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Structural and Dielectric Properties of Glass – Ceramic Substrate with Varied Sintering Temperatures

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1. Introduction

The main requirements of microwave circuit technology for wireless applications are a combination of high performance circuit, high integration density and frequency stability with a cost effective price [1-2]. Ceramic technology is particularly well suited to these requirements due to the superior performance of their electrical, electromechanical, dielectric and thermal properties in order to satisfy the many complex tradeoffs involved in electronic devices to meet many of today's and future needs [3]. However, as the demand for revolutionary changes in mobile phone and other communication systems using microwave as a carrier is increasing, the usage of ceramics may have reached at a certain limit. Thus, continuous research on this ceramic technology is urgently required in order to get an advanced improvement and innovation in the material properties in conjunction with the rapid change of required device characteristics. Although we may sometimes experience miserable insufficiency of accumulated knowledge in regard to basic research, it is believed that these research activities can contribute immeasurably to give scientific and technological understanding which is very important especially for the new engineer and researcher.

'Ceramic' is derived from the Greek word 'keramos' which means potters clay or pottery [4]. This material is usually used as ceramic-ware such as floor tiles. However the demand for ceramics is becoming more important in helping electronic devices to attain better performance for medical, global communication, military and other uses. Their introduction as engineering components in recent years has been based upon considerable scientific effort and has revolutionized engineering design practice. The development of engineering ceramics has been stimulated by the drive towards higher, more energy-efficient, process temperatures and foreseeable shortages of strategic minerals. Since 1750 ceramics materials have been used for the chemical industry, electrical insulation and especially for being heat resist-

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ant to withstand the heating effects of high frequency electromagnetic fields. The last-mentioned property is crucial for radio and television broadcasting. The electro ceramics such as magnetic ceramics (Ferrites) and electrochemical ceramics (piezoelectric ceramics) were subsequently developed [5]. Presently, the ceramic packaging and multilayer substrate process have received much worldwide attention in response to an increasing demand for circuit miniaturization and higher performance device have led to the development of the Low Temperature Co-fired Ceramic (LTCC) technology.

1.1. An overview of low temperature co-fired ceramic (LTCC) technology

LTCC is a multilayer substrate technology for device integration. This technology has been growing continuously since the appearance of the first commercial cofired ceramic product for robust capacitors in the early 60's [6]. In the standard LTCC technology ceramic green tapes are processed by punching and screen printed to form vertical interconnect and planar conductor patterns, laminated and finally fired at 850 ºC to form a highly integrated substrate. The low sintering temperature provided by the LTCC technology is the key factor enabling its advantageous utilization for today's packaging concepts in microwave modules [2].The main motivation for the use of the LTCC technology is the possibility of fabricating three dimensional circuits using multiple ceramic layers allowing more complex design circuits and device structures. A simple diagram of an LTCC substrate is presented in Figure 1. Through this technology a highly integrated package which contains embedded passive parts which increase the level of circuit function can be realized [7-11]. Besides, LTCC modules or packages provide a hermetic multilayer interconnection structure with very uniform and stable frequency and temperature dependent properties. Furthermore they also allow high density of lines throughout the part, are able to construct various geometries of interconnects by layer cut outs and have good heat transfer ability [12]. In contrast to the conventional ceramic technology, this technology which uses the ceramic material as the main ingredient is growing continuously especially for industrial and telecommunication area due to the low investment and short process development in addition to the flexibility of the technology including obtaining interesting properties of the ceramic material itself by controlled processing methodology [13-14]. Moreover, high fired density with repeatable shrinkage and frequency characteristics are necessary for high performance and low cost modules.
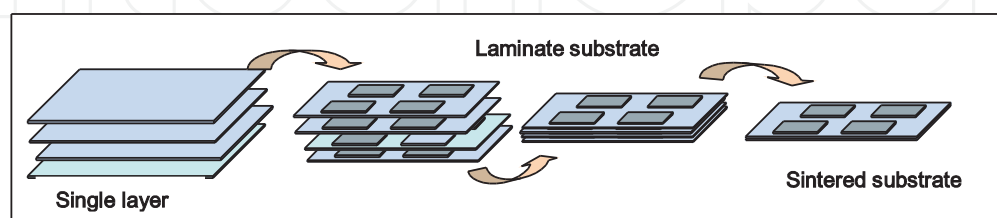
Figure 1. Multilayer ceramic substrates

LTCC is a system consisting of a glass ceramic dielectric composition which can be described as a polycrystalline material formed by controlled crystallization of glass [15-17]. This

composite material consists of multi-components inside the multilayer structure involving more than one component, more than a single phase and complex morphology. The preparation of this composite system is not an easy task because its properties are known to depend significantly on the chemical and physical properties of the starting raw materials [17], chemical composition, chemical purity, homogeneity of particle size distribution and the nature of grains and pores (size, shape, orientation) in the conductor surface and the glass-ceramic composite. Consequently, accurate characterization of the starting powders is essential to achieve high quality and reproducible production of current materials and to development of new materials with optimized or designed properties [18]. Furthermore, the variation of sintering temperatures and chemical composition of the composite also strongly changes the properties of the substrate, so in order to obtain a high quality product, a special working knowledge of ceramic science is needed for a judicious and scientifically reasoned choice of starting constituents that could yield desired properties for required applications.

A multilayer component or microelectronic device requires a highly conductive metal to be used for internal circuitry pattern to obtain a high quality factor and should have a low melting point to co-fire together with the substrate [19]. Conductors are the carriers of electrical current and substrate are the carriers of electromagnetic waves that are related to the current being carried in the conductors. The conductors also must be match with other components in the LTCC substrate in terms of shrinkage and thermal coefficient expansion. So the right selection of the conductor is necessary because it will determine the overall system cost and will impact on the product reliability. A silver conductor is the most commonly used for this purpose due to its low resistivity, low cost, low melting point and being compatible with the high performance substrate, thus providing good electrical properties and good adhesion to the substrate [20-21].

The studies on glass-ceramic systems related to the dielectric and structural properties of $CaO-B_2O_3-SiO_2$ (CBS) for the LTCC technology have been previously reported by some researchers [22-24]. In 1992, the crystallization behavior of a non-alkali glass system was investigated by Ota and his-coworkers, 1992 [25]. They concluded that with an addition of wollastonite ($CaOSiO_2$) powder, the crystallization of the glass can be controlled. Jean et al., 1995 [26] reported a systematic study on the densification kinetic mechanism of glass-composite. They found that the addition of cordierite glass (CG) to the low binary glass (Borosilicate glass-BSG) significantly slowed down the densification kinetics but increased the activation energy of densification. It could be attributed to the strong coupling reaction which takes place between BSG and CG during sintering. More recently Wang et al., (2011) [27] investigated the structure evolution process for CSB glass ceramic powder for LTCC application. The prepared powder exhibits an amorphous network structure with steady Si–O and B–O bonds after heat treatment at 600 °C, in which Ca^{2+} is distributed. They also found that the main phases in the CBS glass ceramic are $CaSiO_3$ and CaB_2O_4, which made the as-sintered CBS glass ceramic to have excellent dielectric properties. Presently research on the CBS system has been carried out by Zhou et al., 2012 [28] on the effect of $La_2O_3–B_2O_3$ on the flexural strength and microwave dielectric properties of the low temperature co-fired CaO–$B_2O_3–SiO_2$ glass–ceramic. They found that LB addition promotes the crystallization of the

$CaSiO_3$ but a highly amount of the LB addition leads to the formation of more pores, which is due to the liquid phase formed during the sintering process.

The effect of sintering temperature variations on microstructure changes of the $CaO-B_2O_3$-SiO_2 glass-ceramic system has been carried out before [29]. In this chapter, an extension of some previous studies has been made to investigate the effect of sintering temperature on the structural properties and the dielectric properties in the range of 10 KHz to 10 MHz at room temperature. The work was constructed as follows: A low temperature co-fired ceramic substrate was prepared by laminating eight layers of ceramic-glass tape to study the relation of different sintering temperatures, 800ºC, 825ºC, 850 ºC, 875 ºC and 900ºC, on density and shrinkage of the whole substrate. The evolution of microstructural changes of the substrate was also studied and observed by using scanning electron microscopy. The density and the shrinkage of the substrate did not show any significant trend with increased sintering temperature. The main aim of this work is to analyze the changes of permittivity, dissipation factor and structural performance with varied sintering temperatures of laminated substrates. Thus these perhaps would provide good information for making high quality substrate materials comparable with those available in the market.
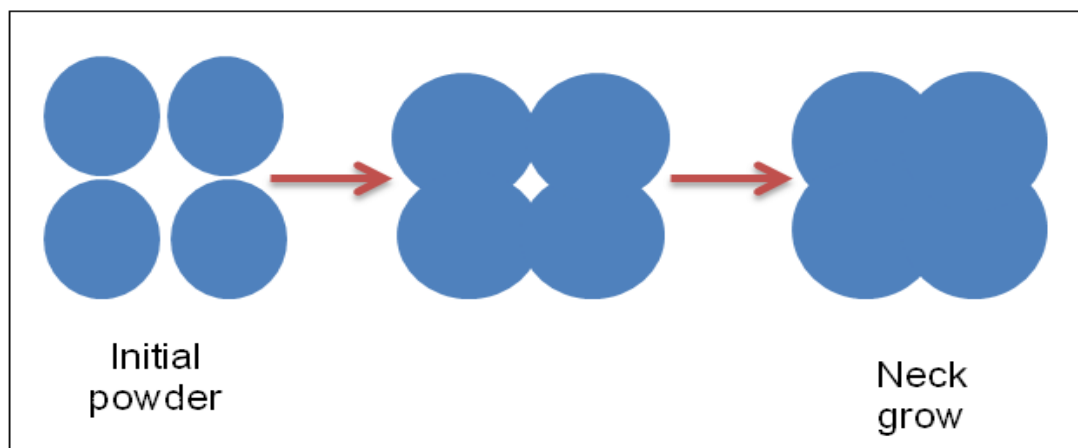
1.2. Sintering

Sintering forms the key stage of the fabrication route in which powder or sample is heated to a certain temperature and converted to the dense body by removal of pores between the starting particles (accompanied by shrinkage of the component) [30]. It involves heat treatment of powder compacts at elevated temperatures, where diffusional mass transport is appreciable which results in a dense polycrystalline solid [31]. The criteria that should be met before sintering can occur are (i) a mechanism for material transport must be present (ii) a source of energy to activate and sustain this material transport must be present. The primary mechanisms for transport are diffusion and viscous flow. Heat is the primary source of energy, with energy gradients due to particle contact and surface tension. A ceramist, physicist, chemist and metallurgist have to work together to produce a material with particular properties, must identify the required microstructure and must then design processing conditions that will produce this required microstructure. The objective of sintering studies is therefore normally to identify and understand how the processing variables such as temperature, particle size, applied pressure, particle packing, composition and sintering atmosphere influence the microstructure that is produced.

Thermodynamically, sintering is an irreversible process in which during this process the constituent atoms redistribute themselves in such a way as to minimize the free energy of the system. It involves consolidation of the powder compact by diffusion on an atomic scale resulting in reduction of surface area by grain boundary formation, neck growth between particles and densification of the system (Figure 2) [32-33]. The principal goal of sintering is the reduction of compact porosity. The effect of sintering temperature variations on the physical properties and microstructure of the finished product has always been a subject of great importance in ceramic literature since several decades ago [34-37]. The development of microstructure and densification during sintering is a direct consequence of mass transport

through several possible paths and one of these paths is usually predominant at any given stage of sintering [38]. They are (i) evaporation/condensation (ii) solution/precipitation (iii) lattice diffusion (iv) bulk diffusion and (v) surface diffusion or grain boundary diffusion with neck surface diffusion and any combination of these mechanisms. Through the different diffusion mechanisms, matter moves from the particles into the void spaces between the particles, causing densification and resulting in shrinkage of the part and thus the micro-structural developments will occur [39-40]. Several variables influence the rate of sintering. Some of them are initial density, material, particle size, sintering atmosphere, temperature, time and heating rate. The sintering phenomena are of two types: 1) Solid-state sintering, where all densification is achieved through changes in particle shape, without particle rear-rangement and 2) liquid-phase sintering, where some liquid that is present at sintering temperatures aids compaction.

Figure 2. Diffusion process.

1.2.1. Sintering of LTCC substrate

In an LTCC technology, the sintering process of a glass-ceramic substrate is one of the most important steps from the green laminate to the final product. In this step, a ceramic and a metal conductor would densify simultaneously at the same firing profile and at similar densification and shrinkage rate. Any mismatch between the sintering shrinkage of the electrode and the dielectric substrate induces stress which later will affects the device performance [41]. During this process particles are bonded together by heating to form sturdy solid bodies [42]. A good sintering profile stage for a dense and crystallized glass-ceramic should consider several factors i.e. 1) the transition temperature of glass, T_g, which determines the starting sintering temperature. For all ceramic materials including LTCC substrates, it is important that no sintering occur before the complete binder burn-out. The binder burn-out stages is complex and historically least understood [43]. This is because mass/heat transport, chemical kinetics and binder distribution interact with each other to determine the binder burn-out characteristics. The volatiles are produced at a rate which depends on the amount of heat available. The binder distribution

is also influenced by the thickness which means that the organics near the surface remove quicker than the inner organics. The binder decomposition temperature is usually in the range of 450 ºC - 750 ºC and recommended for a firing temperature of 850-950 ºC. A melting point below 450 ºC usually causes the organic material to be encapsulated resulting in blister forming in the dielectric layer as the organic decomposes [44]. The glass transition temperature determined by the composition of the glassy phase and is not affected by the presence of the crystal [45]. 2) Crystallization temperature (T_p) which determines the temperature that the crystal phase starts to grow. When the crystallization occurs the densification process rates is decreased. The crystallization of a glass-ceramic system usually occurs below 950 ºC. 3) Sintering rate; glass-ceramic substrates can be fully sintered before densification which depends on the sintering rate. Factor 1) and 2) contribute significantly in the temperature region for efficient densification.

According to Imanaka (2005) [46], the optimum firing temperature for an LTCC material is very important to achieve better performance of the LTCC module. So, the co-firing process of an LTCC substrate should be carefully controlled and monitored. The binder burn-out stage depends on the part size, the number of layers and the amount of metallization and should be considered as a starting point for the co-firing process of LTCC materials. At this stage the binder in the laminates must be completely removed after binder burn-out to make sure the joining of the layers are in good condition. The driving force for the joining of the tape is generally attributed to the surface tension of particles that exists during the burn-out process. The mechanism of binder removal transport are limited to the viscous flow, evaporation, condensation, volume diffusion and surface diffusion of binder phase which occurs at the interphase of the porous microstructure of the green tape and these causes capillary forces to arise [47]. These forces result in an approach of the ceramic layers towards to each other. Ceramic particles close enough after binder removal between ceramic layers, the particles at the edge can rearrange and move so that the ceramic layers interpenetrate each other and make a homogenous junction due to capillary force resulting in a laminate free of defects [48].

1.3. An overview of dielectric properties

The ceramic material provides the dielectric properties where the relative permittivity and dissipation factor of LTCC dielectrics become more important as frequency increases. It has been found that this parameter can be varied, therefore their values have to be determined before the design of any module or circuit can be started. In the microelectronics industry, the development of high speed interconnects for semiconductor devices demands new packaging-style technology to meet high-speed signal processing with high density and high frequency pulse requirements for multi-chip modules. To improve the performance of high speed systems, not only must high speed IC devices be exploited but also the signal delay in the substrate has to be reduced because the propagation delay time greatly depends upon the dielectric constant of the substrate [49-51]. The signal propagation delay time is given by [52]:

$$T = \frac{l x \sqrt{\varepsilon_r}}{C} \tag{1}$$

Where:

T_d: time delay

l: signal transmission length

ε_r dielectric constant of the substrate

c : speed of light

There are two ways to reduce the delay time by shortening the transmission length by:

1. forming fine patterns and many multilayers

2. lowering the dielectric constant

The relative permittivity values of commercial LTCCs which are usually measured at low frequency are in the range 3-10 as shown in Figure 3.
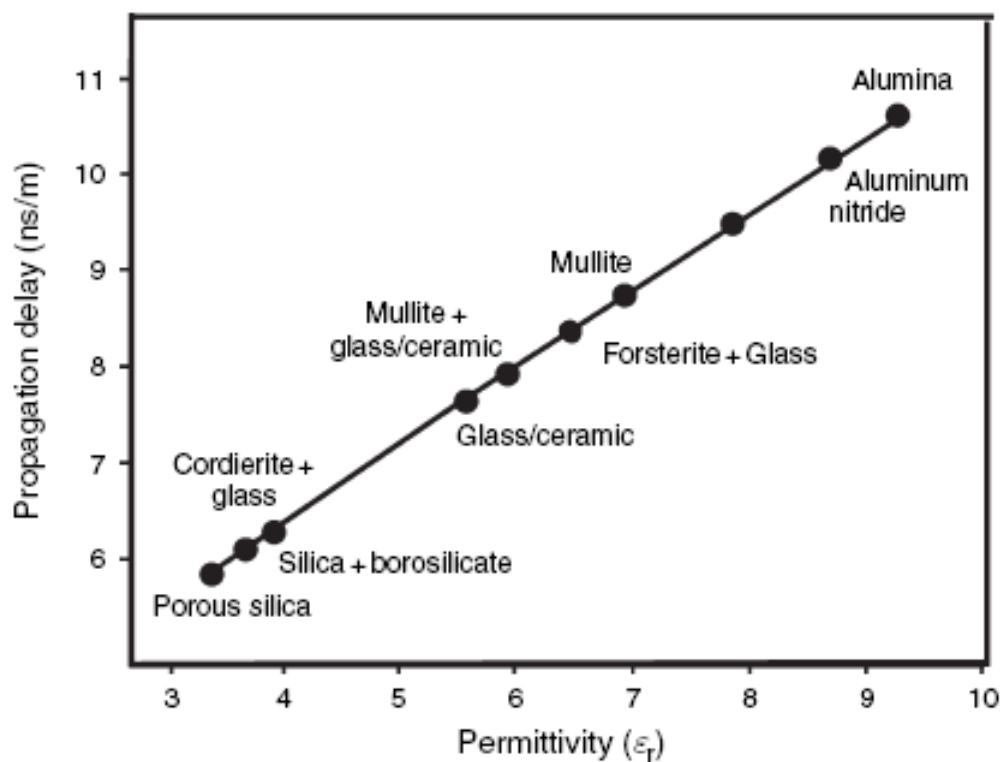
Figure 3. Variation of propagation delay as a function of permittivity of ceramic materials [50]

According to Wakino et al., (1987) [53], the permittivity is especially important because the length of a resonator is inversely proportional to the square root of the permittivity. 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. In a later work by Sasaki and Shimada, 1992 and Kellerman et al., 1998, they noted that the low dielectric is necessary to shorten the delay per unit length and the total wiring length in order to reduce propagation delay for signal transmission speed with minimum attenuation [54,55]. Besides, the dielectric constant is also important to control the impedance of microwave and RF circuits to within a few percent of a nominal value so as to minimize energy reflections at interfaces between the circuit tracks and circuit components. In the RF world, circuit components, as well as input and output impedance, are generally 50Ω. Therefore circuit track impedance should be 50Ω as well [16]. The recent progress in microwave telecommunication, satellite broadcasting and intelligent transport system has resulted in an increasing demand for a dielectric resonator with low loss pucks which are used mainly in wireless communication devices [56]. NIL (Figure 3).

Besides appropriate dielectric constant, low dielectric loss is also an important property of the substrate material for microelectronic packaging with high propagation speed [57-58]. The dielectric constant (permittivity) describes the material behavior in the electric field and consists of a real part, ε', called the dielectric constant, and an imaginary part, ε'', called the dielectric loss factor. Thus, the permittivity is expressed as;

$$e* = e' - je'' \tag{2}$$

where the dielectric constant represents the ability of a material to store electric energy and the dielectric loss factor describes the loss of electric field energy in the material. At microwave frequencies, ionic and electronic polarization mechanisms contribute predominatly to the net dipole moments and the permittivity as depicted in Figure 4 which basically have four basic mechanisms contributing to polarization [16]: 1) Electronic polarization, 2) Ionic/atomic polarization, 3) Molecular/dipole/orientation polarization and 4) Space charge polarization.

A low dissipation factor, DF is also required for low electrical losses in dielectric materials particularly at high frequency [59]. Dissipation factor or loss tangent (tan δ) is the ratio of the dielectric constant's imaginary part to the real part, given by:

$$Tan\delta = \frac{\varepsilon''_r}{\varepsilon'_r} \tag{3}$$

The loss tangent or loss angle may be used to determine how lossy a medium is. A medium is said to be a good (lossless or perfect) dielectric if tan δ is very small ($\sigma \ll \omega\varepsilon'$) or a good conductor if tan δ is very large ($\sigma \gg \omega\varepsilon'$). The characteristic behavior of a medium also depends on the operational frequency ($f = \omega/2\pi$). A medium that is regarded as a good conduc-

tor at low frequency may be a good dielectric at high frequencies. The simplest way to define dissipation factor (loss tangent) is the ratio of the energy dissipated to the energy stored in the dielectric material. The more energy that is dissipated into the material the less is going to make it to the final destination. This dissipated energy typically turns into heat or is radiated as RF (Radio Frequencies) into the air. The optimal goal is to have 100% of the signal pass through the interconnection network, and not be absorbed in the dielectric. With "high power" signals, a material with a large dissipation factor could result in the development of a tremendous amount of heat, possibly culminating in a fire (advanced dielectric heating). When the signals are very weak a high loss material means that little or no signal is left at the end of the transmission path. In order to retain maximum signal power, a low loss material should be used [61].
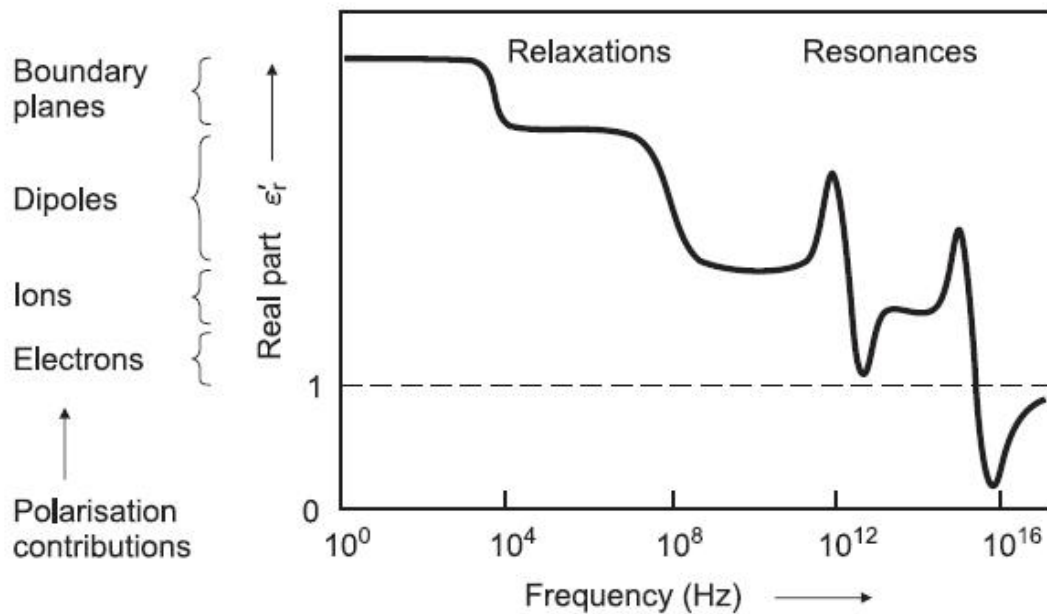
Figure 4. Polarization mechanisms [32].

As well known, the dielectric loss tangent of materials denotes quantitatively dissipation of the electrical energy to the different physical process such as electrical conduction, dielectric relaxation and loss from linear processes. The total dielectric loss is the sum of intrinsic and extrinsic loss. Intrinsic dielectric loss depends on the crystal structure and can be described by the interaction of the phonon system with the AC electric field. The ac electric field alters the equilibrium of the phonon system and the subsequent relaxation associated with energy dissipation. The extrinsic losses are associated with the imperfections in the crystal lattice such as impurities, microstructural defects, grain boundary, porosity, microcrack, random crystallite orientation, dislocations, vacancies, dopant etc. The extrinsic losses are caused by lattice defects and therefore can be in principle eliminated or reduce to the minimum by proper material processing [62].

2. Experimental procedure

2.1. Multilayer substrate process

The multilayer process was carried out using the LTCC process flow as shown in Figure 5. It started with cutting the Ferro A6S tape for the required dimension (204 mm x 204 mm) using a die cutting machine ATOM SE 20C to suit with the printing table dimension. Via hole filling with CN 33-407 was carried out using the manual filling process before printing the pattern onto the substrate using the suggested printing parameter with CN 33-391 for the surface and inner conductor on a KEKO P-200Avf Screen Printer Machine. The printed pattern and via hole filling were dried in an oven at 70 ºC for 10 minutes to avoid the printed pattern in one layer from adhering to each other during the stacking process. The printed pattern was then stacked using a manual stacker plate as shown in Figure 6. A simple and low cost mechanical fixture with alignment pins can be used to accomplish the stacking process layer by layer before insertion into an aluminum bag and vacuumed to remove the air in order to avoid the presence of warpage and delamination problems.
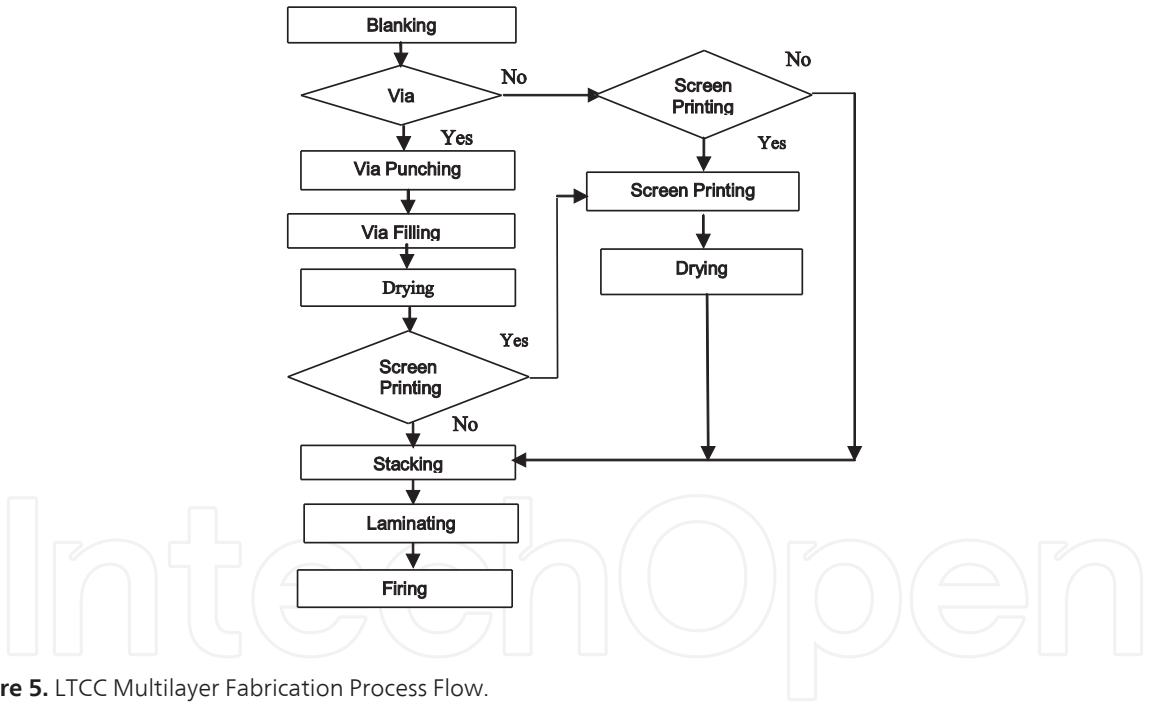

Figure 5. LTCC Multilayer Fabrication Process Flow.

Then the lamination process was performed by using an isostatic laminator system under pressure and temperature of 21 MPa and 70 ºC respectively to ensure that the layers of the stack were well adhered to each other to form a compact multilayer substrate. This process used heated water which acted as a medium to uniformly distribute the force of lamination. It minimized the delamination and gave more uniform shrinkage which improved the yield of complex parts. Finally, the laminated substrate was placed on the setter material in a Naberthem tube furnace and fired using a sintering profile as suggested by the tape manufacturer [63]. The setter material must be properly selected to suit the LTCC material set and

fabrication process [64]. This sintering stage for cofiring the materials is very important in the process methodology and can affect the microstructure and properties of ceramics. Through the sintering process, a transformation from the original porous compact to a dense ceramic takes place.In this process a specific temperature time profile which depends of the glass-ceramic mixture has to be observed during the firing process. A typical practice for the sintering cycle is to heat up the furnace from room temperature to 450 ºC with a gradient of about 2 ºC/min to remove the organic solvent and 6-8 ºC/min from 450 ºC to 850 ºC at which the sintering process of the composite material starts. The temperature remains constant for 10 minutes to finish the sintering. A controlled cooling of the furnace which takes at least three to eight hours (depending on material; thick or large size) causes the need to modify the firing profile. The process was repeated for sintering at 800 ºC, 825ºC, 850 ºC, 875 ºC and 900ºC using the same profile as shown in Figure 7.
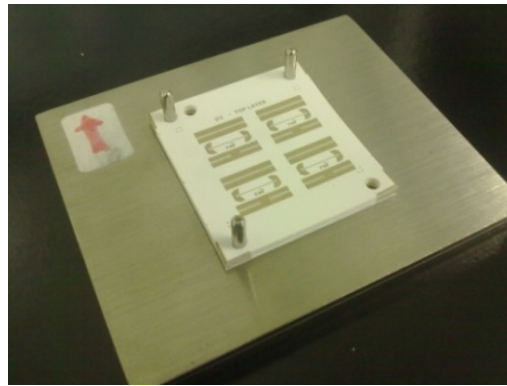
Figure 6. The manual stacker for collating and stacking process.
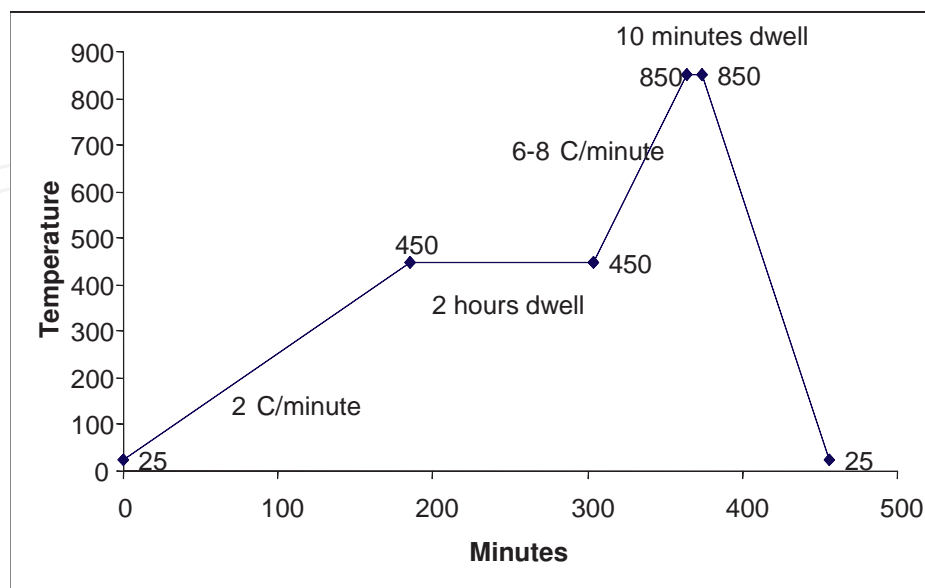
Figure 7. Firing profile for multilayer structure [63]

2.2. Sample characterizations

The density of the samples was measured using an electronic densitometer. The microstructure of the top surface of the ceramic dielectric tape was observed by FEI-Nova NanoSEM Field-Emission Scan (FE-SEM). Most of the samples were imaged several times, with at least three pictures in each case, from different areas of the sample holder. The average grain size was calculated using the line intercept method. The EDX spectrum was used to identify elements within a sample.

The shrinkage along the compaction direction and the diametrical shrinkage were measured from the geometry of the samples. The shrinkage was then calculated using equation.1 below.

$$\text{Shrinkage} = \left(\frac{\text{Length}_{\text{before fired}} - \text{Length}_{\text{after fired}}}{\text{Length}_{\text{before fired}}} \right) \times 100\% \tag{4}$$

The shrinkage during firing depends on the reactivity of material, binder content and the firing conditions (temperature, time and atmosphere). So the control of all the parameters is important to achieve acceptable values of shrinkage which will finally be used for circuit designing. The set of data for density and shrinkage percentage for all substrates will be discussed; this will take into account the composition of LTCC materials and the effect of sintering temperatures on microstructure.

Dielectric properties measurements (dielectric loss, dielectric constant and loss tangent) of the eight layers of the substrate materials were measured using Novocontrol Impedance/ Material Analyzer in the range of 10 KHz to 10 MHz at room temperature. The eight dummy layers were used to make sure an easy handling due to single layer tape is only about 10 micron in thickness. This instrument is very useful and has high accuracy for dielectric properties measurement. Before the substrate material was measured, the analyzer should be warmed up for about 30 minutes after switching on the analyzer for all specifications. The dielectric measurements were made using flat substrate surfaces. The top and bottom surface of the substrate were coated with silver conductive paint to make sure they had a good contact with the sample holder plates.

3. Results and discussion

3.1. Shrinkage and density

The properties of the final ceramic composite materials depend on the sintered density of the whole substrate. A stacked and laminated LTCC substrate before firing consists of a relatively porous compact of oxides in combination with a polymer solvent. During sintering the organic solvent evaporates and the oxides react to form crystallites, or grains of the re-

quired composition, the grains nucleating at discrete centers and growing outwards until the boundaries meet those of the neighboring crystallites. During this process, the density of the material rises; if this process were to yield perfect crystals meeting at perfect boundaries the density should rise to the theoretical maximum, i.e. the x-ray density, which is the material mass in a perfect unit crystal cell divided by the cell volume. In practice imperfections occur and the sintered mass has microscopic voids both within the grains and at the grain boundaries. The resulting density is referred to as the sintered density. The density of the sample was measured using the Archimedes principle shown in equation (5);

$$\rho = \left(\frac{W_a}{W_w}\right)\rho *_w \tag{5}$$

where W_a = weight of sample in air; W_w = weight of sample in water;

$\rho *_w$ = density of water = 1 gcm^{-3}

Sintering Temperature (ºC)	Green Density (g/cm)	Sintered Density (g/cm)$_3$	Densification factor (D_f)	Shrinkage	% porosity
800	1.725	2.379	1.023	16.445	0.211
825	1.733	2.372	0.989	16.3	0.214
850	1.733	2.415	1.131	16.42	0.20
875	1.731	2.365	0.971	15.52	0.217
900	1.785	2.412	1.034	16.79	0.201

Table 1. Physical properties of LTCC tape samples fired at various sintering temperatures

The densification behavior is described as densification factor (DF) as a function of time. The DF which represents the porosity removed during densification is defined as

$$D_f = \frac{\left(D_s - D_g\right)}{(D_{TH} - D_g)} \tag{6}$$

Where Ds is the instantaneous sintered density, Dg is the green density and D_{TH} is the theoretical density calculated for the composite by the mixture rule. The data of green density, sintered density, shrinkage, percentage of porosity and the densification factor of the LTCC substrates fired at various temperatures are tabulated in Table 1. The density and linear shrinkage as a function of sintering temperature for all the substrates is plotted in Figure 8. The sintered density of the substrates material was between 2.365 -2.412 g/cm^3 or about 79%

of the theoretical density of 3.018 g/cm^3. The density obtained is found to be lower than that produced by other researchers [65-66].The total pores are directly related to the density. Therefore the higher heat treatment is believed to have removed a fraction of the pores. In this work all the samples had roughly similar amounts of porosity.

The linear shrinkage of the substrate material also fluctuates with increased sintering temperature. However, it is still in the standard values within the XY shrinkage range of about 14-17 %. In commercial production, the designed shrinkage is generally between 12-16 % for the XY direction and 20-25 % for the Z direction. The shrinkage is the key factor and the major technical problems in the LTCC technology. The repeatability and consistency of the shrinkage percentage must be the top criteria when designing an LTCC product. This is because the shrinkage of the LTCC substrate depends on the reactivity of the co-fired material containing ceramic oxides, glass, metal, organic solvent and also the firing conditions such as temperature, time and ambient air [29]. Better reproducibility increases the uniformity of finished product characteristics and therefore increases the process yield. It is not an easy task because all process parameters (lamination, binder burnout, sintering, etc) and material properties (high temperature reactivity, thermal expansion, etc.) must be matched [67].
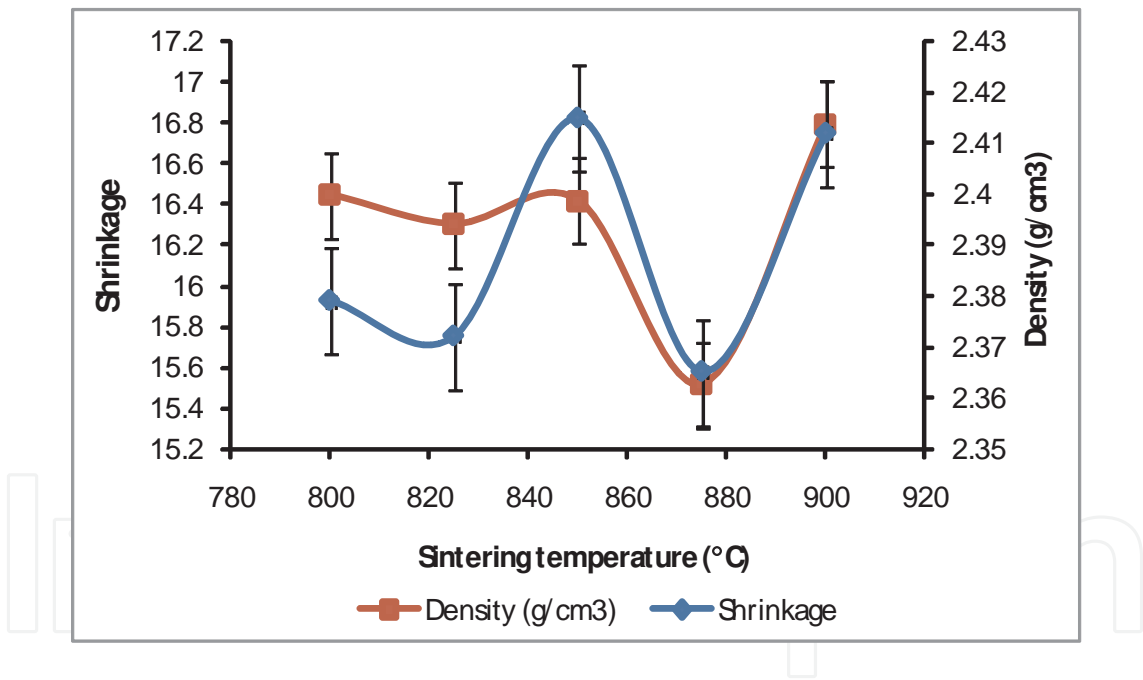
Figure 8. Relation of densification and shrinkage as a function of sintering temperature.

The density and shrinkage are highly microstructure sensitive. They are very much influenced by the way the samples are processed, grain size, chemical homogeneity and the presence of pores where all of these characteristics depend on the particle size, size distribution, particle packing density and particle orientation in ceramic powders and reactivity of the powder including the physical attributes of the green compacts [68]. Apart from the size distribution of the powder employed, the outcome is impacted by the other factors such as dispersion, solid loading and the heterogeneities in multicomponent systems [68-71]. Small

particle size and narrow size distribution may increase the shrinkage rate. A higher shrinkage rate means a good densification process which is due to a good particle distribution contributing to the good particle packing of the samples and giving high density of the tape. These results may be attributed to the preparation condition and the problem of starting raw material used in this work. It finally produced a bad substrate. Keizer and his co-workers in 1973 mentioned in their work that the electrical properties of a ceramic material of a given composition depend primarily on the chemical homogeneity and the average particle size. The value of these characteristics is considered to be the results of quality of starting raw materials as well as of the preparation condition since the density is considered as the most sensitive property [72]. Furthermore, the material quality of the finished product and process conditions also must be optimized in micro and macro structures in order to make sure the work in progress is highly repeatable at each process step [46]. All science and technology knowledge including technical skills regarding the LTCC fabrication process should be applied to achieve desired shrinkage data; the process engineer must have proper protocol to control the critical process variables.

3.2. Microstructure

Microstructural characterization has been used since many years ago in attempts to understand the crystallization mechanism of complex and multiphase ceramics which plays an important role in the improvement of the thermal, electrical and mechanical properties [73]. It covers by the microstructural features such as phases, crystalline morphology, crystallography and the chemistry of the interfaces. According to Yamaguchi, 1987, the desirable properties at high frequency cannot be determined only by chemical composition or crystal phase alone but also require the true characteristics of the microstructure which depend primarily on the sintering temperature, packing density and packing homogeneity of the green body which, in turn, are controlled by the powder characteristics and the method used to form the green body [42]. Generally, microstructure control during firing becomes less difficult when the homogeneity of the green body is improved since a sintered structural ceramic body should have a chemically and physically homogeneous microstructure [74]. Thus for the same green density, improved packing homogeneity leads to improved sinterability in the form of higher sintered density at a given sintering where fine particles tend to be active and sinter more readily at a given temperature especially in the presence of a liquid phase [75-76].

The effects of sintering temperature on microstructure of glass-ceramic tape are shown in Figure 9. It is clearly seen that there is inhomogeneous microstructure for the entire sample with some sample showing a big size pore meaning that probably only a few crystallite sizes are present in the bulk samples. This feature of the microstructure could be due to the presence agglomeration within the sample. The agglomerated tape however leads to lower densities with large shrinkage deviations in particular direction giving a poor quality [77]. NIL. In the LTCC process, some particles are densely packed and some particles are loosely packed due to the agglomeration of particles at some places. The presence of agglomeration is a common problem in ceramics processing and influences the microstructure behavior of

the whole substrate. As mentioned by Lange (1984) and Hirata et al., (2009) [78-79], when a laminated substrate or powder compact is heated, the inhomogeneity of the packing provides the different densification rates producing a microstructure which is usually not uniform when agglomeration is severe. An inhomogeneous distribution of particles leads to an inhomogeneous liquid distribution such that there is no driving force for redistribution of the liquid, so the densification rate is not homogeneous and the microstructure development also becomes inhomogeneous. Agglomeration promotes uneven sintering which sometimes results in a mechanically weak and porous product. Thus, to achieve a high density material and good microstructure development, the agglomeration needs to be controlled [80].

(a) 800 °C   (b) 825 °C   (c) 850 °C

(d) 875 °C   (e) 900 °C
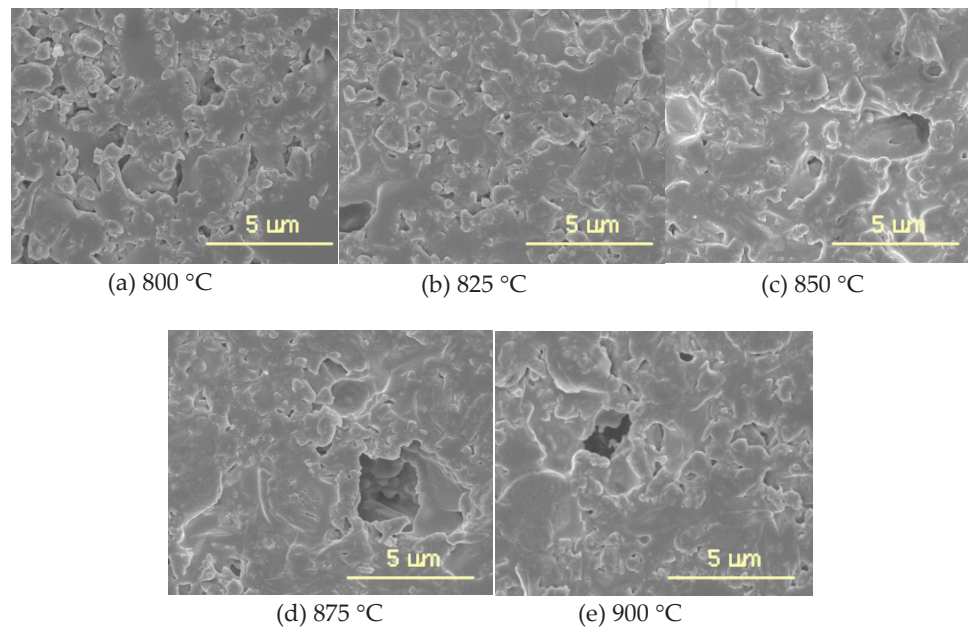
Figure 9. SEM micrograph of laminated sample sintered at a) 800 ºC, b) 825 ºC, c) 850 ºC, d) 875 ºC and e) 900 ºC.

The densification process of the glass-ceramic composite in general can be described by the conventional three-stage liquid phase sintering as previously suggested in the early work [81-82]: particle rearrangement, dissolution and precipitation and solid state sintering. Compared to solid state sintering, each of the three stages is connected with the dominant microstructural changes; however, each stage in a liquid phase sintering is identified with that which occurs in the stages [18]. As previously mentioned the presence of glass phase ($CaSiO_3$) in this composite system produces liquid phase formation at a temperature lower than the sintering temperature and may considerably increase the rate of sintering [29]. The importance of the rearrangement of particles under the action of liquid surface tension and the solution precipitation mechanism has been considered essential features of the liquid phase sintering which finally affects the sintering. The redistribution of liquid during densification is more problematic since it depends on the initial particle packing which is difficult to identify [83]. The presence of this secondary

phase may probably restrain the growth of the grain. Compared to the solid state sintering, the effectiveness of liquid phase for enhancement of sintering rates depends on the introduction of new densification process. When a liquid is added which is present in sufficient amounts at a sintering temperature, it might completely wet and penetrate between solid particles; rapid densification can be obtained by the rearrangement of solid particles under capillary forces and by the solution at the contact points and precipitation elsewhere [84].

The whole densification rate at the final stage, is a summation of the developed local internal defect such as the presence of pores that are no longer large enough to prevent grain growth and this is the major process going on in addition to the final densification. With the increasing grain size, the densification rate decreases as the distance of the defects to the grain boundaries increases. Grain growth also gives pore coalescence where smaller pores are merged together into larger ones: this also reduces the densification rate and explains the density results obtained. In the case of the sintering process of glass ceramic material, if crystallization occurs before densification, the viscosity of samples will be increased. It is due to the contribution of glass composition into a crystalline phase structure, resulting in the reduction of viscous flow of the system. As a result, densification through viscous flow sintering will not occur properly and a porous body will be formed [85].

3.3. Dielectric properties

The ceramic substrate acts as a support material for active and passive devices and the interconnecting conductors that makes up the substantial subsystems. Discrete components integrated into the substrate also may be involved. Signal transmission from one chip pad to another chip pad is governed by the dielectric properties of the substrate or the interlayer and the electrical conductivity of the metal strip. If the total resistance is low, signals will be propagated with the speed of light, with a delay that is proportional to $n = \varepsilon^{1/2}$. Line termination is important to control reflections. If the resistance is large (greater than several ohms), transmission is slower and the effect of the dielectric constant exponent is even greater. Thus, the dielectric properties of the substrate play a crucial role in determining circuit speed.

Dielectric properties of substrates are dependent upon the several factors including the method of preparation, chemical composition and microstructure. Based on these factors, the dielectric materials have to have proper firing, so that a dense and nonporous product has to be obtained [86]. Besides, the dielectric properties are also affected by the bonding mechanism and crystallinity in the materials. The primary bonding mechanism in ceramic is ionic bonding while for the other material the bonding mechanism is covalent bond. In former times the dielectric constant and loss were measured at 1 MHz, the dependence of these data on frequencies up to GHz range is of high interest today, due to the dynamic development of mobile communications [87].

3.3.1. Effect density on the dielectric properties

The variation of dielectric constant and loss tangent with increased the sintering temperature are illustrated in Figure 10. The relation between dielectric properties and sintering did not show a similar trend to those the relation of density and sintering temperature. The decreasing trend of dielectric constant up to 850 ºC can be correlated to the presence of $CaSiO_3$ as a main phase in glass-ceramic system. It was reported in the previous work [29]. Chang and Jean (1999) [88] have noted from their studies and concluded that the presence of Ca-SiO_3 phases at temperature 850 ºC and above would cause some defects in microstructure due to the formation of liquid phase. This behavior will hinder the polarization which finally affects the dielectric constant of the sample sintered at 850 ºC. It was consistent with results by Lo and his team in 2002 and noted that the changes of permittivity attributed to the crystallinity presence in the NIL glass-ceramic samples which made the dielectric constant decline slightly [65]. It was later confirmed by Wang et al., 2009, for their research on the relation of dielectric properties and microstructure of $CaSiO_3$ in the presence of B_2O_3 additives. They found that the dielectric constant was decreased in the presence of $CaSiO_3$ at sintering temperature of 1100 ºC. They are the stable phases when crystallization is complete [89]. Thus, a decrease in the dielectric loss with an increase in the sintering temperature must have been caused by the phase reaction between the ceramic and the glass phase, resulting in an ionic exchange between Si2+, Ca2+ ions in the composite. This would cause a decrease in the electrical resistivity of the glass phase, which in turn would yield a decrease in dielectric loss.
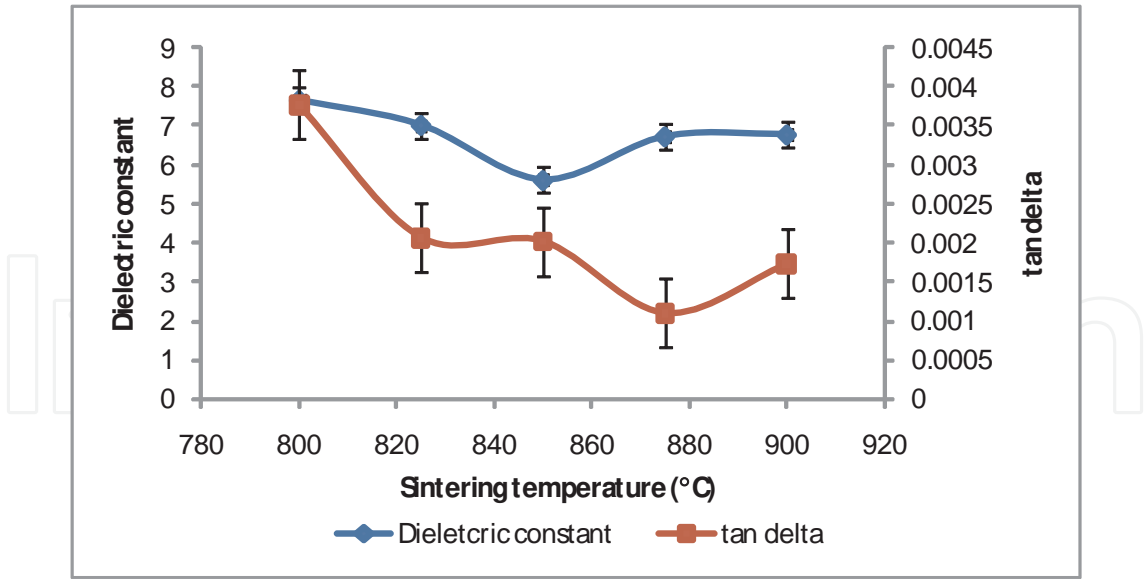
Figure 10. The relation of density and dielectric constant as a function of sintering temperatures.

Since LTCCs are basically composite structures of glass and crystals, controlling their dielectric constant depends largely on the combination of constituent materials of the composites and its material composition (i.e. volume fraction of the constituent materials)

[46]. Each constituent in the glass composition is crucial to the crystallization, densification and thus the microwave dielectric properties. Lo and Yang (1998) have studied the sintering characteristics of Bi_2O_3 added MgO-CaO-Al_2O_3-SiO_2 glass powder. They found that for a glass-ceramic, many factors affect the permittivity including of individual crystalline glass phases and the level of porosity or the degree of densification [90]. However, their effects are intercorrelated and sometimes unable to distinguish the contributions from an individual constituent.

Such a microstructural arrangement can affect the dielectric properties due to inhomogeneities phenomena which usually occur during sample preparation. Pores and grain boundary relaxation was found to be the major features that cause the dielectric loss in LTCC substrate in the low frequency region of dielectric where the response can be noted in the imaginary part of the dielectric constant [91]. Some factors such as the inclusion of the powder impurities, non-uniform density of green compact and controlled atmosphere is very important. The formation of second phases generated from the reaction between dielectric composition and the glass fritz does influence the dielectric constant of materials. As an example in the CaO-B_2O_3-SiO_2 system glass ceramic, the system with high SiO_2 content tend to possess lower dielectric constant at microwave frequency. It is because a higher SiO_2 content favors the formation of wollastonite ($CaSiO_3$) associated with the crystallization of cristobalite, trymidite or quartz depending on the sintering temperature and cooling rate. However after a certain weight percent addition of SiO_2 (65 wt%), the formation of wollastonite is prevented. Chiang et al reported that the formation of wollastonite will decrease the dielectric constant of a material. The reason is that wollostonite phase itself has a low dielectric constant which is ≈ 5. Thus one should determine the composition and the amount of glass fritz composition so that the second phase formation could be minimized, maintaining sufficient densification [92].

Figure 11 and 12 show the variation of dielectric constant and the dissipation factor with the variation of sintered density. The dielectric constant decreased up to the sintering temperature of 850 ºC and increased beyond that point. A closer look at the graph shows that only the sample sintered at 850 ºC has a reverse trend compared to others. The results are not consistent with the results found by Wang et al., 2009, Louh et al., 2005 and Zhang et al., 2005 which noted that the dielectric constant increases with a similar trend to the increase of density as a function of sintering temperature [89, 92, 93]. According to Yang et al., 2003, the dielectric constant increases as the sintered density increase. As the sintered substrate becomes denser, its dielectric constant tends to increase, which indicates that less air entrapment in the substrate favors the permeation of electromagnetic waves [94]. It was confirmed by Sun et al., 2009 [95] who's mentioned that the dielectric properties are affected by the density of the compact body. However in this work, the dielectric constant initially decreased up to sintering temperature of 850 ºC and then increased again beyond this turning point. The drop in dielectric constant value at slightly high sintered density could be attributed to the presence of pores within the substrate. Dielectric constant is linearly dependent on its density which is associated with the porosity; the greater the porosity, the smaller the dielectric constant [92].
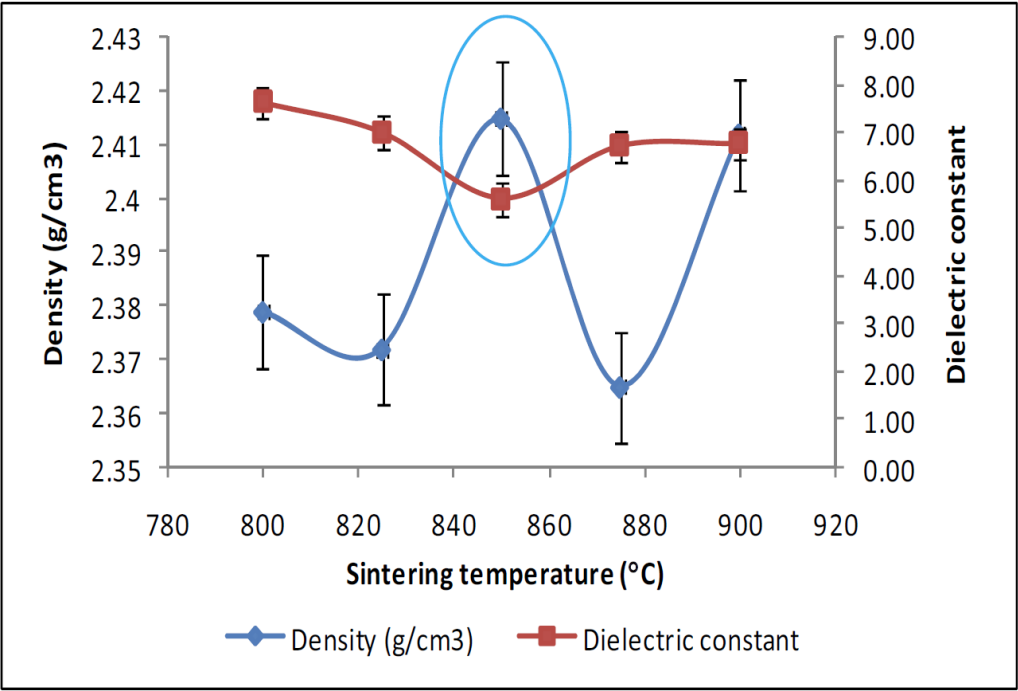
Figure 11. The relation of density and dielectric constant as a function of sintering temperatures.
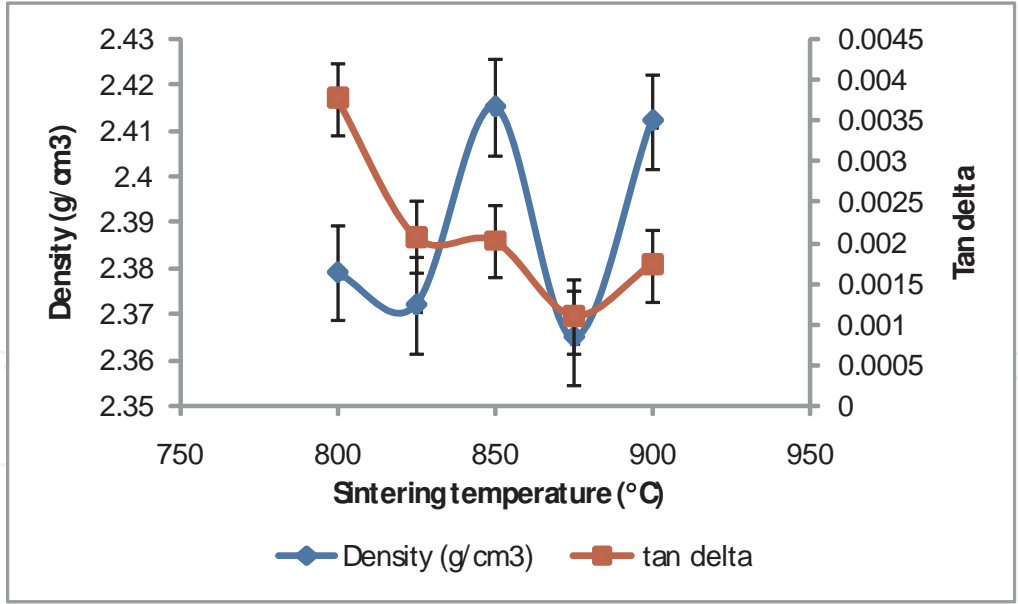

Figure 12. The variation of density and loss tangent as a function of sintering temperatures.

The dependence of the dielectric constant upon the properties of the material may be summarized in the statement that the dielectric constant depends upon the number and the mobility of the electron per cm³ of material and when the molecules contain electric dipole, to

much a greater extent upon the size and arrangement of the dipoles in the molecules, upon the freedom of the molecules to orient, and upon the number of molecules per cm³ [96].

3.3.2. Dielectric properties with frequency

The dielectric properties of glass ceramic system were studied in the frequency range from 10 KHz to 10 MHz at room temperature. Figure 13 show the variation of the dielectric constant as a function of frequency for all samples. Obviously, the dielectric constant shows a decreasing trend for all the samples. The decrease is rapid at lower frequency and slower and stable at higher frequency. The decrease of dielectric constant with increasing frequency is a normal dielectric behavior which is also observed by other researchers [97-99]. A glass ceramic system is considered as heterogeneous material that can experience interfacial polarization as predicted by Maxwell and Wagner. They pointed out that at low frequency region (refer to Figure 3) the movement of charge carriers trapped at interfacial region which is caused by inhomogeneous dielectric structure. At high frequency, the dominant mechanism contributing to dielectric constant is the hopping mechanism in their respective interstice under the influence of alternating current. The frequency of hopping between ions could not follow the frequency of applied field and hence it lags behind, therefore the values of dielectric constant become reduced at higher frequency [100].
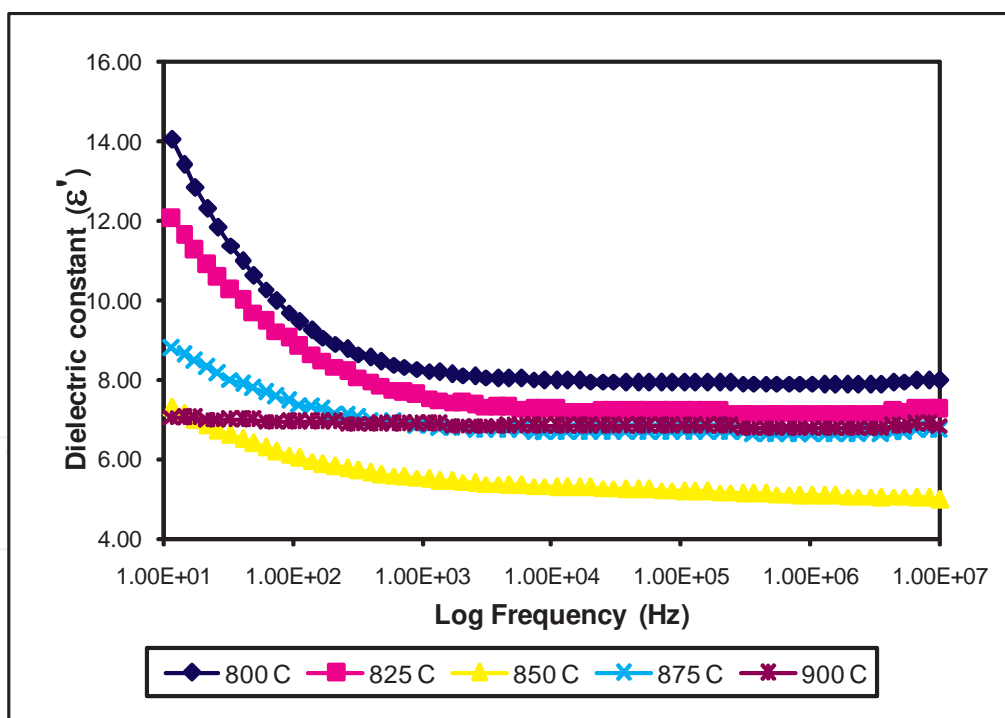

Figure 13. The variation of dielectric constant with frequency.

A low loss factor is desirable for a dielectric material so that the dissipated electric power to the insulator is minimized. This type of consideration is very important for high power circuits operating at high speed. Dissipation factor is a ratio of the energy dissipated to the en-

ergy stored in the dielectric material. The more energy that is dissipated into the material, the less is going to make it to the final destination. This dissipated energy typically turns into heat or is radiated as radio frequency (RF) into the air. The optimal goal is to have 100% of the signal pass through the interconnection network and not be absorbed in the dielectric. A high loss material means a little or no signal is left at the end of the transmission path. In other to retain maximum signal power, a low loss material should be used. The defect, space charge formation and lattice distortion is believed to produce an absorption current resulting in a loss factor and at high alternating frequency those could follow the field applied and later values the trend saturated [100].

Figure 14 show the variation of dissipation factor for all samples with frequency. The decreasing trend of loss tangent may be explained as follows: When the frequency of applied AC field is much larger than the hopping frequency of electron, the electron do not have an opportunity to jump at all and the energy loss is small. In general, the local displacements of electronic charge carriers (jumping electrons in case of ceramic substrate) cause (or determine) the dielectric polarization in materials. Since the dielectric polarization is similar to that for conduction and are mainly by the hopping conduction mechanism. Therefore the marked decrease in tan δ is due to the decreasing ability of the jumping electron (charge carrier) to follow the alternating frequency of AC electric field beyond certain critical frequency. This explains the decreasing trends for tan δ with increasingly frequency.
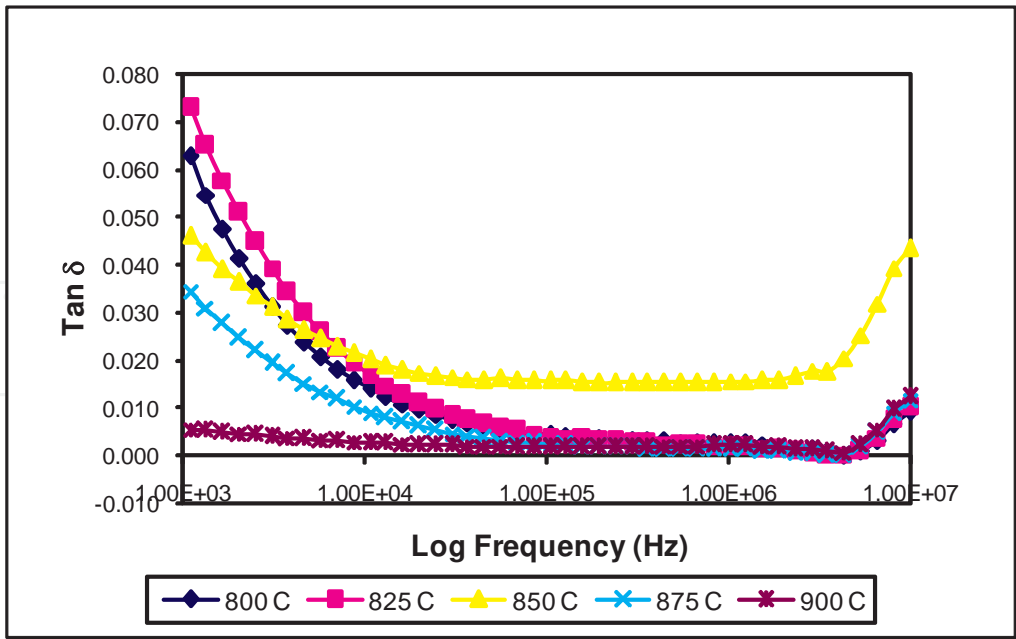
Figure 14. The variation of tan δ with frequency.

4. Conclusion

The effect of various sintering temperatures on some properties of laminated substrates has been successfully studied. It can be concluded that the sintering temperature strongly influenced the dielectric properties and some physical properties of the laminated substrate. The result of dielectric constant was decreased with increasing sintering temperature up to 850 °C but increased again beyond that point. It was also noticed that the dropped value of dielectric constant with higher sintered density at 850 °C is due to the presence of crystalline $CaSiO_3$ phases during the sintering process. The relation for the loss tangent and the density is generally a decrease with increased sintering temperature. It may be due to presence of crystalline phase and the porosity inside the substrate. The sintering process of glass-ceramic substrate is a complicated process because phase changes were involved. Thus the understanding of material behaviors such as binder burnout, densification of LTCC, grain growth behavior and the deformation of suspended LTCC is important in optimizing the fabrication process for multilayer LTCC substrate in order to achieve the required performance.

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References

[1] Lecheminoux, L. "Advanced Design, Technology & Manufacturing for High Volume and Low Cost Production", IEEE Proceeding of International Electronic Manufacturing Technology Symposium, 2003.

[2]   Joseph, T. And M. T. Sebastian (2010) "Effect of glass addition on the microwave dielectric properties of CaMgSi$_2$O$_6$ Ceramics" Int. J. Appl. Ceram. Technol. 7 [S1] E98-E106.

[3]   El-Kheshen, A.A. and M.F. Zawrah (2003), 'Sinterability, microstructures and properties of glass/ceramic composites' *Ceramics International*, 29, 251-257.

[4]   Smallman, R.E., R.J. BiShop (1999) "Ceramic and glass" Modern Physical Metallurgy and Materials Engineering (Sixth edition),1999, 320-350

[5]   Haertling, G. H. (1999) "Ferroelectric Ceramics: History and Technology" J. Am. Ceram. Soc. 82(4) 797-818.

[6]   Rodriguez, A. R., Franklinville and A. B. Wallace (Aerovox Corporation),1961. *Ceramic capacitor and method of making it.* United States Patent 3004197, 10/10/1961

[7]   Modes, C., S. Malkmus and F. Gora (2002), "High-K low loss dielectric co-fireable with LTCC" Active and Passive Elec. Comp., 25, pp. 141-145.

[8]   Kim, S.-H. and Koh, J.-H. (2008), 'ZnBo-doped (Ba,Sr)TiO$_3$ ceramics for the low-temperature sintering process', *J.of Eur. Ceram. Soc.*, 28, 2969-2973.

[9]   Tok, A.I.Y., F.Y.C. Boey and K.A.Khor (1999), "Tape Casting Process of High Dielectric Ceramics Composite/Hybrid Substrate for Microelectronics Applications" Journal of material Processing Technology 89-90 pp 508-512.

[10] Roosen A (2000) "Ceramic Substrate: Trends in Materials Applications" Ceramics Transaction, 106, pp: 479-492.

[11] Stiegel Schmitt, A, A. Roosen, C. Ziegler, S. Martius and L. –P. Schmidt (2004) "Dielectric Data of Ceramic Substrates at High Frequency" J. European Ceramic Soc., 24, pp: 1463-1466.

[12] Morrison, D. G. (2000) "Low Temperature Co-fired Ceramic Fuel Growth of High Frequency" Technical Report. – http://www.elecdesign.com/article

[13] Schubert, H. and G. Petzow (1990) "Preparation and Characterization of Ceramic Powders in Advanced Ceramic III", S. Somiya, ed., Elsevier, pp. 45-56.

[14] Sigmund, W. M., N. S. Bell and L. Bergstrom (2000) "Novel Powder-Processing Methods for Advanced Ceramics" J. Am. Ceram. Soc. 83(7), 1557-1574.

[15] McMillan, P. W. G. PAartridge and F. R. Ward (1969) "Glass ceramics for the coating and bonding of silicon semiconductor material" *Microelectronics and Reliability*, Vol. 8, pp. 113-119.

[16] Charles A. Harper, "Handbook of Material for Product Design", Mc-Graw-Hill. Third Edition (2001).

[17] Chen, G.-H. and X.-Y. Liu (2007) "Sintering, crystallization and properties of MgO-Al2O3-SiO2 system glass-ceramics containing ZnO" J. Alloy & Comp. 431, 282-286.

[18] Rahaman, M.N. (1995) *Ceramic Processing and Sintering* Marcel Dekker, Inc. NY.

[19] Hamzawy, E.M., A.A. El-Kheshe, M.F. Zawrah (2005) "Densification and properties of glass/cordierite composites" Ceram. Int. 31, 383–389

[20] Lin, J. C. and C. Y. Wang (1996) "Effect of surface properties of silver powder on the sintering of its thick-film conductor" Matr. Chem. & Phys. 45, 253-261.

[21] Vu K., "Silver Migration – The Mechanism and Effects on Thick-Film Conductors" Materials Science Engineering, (2003).

[22] Wang, S.-H. and He.-P. Zhou (2003) "Densification and dielectric properties of CaO-B_2O_3-SiO_2 system glass ceramics" Mater. Sci. Eng. B99, 597-600.

[23] Chiang, C. C. S. F. Wang, Y. R. Wang, W.-C J. Wei, (2008) "Densification and Microwave Dielectric Properties of CaO-B_2O_3-SiO_2 System Glass Ceramics", Ceramics International 34, 599-604.

[24] Zhu, H., Liu, M., Zhou, H., Li, L. & Lv, A. (2007). Study on Properties of CaO-SiO_2-B_2O_3 System Glass-Ceramic. *Materials Research Bulletin*, Vol. 42, Issue 6, pp. 1137-1144.

[25] Ota, R., H. Kuribayashi, J. Fukunaga and T. Taguchi (1992) "Crystallization behavior of non-alkali glasses in the SiO_2-CaO-Al_2O_3-ZnO-TiO_2-B_2O_3 system" Journal of Non-Crystalline Solids 144 (1992) 81-88.

[26] Jean, J.-H. J.-I Shen, C.-R. Chang and C.H. Lin (1995) "Densification kinetics and mechanism of a low-dielectric glass composite" Materials Chemistry and Physics 41 (1995) 260-265

[27] Wang, M., R. Zu, J. Jin, S. Su, J. Zhai (2011) "Investigation of the structure evolution process in sol–gel derived CaO–B_2O_3–SiO_2 glass ceramics" Journal of Non-Crystalline Solids 357 (2011) 1160–1163

[28] Zhou, X., E. Li., S. Yang, B. Li, B. Tang, Y. Yuan and S. Zhang (2012) "Effects of La_2O_3–B_2O_3 on the flexural strength and microwave dielectric properties of low temperature co-fired CaO–B_2O_3–SiO_2 glass–ceramic" Ceramics International 38 (2012) 5551–5555.

[29] Alias, R (2012). The Effects of Sintering Temperature Variations on Microstructure Changes of LTCC Substrate, Sintering of Ceramics - New Emerging Techniques, Dr. Arunachalam Lakshmanan (Ed.), ISBN: 978-953-51-0017-1

[30] Kingery, W.D., Bowen, H. K., & Uhlman, D.R. (1976). *Introduction to Ceramics*, (2nd Ed.), John Wiley and Sons, New York

[31] Kang, S. J. L. (2005) Sintering; Densification, grain growth and microstructure Elsevier Butterworth-Heineman.

[32] Varela, J. A. and O. J. Whittemore (1983), 'Structural rearrangement during the sintering of MgO' *J. Am. Ceram. Soc.*, Vol. 66, No. 1, pp. 77-82.

[33] Thummler, F. and Thomma, W. (1967) Sintering processes, Metall. Review vol. 12, 69-108.

[34] Quirk, J. F. (1959) "Factors affecting sinterability of oxide powders": BeO and MgO" *J. Am. Ceram. Soc.*, Vol. 42, No. 4, pp. 178-181

[35] Gupta, T. K. and R.L. Coble (1968) "Sintering of ZnO: Densification and grain growth" *J. Am. Ceram. Soc.*, Vol. 51, No. 9, pp. 521-525.

[36] Kang, S.-J.L., Kim, K.-H. & Yoon, D.N. (1991). Densification and Shrinkage during Liquid Phase Sintering. *J. Am. Ceram. Soc.*, Vol. 74, No. 2, pp. 425-427.

[37] Huang, C.-L. & Tsai, J.-T. (2001). Effects of Sintering Temperature on CaO-Li_2O-Sm_2O_3-TiO_2 Microwave Dielectric Ceramic. *Proc. Natl. Sci. Counc. ROC (A)*, Vol. 25, No. 5, pp. 317-321.

[38] Coble, R.L. (1961). Sintering Crystalline Solids. I. Intermediate and Final State Diffusion. *J. Appl. Phys.*, Vol. 32, No. 5, pp. 787-792.

[39] Lance, D., F. Valdivieso and P. Goeuriot (2004), 'Correlation between densification rate and microstructural evolution for pure alpha alumina' J. of Europ. Ceram. Soc. 24, pp. 2749-2761

[40] De Jonghe, L. and M. N. Rahaman (2003) Handbook of Advanced Ceramics, vol 1, 187-264

[41] Chen, S. Y., C.-H. Chou and S. –Y. Cheng (2002) "Effect of metal oxide precurcor on sintering shrinkage, microstructure evolution and electrical properties of silver-based paste" J. Of Mater. Sci, 37, 169-175.

[42] Yamaguchi, T. (1987), 'Pores in ceramic processing in ceramic databook by Seihin, K. and G. Kyokai, Gordon and Breach Scientific Publishers, Switzerland

[43] Wersing W. and Oliver Dernovsek, "Multilayer Ceramic Technology" in Ceramic Materials for Electronics: Third Edition, Revised and Expanded, edited by Relva C. Buchanan, Marcel Dekker Inc., New York, (2004) 581-642

[44] Nebe, W.J. and T. R. Suess (2007), 'Photo-defined and photo-imaged films' in Ceramic Interconnect Technology Handbook, F. D. Barlow and A. Elshabi9ni, CRC Press, London.

[45] Higby, P.L. and J. E. Shelby (1984), 'Properties of some simple glass/ceramic system' J. Am. Ceram. Soc. 67 (7), pp. 445-449.

[46] Imanaka, Y. (2005). *Multilayered Low Temperature Co-fired Ceramic (LTCC) Technology*. Springer, New York.

[47] Wilder, D. R. and E. S. Fitzsimmons (1955) "Further study of sintering phenomena" J. Am. Ceram. Soc., 38 (2), 66-71.

[48] Cho, B.J, Park, E.-T. and Lee, J.-M. (2009), 'Novel structure ceramic tape for multilayer devices', *J. Eur. Ceram. Soc.*, 29, 451-456.

[49] Kata, K., Y. Shimada and H. Takamizawa (1990) "Low dielectric constant new materials for multilayer ceramic substrate" IEEE Trans. on Comp., Hybrid & Manuf. Tech. 13 (2), 448-451

[50] Tummala, R.R. (1991). Glass-Ceramic Packaging in the 1990's. *J. Am. Ceram. Soc.*, Vol. 74, pp. 895-908.

[51] Konsowski, G. and A. R. Helland (1997) *Electronic Packaging of High Speed Circuitry* McGraw-Hill, New York

[52] Schwartz, B. (1984), "Review of multilayer ceramics for microelectronic packaging" J. Phy.~. Chm Solid Vol. 45. No. I0 pp. 1051-1068

[53] Wakino K, Nishikawa T, Tamura H & Sudo T (1987) "Dielectric Resonator Materials and their Applications" Microwave Journal, 30(6): 133–159.

[54] Sasaki, A and Y. Shimada (1992) "Electrical Design Technology for Low Dielectric Constant Multilayer Ceramic Substrate" IEEE on Components, Vol 15(1) pp: 56-62.

[55] Kellerman, D., D. J. Nabatian, L. Retherford and A. Elshabini (1998) "Characterization and Processing of Low Dielectric Constant Thick-film Substrate for MCM-C Modules" International Conference on Multi-chip Modules and High Density Packaging.

[56] Sebastian, M. T. (2008) Dielectric Materials for wireless communication, Elsevier

[57] Shimada, Y., Y. Yamashita and H. Takamizawa (1988) "Low Dielectric Constant Multilayer Glass-Ceramic Substrate with Ag-Pd Wiring for VLSI Package" IEEE Transaction on Com… Vol. 11(1), pp: 163-170.

[58] Zhou, X., B. Li and H. Ning (2009), "Effect of Ca/Si ratio on the microstructure and properties of CaO-B2O3-SiO2 glass-ceramics" J. Mater. Sci.: Mater Elcetron 20: 262-266.

[59] Pecht, Michael G., Rakesh Agarwal,Patrick McCluskey, Terrance Dishongh, Sirus Javadpour, Rahul Mahajan. "Electronic Packaging:Material and Their Properties", CRC Press LLC, (1999).

[60] http://www.theeestory.com/topics/861

[61] Sen, D, Mahata. T, Patra A.K., Mazumder. S.and Sharma B.P, "Small angle neutron scattering investigation and the low frequency dielectric response of sintered ZrO_2-8 mol % Y_2O_3 ceramic compacts: the effect of pore characteristics," *Journal of Physics: Condensed Matter* 16, pp 6229-6242 (2004).

[62] Kume, S. M. Yasuoka, S.-K. Lee, A. Kan, H. Ogawa and K. Watari (2007) "Dielectric and thermal properties of AIN ceramics" J. European Ceram. 27, 2967-2971.

[63] Ferro Corporation; Ferro Design Guideline in www.ferro.com

[64] Sunappan, V., A. Periannan, C.K.meng and W.C.Khuean (2004) 'Process issues and characterization of LTCC substrates' Elect. Comp. & Tech. Conf. 1933-1937.

[65] Lo, C.-L.,J. G. Duh and B.-S. Chiou. (2002). Low Temperature Sintering and Microwave Dielectric Properties of Anorthite-Based Glass-Ceramic. *J. Am. Ceram. Soc.*, Vol. 85, No. 9, pp. 2230-2235.

[66] Erol, M., Kucukbayrak, S and Ersoy-Mericboyu, A. (2009). The Influence of the Binder on the Properties of Sintered Glass-Ceramics Produced from Industrial Wastes. *Ceramics International*, No. 35, pp. 2609-2617.

[67] Rabe, T., Schiller, W.A., Hochheimer, T., Modes, C. & Kipka, A. (2005). Zero Shrinkage of LTCC Self-Constrained Sintering. *Int. J. Appl. Ceram. Tech.*, Vol. 2, No. 5, pp. 374-382.

[68] Coble, R. L. and Kingery, W. D. (1956) "Effect of porosity on physical properties of sintered alumina"

[69] Subbanna, M., Kapur, P.C. and Pradip (2002), 'Role of powder size, packing, solid loading and dispersion in colloidal processing of ceramics', *Ceramics International*, 28, 401-405.

[70] Shui, A., L. Zeng and K. Uematsu (2006) " Relationship between sintering shrinkage anisotropy and particle orientation for alumina powder compacts" Scripta Materialia 55 pg; 831-834.

[71] Lee, D. Y., D.-J Kim, B.-Y. Kim and Y.-S Song (2003), "Effect of alumina particle size and distribution on filtration rate and fracture toughness of alumina-glass composite prepared by melt infiltration" Material Science and Engineering A341 pg: 98-105

[72] Keizer, K., E., H. Janssen, K. J. de Vries and A. J. Burggraaf (1973) "Inlfuence of particle size and structure of ZrO_2 on microstructure development and dielectric constant of $PbZr_{0.5}Ti_{0.5}O_3$" Mat. Res. Bull. 8, pp. 533-54.

[73] Lee, W.E., D.D. Jayaseelan and S. Zhang (2008) "Solid–liquid interactions: The key to microstructural evolution in ceramics" J. Eur. Ceram. Soc. 28,1517–1525

[74] Fortulan, C. A. and D. P.F.de Souza (1999), "Microstructural evolution of the Al_2O_3-ZrO_2 composite and its correlation with electrical conductivity" Mater. Res. 2(3), pp. 205-210

[75] Dey, D. and R. C. Bradt (1992) "Grain growth of ZnO during Bi2O3 liquid-phase sintering" J. Am. Ceram. Soc., 75 (9), 2529-2534.

[76] Valant, M. & Suvorov, D. (2003)."Microstructural phenomena in low firing .ceramics" Materials Chemistry and Physics 79, 104-110.

[77] Raj, P.M. & Cannon, R. (1999). Anisotropy Shrinkage in Tape-Cast Alumina: Role of Processing Parameter and Particle Shape. *J. Am. Ceram. Soc.*, Vol. 82, No. 10, pp. 2619-2625.

[78] Lange, F.F. (1984). Sinterability of Agglomerated Powders. *J. Am. Ceram. Soc.*, Vol. 67, No. 2, pp. 83-89

[79] Hirata, Y., Hara, A. & Aksay, A. (2009). Thermodynamics of Densification of Powder Compact. *Ceramics International*, Vol. 35, pp. 2667-2674

[80] Forrester, J.S., Goodshaw, H.J., Kisi, E.H., Suaning, G.J. & Zobec, J.S. (2008). Effect of Milling on the Sintering Behavior of Alumina. *J. Am. Ceram. Soc.*, Vol. 44, No. 1, pp. 47-52.

[81] Cole, Jr. A. S. (1972) "Sintering of Ag-Pd in the presence of a reactive glass" *J. Am. Ceram. Soc.*, Vol. 55, No. 6, pp. 296-299.

[82] Exner, H. E. and E. Arzt (1996) " Sintering processes" in R. W. Cahn and P. Haasen, Powder Metallurgy: fourth, revise and enhanced editin' Elsevier Science

[83] De Jonghe, L. and V. Srikatnth (1988) "Liquid-phase sintering of MgO-Bi2O3" J. Am. Ceram. Soc. 71(7), C-356-C-358.

[84] Kingery, W.D.,J. M. Woulbroun and F. R. Charvat (1963) "Effects of applied pressure on densification during sintering in the presence of liquid-phase" *J. Am. Ceram. Soc*, Vol. 46(3), pp. 391-395.

[85] Banijamali, S., Eftekkhari Yekta, B., Rezaie, H.R. & Marghussian, V.K. (2009). Crystallization and Sintering Characteristics of CaO-Al_2O_3-SiO_2 Glasses in the Presence of TiO_2, CaF_2 and ZrO_2. *Thermochimica Acta*, Vol. 488, No. 1-2, pp. 60-65.

[86] Jantunen, H. (2001) "A Novel Low Temperature Cofire Ceramic (LTCC) Material for Telecommunication Devices" Thesis Department of Electrical Engineering Oulu University

[87] McN Alford, N and Penn S. J. (1996) "Sintered Alumina With Low Dielectric Loss" J. Appl. Phys., 80, pp: 5895-5898.

[88] Chang, C.-R. & Jean, J.-H. (1999). Crystallization Kinetics and Mechanism of Low-Dielectric, Low Temperature, Cofirable CaO-B_2O_3-SiO_2 Glass Ceramics. *J. Am. Ceram. Soc.*, Vol. 82, No. 7, pp. 1725-1732.

[89] Wang, H. P, S.-Q. Xu, S.-Q. Lu, S. L. Zhao and B. L. Wang (2009) "Dielectric properties and microstructures of CaSiO3 ceramics with B2O3 addition" Ceram. Int. 35, 2715-2718.

[90] Lo, S.-H. and C.-F. Yang (1998) "Sintering characteristics of Bi_2O_3 added MgO-CaO-Al_2O_3-SiO2 glass powder" Ceramics International (24), 139-144.

[91] Maex, K., Baklanov, M. R, Shamiryan, D., Iacopi, F., Brongersma, S. H., Yanovitskaya, Z. S., (2003), Low dielectric constant materials for microelectronics, *J. Appl. Phys.*, 93:8793-8841

[92] Louh, S.P., I.C. Leu,, M.H. Hon (2005) "Effects of density and bonding structure on dielectric constantof plasma deposited a-C:H films" Diamond & Related Materials 14 (2005) 1000 – 1004

[93]   Zhang, Q. L. H. Yang, J. L. Zhou and H.P.Wang (2005) "Sintering and microwave di-electric properties of LTCC-zinc titanate multilayers" Mater. Lett. 59, 880-884.

[94]   Yang, T. C. K., Sea-Fue Wang, Chung-Chih Juan (2003) "Effect of lamination conditions on sintered properties of glass ceramic substrates for microelectronic packaging", Journal of Materials Processing Technology 148(2004) 165-17.

[95]   Sun, H.-P., Q.-L. Zhang and H. Yang (2009) "Silver cofirable (Ca0.9Mg0.1) SiO3 microwave dielectric ceramics with Li0O3-Bi2O3 additive" Ceramic Internationals 35, 637-641.

[96]   Smyth,C.P. (1929) "The properties of dielectric. I. Electric moment and molecular structure" J. Franklin Institute, 207 (6),813-824..

[97]   Chenari H. Mahmoudi, Ali Hassanzadeh,*, M.M. Golzan, H. Sedghi, M. Talebian (2011) "Frequency dependence of ultrahigh dielectric constant of novel synthesized SnO2 nanoparticles thick films" Current Applied Physics 11 (2011) 409-413

[98]   Venkataraman, B. H., K.B.R. Varma(2004) "Frequency-dependent dielectric characteristics of ferroelectric $SrBi_2Nb_2O_9$ ceramics" Solid State Ionics 167 (2004) 197–202

[99]   Ravinder D., G. Ranga Mohan, Prankishan, Nitendarkishan, D.R. Sagar (2000) "High frequency dielectric behaviour of aluminium-substituted lithium ferrites "Materials Letters 44 2000 256–260

[100]   Kumar, G. B. and Buddhudu, S. (2010) "Optical, thermal and dielectric properties of $Bi_4(TiO_4)$ ceramic powders" Ceram. Int. 36, pp. 1857-1861.