Tape Casting and Dielectric Properties of Zn$_2$Te$_3$O$_8$-Based Ceramics with an Ultra-Low Sintering Temperature

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The suitability of dielectric ceramics made of zinc tellurate (Zn$_2$Te$_3$O$_8$) and titanium dioxide (TiO$_2$) with an ultra-low sintering temperature (650°C) for tape casting and thus for the multimodule technique with Al electrodes was investigated. The properties of the tape before and after sintering as well as the amount of organic additives for the casting process and a thermal analysis of the tape up to 1000°C are reported. In addition, electrodes on a multilayer module made on stacked tapes were prepared using Al paste and postfiring, followed by relative permittivity and loss tangent measurements to verify the electrical performance of the whole structure. The dielectric properties of the stacked module without any electrodes were also measured. The results show that the composition is well suited for the tape process but extra care should be taken especially with the proper sintering temperature for optimized electrical performance.

Introduction

Low-temperature cofired ceramics (LTCC) have been widely studied for cost-effective, high-performance, reliable multilayer microwave devices composed of dielectric ceramic layers and embedded metal electrodes.$^{1-4}$ In this technique, dielectric layers are commonly fabricated by tape casting, followed by screen printing of the electrodes, lamination, and firing.$^{1,5-7}$ Cast tapes are fairly thin, flat, and self-supporting, with the thickness generally ranging from 0.010 to 1.27 mm.$^{6,7}$ For cofiring, the sintering temperature of the LTCC tapes must be lower than the melting point of the metal electrodes (960°C in the case of Ag electrodes).$^1$ However, to enable wide and inexpensive
multimaterial module integration of dielectric thick films with, for example, a silicon wafer could offer, especially, advantages for applications that enable novel use of high-quality ceramics, such as in integrated MEMS applications. For these reasons, ceramics with ultra-low sintering temperature suitable for tape casting are needed.

Recently, a number of glass-free dielectric tellurium-based materials with an ultra-low sintering temperature (500–750°C) have been reported. Subodh and Sebastian reported the microwave dielectric properties of a low-temperature-sintered (585°C) Zn$_2$Te$_3$O$_8$ ceramic with an $\epsilon_r$ of 16.2, a quality factor $Q_e\times f$ of 66,000 at 4.97 GHz and a temperature coefficient of resonant frequency ($\tau_f$) of $-60$ ppm/°C. Zn$_2$Te$_3$O$_8$ ceramics with 4 wt% TiO$_2$ showed a reasonably good $\tau_f$ of $-8.7$ ppm/°C with a $Q_e\times f$ of 27,000 GHz, and an $\epsilon_r$ of 19.3. However, these materials generally react with Ag and thus a metal electrode made of Al has been proposed, an option making these ceramics especially interesting for semiconductor devices where Al is also commonly used for metallizations. The main aim of this work is to study the suitability of TiO$_2$-doped Zn$_2$Te$_3$O$_8$ ceramics (ZTT) for tape casting. The dielectric properties of stacked and fired tapes with and without Al electrodes at low and high frequencies as well as the tape properties before and after sintering are presented.

**Experimental Procedure**

**Powder and Green Tape Preparation**

Zn$_2$Te$_3$O$_8$ powder with 4 wt% of TiO$_2$ was prepared by a solid-state ceramic route using high-purity ZnO, TeO$_2$ (99 %), and TiO$_2$ (99.9 %, Aldrich Chemical, Milwaukee, WI) as the starting materials. In order to estimate the suitable slurry composition, the specific surface area (SSA) of the ceramic powder was measured using a BET analyzer (OmniSorb 360CX, Coulter Electronics, Luton, U.K.). For the final adjustment, the ceramic powder was mixed with solvents and a dispersant in a ball mill for 24 h, and after addition of plasticizers and a binder, mixing was continued for another 24 h. The solvents used were ethanol and xylene (Aldrich Chemical), the dispersant was Blown Z-3 Menhaden fish oil, the binder was polyvinyl butyral (B98), and the plasticizers were butyl benzy1 phthalate (S160) and polyalkylene glycol (UCON 50HB2000). This slurry composition is denoted as a PVB-based binder system. The average molecular weight of UCON 50HB2000 is 2660 g/mol. All the organic additives were supplied by Richard E. Mistler, Yardley, PA. The tape casting was carried out with a laboratory caster (Unicaster 2000, Leeds, U.K.) with a single 300-μm-wide doctor blade and a casting speed of 0.8 m/min.

**Characterization**

The surface roughness of the green and sintered tapes was measured by Dektak ST (Sloan Technology, Santa Barbara, CA). The microstructures of the green tape and the sintered multilayers were studied with a scanning electron microscope (SEM, JEOL JEM-6400, Tokyo, Japan). The phase purity of ZTT ceramics was studied by the X-ray diffraction technique using CuKα radiation (Phillips X-ray diffractometer, Eindhoven, The Netherlands). The lamination temperature, pressure, and dwell time were 70°C, 17 MPa, and 20–30 min for stacks with 10–18 layers. Shrinkage was estimated from the dimensions of the laminated and fired tapes. Dimensions were measured in micrometers, with an accuracy of 0.001 mm. The heat flow and weight change of the tape were measured using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in the temperature range of 20–1000°C (Netzsch models STA 409PC and QMS 403C, Selb, Germany). The heating rate for the ZTT tape was 20°C/min and the mass of the sample was 32,900 mg. The heating rate for the ZTT powder was 20°C/min. The mass of the sample was 35,700 mg.

Aluminum electrodes (2591-A, ESL, King of Prussia, PA) were screen printed on the surface of the sintered multilayer block, followed by postfiring in the temperature range of 550–600°C (30 min). The thickness of the electrode after firing was 25 μm.

Relative permittivity and dielectric loss in the frequency range of 1 kHz–1 MHz were measured with a precision LCR meter (HP4284A Hewlett-Packard, Palo Alto, CA) and at 1 GHz with an RF Impedance/Material Analyzer (Agilent E 4991A, Palo Alto, CA). Samples for the measurements were prepared by laser cutting the laminate (10 layers) into circular-shaped samples (diameter = 10, thickness < 1 mm), followed by sintering at 650–660°C for 4 h. Conductive paint (Ag) was used as electrodes for the LCR samples (Electrolube SCP, Derbyshire, U.K.).
The microwave dielectric properties of the sample were measured using a cavity perturbation technique with an HP 8510 C Network Analyzer (Agilent Technologies). This technique is widely used to determine the dielectric characterization of thin samples with low and medium dielectric loss. A sample with dimensions of 25 mm x 3 mm x 1 mm was laser cut from a laminate with 18 layers. The validity of the experimental setup was ascertained by measuring the standard RT Duroid substrates. The experimental error was found to be less than 2% and 1.3% of the relative permittivity and dielectric loss, respectively.

Results and Discussion

The method of optimizing the slurry composition was based on a previous report and additional experiments for very different kinds of ceramic powders with the same organic PVB-based system as that presented in the experimental part. Common factors for a good tape are that the casting process yields green tapes with a high density (>50% compared with the sintered full density) and are easy to handle and laminate. A relationship for the amount of organic PVB-based system as a function of SSA of the ceramic powder is shown in Fig. 1 according to our experiments for different ceramic powders (piezoelectric, ferroelectric, and varistor). These results show that the SSA value can thus be utilized for the rough estimation of the desired amounts of dispersant and binder in the tape-casting slurry. Additionally, it can be seen that with small SSA values, the amount of binder can be varied in a moderately wide range, while the amount of dispersant should be maintained at the level of ~1 wt% compared with the amount of ceramic powder.

For the final slurry composition, lamination tests and density measurements were also performed. The lamination of the tapes followed the well-known procedure suitable for PVB-based binder systems with a temperature, pressure, and dwell time of 70°C, 17 MPa, and 20 min, respectively, for stacks with 10 layers. The thickness of the tape was ~80 μm and its surface roughness (RA) was 0.1 μm before lamination. The selected slurry composition is presented in Table I and also marked in Fig. 1. The measured SSA value of 1.28 m²/g for the ZTT enabled a moderately low amount of binder to produce high sintered density. The green density of the laminated stack was 3.4 g/cm³, being approximately 69% when compared with the density of sintered ceramics (4.9 g/cm³). The TGA/DSC results of the high-temperature treatments were analyzed (Fig. 2). Melting of the organic additives starts at a

<table>
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<tr>
<th>Powder</th>
<th>Ethanol+</th>
<th>Xylene</th>
<th>Fish oil</th>
<th>B98</th>
<th>S160</th>
<th>UCON</th>
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<tr>
<td>Zn2Te3O8</td>
<td>62.9</td>
<td>15.4</td>
<td>1.3</td>
<td>3.4</td>
<td>0.8</td>
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Fig. 1. Amount of dispersant and amount of binder as a function of specific surface area (SSA) for several tape-casting slurries.

Fig. 2. Thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) diagram of a green ZT (Zn2Te3O8+4 wt% TiO2) tape (inset TGA/DSC of ZT ceramics).
temperature of 284°C and burning at a temperature of 320°C. Thus, in the 200–600°C range, the heating rate of the stacks was maintained at a level of 1°C/min to ensure the integrity of the microstructure without extra carbon contamination. The endothermic peak at 685°C is due to the melting of the ZTT ceramics, with similar behavior in the inset figure. The bulk ZTT specimen also melted when sintered above 680°C. Hence, the sintering temperature of the stacks was kept below this temperature level.

Figure 3 shows the density of the sintered tape stacks (10 layers) as a function of the sintering temperature. The results show that when the sintering temperature increases, the density of the stacked tapes increases, and reaches a maximum at 660°C. The error values in the measured densities were <0.5%. The decrease in density at higher temperatures can be attributed to partial melting of the specimen, which is supported by Fig. 2.

When sintered at 660°C with a dwell time of 4 h, linear shrinkage in the plane of the layer was 14.6% and in the thickness was 13.7%. Weight loss during sintering was 8.9%, consisting of a burnout of organic additives along with residual solvents. XRD profiles of pure Zn2Te3O8 ceramics and the sintered ZTT tape are presented in Figs. 4a and b, respectively. The optimized sintering temperature for Zn2Te3O8 ceramics for the best properties was 585°C and hence the XRD was recorded from samples sintered at that temperature. Pure Zn2Te3O8 ceramics melt as the sintering temperature is increased above 600°C. A ZT (Zn2Te3O8 + 4 wt% TiO2) tape sample for XRD was sintered at 660°C. The lattice parameters obtained for pure Zn2Te3O8 (ICDD file no. 44-241) ceramics are \( a = 12.97\,\text{Å} \), \( b = 5.19\,\text{Å} \), \( c = 11.78\,\text{Å} \), and \( \beta = 99.62^\circ \), which are in good agreement with the earlier report.20 However, the addition of 4 wt% TiO2 to the Zn2Te3O8 ceramics led to the formation of TiTe3O8 (ICDD file no. 24-1348). TiTe3O8 peaks are marked with T in Fig. 4b. Otherwise, the XRD profile of the sintered tape is similar to the profile of pure Zn2Te3O8 ceramics.

![Fig. 3. Density of the stacked tapes as a function of sintering temperature.](image)

![Fig. 4. XRD profile of (a) pure Zn2Te3O8 ceramics sintered at 585°C and (b) tape of Zn2Te3O8 + 4 wt% TiO2 sintered at 660°C. Peaks corresponding to the TiTe3O8 phase are marked with T.](image)
The microstructure of the ZTT green tape, Fig. 5a, shows that the tape is uniform and consists mainly of particles with a particle size of around 1 μm. The average particle sizes were estimated from SEM micrographs using a computer program. The microstructure of sintered (660°C) and thermally etched ZTT ceramics (Fig. 5b) shows that grain growth has occurred during sintering, but, mainly, the particles are still smaller than 5 μm. Thus, the surface quality decreased slightly during sintering (RA ~ 0.7 μm). The density of the tape is visibly improved during sintered as confirmed by the densities reported in Fig. 3. Figure 5c shows the microstructure of a cross section of the ZTT ceramics and Al electrodes where the ZTT ceramics are sintered at 660°C. It can be noted that no chemical reaction or diffusion has occurred between the ceramics and the metal, as evidenced by the SEM. Additionally, the tapes formed a monolithic multilayer without any trace of lamination. This confirms the practical applicability of the ZTT tapes for multilayer modules. However, in order to use Al as internal electrodes and cofire it with ZTT, there is a need to further decrease the sintering temperature of ZTT or use an aluminum paste that withstands a longer period above 600°C.

Figure 6 shows the variation in the dielectric properties of the ZTT multilayer (10 layers, sintered at 660°C) at low frequencies. The main effect here is the space-charge polarization. At 1 MHz, the sintered tape showed a permittivity of 18.2 and a dielectric loss of

![Fig. 5. Surface morphology of (a) green tape ZT (Zn₂Te₃O₈+4 wt% TiO₂), (b) tape sintered at 660°C, and (c) cross-sectional view of the interface between Al and ZT (660°C). Al is sintered at 600°C for 30 min.](image)

![Fig. 6. Relative permittivity and dielectric loss at low frequencies for Zn₂Te₃O₈+4 wt% TiO₂ sintered at 660°C.](image)
0.006. The variation in relative permittivity and loss tangent as a function of temperature is shown in Fig. 7. It can be noted that as the temperature increases, the loss tangent increases slightly. However, the relative permittivity remains nearly a constant.

The microwave dielectric properties of the stacked and sintered tapes using a cavity perturbation technique at higher frequencies (7 GHz) showed a relative permittivity of 17.3 (± 0.5) and a low dielectric loss of 0.006 (4). One must note, however, that this material is very sensitive to the sintering temperature. Its relative permittivity increases slightly. However, the relative permittivity remains nearly a constant.

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Conclusions

The results showed that tape casting of zinc tellurate (Zn$_2$Te$_3$O$_8$) with 4 wt% of TiO$_2$ and a low amount of binder could produce tapes suitable for stacked structures having a high density (4.9 g/cm$^3$) when sintered at 660°C. However, the measured dielectric, density, and microstructure properties verified that this ceramic material is very sensitive to the sintering temperature. The research related to Al electrodes showed that they could be integrated successfully by the postfiring process. To enable their cofiring, another Al paste suitable for firing at 660°C, however, should be tested.

References