Ultra-Low-Temperature Cofired Ceramic Substrates with Low Residual Carbon for Next-Generation Microwave Applications

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Supporting Information

ABSTRACT: High-temperature cofired ceramics and low-temperature cofired ceramics are important technologies in the fabrication of multilayer ceramic substrates for discrete devices, electronics packages, and telecommunications. However, there is a place and need for materials with lower fabrication temperatures to decrease the associated energy consumption. The present paper studies the feasibility of two ultra-low sintering temperature cofired ceramic materials, copper molybdate and copper molybdate–Ag2O, sinterable at 650 and 500 °C, respectively, for multilayer substrates using tape casting. The slurry composition developed uses environmentally friendly organics and a nontoxic binder and solvent. Additionally, the green cast tapes exhibit very low residual carbon (less than 5%) after sintering on analysis by X-ray photoelectron spectroscopy. The multilayer substrates show a permittivity value of about 8 with a low dielectric loss in the range of 10−5 to 10−4 in the frequency range of 2–10 GHz along with a low coefficient of thermal expansion in the range of 4–5 ppm/°C and good compatibility with an Al electrode. Thus, these proposed substrates have much promise, with good thermal, mechanical, and dielectric properties comparable to commercial substrates while also providing an energy and environment-friendly solution.

KEYWORDS: CuMoO₄, ULTCC, environmental friendly, tape casting, microwave substrates

INTRODUCTION

The ultra-low temperature cofired ceramic (ULTCC) technology has attracted interest recently because of its efficient energy-saving characteristics as compared to the conventional high-temperature cofired ceramic (HTCC) and low-temperature cofired ceramic (LTCC) technologies. The LTCC technology has been the standard technology for the integration of components and substrates for high-frequency applications for several decades. The LTCC technology enables the tape casting of dielectric materials for multilayer structures cofired with metal electrodes at a low temperature (~850 °C). For microwave applications, the used dielectric materials must have a low dielectric constant to increase the signal speed and a low dielectric loss to improve the frequency selectivity and the substrates are expected to meet the requirements imposed by growths in the technology. Compared to the printed circuit board materials, the ceramics can provide better thermal stability with a low thermal expansion coefficient and high thermal conductivity as well as a high integration potential to deliver good performance at high frequencies. In the case of the ULTCC technology, the sintering temperature is commonly much less than 700 °C, thus enabling lower energy consumption and easier integration of different materials into the same multilayer structure while at the same time being feasible for the same application areas as the LTCC technology. This technology provides an alternate path to solve the problem of energy crisis by conserving the existing energy used in the present technology rather than looking for a new source of energy and is a simple, easy, and cheap method.

In the last five years, several ULTCC compositions have been reported, but only a few of them have been explored for multilayer substrates through tape casting with a low burnout temperature, and our work is an attempt to examine this aspect. In this work, the focus is on the investigation of the environmentally friendly processing aspects of tape casting formulations, which are based on the nontoxic chemical solvent dimethyl carbonate (DMC) together with a biodegradable and biocompatible binder poly(propylene carbonate) (PPC). This binder system has been successfully used for tape casting of ULTCC compositions which have a lower burnout temperature. However, no studies on the carbon content of the cast tape before and after sintering have been reported. The carbon analysis gives information about the carbon emission during the processing as well as the residual carbon of the substrate. This is an important aspect of this
work because residual carbon can degrade the dielectric properties of the final product.

In our previous research, it was observed that the CuMoO₄ (CMO) ceramic exhibits good thermal and dielectric properties with an excellent densification of 96% by sintering at 650 °C, and its composite obtained by adding 0.5 wt % of Ag₂O was also a good candidate for substrate applications with a much lower sintering temperature of 500 °C. These studied ceramics also exhibited good chemical compatibility with aluminum, which can be used for embedded electrodes.16,17 Hence, our present work is an attempt to transform these ULTCC materials into ULTCC substrates by tape casting using an environmentally benign slurry composition and postprocessing techniques such as multilayer lamination, screen-printing, and cofiring, together with an investigation of their microstructural, dielectric, and thermal characteristics.

## MATERIALS AND METHODS

### Preparation of CMO Ceramic and CMO–Ag₂O Ceramic Composites

The CMO ceramic was prepared using the solid-state ceramic route by mixing stoichiometric amounts of high-purity CuO (>99%, Alfa Aesar) and MoO₃ (>99%, Alfa Aesar) in an ethanol medium for 12 h, with subsequent drying, followed by calcination at 550 °C. The CMO–Ag₂O (CMOA) ceramic composite was prepared by mixing 0.5 wt % of Ag₂O (99+, Alfa Aesar) into the CMO powder in the ethanol medium for 12 h, followed by drying.

### Preparation of CMO and CMOA Substrates by Tape Casting

To prepare the tape casting slurry, DMC (Sigma-Aldrich, St. Louis, MO) was used as a solvent with PPC (QPAC40, Empower Materials, New Castle, DE) as the binder and butyl benzyl phthalate (S160, Richard E. Mistler, Yardley, Pennsylvania) and polyethylene glycol (UCON 50HB2000, Richard E. Mistler) as the type I and type II plasticizers, respectively. Initially, the ceramic powder (CMO/CMOA) was mixed with DMC and PPC for 12 h by ball milling. The milling was continued for 24 h after the addition of the two plasticizers. The resultant slurry was cast on a silicone-coated Mylar carrier tape at a speed of 0.8 m/min using a laboratory caster (Unicaster 2000, Leeds, UK) and a 400 μm doctor blade. The dried green cast tape was peeled off for further processing. Aluminum ink (AL-PS1000, Applied Nanotech, Inc., USA) coifiable in the temperature range of 500–650 °C was screen-printed, followed by drying at room temperature for cofiring analysis, which is performed in the normal air atmosphere. For further characterization, five green cast tapes were stacked by vacuum lamination and isostatic pressing at 75 °C, 20 MPa for 10 min (Turbovac 450 STE vacuum machine and PTC IL-4008, Isostatic laminator). The stacked tapes were sintered at their respective sintering temperatures (CMO–650 °C/2 h; CMOA–500 °C/2 h) with an optimized sintering profile. The process flow chart is shown in Figure 1.

Two commercial LTCC tapes 9k7 (single green layer thickness 0.249 mm) and 951 (single green layer thickness 0.251 mm) (Dupont, US) were used to compare the X-ray photoelectron spectroscopy (XPS) measurement results. The four-layer stacks were sintered at 850 °C and had thicknesses of 0.822 and 0.864 mm, respectively.

### Characterization

The particle size and specific surface area of the ceramic powders were analyzed using the laser diffraction method (Beckman Coulter LS13320) and a particle surface area analyzer (G.W. Berg & Co. Micrometrics ASAP 2020), respectively. The tensile strength of the green cast tapes was measured by a tensile strength measurement setup (TST 350, Linkam Scientific Instruments Ltd., Survey, 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 burnout of the organic additives was studied using differential scanning calorimetric (DSC) measurement/thermogravimetric (TG) analysis (Netzsch 404 F3, Selb). The bulk density of the sintered samples was measured in an ethanol medium using the Archimedes method. The shrinkage was calculated from the dimensions of the laminated and sintered substrates. For XPS analysis, a Fisher Scientific, ESCALAB 250 Xi using the Mg Kα X-ray source was used, and the spectrometer was calibrated with reference energies of Au 4f7/2 (83.9 ± 0.1 eV) and Cu 2p3/2 (932.7 ± 0.1 eV). An angle of 90° was maintained between the surface and the analyzer (take-off angle) for the measurement. The C 1s peak with a binding energy at 284.8 eV corresponding to the surface contamination was used for binding energy calibration for the sample charging correction.18,19 The surface roughness of the green and sintered substrates were measured using an atomic force microscope (Veeco dimension 3100 130 SPM) operating at 10 MHz to 20 GHz, Rhode & Schwarz, ZVB20, Germany) and their temperature dependence by using a furnace (Espec SU-261) operating at 40 to 80 °C integrated with the microwave measurement setup. With this method, the total uncertainty of the determination of the relative permittivity was about 0.5% and the dielectric loss was in the range of 10⁻³. Microwave dielectric properties of the green and sintered substrates were measured by the split-post dielectric resonator (SPDR) (QWED, Poland) technique using a vector network analyzer (10 MHz to 20 GHz, Rhode & Schwarz, ZVB20, Germany) and their temperature dependence by using a furnace (Espec SU-261) operating at 40 to 80 °C integrated with the microwave measurement setup. With this method, the total uncertainty of the determination of the relative permittivity was about 0.5% and the dielectric loss was in the range of 10⁻³. Cylindrical samples of diameter 8 mm and thickness 15 mm were used to measure the linear coefficient of thermal expansion (CTE) using a dilatometer (NETZSCH DIL 402 PC/4, Germany).

## RESULTS AND DISCUSSION

### Tape Casting and Lamination

The CMO and CMOA powders had an average particle size in the range of 2.3–2.5 μm with a surface area of ~3.5 m²/g. These ceramic powder properties are in the range considered desirable to obtain an optimized slurry composition for tape casting,20 as they have a considerable influence on the green cast tapes by determining their quality, strength, and flexibility.21 The surface area determines the interaction of the ceramic with the organic additives, and the moderately small particle size helps in the uniform dispersion of the fillers in the slurry. Because CMO and CMOA show a similar particle size and density, the slurry composition (Table 1) used is same for both of them.

The chemical nature of the organic ingredients used in the tape casting slurry has an effect on the surrounding environment. Although water would be environmentally the ideal solvent, it has many disadvantages in tape casting because of its slow evaporation rate and agglomeration, etc.22 The
the formation of a new compound, Cu$_2$Ag$_2$(MoO$_4$)$_3$, because of the reaction of Ag obtained by the decomposition of Ag$_2$O.

Also, exothermic peaks could be observed around 200°C and 400°C in the DSC: these were due to the strong decomposition of the organics. Figure 3f,g gives information on the TG of the green cast tapes where a weight loss of about 10% occurred below 250°C. The presence of ceramic is evident as it leaves a low residue after burnout and has a low burnout temperature.

Sintering and Cofiring. The TG/DSC analysis of the green cast tapes shown in Figure 2 gives an overall idea about the burnout temperature of the organic additives. It is necessary to annihilate the organic additives before sintering to prevent their effects on the shrinkage or electrical properties of the sintered substrates. A managed burnout also minimizes defects such as delamination, cracking, and anisotropic shrinkage during sintering.

It was observed that the weight loss was slow for both the tapes up to 150°C with a sharp increase to about 10% in the temperature range of 150–250°C, corresponding to the removal of the binder and plasticizer. Also, exothermic peaks could be observed around 200–230°C in the DSC: these were due to the strong decomposition of the low-molecular-weight organics such as the binder and plasticizer. The TG and DSC curves of both green cast tapes were similar because the type and amount of organics used in the tapes were the same. However, the small peak at around 400°C observed in the DSC of the CMOA tape was due to the formation of a new compound, Cu$_2$Ag$_2$(MoO$_4$)$_3$, because of the reaction of Ag obtained by the decomposition of Ag$_2$O with CMO and was expected to melt around 500°C, as we have reported earlier.27

Figure 3. TG curve of ingredients used in the present tape casting composition (a–d), slurry without ceramic (e), and green cast tapes [CMO (f) and CMOA (g)].

TG analysis of the individual constituents, slurry without and slurry with the ceramic, was done to gain more detailed information on the thermal decompositions (Figure 3). It is clear that the solvent was removed first below 100°C (Figure 3a). After that the binder removal started below 200°C and ended at about 300°C (Figure 3b), when the plasticizers were also removed (Figure 3c,d). The removal phase of the individual components from the slurry without the ceramics are clearly visible from Figure 3e, where a weight loss of 50% occurred below 100°C (solvent) and the rest was removed between 200 and 300°C (because of the binder and plasticizers). Figure 3f,g gives information on the TG of the green cast tapes where a weight loss of about 10% occurred below 250°C. The presence of ceramic is evident as it corresponds to the decrease in the decomposition temperature as compared to the individual constituents shown in Figure 3. The green cast tapes used were dried, and hence, a low weight loss below 100°C owing to the solvent was observed. It is also clear from Figure 3a–e that the weight loss was almost 100%, indicating a high level of burnout of the organics. However, it was difficult to achieve a complete residual-free tape after sintering because of the trapping of the organics, and the corresponding low residual carbon content is further confirmed by XPS.

On the basis of these results, the sintering profile of the substrates was carefully optimized by varying the sintering rates and dwell time to obtain a densified tape with a uniform microstructure affecting the performance of the final module.22,30 Figure S1 in the Supporting Information gives the effect of sintering rate and intermediate dwell time upon densification of the CMO substrate. A faster heating rate with a minimum intermediate dwell time increases the densification, which corresponds to the fast grain growth. Figure 4 shows the optimized sintering profile of the CMO and CMOA substrates. Both substrates had the same sintering profile with a difference only in their sintering temperature because the type and amount of organic additives used were the same. The removal

Table 1. Slurry Composition for the Tape Casting

| ingredients       | materials            | content (wt %) |
|-------------------|----------------------|----------------|
| ceramic powder    | CMO/CMOA             | 50             |
| binder            | PPC—poly(propylene carbonate) | 3.6 |
| plasticizer-I     | BBP—butyl benzyl phthalate | 1.2 |
| plasticizer-II    | PEG—polyethylene glycol | 1.2 |
| solvent           | DMC—dimethyl carbonate | 44 |

Figure 2. TG/DSC curve of CMO and CMOA green cast tapes (inset figure: photographic images of the green cast tapes).
of the organic components was ensured by 1 h dwell time at 350 °C. CMO was well sintered with 95% densification after sintering at 650 °C and about the same value was achieved in CMOA (96%) with a lower sintering temperature (500 °C) because of the formation of a low melting compound.17 These densification values are almost the same as those reported earlier for the bulk samples.16,17 Five-layer stacks of sintered CMO and CMOA substrates were produced with thicknesses of 0.430 and 0.450 mm, respectively. The sintered stacks shown in the inset of Figure 4 were hard and robust with a deep green color.

The sintered substrates had shrinkages of 15 ± 1, 14 ± 1, and 12 ± 2%, respectively, in the X, Y, and Z directions for the CMO stacks and 16.5 ± 1, 16.0 ± 1, and 14 ± 2%, respectively, for CMOA, which are in the desired range for commercial production.31 Shrinkage is important for practical substrate applications as it restricts the substrate size that can be processed, which may create complexity in processing as well as in the embedded passive components.32

XPS surface analysis was performed on the green and sintered substrates (CMO and CMOA) to obtain more information on the residual carbon, and the results were compared with the commercial LTCC substrates 9k7 and 951.18,19 The survey spectra of the green and sintered 9k7, 951, CMO, and CMOA substrates shown in Figure 5a,b provide an insight into the carbon content of these substrates. Highly intense C 1s peaks which are seen for the green substrates (Figure 5a) become barely visible in the spectra of the sintered samples (Figure 5b). High-resolution C 1s spectra of the green and sintered substrates are given as Figure S2 in the Supporting Information. The decrease in the carbon content with sintering is more evident from Table 2, which presents the atomic wt %. It is clear that the carbon content was less than 5 wt % in both the substrates after sintering and can also be accounted within the error limit owing to the surface carbon atoms because of the surface roughness of the substrate compared with the XPS analysis depth. Hence, the results are in agreement with the TG analysis depicted in Figure 3. The results are well in line with the results for the commercial LTCC substrates.

Moreover, the carbon content in the ULTCC green laminates was lower and possibly corresponds to the composition as well as the molecular weight of the organics used to obtain a lower burnout temperature. This in turn can reduce the carbon burnout, which is an added advantage of these ULTCC compositions. These results indicate that the composition used in the present work provides much less carbon burnout as well as less residual carbon, which is both a necessity and a great advantage to the future electronics and communication industry.

| sample name | carbon atomic wt % ± 1.5% |
|-------------|--------------------------|
|             | green | sintered |
| CMO         | 40.2  | 4.5     |
| CMOA        | 44.4  | 4.3     |
| 951         | 65.2  | 5.1     |
| 9k7         | 75.8  | 3.0     |

Table 2. Atomic wt % of Carbon in the Green and Sintered Commercial 9k7 and 951 and CMO and CMOA Substrates
Figure 6 presents the high-resolution Cu 2p, Mo 3d, Ag 3d, and O 1s spectra and the curve level fitting observed for the sintered CMOA ceramic in which the Cu 2p, Mo 3d, and O 1s spectra are similar to those of CMO as it is the major phase. The high-resolution Cu 2p (Figure 6a) shows the spin−orbital splitting components of 2p₃/₂ and 2p₁/₂ by about 19.98 eV, while the full width at half-maximum (fwhm) values of the corresponding peaks are 3.11 and 2.86 eV, respectively. Strong satellite Cu²⁺ peaks are also observed, indicating the oxidation state of Cu. The high-resolution spectrum of Mo 3d (Figure 6b) shows the spin−orbital splitting of 3d⁵/₂ and 3d³/₂ having an orbital split of about 3.15 eV and fwhm of 0.92 and 0.93 eV, respectively. The high-resolution Ag 3d spectrum (Figure 6c) exhibits the spin−orbital splitting of 3d⁵/₂ and 3d³/₂ by about 6 eV with fwhm of 1.25 and 1.24 eV, respectively. This further confirms the presence of Ag in CMO, which is difficult to be observed because of its low amount. The O 1s photoelectron peak at about 530 eV depicted in Figure 6d gives information on the oxide ion in the sintered substrate with different chemical bondings and possibly corresponds to the bridging oxygen atoms, showing good agreement with reported values. The fitted binding energies of Cu 2p, Mo 3d, Ag 3d, and O 1s are given in the Supporting Information (Table S1).

Surface Analysis and Microstructure. The surface quality of the tapes and sintered substrates is critical for
microelectronic applications because it influences the accuracy of the printed electrodes and their performance through the skin depth at high frequencies. Two-dimensional (2D) atomic force microscopy (AFM) images of the green and sintered substrates shown in Figure 7 and the corresponding three-dimensional (3D) images shown in the Supporting Information (Figure S3) indicate that the grains were distributed in the form of hills and valleys. It is also clear that the grains were larger after sintering, which indicates grain growth as well as the removal of organics. Analysis of the topography scans of the sample surfaces provides the roughness parameters, which includes average roughness ($R_a$), root-mean-square roughness (rms), skewness (skew), and kurtosis. The roughness parameters of the tapes are given in Table 3. The CMO and CMOA green tapes exhibited average surface roughnesses of $257 \pm 11$ and $302 \pm 10\%$ nm, respectively, which is reported to be comparable to commercial LTCC tapes. The skew value measures the asymmetry of the surfaces, and both the green tapes had negative skew values of $-0.6$ and $-0.1$, which indicate that they had good bearing surfaces and were suitable for device fabrication. The negative value indicates that the surfaces had a longer tail distribution below the reference plane, that is, the valleys were predominant on the surface of the tapes, which is also evident from the 2D and 3D images. Kurtosis measures the distribution of the spikes above and below the mean line/plane. The green tapes had a kurtosis of $0.9 - 0.7$, meaning that the surface was flatter and is referred to as platykurtic. The kurtosis value indicates that the surface was not spiky but bumpy, which is in agreement with the images. Similarly, for the sintered CMO and CMOA substrates, the average surface roughness decreased to $157 \pm 6$ and $172 \pm 5\%$ nm, respectively. The low average surface roughness may correspond to the uniformity of the surface obtained by sintering after the removal of all organic additives as well as to the increased densification. The positive skew values of $0.6$ (CMO) and $0.3$ (CMOA) indicate the brittle nature of the sintered tapes. Similar to the green substrates, the sintered substrates also had a bumpy surface rather than spikes as their kurtosis value was less than $3$ (0.4 and 0.1), which is also evident from the images.

A more detailed microstructure of the green and sintered substrates was obtained from the SEM image shown in the Supporting Information and Figures S4 and 8. The microstructure of the green CMO and CMOA substrates with different magnifications shown in Figure S4 indicated that the green tape appeared to be dense with little porosity as the polymer binder binds the particles together during thermolamination. The morphology of the thermo-laminated stack revealed that the thermo-lamination conditions resulted in the merging of individual layers into a homogeneous coherent body during sintering. This may correspond to the good slurry composition. The microstructure of the sintered and cofired substrates with Al ink is presented in Figure 8. The sintered tape microstructure appeared to be dense and homogeneous with the removal of all organic additives. Substantial grain growth was observed and was tightly packed with good densification, which is clear from the backscattered secondary electron images shown in Figure 8a,b. Energy-dispersive X-ray spectrum (EDS) line map shown in Figure 8c,d further confirmed that both substrates were free from all organics. The cofired CMO sintered substrate consisted solely of Cu, Mo, and O$_2$, while the presence of a small amount of Ag was observed in the cofired CMOA substrate, as expected.

Aluminum powder does not react with the CMO ceramic as well as with CMOA on sintering at 650 and 500 °C,

### Table 3. Surface Quality of the Green and Sintered Substrates

| Surface parameter | Green tape | Sintered tape |
|-------------------|------------|--------------|
| $R_a$ (nm)        | 257        | 157          |
| rms (nm)          | 329        | 202          |
| skew              | $-0.6$     | 0.6          |
| kurtosis          | 0.9        | 0.4          |

![Figure 8](image_url). BSE images of sintered (a) CMO and (b) CMOA substrates, cofired, and (c) CMO and (d) CMOA substrates with EDS line mapping of the ceramic–metal interface.
respective quantities as reported in our earlier studies. As evident from the backscattered electron (BSE) images and EDS line mapping of the ceramic–metal interface shown in Figure 8c,d, no reaction layer as well as no diffusion of the electrode into the ceramic was observed. These results indicate the chemical compatibility between the electrode and the ceramic in the multilayer ceramic substrate.

**Microwave Dielectric Properties of Substrates.** The dielectric properties of the substrate play a vital role in governing the signal transmission, that is, in determining the circuit speed because it acts as a support material for active and passive devices and for the interconnecting conductors that make up the substantial subsystems. The dielectric properties measured at gigahertz frequencies are of great interest because of the active development of mobile communications. The Supporting Information (Table S2) represents the microwave dielectric properties of green substrates (single-layer and multilayer vacuum laminated) while those of substrates developed in the present work had comparable dielectric properties with those of CMO and CMOA substrates. All these observations are well in line with the results achieved for the bulk samples. These dielectric properties indicate the potential of the developed substrate materials for microwave substrate applications at high frequencies. Figure 9 represents the variation of $\varepsilon_r$, and $\tan \delta$ of the sintered CMO and CMOA substrates over the measured temperature range of $-40$ to $80 ^{\circ}C$ at 9.9 GHz. The relative permittivity increased with the temperature as expected. For both materials, $\varepsilon_r$ increased almost linearly from 7.4 to 7.6 (CMO) and from 7.6 to 7.7 (CMOA) without any abnormality with $\tau_f$ values of 159 and 149 ppm/$^{\circ}C$, respectively. The thermal stability of these substrates could be further improved in the future by adding suitable additives. The $\tan \delta$ showed some variation with increasing temperature. However, both substrates exhibited a low dielectric loss in the range of $10^{-4}$ over the entire measured temperature range. The dielectric properties of these substrates were compared with a commercial LTCC DuPont 9k7 sintered at 850 $^{\circ}C$ and measured by the same SPDR measuring technique, which exhibited $\varepsilon_r = 7.4$, $\tan \delta = 11 \times 10^{-4}$, and $\tau_f = 159$ ppm/$^{\circ}C$ ($-40$ to $80 ^{\circ}C$) at 9.9 GHz. The substrates developed in the present work had comparable $\varepsilon_r$ and $\tau_f$ with lower values of dielectric loss and sintering temperature than the commercial substrates. This highlights the potential of these ULTCC substrates for future micro-electronic substrate applications as an environmentally friendly replacement for LTCC.

**CTE of Substrates.** The sintered CMO and CMOA substrates exhibited average low CTE values of 4.1 and 4.6 ppm/$^{\circ}C$, respectively, in the temperature range of 25–300 $^{\circ}C$ being close to the CTE value of Si (4 ppm/$^{\circ}C$), which enables the integration of these substrates with the semiconductor devices used in the electronics industry. This supports the prospect of these selected materials (CMO and CMOA) for device-level applications.

To highlight the importance of the present work, a comparison in the properties of some commercial substrates (LTCC) and reported HTCC, LTCC, and ULTCC substrates is given in Table 5. It is clear from the table that the ULTCC substrates can achieve properties comparable to those of HTCC and LTCC substrates while having a very low sintering temperature. Moreover, a significant reduction in the sintering temperature of ULTCC systems in comparison with HTCC and LTCC fabrication temperatures further points to a future low-cost and sustainable fabrication technology. The considerable reduction in the fabrication temperature reduces the CO$_2$ emission to some extent. Also, it should be noted that only very few ULTCCs have been used to realize substrates by tape casting as described in this work. The table emphasizes the significance of the present work in the growth of future substrate applications in the high-frequency ranges.

## CONCLUSIONS

The ULTCC CMO and CMOA ceramic substrates were prepared by tape casting using environmentally friendly slurry
compositions, followed by sintering at 650 and 500 °C, respectively. The results showed that the developed slurry composition was feasible for these ULTCCs with completed burnout below 300 °C, leaving very low residual carbon (less than 5%). This was at the same level as measured for the commercial LTCCs. The densification of both ceramics (≥95%) was close to that measured for the bulk samples, as were the dielectric properties (\( \epsilon_r = 8, \tan \delta \times 10^{-4} \) at 2–10 GHz). Moreover, the substrates had a low CTE of 10 ppm/°C, close to that of the Si semiconductor, and could be cofired with embedded Al electrodes. Hence, the results show that the developed substrates fabricated by an environmentally friendly approach fulfill the demands of low residual carbon and also enable the fabrication of multilayer substrates with good mechanical, thermal, and dielectric properties.

### Table 5. Comparison of the Properties of Some of the Commercial and Reported HTCC, LTCC, and ULTCC Substrates with Those of Our Present Work

| commercial and research reports on microwave substrates | S.T. °C | \( R_s \) (nm) | \( \epsilon_r \) | \( \tan \delta \times 10^{-4} \) | Frequency | CTE (ppm/°C) |
|------------------------------------------------------|--------|----------------|---------|----------------|-----------|--------------|
| **microwave properties**                              |        |                |         |                |           |              |
| Al\(_2\)O\(_3\) \(^{45}\)                           | 1700   | 9.5–9.9        | 1–4     | 10 GHz         | 6–8       |
| AlN \(^{43}\)                                        | 1900   | 8.0–9.2        | 10      | 1 MHz          | 4.2–5.8   |
| Zr\(_2\)Si\(_3\)O\(_9\) \(^{43}\)                  | 1600   | 9.2            | 3       | 5 GHz          | −2.5      |
| ZAT \(^{29}\)                                        | 1150   | 9.6            | 8.4     | 5 GHz          | 6.59      |
| Sr\(_2\)ZnTeO\(_6\) (SZT)–5 wt % of ZBPT \(^{37}\)  | 900    | 154            | 12      | 5 GHz          | 7.09      |
| Bi\(_4\)(SiO\(_4\)) \(^{28}\)                      | 900    | 320            | 13.3    | 15 GHz         |           |
| Li\(_2\)MgPO\(_4\) \(^{47}\)                        | 900    | 250            | 6.4     | 5 GHz          | 10.5      |
| indialite/cordierite glass–10 wt % Bi\(_2\)O\(_3\) \(^{46}\) | 900    | 6.1            | 1       | 1 MHz          | 3.5       |
| SrCu\(_3\)O\(_7\)+5 wt % LMZBS \(^{45}\)           | 900    | 560            | 4.8     | 5 GHz          |           |
| Li\(_2\)ZnTi\(_3\)O\(_8\) (LZT)–1 wt % LMZBS \(^{46}\) | 875    | 151            | 21.9    | 5 GHz          | 11.97     |
| Sr\(_2\)ZnSi\(_2\)O\(_9\)+15 wt % LMZBS \(^{47}\)   | 875    |                | 21.5    | 10 GHz         |           |
| DuPont 9k\(^{29}\)present work                       | 850    | 7.4            | 11      | 9.9 GHz        |           |
| Ferro A6 \(^{55}\)                                   | 850    | 5.9            | 20      | 3 GHz          | 7         |
| 40 Al\(_2\)O\(_3\)+60 BBSZ \(^{48}\)                | 850    | 299            | 10.9    | 5 GHz          | 6.9       |
| 40 Al\(_2\)O\(_3\)+60 LABS \(^{49}\)                | 775    | 293            | 4.7     | 5 GHz          | 5.1       |
| Li\(_2\)WO\(_4\) \(^{10}\)                          | 650    | 182            | 5.4     | 0.92           | 16        |
| silicon dioxide–filled zinc borate glass \(^{9}\)   | 650    |                | 6.4     | 1 MHz          |           |
| Zn\(_2\)Te\(_2\)O\(_6\)+titanium dioxide \(^{11}\) | 650    |                | 17.3    | 60 GHz         |           |
| CMO \(^{\text{present work}}\)                      | 650    | 257            | 7.67    | 0.73           | 2.4 GHz   | 4.1         |
| CMO \(^{\text{present work}}\)                      | 650    |                | 7.60    | 1.8            | 5.1 GHz   |
|                                                        |        |                | 7.54    | 2.42           | 9.9 GHz   |
|                                                        |        |                | 7.68    | 4.22           | 9.9 GHz   |

“S.T.—sintering temperature. \(^{b}\)ZAT—0.83ZnAl\(_2\)O\(_4\)+0.17TiO\(_2\) (in moles). \(^{c}\)ZBPT—10 mol % ZnO–2 mol % B\(_2\)O\(_3\)–8 mol % P\(_2\)O\(_5\)–80 mol % TeO\(_2\). \(^{d}\)LMZBS—20Li\(_2\)O/20MgO/20ZnO/20B\(_2\)O\(_3\)/20SiO\(_2\). \(^{e}\)BBSZ—35Bi\(_2\)O\(_3\)/32ZnO/27B\(_2\)O\(_3\)/6SiO\(_2\). \(^{f}\)LABS—40Li\(_2\)O/10Al\(_2\)O\(_3\)/30B\(_2\)O\(_3\)/20SiO\(_2\).

binding energy of Cu 2p, Mo 3d, Ag 3d, and O 1s in electronvolts; and microwave dielectric properties of the green tapes (PDF)

### 2 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b07272.

Sintering profile optimization of the CMO substrate; high-resolution C 1s spectrum of green and sintered substrates (9k\(^{7}\), 951, CMO, and CMOA); 3D AFM images of green and sintered CMO and CMOA substrates; microstructure of green laminated CMO and CMOA substrates at different magnifications; and microwave dielectric properties of the substrates fabricated by an environmentally friendly approach fulfill the demands of low residual carbon and also enable the fabrication of multilayer substrates with good mechanical, thermal, and dielectric properties.

### ASSOCIATED CONTENT

* Supporting Information

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Sintering profile optimization of the CMO substrate; high-resolution C 1s spectrum of green and sintered substrates (9k\(^{7}\), 951, CMO, and CMOA); 3D AFM images of green and sintered CMO and CMOA substrates; microstructure of green laminated CMO and CMOA substrates at different magnifications; and microwave dielectric properties of the substrates fabricated by an environmentally friendly approach fulfill the demands of low residual carbon and also enable the fabrication of multilayer substrates with good mechanical, thermal, and dielectric properties.

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