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Compositions of $MgTiO_3$–$CaTiO_3$ ceramic with two borosilicate glasses for LTCC technology

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Abstract

Mixtures of ZnO–SiO_2–B_2O_3/$MgTiO_3$–$CaTiO_3$ (ZSB/MMT-20) and BaO–SiO_2–B_2O_3/$MgTiO_3$–$CaTiO_3$ (BSB/MMT-20) have been investigated as new candidates for LTCC dielectric materials. Two-stage sintering behaviour was observed in both materials, starting at around 600 and 850°C. Nearly full density (97%) was achieved in ZSB/MMT-20 after sintering at 900°C, while a high porosity of 23% was measured in BSB/MMT-20 after firing at 875°C followed by partial melting of samples during sintering at 900°C. After firing, fully crystalline structure with phases of $ZnTiO_3$, Zn_2SiO_4, $Mg_{4/3}Zn_{2/3}B_2O_5$ and TiO_2 were found in ZSB/MMT-20, while the structure of BSB/MMT-20 consisted of crystalline TiO_2 and $BaTi(BO_3)_2$ and amorphous $SiBa(BO_3)_2$ and SiB_2O_5. ZSB/MMT-20 fired at 900°C showed promising microwave properties having the dissipation factor of 0.001 and a permittivity of 10.6 at 7 GHz. The corresponding values for BSB/MMT-20 fired at 875°C were 0.002 and 8.2, respectively.

Keywords: Dielectric properties; Glass ceramics; $MgTiO_3$–$CaTiO_3$; Sintering; Substrates

1. Introduction

In producing miniaturised devices, ceramic multilayer structures with low sintering temperatures are needed because they can be co-fired with high conductivity, that is low-loss conductors.[1] Low temperature co-fired ceramic (LTCC) technology offers significant benefits over other established packaging technologies for high density, high RF and fast digital applications requiring hermetical packaging and good thermal management.[2] Many new ceramic/glass compositions have recently been developed for microwave purposes, especially low permittivity (ϵ_r) materials using alumina and suitable glass combinations,[3] but also higher ϵ_r (20–100) materials.[1,4,5] Table 1 shows the permittivity and dissipation factors (DF) of some currently available commercial LTCC materials.

There are two approaches to exploiting glasses to achieve ceramic compositions sinterable below 1000°C. The first consists in adding a low softening temperature glass to the crystalline ceramic component (liquid phase sintering); the second is the 'glass-ceramic' approach in which the sole starting component is a glass which crystallises during firing.[6] As compared with liquid phase sintering in which the glass phase remains, the advantages offered by the 'glass–ceramic' approach include shape stability during the sintering stage, improved dielectric properties and mechanical strength and controlled thermal expansivity.[6,7]

The basic microwave requirements for RF applications are low dissipation factor, DF, (or high Q-value), optimum values of permittivity, ϵ_r, and temperature coefficient of resonant frequency, τ_f, all defined by applicational specifications. The sintering temperature should lie between 850 and 950°C for co-firing with high conductivity metals. Although some commercial LTCC compositions are available as shown in Table 1, new low loss dielectric materials are needed especially for high frequency RF applications.

$MgTiO_3$–$CaTiO_3$ ceramic is a well-known dielectric material for microwave applications.[8,9] It combines a

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Table 1
Dielectric properties of commercial LTCC materials[a]

	DuPont 951	Ferro A6-5-M-13	Heraeus CT 700
Permittivity (1 MHz)	7.8	5.9	7.0
DF	0.0015 (1 KHz)	0.002 (10 MHz)	0.002 (1 kHz)

[a] Data from LTCC Design Guide made by CTS Microelectronis, West Lafayette, IN, USA.

high quality factor Q (3000–4600 at 6 GHz), low ϵ_r (18–20) and the ability to adjust τ_f (-10 to $+10$ ppm K^{-1});[8] it can be utilised in antennas, high-performance substrates, microwave filters and resonators. The only disadvantage of this material is its high sintering temperature (about 1360°C) which, as it stands, is unsuited to LTCC technology. Despite this, in this research the $MgTiO_3$–$CaTiO_3$ compound is selected as a basic dielectric material because of its excellent RF.

In the work reported here two different glass/$MgTiO_3$–$CaTiO_3$ ceramic mixtures have been investigated as new ceramic materials for telecommunication purposes utilising LTCC technology. The minimum microwave properties aspired here were those of currently available commercial LTCC material in Table 1. Sintering behaviour, microstructural and microwave properties of the materials were studied. The aim of the research was to identify compositions sinterable at temperatures below 1000°C and thus compatible with pattern layers of the high conductivity metals necessary to achieve the best microwave performance.

2. Experimental procedure

2.1. Glass preparation

After testing several different borosilicate glasses, two compositions were chosen to lower the firing temperature of the $MgTiO_3$–$CaTiO_3$. The first one, 60.3 ZnO–27.1 B_2O_3–12.6 SiO_2 (labelled ZSB), was similar to that used by M. Abe et al.[5] with high permittivity $BaTiO_3$ ceramics. The other glass (labelled BSB) had the eutectic composition, 35 BaO–55 B_2O_3–10 SiO_2.[10] The raw materials used were SiO_2 (99.5% purity), ZnO (99% purity), B_2O_3 (99.9% purity) from Johnson Matthey GmbH, Germany, and BaO (98% purity) from Fluka Chemie AG, Switzerland.

The glasses were produced by weighing the starting materials and mixing them for 1 h in a polyethylene pot mill using agate balls. The mixed powders were pressed into pellets, which were melted in a platinum crucible at 980°C for 1 h. The melts were quenched into water and pulverised in the ball mill for 12 h, dried and screened through a 100 mesh sieve.

The specific surface areas of the powders were measured using a BET analyser (OmniSorb 360CX, Coulter Electronics Inc., Ltd., Luton, UK) and their structures by XRD (Siemens D5000, Karlsruhe, Germany) utilising the JCPDS data file (International Center for Diffraction Data 1992, Swarthmore, PA, USA).

2.2. Glass/MMT-20 mixture and test sample preparation

The starting dielectic material was commercial $MgTiO_3$–$CaTiO_3$ powder (coded by Fuji Titanium Industry Co., Ltd as MMT-20). Its specific surface area was measured using the BET analyser. The mixtures were produced by weighing appropriate amounts of glasses and ceramic, mixing them in the ball-mill for 2 h together with PVA as a binder, PEG as a plasticiser and distilled water. The compositions were dried in a microwave oven and sieved. Uniaxial pressing at 60 MPa resulted in 18 mm long cylindrical compacts of 12.2 mm diameter for dilatometric studies (Orton Automatic Recording Dilatometer, Westerville, OH, USA) and in 5–10 mm long cylindrical compacts of 25.5 mm diameter for XRD, SEM/EDS (Jeol JSM-640, Tokyo, Japan), FESEM (Jeol JSM-6300F, Tokyo, Japan), density, shrinkage and microwave property studies.

Pure MMT-20 samples (fired at 1360°C) and samples of commercial LTCC-material (fired at 875°C) were also prepared in a similar way for the measurement of ϵ_r and Q-values. The commercial LTCC powder was derived from 'green' sheet material (duPont green tape code 951)[3] following binder burn-out. This powder was granulated in isopropanol as mentioned earlier.

The optimum glass/$MgTiO_3$–$CaTiO_3$ ceramic ratio required for low temperature firing was determined using dilatometry. The densities and shrinkages of the samples were calculated from their dimensions and weights following the various firings. The porosity of the samples was estimated from the SEM images using the line intercept method.

XRD was used to identify crystalline phases. Microstructural and phase analysis was done using SEM/EDS on ground and polished surfaces. Boron contents were derived by the difference between the total determined constituents and 100%.

The dielectric characteristics in the microwave frequency range were measured by the Hakki–Coleman dielectric resonator method, where a cylindrically shaped specimen is positioned between two copper plates.[11] An HP8719C network analyser was used for the microwave measuring system. The dielectric properties were calculated from the frequency of the TE_{011} resonant mode.

3. Results and discussion

The specific surface areas of the MMT-20 powder and the ZSB and BSB powders were 4.1, 2.6 and 2.4 $m^2\ g^{-1}$, respectively.

After several sintering experiments it was concluded that 70 wt.% glass phase in the ceramic was needed to lower the effective firing temperature to the desired 900°C. Fig. 1 shows shrinkage data for three mixtures, demonstrating an interesting, two-stage densification behaviour starting respectively at around 600 and 850°C. The SEM/EDS and XRD data for the materials in the as-mixed and dried condition, and after firing at 620, 875 and 900°C are summarised in Table 2. The as-received MMT-20 powder was composed of $MgTiO_3$ grains with a very small amount (about 6 mol%) of separate $CaTiO_3$ grains; the $CaTiO_3$ could not be detected by XRD in the prepared glass/MMT-20 mixtures. The BSB was totally amorphous, but the ZSB had also crystallised Zn_2SiO_4. The compact densities of both mixtures before firing were 1.9 Mg m^{-3}.

3.1. BSB/MMT-20 mixture

In the first firing step (620°C, dwell time 10 min) of this mixture, the glass started to sinter causing slight shrinkage. The only crystalline phase observed by XRD (Fig. 2) was $MgTiO_3$. The densities of the samples were 2.0 Mg m^{-3}.

After the second firing step (875°C, 80 min), the microstructure of the composition consisted of needle-like $BaTi(BO_3)_2$ crystals and precipitated TiO_2 crystals surrounded by amorphous $SiB2O_5$ and $SiBa(BO_3)_2$ phases. The original $MgTiO_3$ phase had disappeared. These observations are deduced from an examination of Figs. 2 and 3 taken together.

The density had increased to 2.8 Mg m^{-3} with linear shrinkage about 12% and the porosity of the samples was still quite high (about 23 vol.%). After each firing, the microstructure was found to be uniform. After the last firing step (900°C, 80 min), the samples started to lose their shape, and at 920°C they were totally molten.

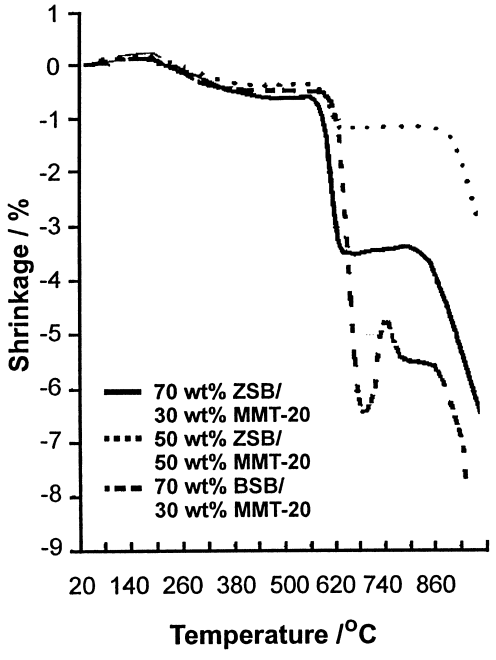

Fig. 1. Shrinkage behaviour of different compositions.

3.2. ZSB/MMT-20 mixture

After firing at 620°C, the microstructure contained densified areas, where glass had started to react with the crystalline material producing different amorphous and crystalline phases composed of the original glass

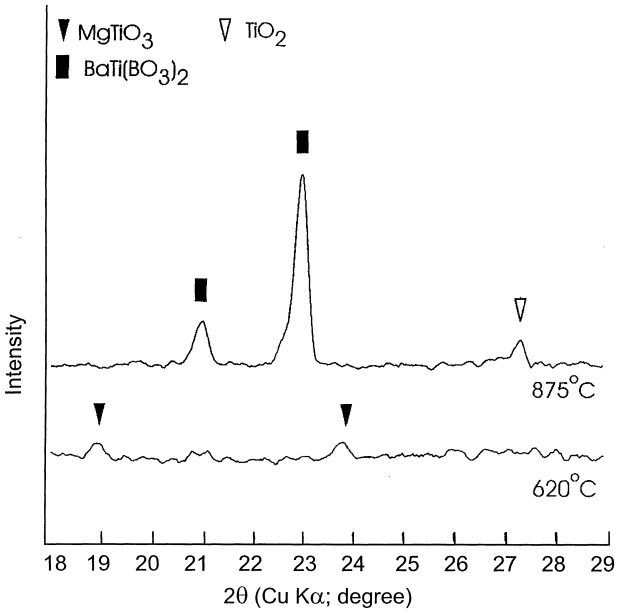

Fig. 2. XRD patterns of BSB/MMT-20 mixture.

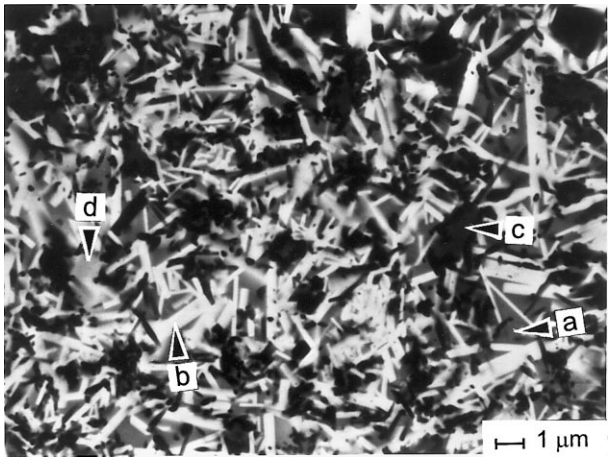

Fig. 3. SEM/BE image of BSB/MMT-20 mixture after 875°C firing. (a) TiO_2 crystal, (b) $BaTi(BO_3)_2$ crystal and amorphous (c) SiB_2O_5 and (d) $SiBa(BO_3)_2$.

Table 2
Densities and SEM/EDS and XRD results for the samples after various process steps

Sample	Compacts before firing	After firing at 620°C for 10 min	After firing at 875°C for 80 min	After firing at 900°C for 80 min
MMT-20	Crystalline $MgTiO_3$, $CaTiO_3$			
BSB	Totally amorphous			
ZSB	Glass and crystalline Zn_2SiO_4			
BSB/MMT-20 mixture (70 wt.%/30 wt.%)		Crystalline $MgTiO_3$ and amorphous $SiBa(BO_3)_2$ and $Ba_2B_6O_{11}$	Crystalline TiO_2, $BaTi(BO_3)_2$ and amorphous $SiBa(BO_3)_2$ and SiB_2O_5	–
Density/Mg m^{-3} (Porosity vol.%)	1.9 (47)	2.0 (44)	2.8 (23)	
ZSB/MMT-20 mixture (70 wt.% /30 wt.%)		Crystalline $ZnSiO_4$, $MgTiO_3$ and amorphous $54ZnO + 9SiO_2 + 37B_2O_3$, $ZnO + 3TiO_2 + 6B_2O_3$ and $35CaO + 41TiO_2 + 6ZnO + 18B_2O_3$	Crystalline $ZnTiO_3$, Zn_2SiO_4, $Mg_2ZnTi(BO_3)_2O_2$, TiO_2 and no amorphous phases found	Crystalline $ZnTiO_3$, Zn_2SiO_4, $Mg_{4/3}Zn_{2/3}B_2O_5$, TiO_2 and no amorphous phases found
Density/Mg m^{-3} (Porosity vol.%)	1.9 (47)	2.2 (39)	3.1 (14)	3.5 (3.5)

material, together with titanium and calcium. The original $MgTiO_3$ crystals and the original Zn_2SiO_4 crystals could also easily be observed in XRD (Fig. 4). The sample density values were 2.2 Mg m^{-3}.

In the second step (875°C), no amorphous phases could be found and the density of the samples was 3.1 Mg m^{-3}. The microstructural variation was still present (Fig. 5) showing uniform, matrix-like areas and large areas, (even >100 μm diameter), in which the inner parts were composed of the original crystalline material and $MgO–TiO_2–B_2O_3$ crystals, and the outer areas contained $ZnTiO_3$, $Mg_2ZnTi(BO_3)_2O_2$ and TiO_2 crystals. The matrix-like uniform area consisted mainly of Zn_2SiO_4 and $Mg_2ZnTi(BO_3)_2O_2$ crystals. All these phases were positively identified by XRD (Fig. 4), except

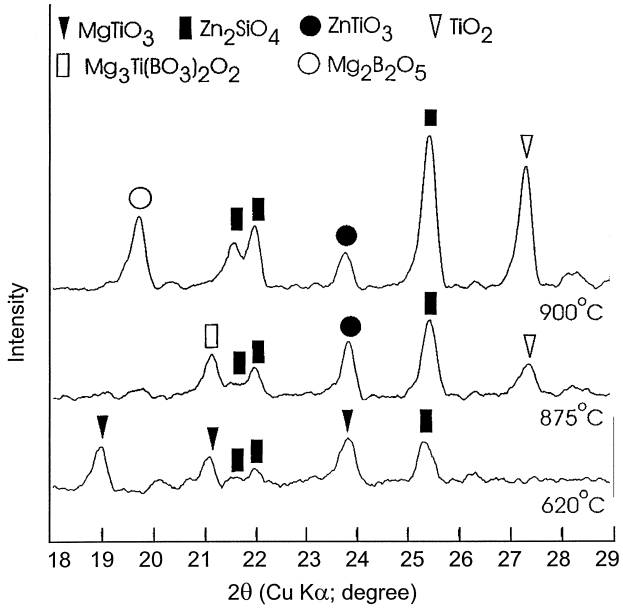

Fig. 4. XRD patterns of ZSB/MMT-20 mixture.

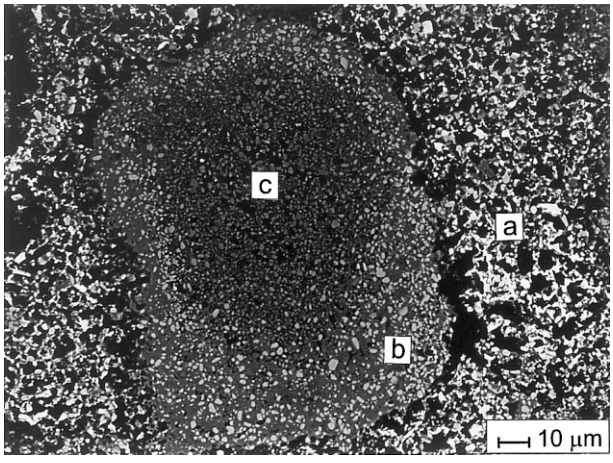

Fig. 5. SEM/BE image of the ZSB/MMT-20 mixture after firing at 875°C. (a) Crystalline Zn_2SiO_4 and $Mg_2ZnTi(BO_3)_2O_2$; (b) crystalline $ZnTiO_3$ and $Mg_2ZnTi(BO_3)_2O_2$; (c) $MgTiO_3$, $CaTiO_3$, $CaTiO_3$ and mixtures of $MgO–TiO_2–B_2O_3$ crystals.

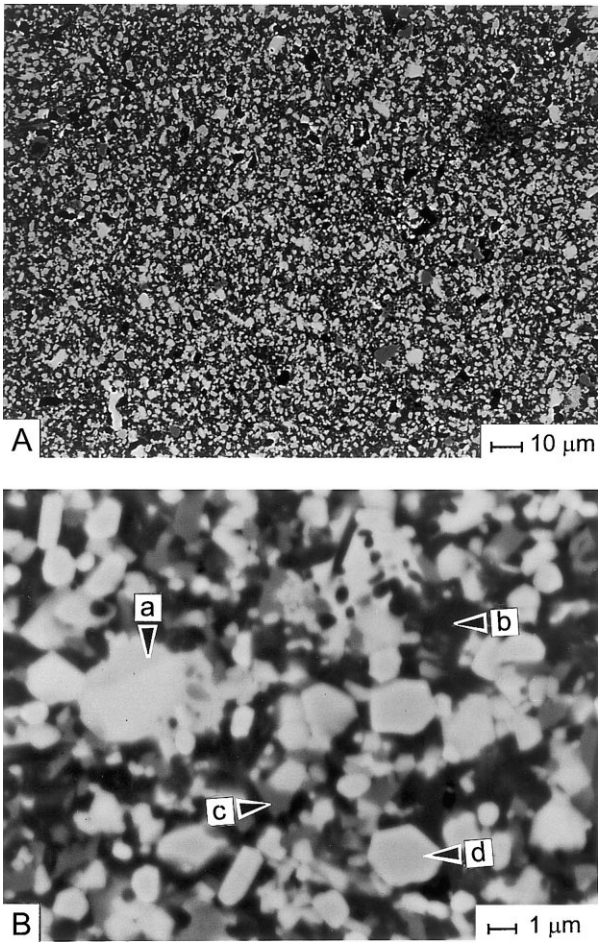

Fig. 6. (A). SEM/BE and (B) FESEM/BE images of the ZSB/MMT-20 mixture after firing at 900°C. (a) Zn_2SiO_4; (b) $Mg_{4/3}Zn_{2/3}B_2O_5$; (c) TiO_2 (with 5–6 wt.% ZnO); (d) $ZnTiO_3$.

for $Mg_2ZnTi(BO_3)_2O_2$ the presence of which was inferred from the JCPDS file for $Mg_3Ti(BO_3)_2O_2$. According to the EDS analyses, the TiO_2 crystals contained about 5–6 wt.% ZnO.

After the 900°C firing step, the large scale microstructural variation totally disappeared (Fig. 6A) and the material consisted of crystals smaller than 5 μm in size with no amorphous phases (Fig. 6B). Compared to the earlier step, the $ZnTiO_3$ and Zn_2SiO_4 crystals were still present and the amount of TiO_2 crystalline phase had increased as well as Zn_2SiO_4. A tentative explanation is that $Mg_2ZnTi(BO_3)_2O_2$ decomposed mainly to TiO_2 and $Mg_{4/3}Zn_{2/3}B_2O_5$, which was inferred from the JCPDS file for $Mg_2B_2O_5$. This explanation is based on the XRD analysis evidence for the presence of $Mg_2B_2O_5$ (Fig. 4) after firing at 900°C but absent earlier. The density of the samples was 3.5 Mg m^{-3} with linear shrinkage about 20%.

Table 3
Measured dielectric properties

Sample	Permittivity	Q-value	DF × 10^{-3}
MMT-20, fired 1360°C	21.4	3700	0.3
BSB/MMT-20 mixture, fired 875°C	8.2	430	2.3
ZSB/MMT-20 mixture, fired 875°C	8.5	830	1.2
ZSB/MMT-20 mixture, fired 900°C	10.6	880	1.1
Commercial LTCC, fired 875°C	7.4	320	3.1

3.3. Dielectric properties

The dielectric properties were measured at approximately 7 GHz except for the MMT-20 samples, and for the commercial LTCC samples where the frequency was 6 GHz. The results are given in Table 3.

Although the amounts of glass in both mixtures required to decrease the firing temperature from 1360 to 900°C were large, the electrical properties were promising compared to those of the commercial LTCC material. When other comparing the effectiveness of the ZSB and BSB additions to MMT-20 ceramic the former is the more promising since it produced nearly fully dense and crystalline material. This composition also had higher permittivity and lower dissipation factor, both parameters improving the higher the firing temperature and the attendant increasing TiO_2 crystalline phase.

Generally speaking, because of differences in specimen geometries and measuring systems, dielectric properties reported in different studies are difficult to compare.[1,3–5] In spite of this, although the glass addition decreased the permittivity and the increased DF from the values for the pure MMT-20 ceramic, the modified materials are competitive with materials having similar glass content[1,5] and with the commercial ones in Table 1. The firing temperature is still slightly too high, but a minor change in glass composition could remedy this. In future, it might prove possible to even lower the glass addition, which should improve microwave properties bringing them closer to those of the original MMT-20 ceramic. Also, in the case of BSB glass addition, combinations of BaO, SiO_2 and B_2O_3 are possible[10] and these might lead to a totally crystalline structure and improved microwave properties.

The study is a preliminary investigation of these mixtures and will be continued with profound measurements of thermomechanical, microstructural and microwave properties of at least the ZSB/MMT-20 mixture.

4. Conclusions

The BSB/MMT-20 and ZSB/MMT-20 mixtures showed two shrinkage behaviours, the first one starting

near 600°C and the second one near 850°C. In the case of the BSB/MMT-20 composition, the first stage shrinkage is caused by the onset of liquid phase sintering. The final state of this composition consisted of amorphous SiB_2O_5 and $SiBa(BO_3)_2$ phases, crystalline TiO_2 and needle-like $BaTi(BO_3)_2$ phases. Although this composition did not reach the full density (porosity about 23%) before melting, its DF was still lower (0.002 at 7 MHz) than that measured for the commercial LTCC material (0.003 at 6 GHz), while values for the permittivity (8–9) were rather similar. This composition did not reach the intended totally crystalline structure.

The first stage shrinkage of the ZSB/MMT-20 composition evidenced the onset of liquid phase sintering coupled with solution-precipitation reactions. At higher temperatures (875°C), all amorphous phases had vanished and the microstructure was composed of crystalline Zn_2SiO_4, TiO_2, $ZnTiO_3$ and $Mg_2ZnTi(BO_3)_2O_2$ phases. In a firing at 900°C, the $Mg_2ZnTi(BO_3)_2O_2$ phase seemed to decompose to $Mg_{4/3}Zn_{2/3}B_2O_5$ and TiO_2 phases and the samples had low porosity (3.5%). The microwave properties also changed showing higher permittivity ($\epsilon_r = 10.6$) and low DF (0.001 at 7 GHz), observations which were consistent with the microstructural development.

Acknowledgements

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