ULTC Glass Composites Based on Rutile and Anatase with Cofiring at 400 °C for High Frequency Applications

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Supporting Information

ABSTRACT: The article presents the very first materials to the ultralow temperature cofired ceramic (ULTCC) technology with the sintering temperature of 400 °C. The dielectric composites are based on a rutile and anatase with commercial GO17 sealing glass. In addition to the bulk samples, the tape casting procedure is also introduced to show its feasibility to cofiring with commercial Ag electrodes at 400 °C. The structural, microstructural, thermal, and microwave dielectric properties in the green and sintered samples were investigated. The optimum amount of glass to fabricate substrates was found to be 30 vol %. The ULTCC substrates with the anatase TiO₂A-30GO17 and rutile TiO₂R-30GO17 that were sintered at 400 °C showed a relative permittivity of 9.9 and 15 and a dielectric loss of 0.006 and 0.003, respectively, at the measurement frequency of 9.9 GHz. The temperature dependences of the relative permittivity were +70 and −400 ppm/°C, respectively. Moreover, the coefficients of the thermal expansion of the substrates were 7.4 and 8.3 ppm/°C in the measured temperature range of 50–300 °C. A preliminary test to study the feasibility of the anatase TiO₂A-30GO17 for a dual band antenna was performed due to its relatively stable temperature behavior.

KEYWORDS: ULTCC, Ceramic–glass, Microwave substrates, Cofiring, Tape casting

INTRODUCTION

The era of multilayer capacitor technology has led to the utilization of multilayer ceramic processes in high temperature cofired ceramics (HTCC), low temperature cofired ceramics (LTCC), and, very recently, in ultralow temperature cofired ceramics (ULTCC) 1–11. This change has been due to the continuous and rapid growth in the electronic and telecommunication fields, with corresponding demands for new ways to use ceramics to enable miniaturization, high packing density, and reduced cost for devices. The newest concept, ULTCC, enables high performance and low-cost devices, which are especially suitable for the future generation of telecommunications. It is also found to be environmentally friendly due to its low energy consumption in fabrication.

Nowadays, there are nearly 200 ULTCC compositions reported, especially for high-frequency applications. 1,3,6 In 2016 and 2017, the first tape casting procedures were introduced. Grabey et al., in 2016, showed the material solutions and processing requirements by fabricating light-emitting diodes (LEDs) using the ULTCC process. 12 The main advantages listed were low-cost of fabrication and an improved thermal performance, which resulted in a longer lifetime as compared to a traditional metal core-printed circuit board. 13 In 2017, Chen et al. rendered the first accurate slurry composition for tape casting of ULTCC multilayers and multimaterials with embedded electrodes. 13 Very recently, the same slurry composition was successfully used for a functional ULTCC substrate cofired at 450 °C. 14 However, more research should be focused on tape casting of ULTCCs and commercial electrode compatibility to make the multilayer devices feasible for the future generation of telecommunications.

On the other hand, the commercial production and utilization of titanium dioxide has increased rapidly due to its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its utilization of titanium dioxide has increased rapidly due to its availability; low cost; chemical stability; nontoxicity; and its utilization of titanium dioxide has increased rapidly due to its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availability; low cost; chemical stability; nontoxicity; and its availab
compositions, such as DuPont, Schott AG, Fujitsu, Asahi glass, Murata, Kyocera, etc. Following this approach, we used a commercial low melting sealing glass (GO17) with the rutile and anatase TiO2 powder. The selection of commercial GO17 glass is due to its low melting temperature of 400 °C and low dielectric loss in the order of 0.001. The present article reveals a new TiO2−GO17 composition, together with the tape casting process and cofiring with commercial Ag ink at 400 °C. In addition to the microwave properties, green tape stability, sintering profile, the linear coefficient of thermal expansion, shrinkage, and AFM surface roughness were also studied. Additionally, very preliminary results on the utilization of the developed anatase-based substrate for microwave devices are presented.

# MATERIALS AND METHODS

## Materials

The raw materials used in the development of theULTCCs included high purity TiO2 ceramic (Anatase, 99.9%, Alfa Aesar, ~325 mesh) and low melting-point sealing glass (GO17-340, SCHOTT technical glasses with Pb2O3, Li2O, Al2O3, and Si2O3). The anatase TiO2 powder was converted to rutile by heat treating at 1050 °C/5 h, followed by ball milling using yttrium-stabilized zirconia balls and a zirconia container with an 100 rpm rotation in an ethanol medium for 12 h, drying, and then sieving. Different amounts of GO17 (20, 30, and 40 vol %) were mixed separately with the rutile and anatase TiO2 powders by 12 h ball milling to find the best densification and sintering temperatures for both TiO2−GO17 compositions. Samples with a diameter of 14 mm and thickness of 2 mm were pressed (150 MPa, 10 min) followed by binder burnout (200−350 °C) and sintering at 400 °C. The detailed flowchart of the tape casting process, screen-printing, and cofiring is shown in Figure 1a.

## Methods

### Tape Casting

The tape casting slurry was made of dimethyl carbonate (DMC; Sigma-Aldrich, St. Louis, MO) as a solvent, poly(propylene carbonate) (QPAC40; EMPOWER MATERIALS, New Castle, DE) as a binder, butyl benzyl phthalate (S160; Richard E. Mistler, Yardley, Pennsylvania) as a plasticizer-1, and polyethylene glycol (UCON 50HB2000; Richard E. Mistler) as a plasticizer-2 together with the mixtures of TiO2 and glass. The names of the research compositions indicate the amount of GO17 (20, 30, 40 vol %) and rutile (R) and anatase (A) phase TiO2, for example, TiO2A−30GO17 and TiO2R−20GO17.

### Characterizations

The crystal structure of the sintered samples and the powders was analyzed by an X-ray diffractometer (XRD) (Rigaku SmartLab 9 kW) using Cu Kα radiation. The analysis of the XRD results was done with PDFX2 software for Rietveld refinement using the ICDD PDF+ 2018 database for the powder diffraction patterns. The bulk density of the sintered samples was studied by the Archimedes method. The dimensional shrinkage of the developed ULTCC substrate was measured using Vernier calipers with an accuracy of 0.02 mm using the standard eq 1

\[
\% \text{ of shrinkage} = \frac{\text{dimension before sintering} - \text{dimension after sintering}}{\text{dimension before sintering}} \times 100
\]

The particle size and surface area analyses of the TiO2−GO17 mixtures were performed using the laser diffraction method (Beckman Coulter LS13320) and a particle surface area analyzer (G.W. Berg & Co. Micrometrics ASAP 2020). Differential scanning calorimetric measurement (DSC)/thermogravimetric analysis (TGA) (Netzsch 404 F3, Selb, Germany) with a heating rate of 2 °C/min for samples of 15.4 mg was used to study the burn out of the organic additives. Tensile strength measurements of the green tape were performed using a temperature-controlled tensile strength measurement stage (TST 350, Linkam Scientific Instruments Ltd., Surrey, UK) and Linksys 32 software at room temperature with a speed of 100 μm/s using standard dumbbell-shaped samples (length 36.2 mm and width 3.1 mm). The microstructure of the sintered sample was studied using field emission scanning electron microscopy (FESEM, ZEISS Ultra Plus, Germany) with EDS analysis. Microwave dielectric properties of the green and sintered multilayers were measured using the split post dielectric resonator (SPDR) (QWED, Poland) technique with a Vector Network Analyzer (10 MHz−20 GHz, Rohde & Schwarz, ZV2B20, Germany). The total error in measuring the relative permittivity was about 0.5%, with an accuracy of measurement of

![Figure 1. (a) ULTCC process flowchart and (b) antenna fabrication steps.](image-url)
the dielectric loss in the range of $10^{-5}$. The total errors associated with relative permittivity and dielectric loss measurements were $\pm 5$ and $\pm 10\%$. The temperature dependence of the microwave dielectric properties was measured using a furnace (Espec SU-261) operating at $\pm 5\%$ with respect to the TiO$_2$A-30GO$_{17}$ substrate for practical applications was verified in this study.

To investigate the temperature dependence of the microwave dielectric properties, the relative permittivity and dielectric loss measurements were conducted in the temperature range of 50 $\degree$C to 80 $\degree$C. The insets show the indexed XRD of ceramic (anatase and rutile) used in this study.

Figure 2. (a) The bulk density of (a) TiO$_2$R-20, 30, 40GO$_{17}$, and (b) TiO$_2$A-30GO$_{17}$ as a function of sintering temperature. X-ray diffraction pattern of (c) TiO$_2$A-30GO$_{17}$ and TiO$_2$R-30GO$_{17}$ sintered at 400 $\degree$C. The insets show the indexed XRD of ceramic (anatase and rutile) used in this study.

The total antenna efficiency of the antenna as a function frequency was plotted including its radiation and mismatch efficiencies. This thus covers the resistive losses and the mismatch losses of the antenna. In eq 3, $P_{\text{input}}$ is the power fed into the antenna, and $P_{\text{radiated}}$ is the integral of power measured over $4\pi$ steradian. The coaxial cable from the test instrument to the antenna input was calibrated out when the measurement was performed.

$$\eta = \frac{P_{\text{radiated}}}{P_{\text{input}}}$$  

$\eta$ is the antenna efficiency.

Device Fabrication. The feasibility of the developed ULTCC TiO$_2$A-30GO$_{17}$ substrate for practical applications was verified by using it in the construction of a dual-band patch antenna. A predesigned and simulated dual band antenna was fabricated on the optimized ULTCC substrate developed in these studies. The fabrication steps of the antenna are shown in Figure 1b, including the screen-printing of the antenna geometry using Ag paste on the green tape, cofiring, and cutting to the desired shapes with a laser (LPKF ProtoLaser U3) with a machining precision of 2 $\mu$m. The shaped ULTCC substrates were integrated with a standard FR4 substrate working as a ground plane (Figure 1b).

A small copper tape was soldered to the FR4 substrate and attached to the Ag layer of the radiator using conductive glue (EPO-TEK, H20E-PFC). The prototype was dried in the oven at a temperature of 120 $\degree$C for 1 h. Finally, a coaxial cable was soldered to the fabricated antenna for the measurements.

### RESULT AND DISCUSSIONS

Optimization of the TiO$_2$-GO$_{17}$ Mixtures. Figure 2a,b represents the variation of bulk density with respect to the sintering temperature of the rutile TiO$_2$R-20GO$_{17}$, TiO$_2$R-30GO$_{17}$, and TiO$_2$R-40GO$_{17}$ composites. To establish the optimal conditions, various sintering temperatures from 350 to 500 $\degree$C (based on the glass softening and melting temperature of 350$\pm$420 $\degree$C) were used. In addition, the anatase phase TiO$_2$ with 30 vol % GO$_{17}$ glass (TiO$_2$A-30GO$_{17}$) was also prepared, and its density was studied (Figure 2b). Figure 2c,d reveals the X-ray diffraction pattern of the TiO$_2$A-30GO$_{17}$ and TiO$_2$R-30GO$_{17}$ samples, respectively, sintered at 400 $\degree$C. Moreover, Figures S1, S2, and S3 represent the Rietveld-refined XRD pattern of TiO$_2$R-40GO$_{17}$ sintered at 400, 450, and 500 $\degree$C to demonstrate the effect of secondary phases after sintering at 400, 450, and 500 $\degree$C. The refined diffraction pattern suggests that when the sintering temperature increased from 450 to 500 $\degree$C, the amount of rutile TiO$_2$ phase decreased due to the formation of the ternary crystalline phase of PbTiO$_3$. However, after a sintering temperature at 400 $\degree$C, only a secondary phase of LiAl(SiO$_4$)$_2$ is nucleated from the GO$_{17}$ glass. The summary of refinement, phase details along with XRD compositions is listed in Tables S1, S2, and S3, respectively. The X-ray diffraction and the bulk density studies revealed that 30 and 40 vol % glass showed the best bulk density. On the basis of the densification and structural studies, the optimized compositions selected for the further
studies were thus TiO₂R-30GO17, TiO₂R-30GO17, and TiO₂R-40GO17 with a sintering temperature of 400 °C.

**Tape Casting and Post Processing.** The compositions selected for the tape casting were TiO₂R-30GO17, TiO₂A-30GO17, and TiO₂R-40GO17, and the amount of additive was calculated according to the composite density, particle size, and surface area of the powders shown in Table 1. Fine optimization of the slurries was carried out during the casting trials to obtain high quality tapes (Table 1).

| Table 1. Optimized Slurry Compositions for the Ceramic–Glass Mixtures |
|------------------------------------------------|
| **filler ceramic–glass mixture properties** | **materials** |
| density (g/cm³) | average particle size (μm) | average surface area (m²/g) | compositions (wt %) |
| TiO₂R-30GO17 | 4.4 | 13 | 2.0 | 54 |
| TiO₂A-30GO17 | 4.2 | 6 | 5.0 | 45 |
| TiO₂R-40GO17 | 4.5 | 14 | 1.9 | 40 |
| DMC (solvent) | 4 | 5 | 1.2 | 40 |
| polypropylene carbonate, QPAC40 (binder) | 4 | 4 | 1.0 | 40 |
| butyl benzyl phthalate, BBP (plasticizer-1) | 4 | 1 | 0.8 | 40 |
| polyethylene glycol, PEG (plasticizer-2) | 4 | 1 | 0.2 | 40 |

Figure 3 shows the photograph of process steps (a) with the tape after casting and drying, (b) after peel off from the carrier film, (c) screen printed pattern on the tapes, (d) vacuum sealed multilayers after the lamination and isotatic pressure, and (e) the shaped expediters. The cast green tapes have a thickness in the range of 137–145 μm. The mechanical properties of the green tapes are important in the postprocessing stages, such as lamination, screen printing, shaping, etc. The average tensile strengths of a single cast layer of TiO₂R-30GO17, TiO₂A-30GO17, and TiO₂R-40GO17 in the green stage were in the range of 0.3–0.6 MPa with a standard deviation of 0.03 MPa. These mechanical properties are lower when compared with commercial tape (example DuPont 951, 1.8 MPa measured with the same setup) due to the new QPAC40 binder system. The difference is attributed to the low strength of the used binder since the slurry system needs to have a low burn out temperature, while for polyvinyl butyral, commonly used for LTCC casting, it is much higher. Despite the lower strength, the developed ULTCC tapes were feasible for the postprocessing.

The reason for the selection of this slurry system was the exceptionally low burnout temperature needed for the developed ULTCCs. The endothermic and exothermic peaks in the DSC analysis of the cast tapes (Figure 4a) relate to the evaporation of the solvent and the melting of the binders and plasticizers until they burn out until 350 °C. The GO17 glass has softening and melting temperatures of 375 °C and 400–415 °C, respectively, which improve the density of the microstructures. The TG analysis showed a low weight loss up to 150 °C, followed by saturation when a temperature of 400 °C was approached. The mass loss can be explained by the decomposition of the binder (QPAC40) and the plasticizers BBP and PEG (decomposition temperatures 208–340 and 165–270 °C, respectively). The total weight loss accounted for the newly developed ULTCC tape was around 11.2%. The optimized sintering profile is shown in Figure 4b based on the TG/DSC analysis and the highest bulk density observed. The inset figure shows a photograph of the substrate after sintering at 400 °C.

The dense sintered microstructure of the developed substrates was further confirmed by the SEM studies. Figure 5a shows the cross-section microstructure of a TiO₂A-30GO17 ULTCC substrate sintered at 400 °C. It reveals that the glass phase melted over the anatase TiO₂ to provide a dense microstructure. There are similar observations for TiO₂R-30GO17 in Figure 5b.

Figure 5a shows the cross-section microstructure of the sintered TiO₂R-40GO17 sample in general. With the larger magnification (Figure 5b), it can be seen that the glass and the secondary phase (LiAlSiO₄) are located on the grain boundaries of TiO₂. Figure 5c,d shows the microstructure and EDS line mapping analysis of ULTCC tape (TiO₂R-30GO17) co-fired with Ag at 400 °C. The SEM microstructure and EDS analysis further confirmed that the developed ULTCC substrates were cofirable at their sintering temperatures without any detectable reactions or diffusion of Ag to the developed composites. The observations with TiO₂A-30GO17 and TiO₂R-40GO17 multilayer substrates sintered at 400 °C were similar. Figure 5a,b shows the cross-section microstructure of multiple Ag lines co-fired with different spacings and the magnified SEM. Figure 5c,d represents the TiO₂A-30GO17 and TiO₂R-40GO17 co-fired microstructures. The four layers of TiO₂R-GO17 and TiO₂A-GO17 tapes have a laminated thickness of about 456 and 465 μm, respectively, after sintering at about 449 and 458 μm. The average sintering shrinkages in the x-, y-, and z-directions were of 0.4 and 0.5 (±1), 0.4 and 0.6 (±1), and 1.5 and 1.6 (±1) %, respectively. This low sintering may be attributed to the formation of low-density LiAlSiO₄ crystallites (2.35 g/cm³) in the grain boundary regions in addition to the high-density glass matrix and TiO₂ rutile and anatase phases. In order to confirm this effect, the z-direction shrinkages of cast TiO₂R-30GO17 and TiO₂R-40GO17 tapes were measured using a dilatometer. These results confirm the low shrinkage of present ULTCC systems (Figure 6). Previously, it has been reported that during the firing process after binder burnout, the low melting glasses help to form a self-constrained layer in the multilayer modules to reduce the shrinkage. Additionally, Roosen et al. reported in a detailed investigation upon the particle size, shape, binder, or reduced solvent also led to higher shrinkage anisotropies. However,
the low shrinkage values observed in the present ceramic–glass ULTCC compositions need further detailed investigation to prove the existence of a self-constrained mechanism in the matrix filler networks.

**Microwave Dielectric Properties of Green and Sintered Tapes.** The microwave dielectric properties of the green cast TiO\(_2\)-R-30GO17, TiO\(_2\)-R-40GO17, and TiO\(_2\)-A-30GO17 tapes at 2.4, 5.1, and 9.9 GHz frequencies are shown in Table 2. The measured results were also compared with commercial 951 LTCC green tape. The low relative permittivity and high dielectric loss in all of these cases were due to the organic additives in the tapes. These measurements were done for the green tapes to open discussion on the possibility of using these values for lot-to-lot variation tests as well as for aging studies after storage.

The microwave dielectric properties of the TiO\(_2\)-R-30GO17, TiO\(_2\)-R-40GO17, and TiO\(_2\)-A-30GO17 substrates after multilayer lamination and sintering at 400 °C are shown in Table 3 along with commercial 951 sintered at 850 °C. The microwave dielectric properties of the commercial Dupont 951 LTCC were comparable to those of the newly developed rutile- and anatase-based substrates sintered at 400 °C. All the developed ULTCC substrates had suitable dielectric properties for high frequency applications.

In addition to this, the temperature dependent microwave dielectric properties of the developed ULTCC substrates are also crucial for practical telecommunication applications. Figure 6a,b,c,d shows the temperature dependence of the relative permittivity and dielectric loss at 9.9 GHz in the temperature range of −40 to 80 °C. It is clear, that the relative permittivity of the TiO\(_2\)-R-30GO17 decreased with the increasing temperature, while the linear fitted lines for the dielectric loss showed an increase as expected. In the case of the TiO\(_2\)-A-30GO17, the behavior of the permittivity as a function of temperature was opposite with the less variation. However, the variation of its dielectric loss values was too large for a clear conclusion. The calculated temperature coefficient of relative permittivity of TiO\(_2\)-R-30GO17 and TiO\(_2\)-A-30GO17 substrates were −400 and 70 ppm/°C, respectively. It is well-known, that rutile TiO\(_2\) has a high temperature coefficient of

| ULTCC/LTCC green tape | single layer thickness (μm) | \(\varepsilon_r\) | \(\tan\delta\) | \(\varepsilon_r\) | \(\tan\delta\) | \(\varepsilon_r\) | \(\tan\delta\) |
|------------------------|-----------------------------|------------------|----------------|------------------|----------------|------------------|----------------|
| TiO\(_2\)-R-30GO17     | 140                         | 8.5              | 0.04           | 8.4              | 0.03           | 7.9              | 0.03           |
| TiO\(_2\)-R-40GO17     | 135                         | 7.3              | 0.05           | 7.1              | 0.04           | 6.9              | 0.03           |
| TiO\(_2\)-A-30GO17     | 113                         | 6.6              | 0.01           | 6.4              | 0.02           | 5.9              | 0.02           |
| Dupont 951             | 251                         | 4.7              | 0.008          | 4.7              | 0.008          | 4.7              | 0.008          |
resonant frequency ($\tau_f$), being about 450 ppm/°C, which explains the negative $\tau_e$ for TiO$_2$R-30GO17. However, although a $\tau_f$ value is reported for the thin film anatase, the exact value after sintering is not available since it is not stable and turns to rutile at a high temperature." Figure 6c,d shows $\tau_e$ values of $-280$ and $200$ ppm/°C for the TiO$_2$R-40GO17 and Dupont 951 substrates, respectively. A 10 vol % increase in GO17 glass decreased the $\tau_e$ value by $-120$ ppm/°C. However, a further increase of the glass content is not desirable. The same feasible sintering temperature for the TiO$_2$R and TiO$_2$A glass composites raises a new suggestion of how to make the $\tau_e$ value near zero. Since, the sintering temperature in both cases is 400 °C, the TiO$_2$A-30GO17 substrate could be modified by relatively small additions of the TiO$_2$R phase with a negligible effect on the measured permittivity and loss values of $\varepsilon_r$ of 9.9 and 0.003 at 5.1 GHz, these being at the same level as those achieved for the commercial Dupont 951 LTCC substrate sintered at 850 °C.

**Table 3. Microwave Dielectric Properties of the Sintered ULTCC Substrates in Comparison to Dupont 951**

| ULTCC/LTCC       | ST (°C) | T (µm) | $\varepsilon_r$ | tan $\delta$ (*) | $\varepsilon_r$ | tan $\delta$ (*) | $\varepsilon_r$ | tan $\delta$ (*) |
|------------------|---------|--------|-----------------|-----------------|----------------|-----------------|----------------|-----------------|
| TiO$_2$R-30GO17  | 400     | 449    | 15.6            | 4               | 15.5           | 3               | 15.5           | 3               |
| TiO$_2$R-40GO17  | 400     | 459    | 14.4            | 5               | 14.3           | 6               | 14.3           | 6               |
| TiO$_2$A-30GO17  | 400     | 434    | 10.0            | 1               | 9.9            | 3               | 9.9            | 6               |
| Dupont 951       | 850     | 822    | 7.5             | 5               | 7.5            | 5               | 7.5            | 5               |

*ST, sintering temperature; T, thickness; and (*) in the order of $10^{-3}$.

**Figure 6.** Dielectric properties of (a, b) TiO$_2$R-30GO17 and TiO$_2$A-30GO17 and (c, d) TiO$_2$R-40GO17 and Dupont 951 substrates as a function of temperature.

**Figure 7.** Linear coefficient of dimensional thermal expansion of TiO$_2$R-30GO17 and TiO$_2$A-30GO17 ULTCC substrates sintered at 400 °C.

**Linear Coefficient of Thermal Expansion.** The linear CTE is important for device level integration, cofiring with conductor electrodes, etc.

**Figure 7** shows the linear change in dimensions for the TiO$_2$A-30GO17 and TiO$_2$R-30GO17 bulk samples within the temperature ranges of 100–300 °C. The measured CTE values for the TiO$_2$A-30GO17 and TiO$_2$R-30GO17 samples were 7.4 and 8.3 ppm/°C, respectively. The CTE values also play an essential role in the ULTCC device fabrication, especially during cofiring with metal electrodes. In addition, the CTE is also crucial in the case of all multilayer and multimaterial
Figure 8. AFM surface roughness image of (a) 2D and (b) 3D green tapes and (c) 2D and (d) 3D sintered TiO₂-A-30GO17 ULTCC substrate.

Figure 9. (a) The simulated antenna pattern, (b) photograph of the fabricated antenna based on TiO₂-A-30GO17 ULTCC substrate mounted on the surface of FR4 with the inset showing the screen printed and cofired antenna pattern on ULTCC substrates, (c) simulated and measured S11 parameters of the antenna, and (d) the simulated and measured total efficiency of the antenna.
integrations in the cofiring process. Large CTE differences can cause delamination, warping, and even cracking during the firing process. The CTE of the developed ULTCC substrates was close to the values of commercial LTCCs and silicon.

Utilization of ULTCC TiO2A-30GO17 in a Dual Band Antenna. The feasibility of the TiO2A-30GO17 as a substrate for a WiFi dual band antenna operating at 2.42–2.48 GHz and 5.1–5.9 GHz frequencies was also demonstrated. The antenna design was based on the dielectric values and dimensions after sintering at 400 °C. The detailed fabrication steps of the antenna are discussed in the Materials and Methods section. The surface roughness of the green and sintered tapes are crucial parameters which control the postprocessing stages, such as screen-printing of the electrodes suitable for telecommunication device fabrications. Figure 8 shows 2D images of AFM surface roughness of (a) green and (b) sintered TiO2A-30GO17 substrates. These average surface roughness values were about 110–140 and 430–520 nm, respectively, being comparable or lower than those reported for the commercial LTCCs used for telecommunication applications. For example, the surface roughness of DuPont 951 and 9k7 has a value <0.34 and 0.52 μm, respectively.30,31 The surface roughness of the electrodes was also low, which is important at high frequencies with regard to the skin depth and transmission line delay.32–36 Figure S7a,b,c,d presents the AFM surface roughness images (2D and 3D images) of the room temperature-dried screen-printed Ag pattern and co-fired Ag pattern at 400 °C. The dried screen-printed Ag pattern showed an average surface roughness in the range of 60–80 nm. The cofired Ag surface showed the roughness in the range of 140–190 nm.

Figure 9 depicts (a) the 3D model design of the simulated antenna pattern and (b) a photographic image of the developed antenna based on a TiO2A-30GO17 ULTCC substrate mounted on the surface of FR4. The total dimension of the FR4 was ∼ 65 × 52 × 0.8 mm3, with ∼ 0.3 mm copper cladding. The ULTCC substrate dimensions in the antenna design were ∼ 15 × 4.5 × 0.4 mm3 with cofired Ag with a thickness of ∼ 12–15 μm. The relative permittivity and loss values of the standard FR4 used for the simulation were 4.3 and 0.02, respectively. Figure 9c,d shows the simulated and measured S11 parameters and the total efficiency of the antenna. The S11 results showed some deviation compared to the simulated results. This can be attributed to the connection point between the PCB and the radiator. The junction was modeled as an ideal galvanic connection in the simulation, whereas in the prototype, a small copper tape was soldered to the PCB and attached to the Ag layer of the radiator using conductive glue. Figure 9d shows the simulated and measured total efficiency of the antenna. These results showed good correlation, which indicates that the substrate properties used in the simulations were a close match to the measured antenna substrate. The fabrication of the ULTCC substrate material to form an antenna at 400 °C, i.e., close to the temperatures encountered in PCB fabrication, focused on the future integration of ceramic modules on polymer composites by overcoming the balanced thermal property cycle. Hence, the present ULTCC research is the first step toward the use of ULTCC materials in device level fabrication for telecommunication applications.

CONCLUSION

This article describes the very first report on rutile- and anatase-based ceramic–glass composites sinterable at 400 °C for ULTCC telecommunication applications. A casting composition suitable for the burnout of the organic additives at 250–350 °C together with moderately good mechanical stability for post processing is presented. The developed ULTCC tapes are cofirable with commercial Ag electrodes at 400 °C. In addition, the developed substrate showed nearly zero sintering shrinkage along the x-, y-, and z-axes, probably due to the low-density intermediate glass crystallization together with the proximity of the organics’ burnout and the glass melting temperatures in the region of 400 °C. The sintered ULTCC substrates, such as TiO2R-30GO17, TiO2R-40GO17, and TiO2A-30GO17, showed excellent microwave dielectric properties suitable for telecommunication applications. The relative permittivity values were in the range of 10–15, and the dielectric loss was 0.006–0.003 at 9.9 GHz. The developed anatase ULTCC substrate had a positive temperature-dependent relative permittivity of +70 ppm/°C measured in the temperature range of −40 to 80 °C. In the future, it could be possible to decrease this dependence close to zero by relatively small additions of rutile TiO2 with negligible effect on the achieved permittivity and loss values. The measured CTE values were also close to those reported for commercial LTCCs. Moreover, the developed substrates had low surface roughness values. The developed ULTCC anatase substrate was further processed for dual band antenna fabrication and testing. The return losses of the simulated and the fabricated antenna were similar to moderately good efficiency. In conclusion, the research gives an opportunity to fabricate microwave antennas at an ultralow sintering temperature (400 °C), with integrated electrodes resulting in lower energy consumption without loss of the electrical performance of the devices.

ASSOCIATED CONTENT

Supporting Information

Rietveld-refined XRD pattern of TiO2R-40GO17 sintered at 400, 450, and 500 °C; cross-section microstructure of TiO2R-30GO17 with different magnifications with marked secondary phases and back scattered SEM images; cross-section microstructure with different magnifications and back scattered image of Ag electrode cofired at 400 °C; dilatometry Z-axis shrinkage of TiO2R-30GO17 and TiO2R-40GO17 tape samples; AFM surface roughness analysis of cofired Ag surface; and refinement results of TiO2R-40GO17 sintered at 400, 450, and 500 °C using PDXL software (PDF)

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Notes

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ABBREVIATIONS

ULTCC, ultralow temperature cofired ceramics; LTCC, low-temperature cofired ceramics; HTCC, high temperature cofired ceramics; SPDR, split-post dielectric resonator; AFM, atomic force microscopy; XRD, X-ray diffraction; CTE, coefficient of thermal expansion; ppm, parts per million; SEM, scanning electron microscopy; R, rutile; A, anatase; GO17, commercial glass; TG, thermos gravimetric; DSC, differential scanning calorimetric; BBP, butyl benzyl phthalate; DMC, dimethyl carbonate; PEG, polyethylene glycol; PCB, printed circuit board.

REFERENCES

(1) Sebastian, M. T.; Wang, H.; Jantunen, H. Low Temperature Co-Fired Ceramics with Ultra-Low Sintering Temperature: A Review. Curr. Opin. Solid State Mater. Sci. 2016, 20 (3), 151–170.
(2) Udovic, M.; Valant, M.; Suvorov, D. Dielectric Characterisation of Ceramics from the TiO2–TeO2 System. J. Eur. Ceram. Soc. 2001, 21 (10), 1735–1738.
(3) Yu, H.; Liu, J.; Zhang, W.; Zhang, S. Ultra-lower sintering temperature ceramics for LTCC applications: a review. J. Mater. Sci. Mater. Electron. 2015, 26, 9414–9423.
(4) Valant, M.; Popovic, J.; Mihelj, M. V.; Burazer, S.; Altomare, A.; Molterini, A. Oxide Crystal Structure with Square-Pyramidally Coordinated Vanadium for Integrated Electronics Manufactured at Ultralow Processing Temperatures. ACS Sustainable Chem. Eng. 2017, 5 (7), 5662–5668.
(5) Imanaka, Y. Multilayered low temperature cofired ceramics (LTCC) technology. Springer: US, 2005.
(6) Zhou, D.; Pang, L.-X.; Wang, D. W.; Reaney, I. M. BiVO4 based high k microwave dielectric materials: a review. J. Mater. Chem. C 2018, 6, 9290–9313.
(7) Zhu, X.; Wang, Z.; Su, X.; Vilariinho, P. M. New Cu2TeO2 ceramics: Phase Formation and Dielectric Properties. ACS Appl. Mater. Interfaces 2014, 6 (14), 11326–11332.
(8) Joseph, N.; Varghese, J.; Siponkoski, T.; Teirikangas, M.; Sebastian, M. T.; Jantunen, H. Glass Free CuMoo4 Ceramic with Excellent Dielectric and Thermal Properties for Ultra-Low Temperature Cofired Ceramic Applications. ACS Sustainable Chem. Eng. 2016, 4 (10), 5632–5639.
(9) Varghese, J.; Siponkoski, T.; Teirikangas, M.; Sebastian, M. T.; Uusimaki, A.; Jantunen, H. Structural, Dielectric, and Thermal Properties of Pb Free Molybdate Based Ultralow Temperature Glass. ACS Sustainable Chem. Eng. 2016, 4 (7), 3897–3904.
(10) Joseph, N.; Varghese, J.; Teirikangas, M.; Sebastian, M. T.; Jantunen, H. Ultra-low sintering temperature ceramic composites of CuMoo4 through Ag2O addition for microwave applications. Composites, Part B 2018, 141, 214–220.
(11) Sashidharanpillai, A.; Kim, C. H.; Lee, C. H.; Sebastian, M. T.; Kim, H. T. Environmental Friendly Approach for the Development of Ultra Low Firing Li2WO4 Ceramic Tapes. ACS Sustainable Chem. Eng. 2016, 6, 6849–6855.
(12) Grabey, S.; Shahbazi, S.; Persons, R.; Shahbazi, C. Evaluation of a lead-free ultra low temperature co-fire ceramic (ULTCC) tape designed for lamination on aluminum substrates and a compatible cofireable silver conductor. Int. Symp. Microelectron. 2016, 2016, 000573–000580.
(13) Chen, M. Y.; Vahera, T.; Hsi, C. S.; Sobocinski, M.; Teirikangas, M.; Peräntie, J.; Juuti, J.; Jantunen, H. Tape casting system for ULTCCs to fabricate multilayer and multiregional 3D electronic packages with embedded electrodes. J. Am. Ceram. Soc. 2017, 100, 1257–1260.
(14) Varghese, J.; Siponkoski, T.; Sobocinski, M.; Vahera, T.; Jantunen, H. Multilayer functional tapes cofired at 450°C Beyond HTCC and LTCC Technologies. ACS Appl. Mater. Interfaces 2018, 10, 11048–11055.
(15) Hanaz, D. A. H.; Sorrell, C. C. Review of the anatase to rutile phase transformation. J. Mater. Sci. 2011, 46, 855–874.
(16) Nolan, M.; Iwaszuk, A.; Lucid, A. K.; Carey, J. J.; Fronzi, M. Design of novel visible light active photocatalyst materials; surface modified TiO2. Adv. Mater. 2016, 28, 5425–5446.
(17) Xia, T.; Zhang, C.; Oyler, N. A.; Chen, X. Hydrogenerated TiO2 nanocrystals: a novel microwave absorbing materials. Adv. Mater. 2013, 25, 6905–6910.
(18) Templeton, A.; Wang, X.; Penn, S. J.; Webb, S. J.; Cohen, L. F.; Alfard, N. M. Microwave Dielectric Loss of Titanium Oxide. J. Am. Ceram. Soc. 2000, 83, 95–100.
(19) Pullar, R. C.; Penn, S. J.; Wang, X.; Reaney, I. M.; Alfard, N. M. Dielectric Loss Caused by Oxygen Vacancies in Titania Ceramics. J. Eur. Ceram. Soc. 2009, 29, 419–424.
(20) Sebastian, M. T.; Jantunen, H. Two volume sets; Sebastian, M. T.; Jantunen, H.; Uebic, R., Eds.; Wiley-VCH: Weinheim, Germany, 2017, Vol. 1, Chapter 8.
(21) Langfeld, R.; Kunze, M.; Letz, M. Novel Glass Ceramics for Electronic Applications. Mater. China 2015, 34, 558–564.
(22) Schott, A. G. Technical glasses; physical and technical properties, 2014, https://www.uschott.com/d/tubing/RED51BE4F47/D/857E-SA42CFF131610.10.0002.001/09.schott-brochure-technical-glasses_us.pdf (accessed October 2018).
(23) Koseva, I. I.; Zvetkov, P. T.; Yordanova, A. S.; Marychev, M. O.; Dimitrov, O. S.; Nikovol, V. S. Preparation of Chromium doped LiAlSiO4 Glass-Ceramics. Bulg. Chem. Commun. 2017, 49, 366–370 http://bcc.bas.bg/BCC_Volumes/Volume_49_Number_2_2017/49-2-2017-419-Koseva-366-370.pdf.
(24) Misztler, E. R.; Twiname, R. E. Tape Casting: Theory and Practice; The American Ceramic Society: Westerville, Ohio, USA, 2000.
(25) Das, A.; Madras, G.; Dasgupta, N.; Umarji, A. M. Binder Removal Studies in Ceramic Thick Shapes made by Laminated Object Manufacturing. J. Eur. Ceram. Soc. 2003, 23, 1013–1017.
(26) Rabe, T.; Schiller, W. A.; Hochheimer, T.; Modes, C.; Kipka, A. Zero Shrinkage of LTCC by Self-Constraints Sintering. Int. J. Appl. Ceram. Technol. 2005, 2, 374–382.
(27) Besendorfer, G.; Roosen, A. Particle Shape, Size Effects on Anisotropic Shrinkage in Tape-Cast Ceramic Layers. J. Am. Ceram. Soc. 2008, 91, 2514–2520.
(28) Wypych, A.; Bobowska, I.; Tracz, M.; Opasinska, A.; Kadlubowski, S.; Kaliszewska, A. K.; Grobelny, J.; Wojciechowski, P. Dielectric Properties and Characterization of Titanium Dioxide Obtained by Different Chemistry Methods. J. Nanomater. 2014, 2014, 1–9.
(29) Eberstein, M.; Glatzky, C.; Gemeinert, M.; Rabe, T.; Schiller, W. A.; Modes, C. Design of LTCC with high thermal expansion. Int. J. Appl. Ceram. Technol. 2009, 6, 1–8.
(30) DuPont. Green tape 951 low temperature ceramics. Technical data sheet, 2011, https://www.etsmtl.ca/Unites-de-recherche/LTCC/Services-offerts/Dupont_951.pdf (accessed October 2018).
(31) DuPont. Green tape 976 low temperature ceramics. Technical data sheet, 2009, https://www.etsmtl.ca/Unites-de-recherche/LTCC/Services-offerts/Dupont_976.pdf (accessed October 2018).
(32) Chai, L.; Moroz, M.; Shahk, A.; Stgyar, V. Effect of conductor surface roughness and geometry on microwave loss, Presented at IEEE MTT-S Inter. Microwave. Symp. Phoenix, Arizona, May 2001.
(33) Rautio, J. C.; Rautio, B. J.; Arvas, S.; Horn, A. F.; Reynolds, J. W. The effect of dielectric anisotropy and metal surface roughness,
Presented at IEEE 2010 Asia-Pacific Microwave Conf. Yokohama, Japan, 10 March 2010.

(34) Hildebrandt, S.; Wolter, K. J. Thin Film Structuring on LTCC, Paper presented at 31st Inter. Spring Seminar on Elec. Tec., Hungary, May 2008.

(35) Thomas, D.; Abhilash, P.; Sebastian, M. T. Casting and characterization of LiMgPO4 glass free LTCC tape for microwave applications. J. Eur. Ceram. Soc. 2013, 33, 87–93.

(36) Rajesh, K. B.; Subba, R. T. AFM Studies on Surface Morphology, Topography, and Texture of Nanostructured Zinc Aluminium Oxide Thin Films. Dig. J. Nano. Bio. 2012, 7, 1881–1889.