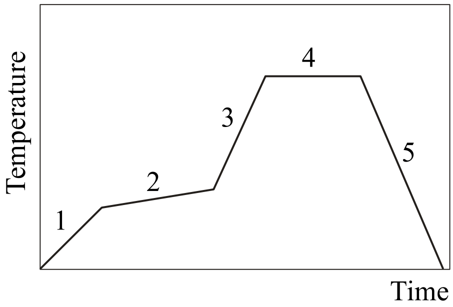


Fig. 2.1. Typical firing profile for LTCC components.

All these steps are typical for commercial LTCCs with only small variations in cooling and heating rates, maximum temperatures and dwell times caused by different compositions and additives. For duPont's 943 material system the recommended co-firing profile is presented in Table 1.

Table 1. Firing profile for duPont's 943 LTCC material system.

Temperature / °C	rate or dwell time
20–400	9.2°/min
400–600	4.7°/min
600–850	11.4°/min
850	15 min
850–20	10°/min
Total time	3 h 24 min

Preliminary information from duPont

The second requirement, dielectric properties, is of course one of the most important factors when LTCCs are developed specially for RF purposes and the most suitable values depend on the applications. For RF components at least the permittivity, ε_r, the dissipation factor, DF, (or Q-factor) and temperature dependence of the resonance frequency, τ_f, have to be considered. These three properties define the quality and size of the RF component. The permittivity is especially important because the length of a resonator is inversely proportional to the square root of the permittivity. [Wakino *et al.* 1987] Thus the footprint of RF components operating at low frequencies can increase to an inconvenient size if the ε_r is low. On the other hand, materials with too large a permittivity can also cause problems because they need narrow and accurate lines for proper impedance matching. [Ludwig & Bretchko 2000, p. 65] The LTCC materials available commercially have permittivities between 4–10 (Table 2), but larger values up to 85 have also been reported in the literature for non-commercial materials. [Kagata *et al.* 1992, Kniajer *et al.* 1997]

Table 2. Dielectric properties of commercial LTCC dielectrics.

Material	ε_r	DF / 10^{-3}	τ_f / ppm/K
duPont 951*	7.8	1.5 @ 1 kHz	–
duPont 943**	7.5	1 @ 1 MHz	–
Ferro A6-5-M-13*	5.9	2 @ 10 MHz	–
Heraeus CT 700*	7.0	2 @ 1 kHz	–
Motorola T2000***	9.1	1 @ 2 GHz	< ± 10

*LTCC design guide made by CTS Microelectronics, West Lafayette, IN, USA,
** Preliminary information from duPont, *** [Barnwell *et al.* 2000].

A low dissipation factor, DF, (or high Q-factor) is also an important property for LTCCs because it makes it possible to design RF filters with low losses. Although this fact is well-known and the values should be and are reported for all commercial LTCCs (Table 2), in multilayer systems the conductive losses are more important. [Barnwell *et al.* 2000] The dissipation factor is also commonly studied as a function of frequency. [Donahue *et al.* 1998]

The temperature dependence of the resonance frequency, τ_f, is rarely reported, but for RF filter applications a value between –10…+10 ppm/K is necessary for a stable frequency response of the component at its operational temperature. [Barnwell *et al.* 2000] This is a universal demand for all dielectric materials used for RF purposes because otherwise the temperature dependence of the component frequency has to be compensated with other arrangements such as special mechanical or electrical design. [Jantunen & Turunen 1994, Wang & Zaki 1999] At the present time only a few commercial LTCC materials fulfilling this demand have been reported. [Barnwell *et al.* 2000, Kagata *et al.* 1992]

The third aspect, thermomechanical properties, should also be considered in dielectric material development. This area includes a large variety of properties, which effect the reliable use of the designed component. A specific requirement is the linear thermal expansivity (LTE) which should be matched closely to the value of the mounting board used. This means that if the LTCC component is mounted on silicon the LTE should be about $4 \cdot 10^{-6}$ K^{-1}, on alumina about $7–9 \cdot 10^{-6}$ K^{-1} and on PCB nearly $20 \cdot 10^{-6}$ K^{-1}. [Tummala 1991, Mattox *et al.* 1988, Gektin *et al.* 1998] Furthermore, LTCCs have to meet a number of mechanical requirements such as flexural strength, σ_f, hardness, H_v, surface smoothness, elasticity (or Young’s modulus), E and toughness, K_{IC}, arising during its fabrication and subsequent use. [Sheen 1999, Mattox *et al.* 1988, Amey *et al.* 2000] The values for commercial LTCCs, pure Al_2O_3 and some glass and glass-ceramics are shown in Table 3.

Table 3. Thermomechanical properties of commercial LTCCs, glasses, glass-ceramics and pure alumina.

Property	E GPa	σ_f Mpa	H_v GPa	K_{IC}MPa/m$^{1/2}$	LTE ppm/K
duPont 951*	152	320	–	–	5.8
duPont 943**	–	230	–	–	4.5
Ferro A6-5-M-13*	82	130	–	–	7.0
Heraeus CT 700*	91.8	240	–	–	6.7
Motorola T2000$^{\#}$	–	230	–	–	6.0
$Al_2O_3^{+}$	~ 400	300–400	13’	~ 5	8.1
Glassceramic G55’	110	200	6.8	–	5.5
Cordierite”	130–150	150–300	–	~ 2.2	2.5^
Celsia”	~ 69	~ 87	–	~ 2.3	–

*LTCC design guide made by CTS Microelectronics, West Lafayette, IN, USA, ** Preliminary Product Data Sheet, $^{+}$ [Bever 1986, p. 155], ‘ [Tagami *et al.* 1997], ” [Sung & Kim 1999], ^ [Jean & Gupta 1994], $^{\#}$ [Scrantom & Gravier 1999].

These three aspects show that the development of the dielectric material for LTCC technology is at least a 3-dimensional problem demanding a large variety of measurements. Additionally, the target values of each property cannot always be taken for granted and depends on the intended application. The way in which the desired values can be achieved also depends on the means by which the low temperature firing properties are obtained. There are two basic ways to arrange dielectric LTCC composition densification at low temperatures. Firstly, crystalline dielectric ceramic is mixed with low melting temperature glass working as a fluxing agent. The final microstructure is then composed of dielectric particles in a glass matrix. [Tummala 1991, Knickerbocker *et al.* 1993] This is a very common method in commercial LTCCs as shown in the literature and, for example, in duPont's 943 dielectric composed of alumina particles in calcium aluminium silicates. [Jones *et al.* 2000] The achieved microstructure is dense and non-porous with properly designed composition and firing, but the glass addition can impair the mechanical and dielectric properties of the material. [Hing & McMillan 1973, p. 184,209] The second method is to use only glasses as starting materials and let them crystallise during the firing [Tummala 1991], thus avoiding glasses in the final microstructure.

In this thesis the target firing temperature was between 850–900°C because this is the most suitable range for commercial silver pastes. The desired dielectric and thermomechanical properties were basically the same as for the commercial LTCCs with some exceptions. The target value for the LTE was allowed to be closer to the value of alumina than silicon or PCB. Also the RF requirement of the τ_f was taken into account very carefully.

To achieve these properties, the basic compositional idea differed slightly from the methods described above. In this thesis the dielectric starting material was crystalline, a well-known mixture of magnesium titanate and calcium titanate (labelled as $MgCaTiO_3$) ceramic. [Katoh & Ozeki 1994, Wood *et al.* 1996] This composition has a sintering temperature at about 1360°C and has been used for RF resonators and antennas because of its excellent dielectric properties. [Katoh & Ozeki 1994, Huang & Lin 2000] The permittivity of this material is ~ 18–20, the Q-factor ~ 3000–4600 at 6 GHz (DF ~ $3.3–2.2 \cdot 10^{-4}$) and the τ_f can be adjusted to be very close to 0 ppm/K by varying the amount of $CaTiO_3$. [Katoh & Ozeki 1994] In this thesis the basic idea was to develop LTCC material using this dielectric composition and its properties as a base and decrease its firing temperature to nearly 900°C, but in this thesis a totally crystalline microstructure was aspired to because of its positive influence on dielectric and mechanical properties. [McMillan 1979, p. 184, 209]

2.2 Test sample preparation and measurements

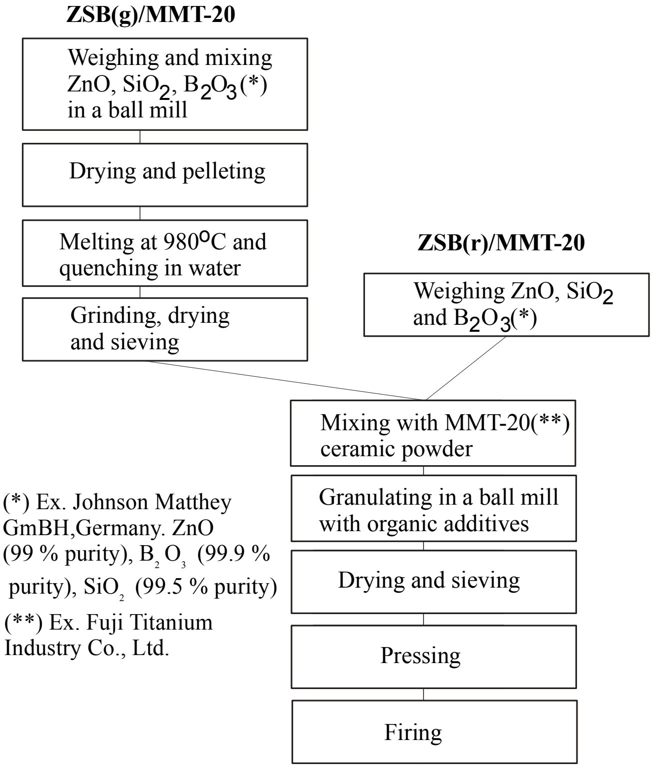
The properties of different compositions were studied using oxide mixing and a dry pressing procedure, because it is a simple method for the preparation of samples with the many different shapes needed for firing, dielectric and thermomechanical measurements. Later on, when the tape casting process was employed, the microstructure of the final dielectric was used as the basic criterion to ensure that the process did not affect the properties of the developed dielectric.

Fig. 2.2 shows the two sample preparation procedure producing compositions labelled as ZSB(g)/MMT-20 and ZSB(r)/MMT-20, respectively. [Paper II] The MMT-20 comes from a commercial name of the dielectric ceramic powder of $MgCaTiO_3$, the firing temperature of which has been decreased by using a mixture of Zinc, Silicon and Boron oxides (ZSB). Index 'g' in bracket denotes that the mixture has been prepared using glass and 'r' denotes the straight utilisation of the raw material oxides.

Following the route for producing the mixture ZSB(g)/MMT-20, glass was first produced by weighing the starting oxides and mixing for 1 h in a polyethylene pot mill using agate balls. The mixed powders were pressed into pellets which were subsequently melted in a platinum crucible. The melts were quenched in water, pulverised in the ball mill for 12 h, dried and screened through a 100 mesh sieve. The test mixtures where then prepared by weighing different amounts of glasses and $MgCaTiO_3$ ceramic, mixed in the ball mill for 2 h together with polyvinyl alcohol (PVA) as a binder, polyethylene glycol (PEG) as a plasticiser and distilled water. The composition was dried in a microwave oven and sieved. Uniaxial pressure and firing were then used to form different shape of compacts for various measurements. [Paper I]

Later on, when the most suitable composition with competitive dielectric properties and a high density, totally crystalline microstructure was found, a straightforward route without any glass preparation was also used (Fig. 2.2.) producing the final mixture of ZSB(r)/MMT-20. The same mixing and sieving procedure was also used for pure $MgCaTiO_3$. [Paper II]

The specific surface area for all prepared powders was studied using a BET analyser (OmniSorb 360CX, Coulter Electronics Inc., Luton, UK) and their phases with x-ray diffraction (XRD) (Siemens D5000, Karlsruhe, Germany) utilising the JCPDS data file (International Center for Diffraction Data 1992, Swarthmore, PA, USA).



(*) Ex. Johnson Matthey GmbH,Germany. ZnO (99 % purity), B_2O_3 (99.9 % purity), SiO_2 (99.5 % purity)

(**) Ex. Fuji Titanium Industry Co., Ltd.

Fig. 2.2. Two different preparation routes for the novel LTCC dielectric. [Paper II]

Cylindrical compacts with length of 18mm and diameter of 10 mm were used for dilatometric studies (Orton Automatic Recording Dilatometer, Westerville, OH, USA) to find the firing properties for each composition. The densities and shrinkages of the samples were calculated from their dimensions and weights after firing and the microstructural and phase analyses were done using a Scanning Electron Microscope with Energy Dispersive Spectrometer (SEM/EDS) (Jeol JSM-6400, Tokyo, Japan) or Field Emission Scanning Electron Microscope (FESEM) (Jeol JSM-6300F, Tokyo, Japan) on ground and polished surfaces. Boron contents were derived by determining the difference between the total determined constituents and 100%. Porosity values were estimated from SEM or FESEM micrographs using the line intercept method.

The dielectric characteristics in the microwave frequency range were measured by the post-resonator method first introduced by B. W. Hakki and P. D. Coleman in 1960. [Hakki & Coleman 1960] This method employs a cylindrically shaped specimen positioned between two copper plates, as shown in Fig. 2.3, which supports several TE and TM modes. The TE_{011} has been used because it has been found most suitable and because identification of this mode is easy. [Dube *et al.* 1997]

In this configuration, probes are situated on opposite side of the sample and the resonance frequency and the unloaded Q-factor are determined with a HP8719C network analyser. The equations required for calculating the permittivity have been detailed by Kobayashi & Katoh [1985] but the calculation is nowadays done with a computer. The experiment is performed with weak coupling so that it does not affect the measured values. This is one of the most accurate methods provided that the conductive losses of the conductive plates are low or their effects can be corrected.

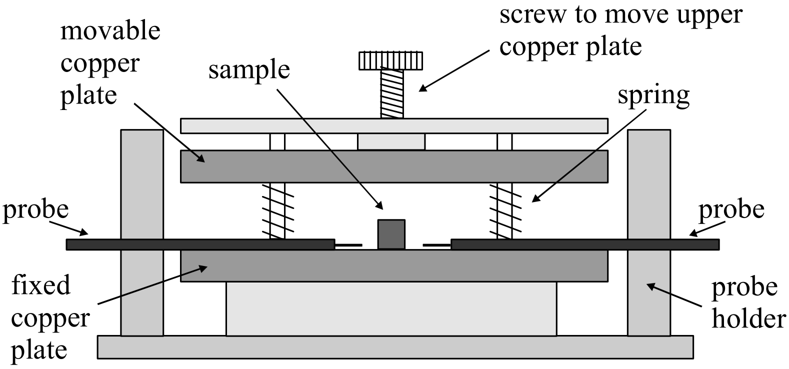


Fig. 2.3. Measurement system of dielectric properties with Hakki-Coleman configuration. [Dube *et al.* 1997]

Also the samples should have suitable and accurate dimensions and the measurement has to be done carefully and with an awareness of its limitations. Taking into account these facts, the Hakki-Coleman method is able to determine the permittivity with high accuracy (~ 0.1%). Also, with large samples (diameter ~ 20 mm) this technique can produce reliable DF results if DF is > 10^{-4} (Q-factor < 10 000) even at low frequencies. [Dube *et al.* 1997]

In this thesis the samples were pressed with a 25.5 mm diameter tool of length between 5–10 mm, fired and lapped and their dimensions were measured. The copper plates were also cleaned before each measurements and the coupling was arranged to produce > 35 dB attenuation. [Papers I, II]

The measurements of the temperature dependence of the resonance frequency, τ_f, were done using coaxial resonators. These samples were also made with the dry pressing procedure and, after firing and dimensional measurements, they were coated with conductive paste (DT1402, Heraeus, West Conshohocken, PA, USA) to form λ/4 resonators. The measuring system is shown in Fig. 2.4.

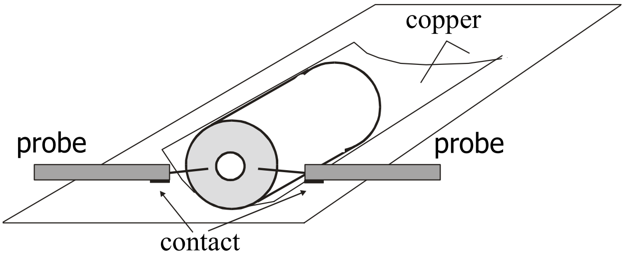


Fig. 2.4. Measurement systems for coaxial resonators. [Kemppinen & Leppävuori 1986]

Also in this case the coupling of the two probes to the electric field was arranged to be low (< –35 dB) to avoid the effects of the measuring system. The resonance frequencies were then measured with a HP8719C network analyser between temperatures of –30°C and +80°C and the τf was calculated. This method was chosen because it takes into account the temperature coefficient of the dielectric constant, τe, as well as the linear thermal expansivity, LTE, of the resonator itself, which is important from the practical point of view. [Wakino *et al.* 1987, Kemppinen & Leppävuori 1986] This well-known relationship is given by the following equation (1).

$$\tau_f = -1/2\ \tau_\varepsilon - \mathrm{LTE} \quad (1)$$

Samples for thermomechanical studies were also made with the dry pressing procedure. At this point the work concentrated on measurements of elastic modulus, E, hardness, H_v, strength, σ_f, fracture toughness, K_{IC}, and linear thermal expansivity, LTE. All these properties are important because they can be correlated with fracture initiation by thermal stress or with the ability of cracks to propagate in material, both conditions being associated with mechanical failure. High values of strength and thermal conductivity and low values of elastic modulus and thermal expansion coefficient increase thermal stress resistance of the material. [Kingery, *et al.* 1976, p. 828] In this case, instead of thermal conductivity, the hardness of the materials was measured. The hardness is basically the ability of a material to resist mechanical transformation, but it has been established for ceramics to correlate with thermal conductivity. [Baesso *et al.* 1999] Furthermore, the fracture toughness characterises the inherent ability of a crack to propagate after its initiation, but it can also be correlated with the size of the plastic zone ahead of the crack. [Kingery *et al.* 1976, p. 787]

The elastic modulus, E, was measured with a scanning acoustic microscope (C-SAM D-9000, Sonoscan Inc., Bensenville, IL, USA) using a method reported by Canumalla & Oravecz. [1997] All samples had a diameter of 8.5 mm, but several different thicknesses between 0.61 and 0.92m mm (standard deviation ± 0.01 mm) were used for each composition to ensure the measuring results. The elastic modulus was calculated using Equation (2)

$$E=\rho v_s^2(3v_c^2-4\, v_s^2)/(\, v_c^2-v_s^2) \tag{2}$$

where ρ is the bulk density. The v_s is the shear velocity and v_c the compressional velocity, which can be calculated if the thickness of the sample and respective wave propagation times from a Scanning Acoustic Microscope (SAM) measurements are known. [Paper III]

The cross-breaking strengths were measured with 3-point loading on several nominally square section rods in the 'as-fired' state using an Instron machine. The spanning was 30 mm and the loading rate 0.5 mm min^{-1}. [Paper III]

The hardness and toughness of each fired composition were derived from polished samples using a Type M Shimadzu Micro Hardness Tester (Shimadzu Seisakuso Ltd., Kyoto, Japan). The average Vickers Hardness values (H_v) and their standard deviations were determined with a load of 100 g and dwell time of 15 s. The fracture toughness was calculated using Equation (3)

$$K_{IC}=0.028H_v a^{1/2}(E/H_v)^{1/2}(a/c)^{3/2} \tag{3}$$

where H_v is the Vickers hardness, E the elastic modulus, 'a' the half length of the indent diagonal and 'c' the radial crack length. [Sung & Kim 1999] Toughness values and standard deviations were determined with a 300 g load. [Paper III]

Finally, the Linear Thermal Expansivities, LTE, were measured using the dilatometer in a temperature range of 20–400°C. [Paper III]

2.3 Investigated compositions and the results

The basic dielectric material MMT-20 ($MgCaTiO_3$) was delivered by Fuji Titanium Industry Co., Ltd. The specific surface area of the powder was 4.1 $m^2\, g^{-1}$ and the XRD showed only $MgTiO_3$ crystals. [Paper I] The $CaTiO_3$ could not be detected because of its small amount (2.3 mol%) in this mixture.

The number of possible different materials and compositions to decrease the firing temperature of crystalline ceramic is countless, but some guiding principles for the selection process can be found. In this thesis a comprehensive literature study of compositions used earlier for other dielectric materials and also for commercial LTCCs was done as a first step. The reported effects of different compounds on the dielectric properties of ceramic materials were also studied. The results showed that the most common method was to use SiO_2 based glass compositions. [Jones *et al.* 2000, Donahue *et al.* 1998, Tummala 1991] Especially with silicon oxide (SiO_2) and aluminium oxide (Al_2O_3)-glasses containing MgO, boron oxide (B_2O_3) and phosphorus oxide (P_2O_5) had good firing properties and totally crystalline structures have been achieved with moderately low amounts of glass addition. [Tummala 1991] Also, in some cases common sintering aids were effective. [Kagata *et al.* 1992] On the other hand, alkaline metals impair the dielectric and mechanical properties and are thus not recommendable. [McMillan 1979, p. 209, Kingery *et al.* 1976, p. 940] Recently the addition of lead has also been avoided because of environmental considerations. [Donahue *et al.* 1998]

In this thesis the efficiency of several different sintering aids such as bismuth oxide (Bi_2O_3), lithium oxide (Li_2O), zinc fluoride (ZnF) and copper oxide (CuO) and glasses such as $CaO-Al_2O_3-B_2O_3$, $Li_2O-ZnO-SiO_2$ and $MgO-Al_2O_3-SiO_2$ were first tested. Some of them were not able to decrease the firing at all and others, although producing quite microstructurally dense samples at low sintering temperatures, degraded the dielectric values. The most promising additions, $BaO-SiO_2-B_2O_3$- and $ZnO-SiO_2-B_2O_3$- glasses, were studied more carefully, but the first one was subsequently rejected. The second glass, consisting of 60.3 mol% ZnO, 12.6 mol% SiO_2 and 27.1 mol% B_2O_3 (coded ZSB(g)), was prepared using high purity oxides and the pellets were melted at 980°C before quenching.[Paper I] The composition is the same as that used successfully for decreasing the firing temperature of $BaTiO_3$. [Abe *et al.* 1996] The specific surface area of the glass powder after milling was 2.4 $m^2\ g^{-1}$ and the XRD analyses showed crystalline Zn_2SiO_4 phase in an otherwise amorphous composition. [Paper I]

Different amounts of the ZSB(g) glass were mixed and granulated with MMT-20 dielectric and the sinterability of this composition was measured using the dilatometer (Fig. 2.5). The results show that 70 wt% of the ZSB glass was needed for good densification, which occured in two stages. [Paper I]

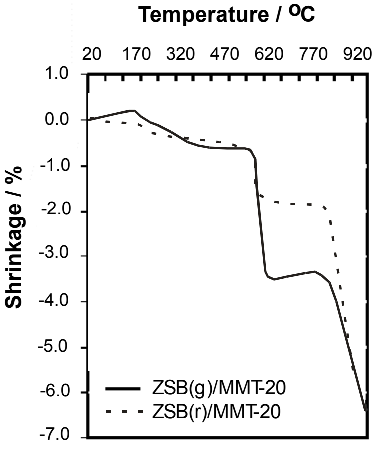


Fig. 2.5. Shrinkage behaviour of the ZSB(g)/MMT-20 and ZSB(r)/MMT-20 compositions. [Paper I, II]

The first stage of sintering started at around 600°C and the second one at about 850°C. The SEM/EDS and XRD data for the materials in the as-mixed and dried condition, and after firing at 620, 875 and 900°C, was studied and the density and porosity of the samples were measured. [Paper I]

As mentioned in Chapter 2.1, the starting material MMT-20 consisted of $MgTiO_3$ and $CaTiO_3$ crystals and the ZSB(g) glass of amorphous phases with Zn_2SiO_4 crystals. Thus the compact before any heat treatments was a mixture of these phases. The compact density was 1.9 Mg m^{-3} with porosity about 47 %. [Paper I]

The set of samples fired at 620°C for 10 minutes showed slight densification with increased density (2.2 Mg m^{-3}) and decreased porosity (39 %). The microstructural analyses showed densified areas where glass had started to react with the crystalline materials producing different amorphous phases such as $47ZnO\text{-}9SiO_2\text{-}37B_2O_3$, $ZnO\text{-}3TiO_2\text{-}6B_2O_3$ and $35CaO\text{-}41TiO_2\text{-}6ZnO\text{-}18B_2O_3$. The original $MgTiO_3$ and Zn_2SiO_4 crystals could also be observed by XRD. [Paper I]

In the second set of samples fired at 875°C for 80 minutes, no amorphous phases could be found and the density of the sample was 3.1 Mg m^{-3} with porosity of 14 %. The observed crystalline phases were the original Zn_2SiO_4 and new $ZnTiO_3$, TiO_2 and $Mg_2ZnTi(BO_3)_2O_2$. All these phases were positively identified by XRD, except for $Mg_2ZnTi(BO_3)_2O_2$, the presence of which was inferred from the JCPDS file for $Mg_3Ti(BO_3)_2O_2$. The TiO_2 crystals also contained about 5–6 wt% ZnO. [Paper I]

In the third test series after firing at 900°C for 80 minutes, the porosity of the sample was about 3.5 % and the density 3.5 Mg m^{-3}. The microstructure (Fig. 2.6a) was very uniform and consisted of crystals smaller than 5 µm. According to the XRD analyses, $Mg_2ZnTi(BO_3)_2O_2$ was decomposed leading to an increase of the amounts of Zn_2SiO_4 and TiO_2 phases as well as a new $Mg_{4/3}Zn_{2/3}B_2O_5$ phase, which was inferred from the JCPDS file for $Mg_2B_2O_5$. [Paper I]

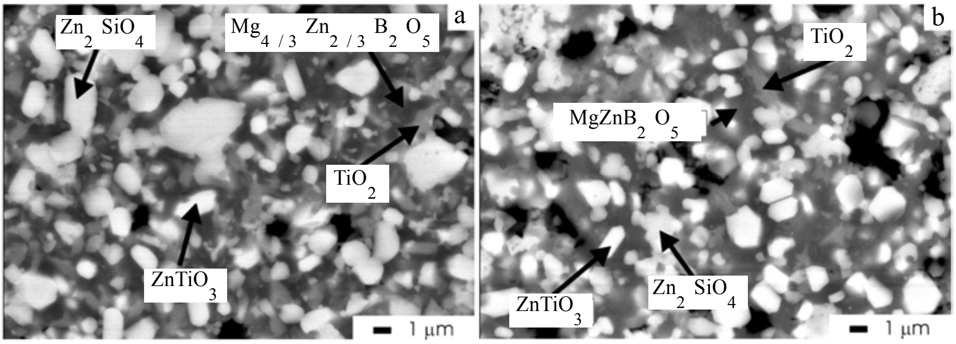


Fig. 2.6. FESEM/BE images of sintered (900°C, 80 min) a) ZSB(g)/MMT-20 and b) ZSB(r)/ MMT-20 mixtures. [Paper II]

The study clearly showed the steps of the firing process and the final microstructure had low porosity and was totally crystalline as desired. As for the applicational point of view, the microstructure also contained large amounts of well-known good dielectric crystals; TiO_2 having permittivity ~104, Q-factor ~ 14 600 (at 3 GHz) and $\tau_f = +427$ ppm K^{-1} and $ZnTiO_3$ having the values of 10 and 3000 (at 10 GHz) and –55 ppm K^{-1}, respectively. [Kim *et al.* 1999, Wakino *et al.* 1987] The only disadvantage was the densification near 600°C, which can cause unwanted carbon residues in the LTCC process.

Using the results of the dilatometer measurements and microstructural studies, the firing profile in Table 4 was chosen for further studies.

Table 4. Firing profile for the novel LTCC dielectric.

Temperature /°C	Rate or dwell time
20–400	3°/min
300–500	1°/min
500–900	3°/min
900	80 min
900–20	3°/min

Total time14 h 26 min

The totally crystalline structure after firing the mixture of MMT-20 ceramic and ZSB(g) glass at 900^{o}C prompted a study of the possibility of preparing the same composition using a simpler and more straightforward method (Fig. 2.2, route 2). In this case the glass preparation step was totally omitted and the compositionally identical mixture was made up of 30 wt% of MMT-20 ceramic and 70 wt% of glass-forming oxides with the same amounts of ZnO, SiO_2 and B_2O_3 as used earlier. Otherwise the same powder preparation route was followed. The mixture was labelled ZSB(r)/MMT-20. [Paper II]

The dilatometer results in Fig. 2.5 show that the main shrinkage of the samples made of ZSB(r)/MMT-20 occurred at temperatures over 800°C. [Paper II] This was encouraging because the optimal LTCC material would be the one in which the microstructure remains open up to about 800°C. This facilitates the burn out of the organics associated with the ceramic and conductor pastes. [Tummala 1991] The shrinkage behaviour of this ZSB(r)/MMT-20 powder made without any glass preparation is thus more favourable for low firing purposes than the ZSB(g)/MMT-20 mixture.

The ZSB(r)/MMT-20 samples reached the same density and porosity as the ZSB(g)/ MMT-20 samples. The microstructure (Fig. 2.6b) was also very similar. The XRD (Fig. 2.7) studies showed that this new procedure produces basically the same phases (Zn_2SiO_4, $ZnTiO_3$, TiO_2 and $MgZnB_2O_5$) as the final microstructure, but the amount of TiO_2 and Zn_2SiO_4 were markedly lower and the sample was enriched in $ZnTiO_3$. [Paper II]

The dielectric measurements showed that both routes also decreased the permittivity value (21) of the MMT-20. For ZSB(g)/MMT-20 it was 10.6 and for ZSB(r)/MMT-20 it was 8.5. The DF and τ_f, $1.1 \cdot 10^{-3}$ at 7 GHz and –13.3 ppm K^{-1} for the ZSB(g)/MMT-20 and $0.9 \cdot 10^{-3}$ at 8 GHz and +6.2 ppm K^{-1} for the ZSB(r)/MMT-20, respectively, were also impaired although the ZSB(r)/MMT-20 was slightly better. [Paper I, II] The reason for this might be different amounts of the various crystalline phases in the microstructure, and the trace amounts of glass possibly located on grain boundaries. Despite these degradations, the achieved dielectric values of this novel LTCC composition are competitive with commercial LTCC materials. Of special importance, the DF was very low.

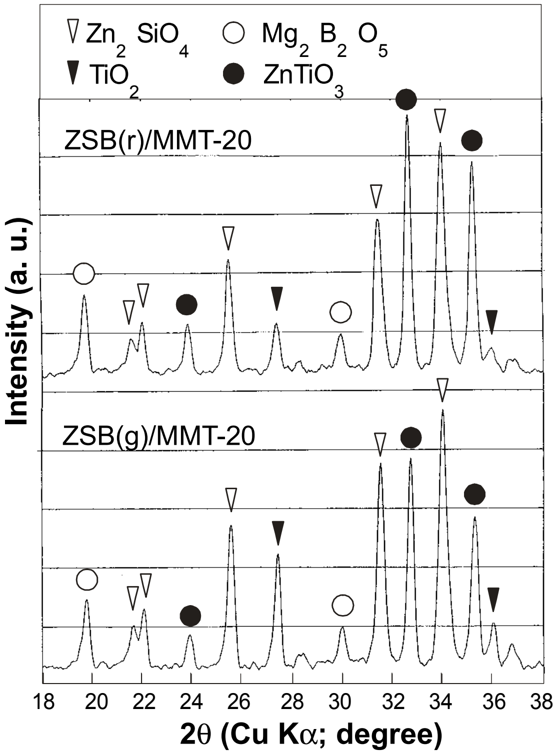


Fig. 2.7. XRD patterns of the ZSB(g)/MMT-20 and ZSB(r)/MMT-20 mixtures after firing at 900°C for 80 min. [Paper II]

Additionally, the effect of the amount of TiO_2 in the ZSB(r)/MMT-20 on the temperature dependence of the resonance frequency, τ_f, was studied. [Paper IV] This is a well-known method [Barnwell *et al.* 2000] and is based on the large τ_f values of crystalline TiO_2 together with its low DF. In this case the method was very probably valid because the microstructure already contained almost pure TiO_2 crystals. The results showed that this compositional variation is able to adjust the τ_f between the values of –62 ppm/K and +8.8 ppm/K without impairment of other dielectric properties. [Paper IV]

The thermomechanical properties showed very small differences, although in both cases the addition led to lower values of elasticity, strength, hardness, fracture toughness and LTE compared to the corresponding values of pure MMT-20. [Paper III]

As a result, the ZSB(r)/MMT-20 composition was chosen for tape casting and multilayer component preparation because it had the same or even better dielectric, thermomechanical and microstructural properties as the ZSB(g)/MMT-20. Its preparation route was also very straightforward avoiding the separate, high-temperature, glass-melting step, which carries the additional risk of component volatilisation. The firing profile and dielectric and thermomechanical properties of this novel LTCC dielectric are shown in Tables 4–5, the sintered microstructure in Fig. 2.8 and the preparation route in Fig. 2.2.

Table 5. Measured dielectric and thermomechanical properties of the developed microwave LTCC ceramic. [Papers II, III]

Property	Value
ε_r	8.5
DF / %	0.09 @ 8 GHz
τ_f / ppm/K	+6.2*
E / GPa	106
σ_f / MPa	120
H_v / GPa	2.9
K_{IC} / MPa/m$^{1/2}$	1.4
LTE / ppm/K	8.5

* adjustable with the amount of TiO_2

3 Material development for the multilayer process

3.1 Demands of the LTCC material systems

The tape casting process, also known as doctor blade or knife casting, is a technique that has been used by the paper and plastics industries for many years. This method was introduced for ceramic materials for the first time by Glenn Howatt [1947] and ever since it has been used to produce multilayer capacitors, ceramic substrates, LTCC and High Temperature Co-fired Ceramic (HTCC) applications and for piezoelectrics.

The tape casting method is able to produce flexible, self-supporting green ceramic sheets with a wide thickness range (10 µm–1 mm) and it can be arranged as a continuous process, although a small scale laboratory route for cost effective tests is possible. The tapes also have smooth surfaces suitable for accurate printing to form e.g. conductive patterns. [Cahn *et al*. 1996, chap. 7]

The method consists of a slurry preparation and its casting followed by component preparation as shown in Fig. 3.1. [Cahn *et al*. 1996, chap. 7] The basic formula for the tape casting slurry includes the ceramic powder, solvents and organic additives. In the fired product the ceramic material is all that remains and thus the solvents and additives have to be removed in earlier process steps. These ingredients are added only to facilitate the fabrication of the tape with an appropriate thickness and density and to make the tape strong enough for subsequent processing. [Berry *et al*. 2000]

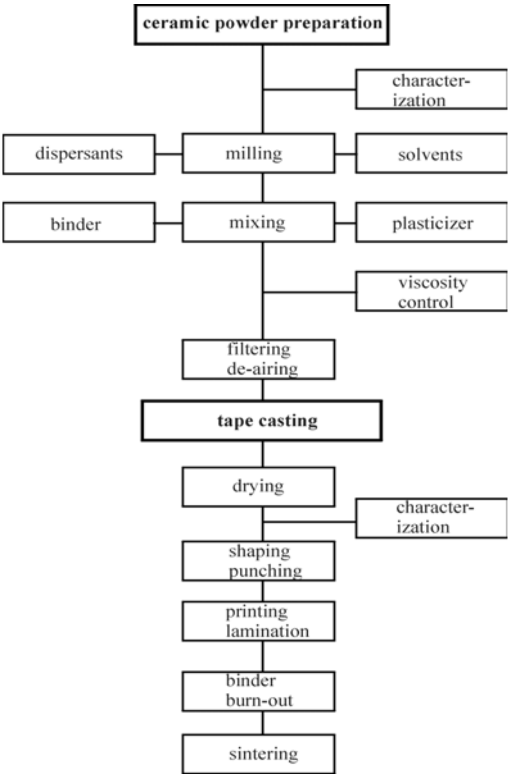


Fig. 3.1. General production process of cast ceramic tapes and tape-based multilayer components. [Cahn *et al.* 1996, chap. 7]

There are many different possible formulations of the solvent/additive system for the tape casting slurry. The role of the solvents is to dissolve the organic additives, provide suitable viscosity for the slurry and also slightly disperse the ceramic powder particles. The solvents should also evaporate at moderate temperatures immediately after the casting process.

The organic additives consist of dispersant, binder and plasticizer, which are added in consecutive phases as shown in Fig. 3.1. The dispersant provides a stable suspension of the ceramic powder helping to produce a uniform and homogeneous tape. The binder coats the ceramic powder particles and holds them together and the plasticizer imparts the flexibility necessary for the multilayer component preparation. [Cahn *et al*. 1996, chap. 7] The amounts of additives and solvents should be kept to a minimum because large excess amounts can cause burnout difficulties, carbon residuals and a low fired density. [Berry *et al*. 2000, Tummala 1991] Typically, the binder system is based on either acrylic or poly(vinyl butyral) (PVB) plastics and non-aqueous solvents. Both these systems have been successfully used to prepare the commercial LTCC tapes [Jones *et al*. 2000] and also electroceramic sheets. [Szafran & Rokicki 2001, Feng & Dogan 2000]

Before slurry preparation the properties of the most important component, the ceramic powder, have also to be measured. This normally includes particle size and distribution as well as specific surface area (SSA) determinations. These characteristics govern how the particles pack together in the green state and determine the formulation of organics and solvents added to the slurry. [Cahn *et al.* 1996, chap. 7]

After preparation, the slurry is spread onto a temporary substrate such as glass or carrier film by forcing it to pass through a gap of accurate width, which is the determining factor for the thickness of the tape. In this state the casting speed and the viscosity of the slurry are also important. [Berry *et al.* 2000, Cahn *et al.* 1996, chap. 7]

After drying the tape in air, it is further processed to form multilayer components as shown in Fig. 3.1. The tape is first blanked to size and required vias are formed using, typically, punching or drilling. After via filling and screen printing of the conductive patterns on each separate layer, they are stacked together, laminated and co-fired. [Amey *et al.* 2000]

All these phases impose several demands on the green tape. The mechanical strength, flexibility, surface smoothness, dimensional stability, sinterability and good binder burnout behaviour are requirements which ensure that the tape can be handled, that accurate patterns on its surface can be printed and that the firing state can be carried out to produce a dense and accurately dimensioned product. In an ideal lamination, the boundary between two adjacent tapes should be undetectable after compression. This can only be guaranteed by use of the correct lamination parameters and sufficient slurry formulation and preparation. Because these depend very much on materials and production parameters, they have to be defined empirically from case to case and are therefore often a proprietary secret for commercial materials. [Cahn *et al.* 1996, chap. 7]

There are two typical problems arising from the printing of the green tapes with conductive paste to form the desired patterns and electrodes. The first one appears when the additives and solvents of the paste and tape systems are not compatible. The paste pattern does not anchor on the tape surface or, in the opposite situation, the paste system dissolves the ceramic sheet. The second and very general problem is warping of the multilayer component arising from density gradients generated during pressure lamination of the electroded green tape. Although this can be avoided to some degree by careful design of the electrodes e.g. using meshed, non-uniform areas [Thust *et al.* 1998], a basic answer for both problems is the optimum formulation of the slurry and correct tape casting, lamination and firing parameters in addition to successful paste selection. [Cahn *et al.* 1996, chap. 7]

Although the development of the novel LTCC dielectric material presented in Chapter 2 is in a key position for microwave applications, this chapter shows that the tape casting and subsequent lamination and firing procedures and conductive paste selection have also to be designed and studied carefully so that proper multilayer components can be successfully prepared. In the case of commercial LTCC material systems, the suitable pastes, as well as their design and process parameters, are support with information given by material manufacturers.

After development of the low firing dielectric ceramic, all the multilayer component production stages described above have to be studied. The large variety of possible additives and solvents for tape casting slurry and pastes and the casting process itself make this work very empirical and laborious. Despite these facts, there are some objectives. In this thesis they have been as follows:

1. The same high fired density (3.5 Mg m^{-3}) and low porosity (3.5 %) values have to be achieved as in the material development stage. [Paper II]
2. The same microstructural phases ($ZnTiO_3$, Zn_2SiO_4, $MgZnB_2O_5$, TiO_2) as for dry pressed samples have to be achieved. [Paper II]
3. The surface smoothness of the green tape should be comparable to the values of commercial tapes (RA < 0.7 μm).
4. The conductive paste used should be compatible with the green tape and the lamination and co-firing should be successful.

The first two goals are to ensure that the ceramic tape after firing has the same dielectric properties through the same microstructural details as those measured for the samples prepared with the dry pressing procedure when the dielectric ceramic itself was developed. [Paper II] To verify the microstructural properties the same methods as in the Paper II (XRD, SEM/EDS, dimensional and weight measurement and line inspection) have been used.

The third objective enables accurate conductive patterns to be printed on its surface and was studied using a Dektak^{3}ST (Sloan Technology, Santa Barbara, CA, USA).

The final objective is elementary for the preparation of multilayer components and in this thesis commercial silver pastes were selected to be tested. The quality of the printed patterns with different pastes was inspected visually before lamination and after firing, and the inner layers were studied with an acoustic microscope. Any marks indicating decomposition, melting or dissolving of the green tape or of the printed pattern in the green state or during the firing, caused the tested paste to be rejected.

The other requirements, such as self-supporting, flexible tapes with appropriate strength for handling, exact determination of the lamination and firing procedures and strong, base-like final products were taken for granted because fabrication and measurements of multilayer components are impossible below a certain level of these properties. The target thickness of the fired tape was set to be near 100 μm to ensure convenient electrical design and preparation of the multilayer components. The binder system based on PVB was chosen since it burns out well leaving no residual carbon, contrary to other system. [Nufer, 1992]

3.2 Determination of the process parameters

A successful slurry for tape casting was prepared using ceramic powder (30 wt% commercial $MgCaTiO_3$ dielectric and 70 wt% of glass-forming oxides of 60.3 ZnO- 12.6 SiO_2- 27.1 B_2O_3 as in Chapter 2) and a PVB based binder system with solvents and organic additives as listed in Table 6. [Papers II, VI]

Table 6. Composition of the slurry for tape casting. [Paper VI]

Component	wt%	Function
Ceramic powder	55.66	Dielectric
Xylene	18.55	Solvent
Ethanol	18.55	Solvent
Butvar 98*	4.08	Binder
Menhaden oil*	1.12	Dispersant
Santicizer 160*	1.02	Plasticizer
UCON*	1.02	Plasticizer

*ex. Richard E. Mistler, Inc., USA

The ceramic powder, solvents and dispersant were first mixed in a ball-mill for 24 h, the binder and plasticizers were added and mixing was continued for another 24 h. The casting was made using a laboratory caster (Unicast 2000, University of Leeds, Leeds, UK) with a speed of 4 cm s^{-1} on coated paper (715H90 Hexenyl, Sterling Coated Materials Ltd., Derbyshire, UK) and allowed to dry naturally. The firing profile was the same as that used for the dry pressed samples (Table 4). [Paper VI]

After tests with different formulations of the slurry and different casting procedures, it was found that the free B_2O_3 in the ceramic composition reacted with the solvents and lead to a low density of the green test tapes. This problem, also reported earlier [Su & Button 2000], was solved by calcinating the ceramic powder at 620°C for 10 min which eliminated the free B_2O_3. [Paper I] After milling, the calcinated powder had a specific surface area ~ 2 m^2 g^{-1} and the cast and dried tape had a thickness of 110 µm and a green density of 2.1 Mg m^{-3}. The casting was made using a 400 µm gap. The best lamination result was achieved using 20 MPa pressure at 90°C for 1 h, after which the scanning acoustic microscope and cross-sectional surface studies showed uniform ceramic materials with no de-laminations. The phases after sintering (Fig. 3.2) were also identical with those achieved at the state of the dielectric material development [Papers I, II] and the fired density was high (3.7 Mg m^{-3}) with low porosity (0.5 %). [Paper VI]

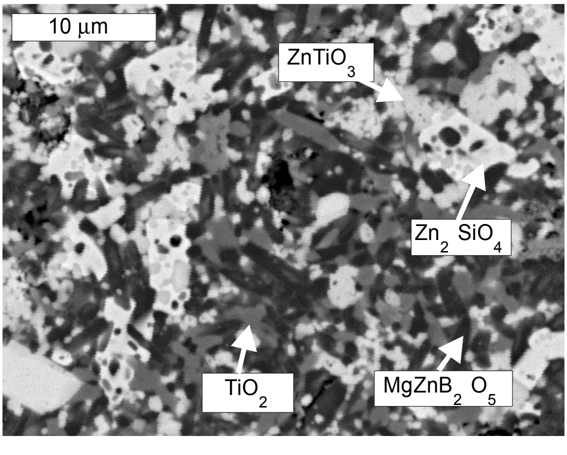


Fig. 3.2. SEM/BE image of the tape cast and sintered dielectric material. [Paper VI]

The linear shrinkages in x-, y- and z-directions were about 18 %. All these results indicated that the developed tape casting procedure for this novel LTCC dielectric was successful. [Paper VI]

The tested silver conductor pastes were duPont HF602, Heraeus C1075 and duPont 6160. According to the manufacturer's information, the first one is meant for duPont's green tape 943 in a co-firing process and the last two for the post-firing process of ceramic components. The paste 6160 was the one found to able to be co-fired with the novel LTCC tape at 900°C without being exposed to diffusion or dissolving. This paste has a low square resistance (Data Sheet: 1–2 mΩ/ for 16 µm thick film) and it was used for all conductive areas including vias and inner and outer patterns. After lamination and firing the conductive layer showed good compatibility with the dielectric (Fig. 3.3). The most probable reason for the large thickness variation (5–9 µm) of the conductor lines was that the paste printing was done by hand. A more accurate technique would have certainly improved its quality. The fired samples also had good flatness without any warping although large uniform areas were printed with this conductor paste. The as-fired surface smoothness was 0.5 mm. [Paper VI]

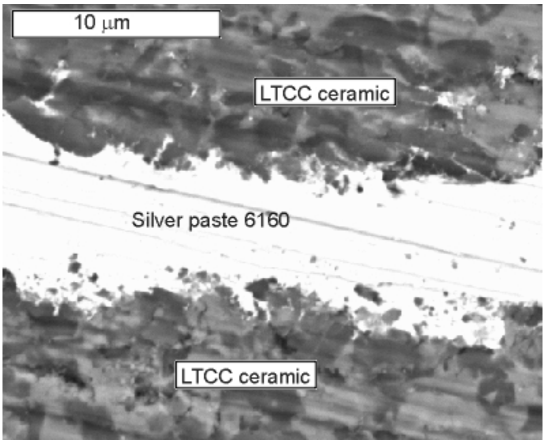


Fig. 3.3. Typical cross-section view of the inner conductive line between dielectric layers.

As a result, the properties and processing parameters for the novel LTCC tape are listed in Table 7. As a comparison, the same parameters for the commercial LTCC material system, duPont 943, are shown, because this material system was also used to prepare multilayer components.

Table 7. Tape properties and process parameters for the novel LTCC and duPont's 943 material systems.

Property	novel LTCC tape*	duPont 943**
green thickness / µm	110	125
fired thickness / µm	90	110
surface smoothness (RA) / µm	0.5	0.7
xy-shrinkage / %	17.8	9.5
z-shrinkage / %	18.2	10.3
lamination pressure / MPa	20	20
lamination temperature / °C	90	70
lamination time / min	60	10
inner conductor paste	duPont 6160	HF602
outer conductor paste	duPont 6160	HF615
via paste	duPont 6160	HF600
firing profile	900°C/Table 4	850°C/Table 1

* [Paper VI]

** Preliminary information from duPont

4 Properties of the multilayer RF components

The final target of this thesis was to demonstrate the advantages of the developed LTCC system in a real telecommunication application. Although the microwave properties of the dielectric material itself were measured during its development work, the actual function of the novel LTCC material system can only be verified if true multilayer components with practical specifications are designed, prepared and measured.

The commercial, and some non-commercial, LTCC material systems have already been studied and used for RF applications [Barnwell *et al.* 2000, Ishizaki & Kagata 1994, Miyake *et al.* 1999, Amey *et al.* 2000, Sutono *et al.* 2000], but the results are difficult to compare because the electrical specifications and especially the operational frequencies are different for each component. To evaluate the properties of the novel LTCC material, RF resonators utilising the commercial LTCC material system, duPont's 943, and the novel system were prepared using the same electrical specifications.

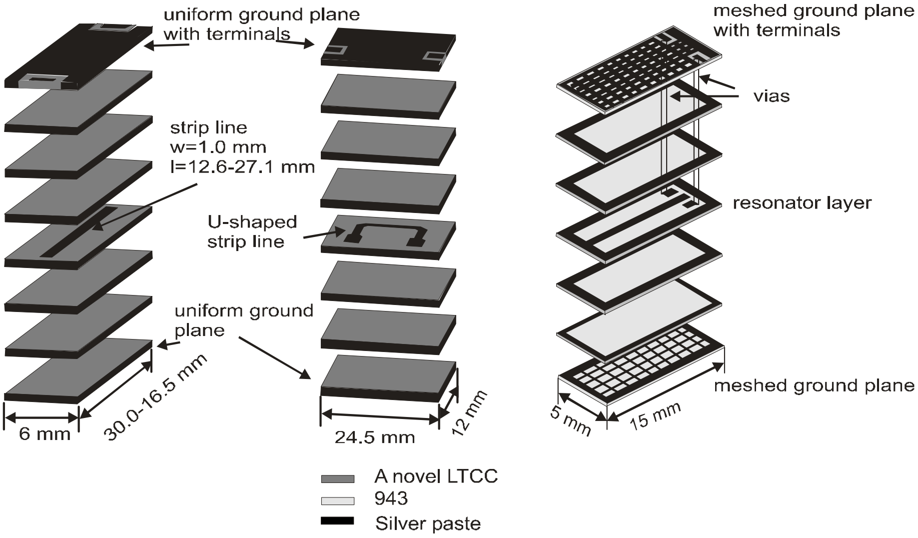
The final target was a filter, with electrical specifications as follows:

1. passband centre frequency near 2 GHz having a fractional bandwith of 3 %, insertion losses < –3 dB and ripple > 1 dB
2. stopband centre frequency 190 MHz higher than the passband and having attenuation > 20 dB

This kind of filter can be used in the next generation of telecommunication applications [Ishizaki & Kagata 1994, Miyake *et al.* 2000].

As a first step with the novel LTCC material system, two multilayer resonator structures were designed using the Sonnet electromagnetic simulator. Their structures formed balanced 1 mm wide λ/2 strip line resonators consisting of either straight (Fig. 4.1a) or U-shaped (Fig. 4.1b) conductive line at the centre of the LTCC module. The input and output pads, situated at the capacitive ends on the top layer, were loosely coupled (< –35 dB) to the strip line. The resonators, which had straight-shaped strip lines, were made with different lengths (12.6–27.1 mm) to determine the Q-factor as a function of the resonance frequency. One length of the U-shaped resonator, working at about 2 GHz, was also studied because of its more conformable footprint for the filter application. Furthermore, for the U-shaped resonator, stepped widening at both of its capacitive ends was also designed, because this enabled easier coupling arrangements and more suitable impedance matching. This resonator was thus basically the well-known stepped impedance resonator.

The values needed for electrical and structural design of the components, the firing profile and materials used are presented in Tables 4–6 in Chapters 2–3 of this thesis. In both cases all outside areas were made uniformly conductive in the co-firing process except for the side walls, which were coated using low firing silver-based paste Heraeus DT1402 and post-fired at 600°C. The final thickness of the strip line type resonators was 720 µm. [Papers V, VI] Otherwise the preparation followed the common LTCC process. [Ishizaki & Kagata 1994]



(a) (b) (c)

Fig. 4.1. Resonators prepared for the Q-factor measurements. a) straight and b) U-shaped λ/2 resonators and c) straight λ/4 resonators. [Papers V, VI]

The commercial LTCC material, duPont 943, was also used to study its Q-factor. This λ/4 resonator in Fig. 4.1c, the structure of which was the well-known balanced strip line with a conductive strip at the centre of the LTCC module, was prepared using the following information from the material manufacturer and the commonly described LTCC process. [Ishizaki & Kagata 1994] The electrical values of this dielectric are in Table 2 (Chapter 2), the firing profile in Table 1 (Chapter 2) and the other parameters in Table 7 (Chapter 3). The designed frequency of the resonators was also near 2 GHz, but the components were first prepared with meshed grounds, measured and then one upper ground was coated with DT1402 paste and post-fired to be uniform. This was done to exclude effects of the ground planes on the electrical performance and also to produce some comparative information. The input and output was arranged as mentioned earlier with loosely coupled capacitive pads. [Paper V]

The Q-factors of the resonators are shown in Fig. 4.2. The RF measurements were made using a HP8719C network analyser. The straight-line resonators made of the novel LTCC material system had a Q-factor of over 100 at 2 GHz. [Paper VI] This value is very high compared to those reported for the commercial materials, especially if the total thickness of the component (720 μm) is considered. Liang at al. [1999] were able to achieve Q-factors over 70 for λ/4 resonators at 1.9 GHz made of duPont's LTCC material system, but only when the component thickness was about 900 μm. The strip line width was, in their study, 400 μm, but it was demonstrated that within these dimensions the total thickness is more important. Miyake *et al.* [Miyake *et al.* 1999] have also reported unloaded Q-factor values of 80 for λ/4 resonators at 900 MHz made with a non-commercial Bi-Ca-Zn-Nd system with thickness of 2 mm. In this study, the 750 μm thick resonators made of duPont's 943 system had a Q-factor of 70 at 1.89 GHz, but this increased to the value of 80 after uniform ground plane preparation with an increased resonance frequency of 1.9 GHz. [Paper V]

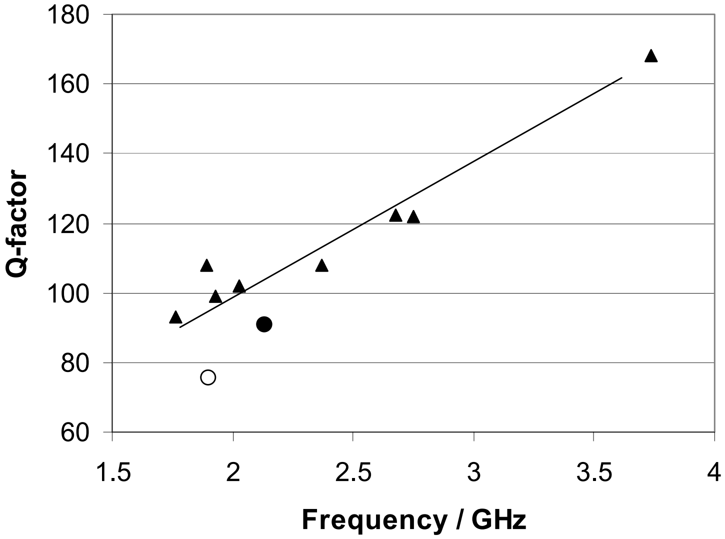


Fig. 4.2. Simulated (solid line) Q-factors and measured Q-factors as a function of resonance frequency for straight-line shape λ/2 resonator (▲) and U-shape λ/2 resonator (●) resonators made of the novel LTCC material system and for a resonator made of 943 material (○). [Papers V, VI]

A minor detail is that the Q-factor of the straight-line resonators made of the novel LTCC material system did not correlate to the square root of the frequency, as is commonly indicated for TEM resonators. At high frequencies the measured Q-factor was higher than expected. Because the simulations gave the same results as the measurements, a possible explanation could be related to the resonator structure.

The Q-factor of the U-shaped resonator at 2 GHz was also high (90) and it was chosen to be used in the practical filter application. [Paper VI]

In conclusion, the results showed that the novel LTCC material system produced at least 20% higher Q-factors when compared to the resonators made of commercial material with the same component thickness. The basic reasons for these higher Q-factors could be the lower losses of the dielectric material ($0.9 \cdot 10^{-3}$ to $>1.2 \cdot 10^{-3}$) [Bailey *et al.* 1997] and the fact that the $\lambda/2$ resonator structures needed no low-conductive grounds at one end of the resonator. This proposed explanation requires further studies.

These U-shaped $\lambda/2$ resonators were used in the designed filter structures. The equivalent circuit diagram of the filter is shown in Fig. 4.3.

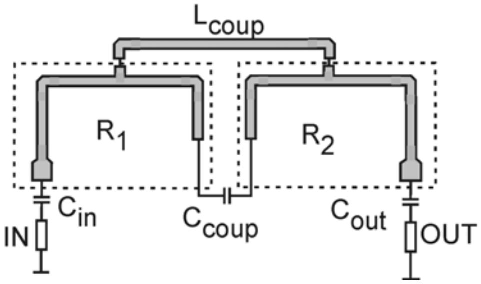


Fig. 4.3. The equivalent circuit diagram of bandpass filter using the novel LTCC material system. [Paper VI]

The filter comprised a bandpass structure (Fig. 4.3) with two resonators (R_1 and R_2), capacitive inputs and outputs (C_{in} and C_{out}) and an excess notch (L_{coup}) improving the stop band attenuation. The coupling between the resonators was arranged using a capacitance (C_{coup}). [Paper VI]

The multilayer structure (Fig. 4.4) of the filter was designed with the Sonnet simulator.

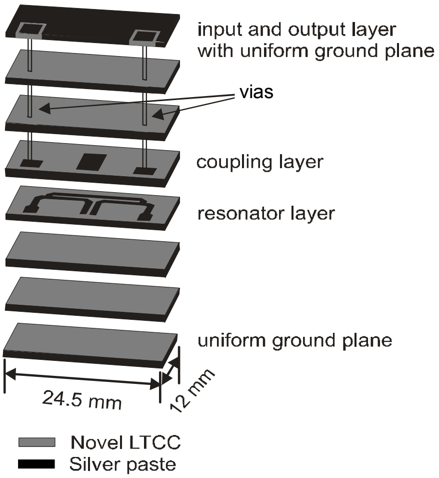
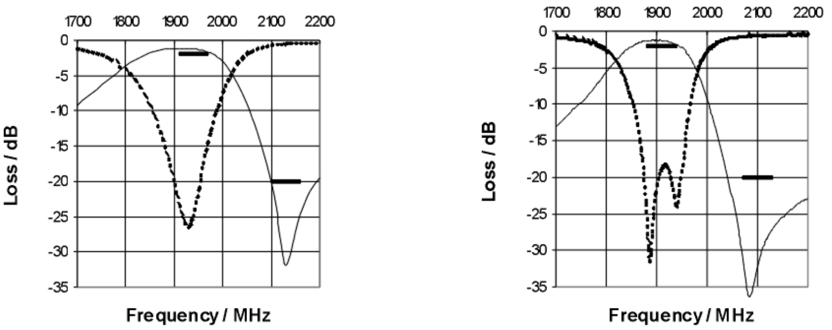


Fig. 4.4. 3-dimensional structures of the 2-pole bandpass filter made of the novel LTCC material system. [Paper VI]

The resonators (R_1 and R_2) were situated in the middle of the multilayer LTCC module and the same layer included the notch-forming transmission line (L_{coup}). The coupling pads (C_{in} and C_{out}) were located on the coupling layer with the capacitive input and output pads connected through vias to the terminals of the top layer. The thickness of the structure was the same as for the measured U-shaped resonator as were the preparation and structural routes and values for the electrical design. [Paper VI]

The simulated and measured frequency responses of the filter are shown in Fig. 4.5.



(a)

(b)

Fig. 4.5. The simulated (a) and measured (b) frequency response of the prepared filter (··· S11, — S21) indicating desired bandwidths and attenuation (—). [Paper VI]

The prepared filter had insertion loss in the pass band <–2dB, the ripple was < 1 dB and the attenuation losses in the stopband were more than 25 dB, indicating its superior properties. The difference between the simulated and measured centre frequency values was about 30 MHz and the bandwidth was somewhat narrower. The cause of these deviations was inaccurate positioning of the coupling layer identified by scanning acoustic microscope. [Paper VI] Furthermore, the measured filter had a very high reflection attenuation, which is caused by its double tuned response. This was not found with the Sonnet electromagnetic simulator because the program version used was not able to optimise.

In Paper V, a bandstop filter with two $\lambda/4$ resonators and the same capacitive coupling system but using duPont's 943 materials was also prepared. Although it is difficult to compare the properties of different types of filters, a rough comparison of their frequency responses suggests that the same kind of superior properties of this novel LTCC material system may be obtained in a filter as were measured for separate resonators. This study demonstrated that the novel LTCC material system can successfully be used for RF filters for the next generation of telecommunication applications. Further improvements and tests are needed for larger manufacturing.

5 Conclusions

The main target of this thesis has been to develop a novel LTCC dielectric material suitable for microwave and RF telecommunication applications. The two most important research objectives were the development of the dielectric ceramic and its preparation procedure for multilayer components. Also its properties were demonstrated with RF resonators operating in the frequency range between 1.8 and 3.8 GHz and a filter at 2 GHz.

The basic characteristics of a novel LTCC material are set by requirements of the final components. Special attention has to be paid to the values of the permittivity, ε_r, the dissipation factor, DF, and the temperature coefficient of the resonance frequency, τ_f. All these electrical material properties are very important for microwave devices. The permittivity should conform to the process and application demands and limitations, low losses are always desired and the RF components have to give the same frequency response at all operational temperatures. The first two properties have been well reported, but the importance of the temperature stability of the resonance frequency has received only very limited attention. The commercial LTCC materials, for example, have the ε_r between 4–10 and the measured DF > $1.2\cdot10^{-3}$, but the values of τ_f are not normally published.

Although the dielectric properties are essential, the LTCC process itself has fundamental requirements for the dielectric material. First of all the ceramic composition should reach it full density in a low temperature firing process which includes complete burn-out of the organic additives used in tape casting. The tape should also have a smooth surface, it should be self supporting, easy to laminate and be compatible with a low firing, high conductive paste. Only these properties can assure that real multilayer components can be produced. Additionally, the thermomechanical properties of the dielectric material should enable the use of the prepared components with high reliability.

In this thesis all these requirements have been taken into account. The basic study has been done with the development of the dielectric material by decreasing the firing temperature of $MgCaTiO_3$ dielectric, through the addition of ZnO-SiO_2-B_2O_3, from 1360°C to 900°C. The firing and microstructure properties of the composition were investigated using the dilatometer, SEM/EDS and XRD. The dielectric properties were studied with the Hakki-Coleman method and coaxial resonators and finally, the most critical thermomechanical values, linear thermal expansivity, elastic modulus, hardness, fracture strength and toughness, were determined. The results were compare to the corresponding properties of the commercial LTCCs.

The tape casting and multilayer component preparation procedures were studied with the selection of a suitable silver-based paste for the conductors. Finally, multilayer resonators and a bandpass filter were prepared using this novel LTCC material system and process, both introduced in this thesis.

The most important results of the thesis were as follows:

1. The novel dielectric LTCC made of the $MgCaTiO_3$ and $ZnO\text{-}SiO_2\text{-}B_2O_3$ can be prepared without any prior glass preparation route, which makes the powder process very straightforward and minimises the risk of component volatilisation.
2. The fired microstructure was dense with a low porosity composed of totally crystalline phases, which improved the dielectric and thermomechanical properties of the material.
3. The DF of the novel dielectric was lower ($0.9 \cdot 10^{-3}$ at 8 GHz) when compared to the commercial LTCCs and, furthermore, the value of the τ_f is shown to be adjustable with the amount of TiO_2 in the composition. The permittivity was 8.5.
4. The mechanical properties of the dielectric were almost the same as for the commercial LTCCs, but this material had a higher thermal expansivity (8.5 ppm K^{-1}) and is thus especially compatible with alumina substrates.
5. In the tape casting procedure, the common slurry preparation method and additives could be used and the final green tape had a smooth surface and good lamination and firing properties. Additionally, a commercial low resistive silver paste could be used with this LTCC to form the inner and outer conductors and via filling needed for multilayer components.

The studies described in this thesis are fundamental investigations of the development of novel LTCC materials systems. The achieved state of the art offers an opportunity to prepare RF and microwave components with excellent properties in small scale production. The results also compare well with the state of prior art of commercial LTCC dielectrics and in many ways even exceed this. For large scale production however, further work needs to be done.

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