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Optimization of $MgTiO_3$–$CaTiO_3$ based LTCC tapes containing B_2O_3 for use in microwave applications

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Abstract

Optimization of $MgTiO_3$–$CaTiO_3$ based LTCC tapes to be used for microwave purposes was investigated. Three kinds of $MgTiO_3$–$CaTiO_3$ based powders containing B_2O_3 in different forms, and two different slurry systems (PVB and PM) were prepared for tape casting. The results clearly demonstrated that if the powder contained 'free' B_2O_3, no proper tape could be fabricated regardless of the slurry system. With other powders containing pre-reacted B_2O_3, dense tapes as well as multilayer strip line resonators could be fabricated. Difficulties to prepare proper tape from the powder containing 'free' B_2O_3 and different tape properties with different slurry systems are studied and discussed.

Keywords: A. Tape casting; B. Microstructure; B_2O_3; Resonator

1. Introduction

Multilayer Ceramic Modules (MCMs) have recently shown their superiority in telecommunication devices. This technology utilises tape casting procedures, which have been well known for many years [1], since their applications in the paper industry, and have later been developed for ceramic materials. The technology has been especially used with Low-Temperature Co-fired Ceramic (LTCC) materials, where dielectric ceramic layers are co-fired with embedded highly conductive electrodes made of metals, such as silver or copper [2,3]. Several LTCC materials are available commercially in the form of green tape with suitable conductor paste systems [2,4,5]. The materials introduced by DuPont and Heraeus consist of a dielectric phase, such as Al_2O_3 or $CaSiO_3$, with glassy phases containing SiO_2, Al_2O_3, Na_2O, CaO, etc. [6]. The DuPont 943 tape consists of aluminium filler and glasses and forms $CaAl_2B_2O_7$ and $LaBO_3$ after firing [7]. Many of these LTCC compositions also contain B_2O_3 [6,8], which is an important glass former at low temperatures [9]. Since many of these materials are commercially available, the tape casting formula is often proprietary and thus rarely reported. B_2O_3 is, however, known to be a problematic oxide in the presence of the organic additives and solvents needed for slurry preparation [10,11], and thus further studies for successful tape casting are needed.

The properties of commercial green tapes have rarely been reported. Material manufacturers normally give the density, thickness, lamination and firing properties of their green tapes, including advice on suitable conductor pastes; but information such as the tensile strength of green tape, the additives used for purposes of comparison, process qualities, mechanics and compatibility are not reported. Jones et al. [6] studied commercial tapes and showed that the properties of green tape are dependent on the binder system used by the manufacturer.

Different tape casting additives and solvents may have dramatic effects on conductor printing accuracy, which is able to ruin the whole well-designed component preparation route or have an effect on the electrical properties through carbon residuals [4,12].

The main objective of the present work was to study the effects of different forms of one powder and different slurry compositions on the properties of B_2O_3-containing dielec-

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tric LTCC tape. This is an important topic, since the preparation of multilayer ceramic components requires not only satisfactory electrical properties, but also suitable mechanical and process properties for green and fired tape. The basic LTCC powder used was $MgTiO_3$–$CaTiO_3$ dielectric [13], whose sintering temperature was decreased by the addition of a SiO_2, ZnO and B_2O_3 mixture [14]. The present paper reports on the investigation of powder parameters, tensile strengths for green tape and surface roughness and microstructure studies for green and fired tapes. Furthermore, the process parameters, including lamination, firing and selection of suitable conductor paste to produce multilayer components have been studied, and strip line resonators for use at 1.75 GHz frequencies have been prepared and calibrated as demonstrator devices.

2. Experimental

The ceramic tapes were made using three different powder preparation routes and two different slurry systems, as shown in Table 1. The basic ceramic dielectric used was $MgTiO_3$–$CaTiO_3$ obtained from the Fuji Titanium Industry Co., Ltd. (denoted as MCT). The firing temperature was decreased according to composition [60.3 mol% ZnO–12.6 mol% SiO_2–27.1 mol% B_2O_3 (denoted as ZSB)] and added in three different forms: index ‘g’ denotes the glassy form, index ‘r’ the simple mixture of oxides and index ‘c’ the calcined composition. Thus, the MCT/ZSBg powder was made as follows. The starting materials, which were SiO_2 (quartz of 99.5% purity), ZnO (99.0% purity) and B_2O_3 (99.9% purity) from Johnson Matthey GmbH, Germany, were weighed and mixed in a pot mill. After melting at 980 °C in a platinum crucible, the glass was quenched. Subsequent to re-pulverisation in a pot mill for 8 h and passing through a 100 mesh sieve, 70 wt.% of this glassy powder was well mixed with 30 wt.% of the dielectric MCT. The MCT/ZSBg powder has earlier been demonstrated to be composed of crystalline phases of Zn_2SiO_4 and $MgTiO_3$ with several amorphous phases [14].

The MCT/ZSBr and MCT/ZSBc powders were made using the same methods, except that in these cases the ZnO, SiO_2 and B_2O_3 oxides were mixed with the MCT powder without any glass preparation. Additionally the MCT/ZSBc powder was calcined at 620 °C for 2 h, pulverised and sieved again, in order to eliminate any ‘free’ B_2O_3.

Two different slurry systems were used. The first contained polyvinyl butyral 98 (PVB) as a binder, menhaden fish oil as a dispersant, butyl benzyl phthalate (S160) and polyalkylene glycol (Ucon) as plasticizers, and a mixture of ethanol and xylene as a solvent. The additives were supplied by Richard E. Mistler, Inc., USA. The second slurry system utilised a polymethacrylic system, polymethacrylic 685 (PM) as a binder, dioctyl phthalate (DOP) as a suitable plasticizer for the acrylic system, and methyl ethyl ketone (MEK), xylene isomer mixture and *n*-butyl acetate as the solvent. The binder was supplied by Rohm and Haas, and the plasticizer and solvent by Aldrich. Both slurry compositions are well-known in tape casting processing [6,10]. In both cases the amounts of additive and solvent were varied within certain limits until a castable slurry producing flexible and strong green tapes with high green density was obtained. This naturally indicates that if the amount of some component is not correct, the density of the final tape is too low, or the additives are not able to work effectively or do not dissolve totally. Inappropriate composition may also result in cracking or wrapping of the green tape in such a way that it cannot be laminated satisfactorily [12]. The typical amounts were 12.0–37.0 g of solvents, 2.5–6.0 g of binders and plasticizers and 0.1–1.0 g of dispersing agents, added to 30.0 g of powder.

The slurries with PVB system were prepared and casting with a laboratory caster (Unicast 2000, University of Leeds, Leeds, UK) with a single doctor blade and a 250 μm wide gap. For PM slurry system a doctor blade tape-caster, model DP-150, and a 200 μm wide gap was used. The tapes were dried in air. In both cases, the slurry was prepared by the standard route, including mixing of the solvent, dispersant and powder in the pot mill for 24 h followed by further 24 h of mixing after the addition of the plasticizers and binder, as outlined in Fig. 1.

Before the slurry preparation, the specific surface areas (SSA) of the powders were measured with a BET analyser (OmniSorb 360CX, Coulter Electronics Inc., Ltd., Luton, UK) and the shapes of individual particles with STEM (Jeol JEM 100CX II, Tokyo, Japan). These characteristics partly govern the way how particles pack together in the green

Table 1
The composition of the tapes

	MCT/ZSB			
	c-PM	c-PVB	g-PVB	r-PVB
Basic powder	MCT	MCT	MCT	MCT
LTCC additives	Calcined ZSB	Calcined ZSB	Glassy ZSB	Direct mixed ZSB
Solvents	MEK, xylene, *n*-butyl acetate	Ethanol, xylene	Ethanol, xylene	Ethanol, xylene
Binder	PM	PVB	PVB	PVB
Dispersant	No	Fish oil	Fish oil	Fish oil
Plasticizer	DOP	S160, Ucon	S160, Ucon	S160, Ucon

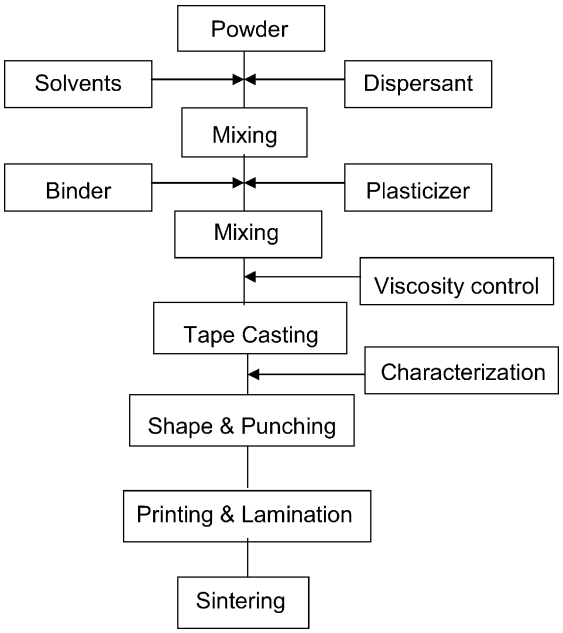

Fig. 1. Preparation route for tape casting slurries and multilayer components.

state and determine the formulation of the organics and solvent added to the slurry [12]. The viscosity of the slurry was measured before casting by using the Brookfield digital viscometer DV-II+ Version 2.0 (Brookfield Engineering Laboratories, INC., Stoughton, USA). The spindle used was SC4-18.

The surface roughness (RA) of the tapes was measured using a Dektak^{3}ST (Sloan Technology, Santa Barbara, CA, USA). The scan parameters used were scan length of 5 mm, measurement range of 131 nm with vertical resolution of 2 nm, medium scan speed of 12 s per scan, and stylus force of 30 mg. Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) were performed by a thermal analyser (NETZSCH STA-409 EP, Selb/Bayern, Germany). Crystal phases was analysed with a XRD (Siemens D5000, Karlsruhe, Germany), and JCPDS (International Center for Diffraction Data 1992, Swarthmore, PA, USA) files. Microstructures were recorded by SEM/EDS (Jeol JEM-6400, Tokyo, Japan). Tensile strengths were measured using an Instron 8801 tensile strength tester (Instron Corporation, UK) at crosshead speed of 5.0 mm min^{-1}. Three samples were measured for each tensile strength test. The specimen gauge length was 40 mm, width 10–12 mm and thickness 0.07–0.16 mm. The results with standard deviation are shown in Table 2. The densities of the green tapes were calculated from the diameters and weights of large pieces. The appropriate lamination conditions were also studied using different dwell times within the temperature range of 70–110 °C, while the pressure remained constant at 20 MPa.

The tapes were fired at 900 °C for 80 min at a heating rate of 4.7 °C min^{-1}, and the organic compounds were given time to burn out in the range of 400–600 °C. The microstructure of the fired tapes was studied with SEM/EDS (JSM-5410, JEOL), and the phases present were identified with XRD (JDX-3530, JEOL), surface roughness with the Dektak^{3}ST, and shrinkage and density based on physical dimensions and weight.

The silver-based conductor pastes used were Heraeus TC2304HQ and DuPont 6160, the first basically meant for co-firing with the LTCC tape Heraeus CT2000 and the second for post-firing processing of ceramic substrates.

Table 2
Measured values for different powder forms and tapes

	MCT/ZSB			
	c-PM	c-PVB	g-PVB	r-PVB
Powder				
SSA ($m^2 g^{-1}$)	3.6	2.6	2.3	2.7
Particle shape	Angular, cubic	Angular, cubic	Angular, cubic	Angular, cubic
Green tape				
Surface roughness RA (μm)	0.2	0.5	0.3	0.1
Tensile strength (MPa)	0.28 ± 0.01	1.18 ± 0.05	2.03 ± 0.20	1.63 ± 0.01
Crystal phases from XRD	$MgTiO_3$, ZnO, SiO_2	$MgTiO_3$, ZnO, SiO_2	$MgTiO_3$, Zn_2SiO_4, $ZnTiO_3$, amorphous	$MgTiO_3$, SiO_2, ZnO, H_3BO_3
Density (Mg m^{-3})	2.0	2.1	2.1	1.6
Fired tape (900 °C, 80 min)				
Surface roughness RA (μm)	0.2	0.5	0.3	0.4
Shrinkage *X*, *Y* and *Z* (%)	17–20	17–19	17–19	19–20
Density (Mg m^{-3})	3.8	3.7	3.5	3.3
Resonators				
Conductor paste	Heraus TC2304HQ (6160 dissolved green tape)	DuPont 6160 (TC2304HQ did not work in firing)		
Component thickness (μm)	500	720	NA	NA
Q-factor (frequency at GHz)	58 (1.75)	93 (1.76)		

The test resonator structure, a balanced λ/2 strip line resonator consisting of a straight conductive strip line at the centre of the LTCC module, was designed by using the Sonnet electromagnetic simulator. The input and output pads, situated at opposite ends of the strip line on the top layer, were capacitively coupled (<35 dB) to the line with a printed length and width of 27.1 and 1.0 mm, respectively. The arrangement ensured correct measurement of the unloaded *Q*-factor. All outside areas of the component were made uniformly conductive with silver paste before co-firing at 900 °C for 80 min, following the preparation route shown in Fig. 1. The multilayer structure consisted of eight dielectric layers. The frequency response of the components was measured at room temperature using a network analyser (HP8719C).

3. Results and discussion

The main experimental results are shown in Table 2.

The Table 2 shows that all the powders had the same particle shape, and that the SSA was almost equal, with an exception of the MCT/ZSBc powder, which was milled longer. The optimum amounts of additives and solvents for each powder are shown in Table 3. The selection was made on the grounds of the quality of green and fired tapes, mainly by achieved densities, strengths and surface quality.

3.1. Powders containing 'free' B_2O_3

During the investigation, the MCT/ZSBr powder showed several problems and required extensive investigation. The first observation made was that the slurry heated up during mixing, showing exothermal reactions. Furthermore, a larger amount of solvent was needed to produce a castable slurry, which required additional amounts of additives to produce a strong green tape. The final amounts of additives and solvents used, compared to the amount of powder, were almost 18 and 117 wt.%, respectively, which are much higher values than those of commonly used in tape casting, for example, 16 and 51 wt.% [15]. This cannot be explained by the particle size of the powder, because its measured SSA did not differ significantly from the other powders. As suggested by B. Su et al. [11], B_2O_3 can crosslink instantly with the PVA polymer binder during the process, so the crosslink between B_2O_3 and PVB was happened in this case. The need for extra additives was confirmed by the TGA/DTA curve (Fig. 2). The large mass loss (23 wt.%) of the MCT/ZSBr-PVB tape can be seen in the TGA curve. The weight loss at 60–180 °C was obvious, being about 11 wt.%, but not detectable in the other three tapes. This weight loss corresponded to an endothermic peak in DTA and might be due to the evaporation of the solvent molecules weakly linked within the gel matrix of B_2O_3 and PVB. The second weight drop at 200–600 °C was 11.5 wt.% and corresponded to an exothermic peak in DTA, which was related to the decomposition of organics into carbon dioxide. After 600 °C there was very little weight loss and an exothermic peak at 700 °C, which were caused by some phase transformation not any more related to slurry composition.

The crosslink also notable affected the viscosity of slurry. The viscosity of MCT/ZSBr-PVB slurry is much larger than that of the others and out of the measurement range (>9998 mPa s) for the spindle SC4-18. In order to study and get some information about the slurry behaviour, the slurry was added 50 vol.% more solvents and then the viscosity was measured, the results of dilute MCT/ZSBr-PVB slurry shown in Fig. 3. Viscosity decreased with an increasing shear rate, denoting a pseudo-plastics type or shear thinning

Table 3
The optimized amounts of solvents and additives in wt.% for each powder and slurry

	MCT/ZSB			
	c-PM	c-PVB	g-PVB	r-PVB
Powder (g)	30.00	30.00	30.00	30.00
Solvents (g)	13.34	20.00	20.00	35.00
Binder (g)	1.92	2.20	2.20	3.00
Dispersant (g)	–	0.60	0.60	0.80
Plasticizers (g)	0.64	1.10	1.10	1.50

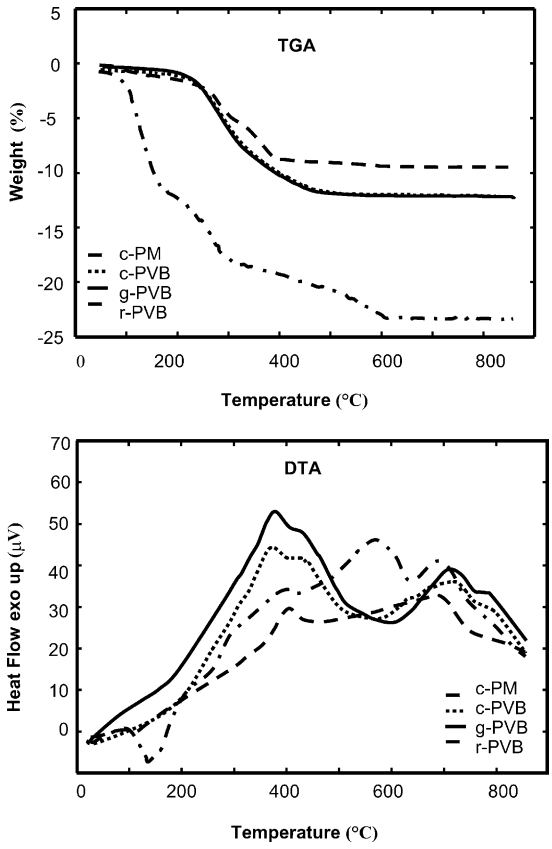

Fig. 2. DTA/TGA curves for different tapes.

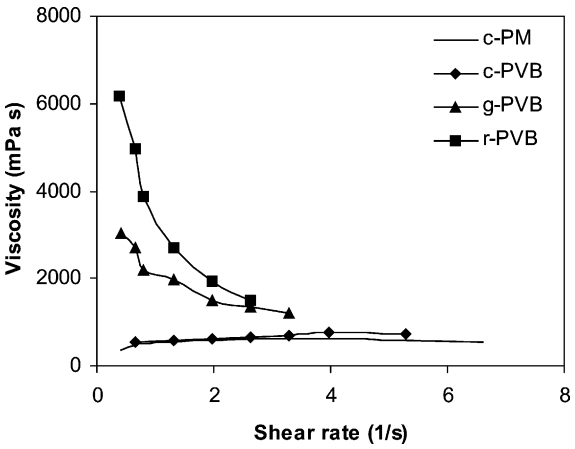

Fig. 3. Viscosity as a function of shear rate for different slurry.

behaviour, which is most commonly seen in non-Newtonian fluids.

The XRD studies of the MCT/ZSBr-PVB green tape (Fig. 4) showed clear peaks indicating $MgTiO_3$, SiO_2 and ZnO crystals, as anticipated, but no peaks of B_2O_3. However, some extra peaks at 6.7 and 12.7° were found, although of moderately low intensity. One possible candidate could be H_3BO_3 with good match to the unknown peaks. Some other boronate or complex compound of boron and PVB are also possible.

The SEM images of the MCT/ZSBr-PVB green tapes (Fig. 5d) were also structurally different compared to the other tapes. There were some small white fragments spreading uniform between the particles. The microstructure was composed of particles 2–3 μm in average size mixed with very small particles, although the measured SSA was not particularly low. The density of the green tape was measured to be 1.6 Mg m^{-3}, which is less than 50% of the desired fired density (3.8 Mg m^{-3}). Otherwise, the tape had good surface quality (RA = 0.1 μm) and almost the highest measured value of tensile strength, which can be explained by the crosslink between B_2O_3 and the hydroxyl group in PVB and gelation in the green state ceramic.

After firing, the microstructure (Fig. 6d) still had high porosity (13%) and, thus, low density (3.3 Mg m^{-3}) compared to the tape series prepared, and this composition was therefore not chosen for microwave studies.

Similar properties were also observed with the combination of MCT/ZSBr-PM, although they are not indicated in detail in the results.

3.2. Powders without 'free' B_2O_3

The slurry preparation and tape casting processes for the other powder and slurry system combinations, MCT/ZSBc-PM, MCT/ZSBc-PVB and MCT/ZSBg-PVB, were quite different compared to MCT/ZSBr-PVB. First of

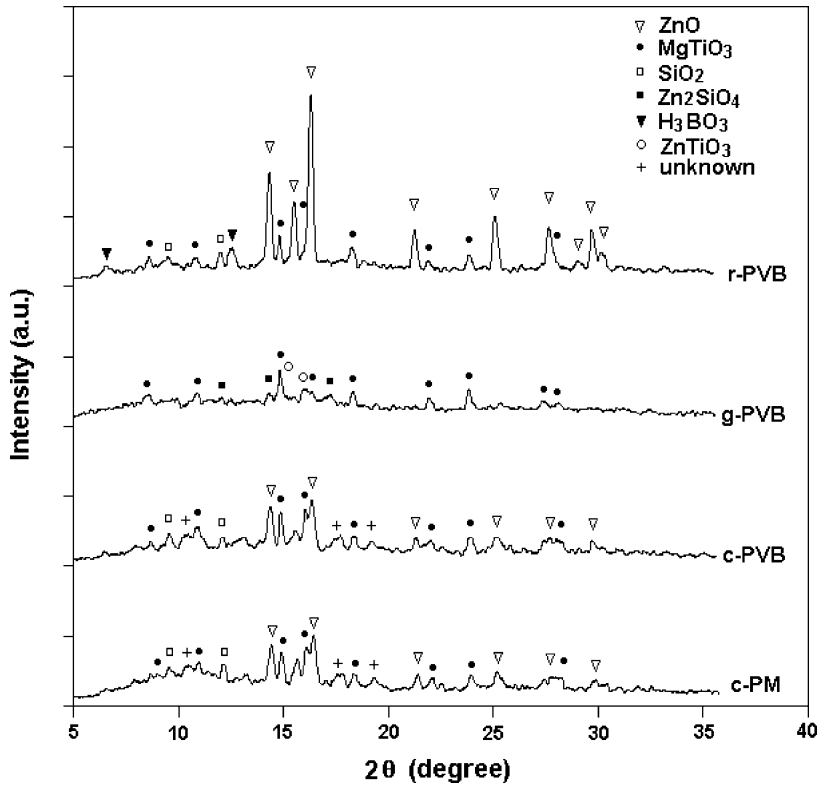

Fig. 4. XRD results of different green tapes.

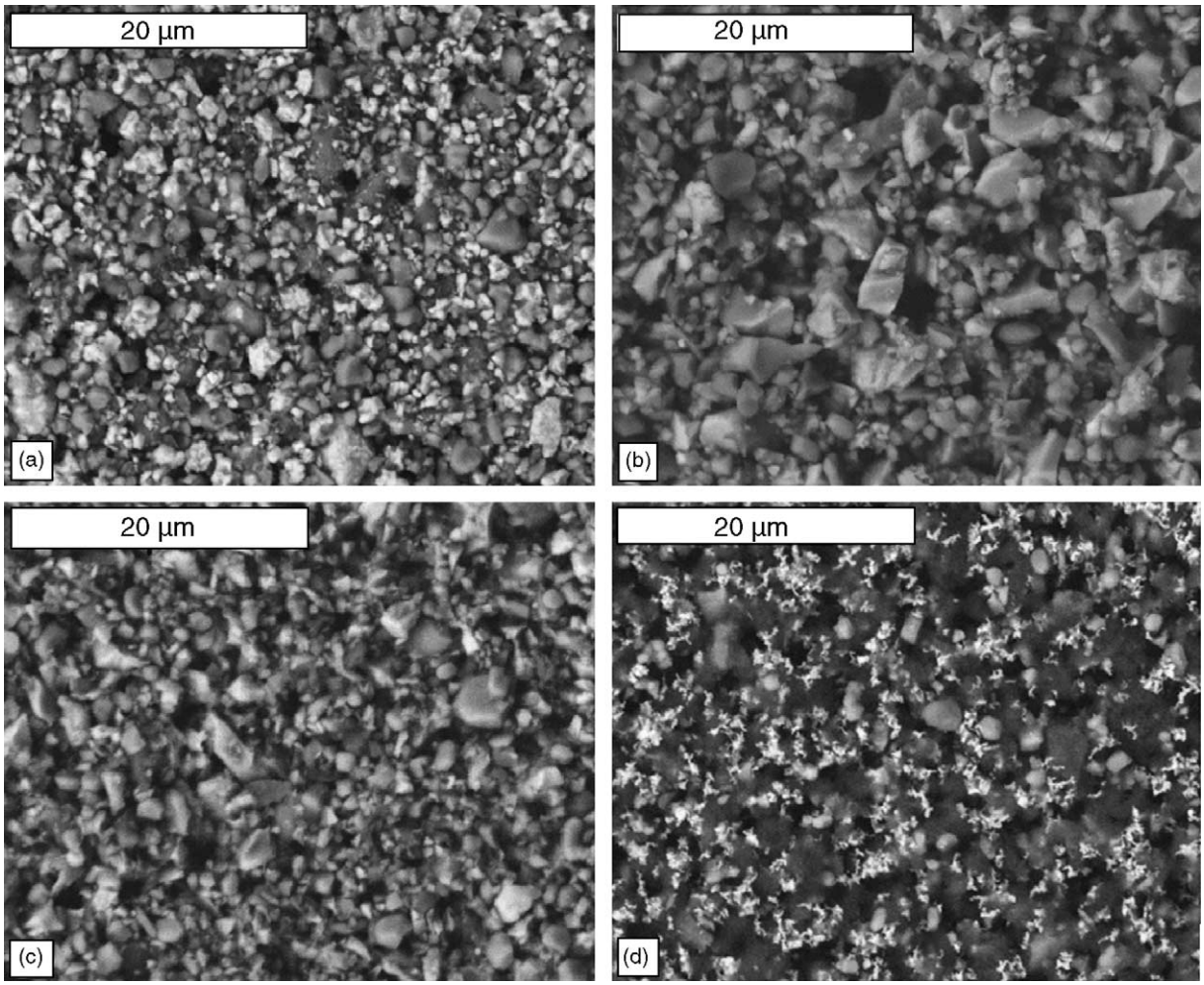

Fig. 5. SEM images of MCT/ZSB green tapes: (a) c-PM, (b) c-PVB, (c) g-PVB, and (d) r-PVB.

all, no heating up during the mixing of powders with solvents or additives was observed. Secondly, the commonly presented amounts of additives and solvents [12,16,17] were straightaway recognised to be a good starting point. Several tests with these powders and slurries also showed that too large an amount of additives caused tape wrapping during drying or too low green density. A small amount of additives, on the other hand, caused powdery tape and low tensile strength. The strongest tapes with the highest green densities prepared from MCT/ZSBc and MCT/ZSBg powders with PVB-based system additives were achieved in both cases using slurries with 13 wt.% additives and 67 wt.% solvents compared to ceramic loading. The tensile strength of MCT/ZSBc-PVB, however, remained low (1.2 MPa), being only sufficiently high to stand the subsequent handling of conductor printing, stacking and lamination. The MCT/ZSBg-PVB tape was much stronger (2 MPa), which is believed to be due to the different surface properties of the powders, thus allowing more effective reactions of additives. Both tapes, however, had similar and high green density (2.1 $Mg\,m^{-3}$), which was more than the optimal 50% of the fired density.

The amounts of additives and solvents needed for a PM-based system with MCT/ZSBc powder were 9 and 45 wt.%, respectively. In this case, the achieved strength of the green tape was very low (0.3 MPa) and could have been increased by adding a larger amount of binder. This was, however, not done because this action would have decreased the green density (2.0 $Mg\,m^{-3}$).

As shown in Fig. 3, the viscosity values of MCT/ZSBc-PM slurry and MCT/ZSBc-PVB slurry were almost identical. Viscosity increased slightly along with shear rate, increasing as dilatant fluid behaviour. The rates of increase, however, were very small, both being close to the Newtonian type. For the MCT/ZSBg-PVB slurry, viscosity decreased when the shear rate increased, denoting a pseudo-plastic type.

From the TGA measurements (Fig. 2), the three tapes prepared from MCT/ZSBg-PVB, MCT/ZSBc-PVB and MCT/ZSBc-PM powders showed low mass losses (<12 wt.%) caused by low addition of organics and solvents, which was important point since large excess amounts can cause burnout difficulties, carbon residuals and low firing density [18,19]. The DTA/TGA measurements of the tapes also showed identical behaviours of MCT/ZSBg-PVB and

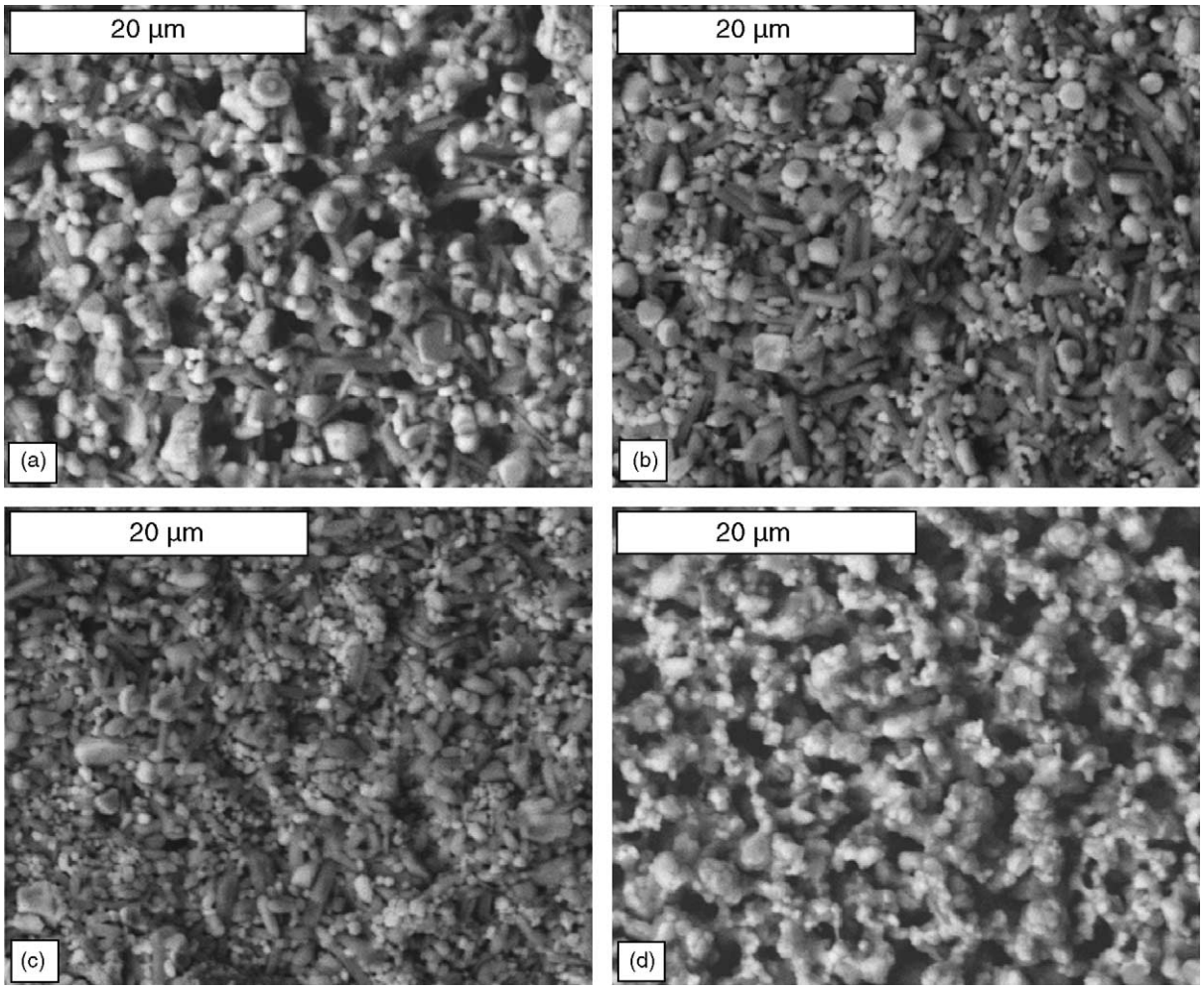

Fig. 6. SEM images of MCT/ZSB fired tapes: (a) c-PM, (b) c-PVB, (c) g-PVB, and (d) r-PVB at 900 °C for 80 min.

MCT/ZSBc-PVB. There was only one weight drop between 200 and 600 °C, corresponding to an exothermic peak at 375 °C in DTA denoting the decomposition of organic compounds. The MCT/ZSBc-PM tape had a small 1 wt.% weight drop at 100 °C due to the solvents and a 9.2 wt.% drop in the range of 180–460 °C related to the decomposition of organic compounds, but the exothermic peak of MCT/ZSBc-PM was 406 °C, which was higher than the others because of its different organic additive. There was also a large exothermic peak at 700 °C for MCT/ZSBc-PVB, MCT/ZSBg-PVB and MCT/ZSBc-PM, the same as MCT/ZSBr-PVB shown in the DTA curve. These exothermic peaks corresponded to the phase transformation of ceramics.

The better surface quality of the MCT/ZSBc-PM tape (RA = 0.2 μm) compared to the others can be explained by the longer period of milling, which also explained the high SSA value of this powder. These properties can also be correlated with the SEM images of the corresponding green tapes (Fig. 5). The PVB-based additive system for all powders, however, produced stronger green tape than PM, suggesting a more effective binding system.

The XRD results for these green tapes, MCT/ZSBg-PVB, MCT/ZSBc-PVB and MCT/ZSBc-PM, were also as expected. The two tapes made of calcined powder, MCT/ZSBc-PVB and MCT/ZSBc-PM, consisted of the crystalline phases such as $MgTiO_3$, ZnO and SiO_2 and had no peaks representative of the 'free' B_2O_3 crystals, as was desired. Additionally some unidentified peaks were observed. The MCT/ZSBg-PVB tape mainly consisted of amorphous phases with some $MgTiO_3$, $ZnTiO_3$ and Zn_2SiO_4 crystalline. These results were also demonstrated earlier by SEM/EDS studies in Ref. [14]. After firing, the tapes made of calcined powder, MCT/ZSBc-PM and MCT/ZSBc-PVB, had higher density (>3.7 Mg m^{-3}) than the MCT/ZSBg-PVB tape made of ceramic with glass (3.5 Mg m^{-3}), and this was used as a selection criterion at the following stages.

The best lamination conditions were almost the same for all tapes. Under a pressure of 20 MPa, the MCT/ZSBc-PVB tape needed a temperature of 90 °C and 1 h of pressing for consolidation. For the MCT/ZSBc-PM tape, the corresponding values were 100 °C and 30 min at the same pressing

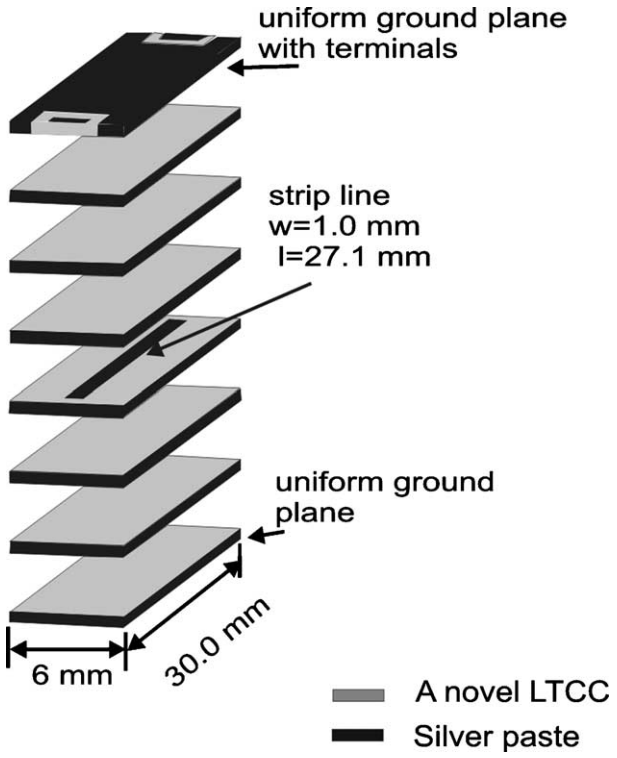

Fig. 7. Structure of the λ/2 resonator.

pressure. In all cases, the laminated compacts were uniform without excess deformation of the structure. The absence of delamination was confirmed with a scanning acoustic microscope. The thickness of the MCT/ZSBc-PVB tape after casting and drying was 110 μm and after lamination and firing 90 μm. The corresponding values for the MCT/ZSBc-PM tape were 80 and 62.5 μm, respectively.

3.3. Microwave application

Fig. 7 showed the structure of λ/2 resonators. The conductor pastes, Heraeus CT2304HQ and DuPont 6160, were tested for both these tapes with λ/2 resonators. The pastes worked well with the MCT/ZSBc-PVB tape in printing, but after firing, the resonators made with the Heraeus TC2304HQ paste showed no resonance in the frequency range of 1–4 GHz. Non-destructive testing under a scanning acoustic microscope, X-ray studies or cross-sectional SEM studies of the samples failed to explain this behaviour. Consequently, further investigations are required to explain this specific phenomenon. However, the combinations of MCT/ZSBc-PVB tape and DuPont 6160 paste produced good-quality resonance at about 1.76 GHz with *Q*-values of 93. The measured values were almost the same as the simulated ones (1.75 GHz and 82) with a component thickness of 720 μm. No interface reactions were seen in the cross-sectional images (Fig. 8a). The thickness of the central conductor was about 5–9 μm.

Heraeus TC2304HQ paste, however, worked better with the MCT/ZSBc-PM tape. The fired conductor inside the multilayer structure showed good line accuracy (Fig. 8b) at a thickness of 8–11 μm. The frequency of the resonators was about 1.75 GHz with an average *Q*-value of 58. The overall thickness of the fired component was 500 μm, which in simulations produced a *Q*-value of 63 at the measured frequency.

The combination of the MCT/ZSBc-PM tape and the DuPont 6160 paste worked quite differently. Immediately after printing the conductor patterns started to react with the tape material producing obscure borders areas, which can be explained on the basis of incompatibility of the additive and solvent systems of the paste and the tape. The reaction was so strong that resonators could no longer be prepared and the process was discontinued.

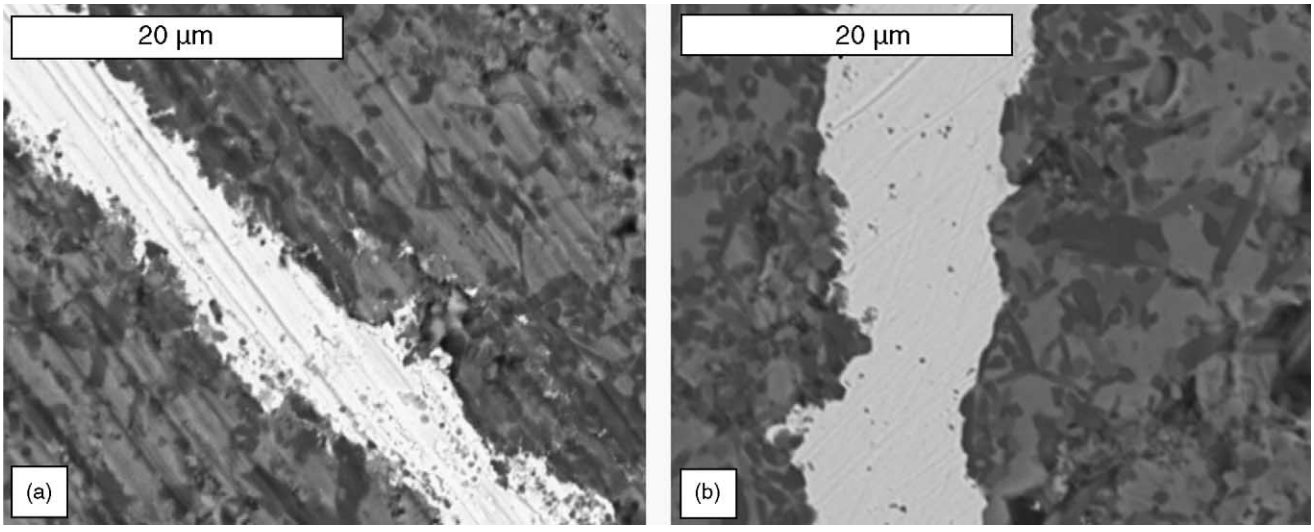

Fig. 8. Cross-section of the resonator: (a) MCT/ZSBc-PVB tape and DuPont 6160 silver line, (b) MCT/ZSBc-PM tape and Heraeus TC2304HQ silver line.

4. Summary

The results of this research showed the condition of the ceramic powder and, especially, the state of the B_2O_3 effect on the whole tape casting procedure and on the achieved tape properties. In particular, 'free' B_2O_3 was able to change the properties of the additives and solvent in both organic systems, causing a need for further additions until the density of the cast green tape was too low to be able to shrink homogeneously on firing into a high-density ceramic. The presence of 'free' B_2O_3 also caused heating up of the slurry during its mixing. The XRD data also included several odd peaks that could not be identified with certainty. No such peaks were observed in the XRD measurements made on the tapes where B_2O_3 reacted with prior calcinations or glass preparation before slurry preparation.

The powder forms where B_2O_3 reacted with the other compounds at an early stage in the process before slurry preparation needed only the usual amounts of additives and solvents regardless of the binder system used. The tapes cast from these slurries had high green and fired densities and were easy to laminate.

The resonance frequencies and the *Q*-values of the multilayer strip line resonators made of the calcined powder compositions with a different slurry system were close to the simulated values. This indicates that the process in both cases worked well, including successful burnout of the organics and good fired microstructures. However, the use of different commercial conductor pastes was necessary. The tape made with PVB-based additives was more compatible with the DuPont silver paste 6160, whereas in the experiment where PM was used, this paste dissolved the tape and it was replaced by the Heraeus silver paste TC2304HQ.

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References

[1] G.N. Howatt, R.G. Breckenridge, J.M. Brownlow, Fabrication of thin ceramic sheets for capacitors, J. Am. Ceram. Soc. 30 (8) (1947) 237–242.

[2] P. Barnwell, W. Zhang, J. Lebowitz, K. Jones, N. MacDonald, C. Free, Z. Tian, An investigation of the properties of LTCC materials and compatible conductors for their use in wireless applications, in: International Symposium on Microelectronics, IMAPS, 2000, pp. 659–664.

[3] J.W. Sheen, LTCC-MLC Duplexer for DCS-1800, IEEE Trans. Microwave Theory Tech. 47 (9) (1999) 1883–1890.

[4] N. McN. Alford, S.J. Penn, A. Templeton, X. Wang, J.C. Gallop, N. Klain, C. Zuccaro, P. Filhol, Microwave dielectrics, in: Proceeding of IEE Colloquium on Electro-technical Ceramics—Processing, Properties and Applications (Ref. No.: 1997/317), vol. 9, 1997, pp. 1–5.

[5] M. Lahti, V. Lantto, Passive RF band-pass filters in an LTCC module made by fine-line thick-film pastes, J. Eur. Ceram. Soc. 21 (2001) 1997–2000.

[6] W.K. Jones, Y. Lie, B. Larsen, P. Wang, M. Zampino, Chemical, structural and mechanical properties of the LTCC tapes, in: Proceeding of International Symposium on Microelectronics, IMAPS, Boston, USA, 2000, pp. 669–804.

[7] P.C. Donohue, B.E. Taylor, D.I. Amey, R.R. Draudt, M.A. Smith, S.J. Horowitz, J.R. Larry, A new low loss lead free LTCC system for wireless and RF applications, IEEE Digest (1998) 196–199.

[8] H.T. Kim, S.H. Kim, S. Nahm, J.D. Byun, Y. Kim, Low-temperature sintering and microwave dielectric properties of zinc metatitanate-rutile mixtures using boron, J. Am. Ceram. Soc. 82 (11) (1999) 3043–3048.

[9] P.W. McMillan, Glass-Ceramics, Academic Press, London, 1979, pp. 184–209.

[10] C.W. Cho, Y.S. Cho, J.G. Yeo, J. Kim, U. Paik, Effect of PVB on the gelation behaviour of $BaTiO_3$-based dielectric particles and glass suspension, J. Eur. Ceram. Soc. 23 (2003) 2315–2322.

[11] B. Su, T.W. Button, Interactions between barium strontium titanate (BST) thick films and alumina substrates, J. Eur. Ceram. Soc. 21 (2001) 2777–2781.

[12] R.W. Cahn, P. Haasen, E.J. Kramer, Tape casting, in: R.J. Brook (Vol. Ed.), Materials Science Technology, vol. 17A: Processing of Ceramics, VCH Verlagsgesellschaft mbH, 1996 (Chapter 7).

[13] T. Katoh, H. Ozeki, Microwave dielectric ceramic composition, US Patent 5 340 784 (23 August 1994).

[14] H. Jantunen, R. Rautioaho, A. Uusimäki, S. Leppävuori, Compositions of $MgTiO_3$–$CaTiO_3$ ceramic with two borosilicate glasses for LTCC technology, J. Eur. Ceram. Soc. 20 (14–15) (2000) 2331–2336.

[15] R.E. Mistler, E.R. Twiname, Tape Casting: Theory and Practice, The American Ceramic Society, Westerville, OH, 2000, p. 240.

[16] A. Dziedzic, L.J. Golonka, J. Kita, J.M. Kozowski, Macro- and microstructure of LTCC tapes and components, in: Proceedings of XXIV Conference of IMAPS, Poland, 2000, pp. 163–168.

[17] J.-H. Feng, F. Dogan, Effect of solvent mixtures on dispersion of lanthanum-modified lead zirconate titanate tape casting slurries, J. Am. Ceram. Soc. 83 (7) (2000) 1681–1686.

[18] C. Berry, D. Parlow, T. Vasilow, S. Gurkovich, A. Barley, A design of experiment for a tape casting process, in: Proceedings of the International Symposium on Microelectronics, IMAPS, Boston, MA, USA, 2000, pp. 150–155.

[19] R.R. Tummala, Ceramic and glass packaging in the 1990s, J. Am. Ceram. Soc. 74 (5) (1991) 895–908.