Low temperature sintered ZnTiO$_3$ dielectric ceramics with temperature coefficient of dielectric constant near zero

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Abstract

ZnTiO$_3$ compound is an attractive dielectric ceramics owing to its interesting dielectric properties in high frequency range ($\varepsilon_r = 19$, $Q\times f = 30,000\text{GHz}$, $\tau_\varepsilon \approx +120\text{ ppm/°C}$). The structure, microstructure and dielectric properties of sintered ZnTiO$_3$, with a mixture of ZnO-B$_2$O$_3$ glass phase and CuO oxide as sintering aids, have been investigated. For all compounds, the sintering temperature becomes 850°C due to the glass addition. It is also shown that the addition of CuO oxide allows a control of the temperature coefficient of the permittivity ($\tau_\varepsilon$). This parameter varies from positive to negative values with increasing the CuO content. The ZnTiO$_3$ composition sintered at 850°C with 5 wt.% ZnO-B$_2$O$_3$ glass phase and 2.2 wt.% CuO addition exhibits attractive dielectric properties ($\varepsilon_r = 23$, tan $\delta < 10^{-3}$ and a temperature coefficient of the dielectric constant near zero, $\tau_\varepsilon = 3\text{ ppm/°C}$) at 1 MHz. All these properties lead this system compatible for manufacturing Ag based electrodes multilayer dielectrics devices needed for LTCC application or other multilayer dielectric components.

Keywords: zinc titanate, sintering, dielectric properties, glass additive

I. Introduction

Microwave devices such as resonators, filters, oscillators or capacitors play an important role in microwave telecommunication systems. The materials required to fabricate these devices should have a high dielectric constant ($\varepsilon_r > 20$), a low dissipation factor ($\tan \delta < 10^{-3}$), a small temperature coefficient of the resonant frequency ($\tau_f$) or a small temperature coefficient of the dielectric constant ($\tau_\varepsilon$) [1,2] in high frequency range (> 1 MHz). Most of the known dielectrics which are commonly employed for the present applications have a sintering temperature around 1200°C–1500°C. This high temperature forbids the use of cheaper base metals e.g., Cu, Ag, to replace the noble metals like Pd and Pt which are currently employed. Consequently, it is of prime importance to lower down the sintering temperature of the dielectrics at a level enabling a base metal co-sintering. Golovchanski et al. [3] have shown that ZnTiO$_3$ ceramic has excellent dielectric properties ($\varepsilon_r = 19$, $Q\times f = 30,000\text{GHz}$, $\tau_\varepsilon \approx +120\text{ ppm/°C}$) and moreover, this is a promising candidate as base material for low temperature sintering devices owing to its relatively low sintering temperature (~1150°C) without sintering aids. Kim et al. [4] have also investigated the low temperature sintering of ZnTiO$_3$-TiO$_2$ system using B$_2$O$_3$ addition with the aim to control $\tau_\varepsilon$. They also have examined the microstructure and the microwave dielectric properties of alkaline earth modified zinc titanates [5,6]. These modifications improved the temperature coefficient of the dielectric but slightly increased the sintering temperature.

Haga et al. [7] have studied the mixture (1−$x$)ZnTiO$_3$+$x$TiO$_2$ (where $\tau_\varepsilon = +100\text{ ppm/°C}$ for ZnTiO$_3$ [8] and $\tau_\varepsilon = -500\text{ ppm/°C}$ for TiO$_2$ [7]) to tailor the temperature coefficient according to the well-known mixing rule. This rule links the resulting temperature coefficient ($\tau_r$) of a composite versus the temperature coefficients of the compounds belonging to the material and characterised by their volume fractions (respectively $\tau_{\varepsilon1}$, $\nu_1$ and $\tau_{\varepsilon2}$, $\nu_2$): $\tau_r = \nu_1 \tau_{\varepsilon1} + \nu_2 \tau_{\varepsilon2}$. Haga et al. [7] have shown that the temperature coefficient tuning of ZnTiO$_3$ + TiO$_2$ mixture is not trivial because of ZnTiO$_3$ decomposition at high temperature (>945°C) into Zn$_2$TiO$_4$ + TiO$_2$. This leads to a very difficult control of ZnTiO$_3$/TiO$_2$ ratio at the end of the sintering stage.

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In our recent paper [9] it was show that the formula-
lation \( \text{ZnTiO}_3 + 5 \text{ wt.}\% (\text{ZnO-B}_2\text{O}_3) \) could be sintered
at 900°C. The resulting sintered samples exhibit attrac-
tive dielectric properties in high frequency range, e.g. a
relative permittivity around 22 and low dielectric losses
(\( \tan \delta < 10^{-3} \)). However, the \( \tau_e \) value has been measured
to be higher than +100 ppm/°C for this sample.

In previous studies, \( \text{CuO} \) liquid phase is introduced
as sintering aid to lower down the sintering temperature
of several ceramics and obtain good dielectric proper-
ties [10–13]. Xing et al. [14] showed that the increase
the quantity of the liquid phase sintering in \( \text{ZnTiO}_3 \) (ZT)
ceramics, accelerate the decomposition of ZT to TiO_2
and \( \text{Zn}_2\text{TiO}_4 \).

In this work, it is aimed to develop a new strate-
gy for both lowering down the sintering temperature
and controlling the permittivity temperature coefficient
(\( \tau_e \)) using appropriate additives. For this goal, the ef-
effect of a mixture of \( \text{ZnO-B}_2\text{O}_3 \) as glass phase additive
on the decreased sintering temperature has been inves-
tigated. Moreover, the compound \( \text{CuO} \) has been also
added in a view of controlling the temperature coeffi-
cient. Practically, various formulations consisting in a
\( \text{ZnTiO}_3 + 5 \text{ wt.}\% (\text{ZnO-B}_2\text{O}_3) + x \text{ wt.}\% \text{ CuO} \) mixture
with \( x = 0, 0.5, 1, 2, 2.2, 2.3, 2.5, 3 \) and 4 have been pre-
pared. Specimens were then sintered at low temperature
and characterised in terms of density, structure, micro-
structure and dielectric properties.

II. Experimental

\( \text{ZnTiO}_3 \) compound was prepared by solid state re-
action between reagent graded precursors of \( \text{ZnO} \) and
\( \text{TiO}_2 \) (purity >99%). The precursors were appropri-
ately weighted according to the \( \text{Zn/Ti} = 1 \) molar ratio. Mix-
ing was performed in an ammoniac to get very well
dispersed slurry [15,16]. The slurry was subsequently
dried and powder was manually solution at pH=11 us-
ing zirconia balls in teflon jar for 3 hours. These condi-
tions were found to be the optimal reground and heat
treated at 800°C for 2 hours in air. Powder was finally
reground using the same process than before in ammno-
iac solution at pH=11 for 2 hours. For the glass prepa-
ration, the \( \text{ZnO} \) (crystallised, purity >99%) and \( \text{H}_3\text{BO}_3 \)
(amorphous, purity >99%) precursors were appropri-
ately weighted in equimolar ratio and mixed in deionised
water using zirconia balls in a teflon jar for 2 hours. The
mixtures were then melted at 1100°C for one hour in a
platinum crucible and quenched at room temperature in
deionised water. These glasses were grounded in a plan-

![Figure 1. Shrinkage curves versus temperature](image-url)

<p>| Table 1. Symbol and the composition of the studied ceramics |
|---------------------------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Symbol for composition</th>
<th>ZnO-B_2O_3 glass [wt.%]</th>
<th>CuO [wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZT-ZB</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>ZT-ZB-0.5CuO</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>ZT-ZB-1CuO</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>ZT-ZB-2CuO</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>ZT-ZB-2.2CuO</td>
<td>5</td>
<td>2.2</td>
</tr>
<tr>
<td>ZT-ZB-2.3CuO</td>
<td>5</td>
<td>2.3</td>
</tr>
<tr>
<td>ZT-ZB-2.5CuO</td>
<td>5</td>
<td>2.5</td>
</tr>
<tr>
<td>ZT-ZB-3CuO</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>ZT-ZB-4CuO</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>

(1) Pure ZT
(2) ZT-ZB
(3) ZT-ZB-1CuO
(4) ZT-ZB-3CuO
etary grinder for 45 minutes to obtain a fine powder. The mixture \( \text{ZnTiO}_3 + 5 \text{ wt.\% (ZnO-B}_2\text{O}_3 \) glass + \( x \) wt.\% CuO for \( x=0, 0.5, 1, 2, 2.2, 2.5, 3 \) and 4 were prepared by mixing the powders in a planetary grinder for 45 minutes in absolute ethanol. Each formulation is named ZT-ZB-xCuO (Table 1). To shape disks, an organic binder (polyvinyl alcohol, 5 vol\%) was manually added to the powder and disks (8 or 6 mm in diameter, 2 mm thick) were shaped by uni-axial pressing at a load of about 200 MPa. Green samples were finally sintered in air in a tubular furnace for two hours at a dwell temperature determined by TMA (Thermo-Mechanical analysis Setaram TMA 92), with a heating and cooling rates of 150°C/h. The sintered pellets were characterised in terms of density using a He pycnometer (Accupyc 1330) and dielectric properties using a LCR bridge (PM6306). Dependence of the dielectric properties versus temperature has been determined from \(-60^\circ\text{C}\) to \(+160^\circ\text{C}\). Crystallised phase composition has been identified by X-ray diffraction technique using the CuKa copper X-ray radiation (Philips X’ Pert) and microstructures were observed using a scanning electron microscopy (SEM Philips XL’30).

III. Results and discussion

After the calcination step at 800°C, the powder contains \( \text{ZnTiO}_3 \) and \( \text{Zn}_2\text{TiO}_4 \) phases. Reground \( \text{ZnTiO}_3 \) based powder microstructure reveals a very fine microstructure and a very narrow grain size distribution centred at around 400 nm. The shrinkage curves of the \( \text{ZnTiO}_3 \) based powders are given in Fig. 1. The temperature at which the maximum shrinkage is achieved for glass free \( \text{ZnTiO}_3 \) compound is around 1150°C whereas the glass phase containing sample could be sintered at around 850°C. This temperature is from a practical aspect very enable since it autorises a silver co-sintering. Fig. 2 shows the XRD patterns of ZT-ZB-xCuO (x varying from 0 to 4) ceramics sintered at 850°C for 2 hours. For the CuO free sample (x = 0), XRD pattern indicates that the hexagonal \( \text{ZnTiO}_3 \) phase is the unique crystallised phase (Fig. 2a). This confirms that the addition of the glass phase favours the hexagonal \( \text{ZnTiO}_3 \) crystallisation as published elsewhere [9]. For \( x = 0.5 \) to 4 wt.\%, the sintered ceramics is multi-phased. The peaks of \( \text{Zn}_2\text{TiO}_4 \) and \( \text{TiO}_2 \) rutile phases were systematically observed showing that the \( \text{ZnTiO}_3 \) starts to decompose into the cubic \( \text{Zn}_2\text{TiO}_4 \) and \( \text{TiO}_2 \) at 850°C. This decomposition of \( \text{ZnTiO}_3 \) has been also reported by Kim et al. [8]. However, the value of this temperature founded in our work is lower than reported in the Kim’s result. This difference in temperature suggests that the mixture of the glass phase and the CuO addition lowers down the \( \text{ZnTiO}_3 \) phase decomposition temperature which can be understood by the diffusion promoted by the presence of liquid phase, induced by the glass phase addition. If we observe more accurately the XRD patterns, the peaks of the hexagonal \( \text{ZnTiO}_3 \) phase decrease with increasing the CuO amount. In the same time, the characteristic peaks of the \( \text{Zn}_2\text{TiO}_4 \) and \( \text{TiO}_2 \) compounds strongly and simultaneously increase. This shows that the CuO addition enhances the formation of \( \text{Zn}_2\text{TiO}_4 \) and \( \text{TiO}_2 \). Finally, when \( x = 4 \) wt.\%, the hexagonal \( \text{ZnTiO}_3 \) phase has practically disappeared, \( \text{Zn}_2\text{TiO}_4 \) and \( \text{TiO}_2 \) being the major phases (Fig. 2c).

The bulk density of \( \text{ZnTiO}_3 \) based ceramics with various amount of glass phase addition is systematically higher than 95 % of the theoretical value (Table 2). The scanning electron micrographs of a typical sintered sample are presented in Fig. 3. The microstructures reveal a quite dense ceramic with an heterogeneous grain size distribution. Grains having an apparent diameter lower than the micrometer are easily observed whereas some grains have an apparent diameter around 1–2 µm. For samples with high level of additives, the excess glass phase appears clearly on the microstructure of ceramics (Fig. 3d). The Fig. 4 depicts the permittivity versus temperature for the system ZT-ZB-xCuO and Table 2 summarises the main dielectric properties versus temperature has been determined from \(-60^\circ\text{C}\) to \(+160^\circ\text{C}\). Crystallised phase composition has been identified by X-ray diffraction technique using the CuKa copper X-ray radiation (Philips X’ Pert) and microstructures were observed using a scanning electron microscopy (SEM Philips XL’30).

![Figure 2. XRD patterns of ceramics sintered at 850°C: a) ZT-ZB, b) ZT-ZB-2.2 CuO and c) ZT-ZB-4 CuO](image-url)
Table 2. Dielectric properties and density of the sintered ceramics at 1 MHz

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sintering temperature [°C]</th>
<th>Relative density [%TD]</th>
<th>$\varepsilon_r$</th>
<th>$\tan \delta$ [ppm/°C]</th>
<th>$\rho_i$ [Ω·cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZT-ZB</td>
<td>850</td>
<td>95</td>
<td>20.5</td>
<td>$&lt; 10^{-3}$</td>
<td>195</td>
</tr>
<tr>
<td>ZT-ZB-0.5CuO</td>
<td>850</td>
<td>95</td>
<td>20</td>
<td>$&lt; 10^{-3}$</td>
<td>171</td>
</tr>
<tr>
<td>ZT-ZB-1CuO</td>
<td>850</td>
<td>97</td>
<td>20</td>
<td>$&lt; 10^{-3}$</td>
<td>130</td>
</tr>
<tr>
<td>ZT-ZB-2CuO</td>
<td>850</td>
<td>95</td>
<td>23</td>
<td>$&lt; 10^{-3}$</td>
<td>64</td>
</tr>
<tr>
<td>ZT-ZB-2.2CuO</td>
<td>850</td>
<td>98</td>
<td>23.5</td>
<td>$&lt; 10^{-3}$</td>
<td>3</td>
</tr>
<tr>
<td>ZT-ZB-2.3CuO</td>
<td>850</td>
<td>97</td>
<td>24</td>
<td>$&lt; 10^{-3}$</td>
<td>-20</td>
</tr>
<tr>
<td>ZT-ZB-2.5CuO</td>
<td>850</td>
<td>98</td>
<td>25</td>
<td>$&lt; 10^{-3}$</td>
<td>-80</td>
</tr>
<tr>
<td>ZT-ZB-3CuO</td>
<td>850</td>
<td>93</td>
<td>25</td>
<td>$&lt; 10^{-3}$</td>
<td>-83</td>
</tr>
<tr>
<td>ZT-ZB-4CuO</td>
<td>850</td>
<td>93</td>
<td>17</td>
<td>$&lt; 10^{-3}$</td>
<td>-126</td>
</tr>
</tbody>
</table>

Figure 3. Scanning electron micrographs (SEM) of ceramics sintered at 850°C for 2h

![SEM images of ZT-ZB-0.5CuO, ZT-ZB-1CuO, ZT-ZB-2.2CuO, ZT-ZB-4CuO](image)

Figure 4. Dielectric characteristics of ceramics versus temperature at 1 MHz

![Graph showing dielectric characteristics](image)
properties obtained in respect to the composition. For each composition, it is noticeable that higher the CuO content is, the higher is the permittivity. This is well understood considering increased TiO$_2$ amount with increasing CuO content. It is indeed known that TiO$_2$ has a high dielectric constant ($\varepsilon_r$ (TiO$_2$) $\approx$ 100) [4]. The dielectric losses are always lower than $10^{-3}$. The dependence of $\tau_\varepsilon$ versus CuO content is linear (Fig. 5), with a negative slope, passing from positive to negative values. This behaviour can be attributed to the high and negative value of $\tau_\varepsilon$ of TiO$_2$ ($\tau_\varepsilon$ (TiO$_2$) $<$ $-500$ ppm/$^\circ$C) [7,8]. These results unambiguously show that it is possible to control the temperature coefficient of the ZnTiO$_3$ based ceramics by adjusting the CuO content. In particular, it can be underlined the low $\tau_\varepsilon$ value which we obtained on ZT-ZB-2.2CuO sample sintered at 850$^\circ$C which is $\tau_\varepsilon$ = 3 ppm/$^\circ$C with a room temperature permittivity of around 23.

The resistivity of all composition is systematically higher than $10^{10}$ $\Omega$·cm. This value is convenient for most of the applications in dielectric devices (capacitors, LTCC, resonators, etc.). To show feasibility of fabrication silver based dielectric device, a co-sintering has been performed. Fig. 6 shows a SEM microstructure of a cross section of a silver/ZnTiO$_3$ prototype sintered at 850$^\circ$C. No silver diffusion into the ceramics (and vice versa) has occurred showing a good compatibility between the electrode and the ceramics. In addition, this prototype exhibits very attractive dielectric properties, i.e. a room temperature relative permittivity of around 23, a permittivity temperature coefficient of 1 ppm/$^\circ$C and a loss factor lower than $10^{-3}$.

**IV. Conclusions**

The effect of a mixture (ZnO-B$_2$O$_3$) glass and CuO addition on the densification, crystal phase, microstructure and dielectric properties of ZnTiO$_3$ has been investigated. Different weight percentages of CuO have been added to the ZnTiO$_3$ + 5 wt.% (ZnO-B$_2$O$_3$) formulation. The sintering temperature of the glass-added ZnTiO$_3$ samples is lowered down to 850$^\circ$C compared to glass free compound which requires 1150$^\circ$C to be well sintered. This glass phase addition should lead possibly to the co-sintering with silver. In addition to this practical result, it is clearly shown that the addition of CuO allows us to tailor the permittivity temperature coefficient. This parameter linearly varies from positive to negative values when the CuO content varies from 0 to 4 wt.%. This result is explained by the ZnTiO$_3$ partial decomposition into Zn$_2$TiO$_4$+TiO$_2$ when CuO is added. Very attractive dielectric properties are reported for the composition ZT-ZB-2.2 wt.% CuO ceramics: a room temperature permittivity of around 23, permittivity temperature coefficient of 3 ppm/$^\circ$C with low loss factor ($< 10^{-3}$). Finally, a prototype of silver/ZnTiO$_3$ based capacitor has been successfully sintered at 850$^\circ$C from this composition exhibiting similar dielectric properties ($\tau_\varepsilon$ = 1 ppm/$^\circ$C, $\varepsilon_r$ = 24 and $\tan \delta$ < $10^{-3}$). These properties make this formulation suitable to fabricate silver based multilayer ceramic capacitor or other dielectrics devices requiring low sintering temperature and attractive dielectric properties.

**References**

4. H.T. Kim, S.H. Kim, S. Nahm, J.D. Dyun, “Low-temperature sintering and microwave dielectric properties