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# Effects of additives on the sintering temperature and dielectric properties of $ZnTiO_3$ based ceramic

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**Abstract**

The effects of various additives, namely ZnO–$B_2O_3$–$SiO_2$ (ZSB), $B_2O_3$ and $B_2O_3$ + LiF on the lowering of sintering temperature and dielectric properties of $ZnTiO_3$ based ceramics were investigated. From the dilatometric studies, it was shown that the sintering temperature is significantly lowered owing to the addition of 15 mol.% of ZSB or of the addition of 15 mol.% of $B_2O_3$: ZSB added sample can be sintered at 950 °C and $B_2O_3$ added one at 1000 °C whereas pure compound hence can be sintered at 1100 °C. The most interesting result concerns the ZSB added sample sintered at 950 °C during 4 h which exhibits a density higher than 92% of the theoretical one, high dielectric constant ($\varepsilon_r \approx 25$) and low dissipation factor ($\tan(\delta) < 10^{-3}$) in the range −60 °C/160 °C at 1 MHz. The temperature coefficient of the dielectric constant is also reasonable ($\tau_\varepsilon \approx -150$ ppm/°C) as well as the temperature coefficient of the resonant frequency ($|\tau_f| < 100$ ppm/°C). This formulation should be consequently a suitable candidate for low-temperature co-fired ceramics (LTCCs).

*Keywords:* C. Dielectric properties; $ZnTiO_3$ ceramics; Low-temperature sintering

## 1. 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 ($\tau_f$) and a small temperature coefficient of the dielectric constant ($\tau_\varepsilon$) [1–2]. Most of the known dielectrics, which have been employed for the present applications, have been usually synthesised by employing the high sintering temperature, which is usually in the range 1200–1500 °C. High temperature processing hence forbids the use of cheaper base metals, e.g. Cu, Ag, as an electrode, instead of noble metals like Pd and Pt, which is currently employed. Hence, it increases the manufacturing cost, both in terms of money and energy. Hence, it is of prime importance to lower the sintering temperature of the dielectrics in order to replace the noble metals by base metals as an electrode. In principle, two basic approaches can be adopted to reduce the sintering temperature:

(i) to add glass phase or crystallised materials to act as densification promoter (owing to the formation of a liquid phase to improve species diffusion)
(ii) to use liquid phase processing (e.g. sol–gel method) or grinding system in order to reduce the grain size of the powder, which in turn enhances the reactivity of the final powder.

Low-temperature sintering of dielectric materials with glass phase addition have already been successfully developed for several microwave dielectric system, e.g. (Zr,Sn)$TiO_4$, ZnO–$Nb_2O_5$–$TiO_2$, (Ca,Mg)$TiO_3$, BaO–$Nb_2O_3$–$TiO_2$ [3,4]. In this regard, $ZnTiO_3$ is also a potential candidate for microwave devices application because of the fact that it possess high dielectric constant ($\varepsilon = 29$), low dielectric loss ($\tan(\delta) < 10^{-3}$) and requires low sintering temperature (≅1100 °C) [5]. The aim of the present work is to develop a strategy for lowering the sintering temperature by employing suitable additives without degrading its dielectric properties. Hence, $ZnTiO_3$ ceramic could be a good candidate for low temperature co-fired ceramic

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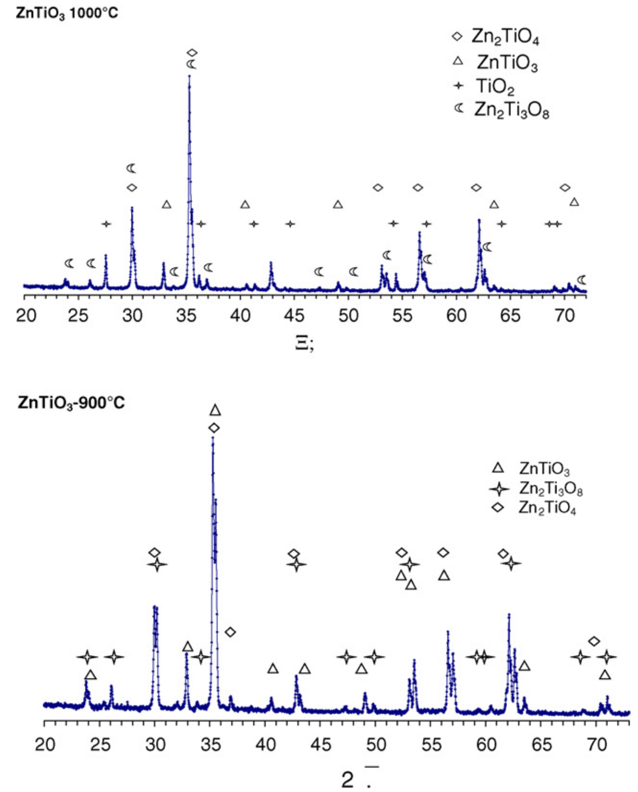


Fig. 1. XRD patterns of $ZnTiO_3$ powders calcined at (a) 900 °C, and (b) 1000 °C.

(LTCC) applications. ZSB (eutectic composition 60 mol.% ZnO + 27 mol.% $B_2O_3$ + 13 mol.% $SiO_2$) glassy phase, $B_2O_3$ and $B_2O_3$ + LiF compounds were chosen as sintering additives. The sintering behaviour and the microwave dielectric properties with different sintering additives were investigated.

## 2. Experimental procedure

The $ZnTiO_3$ compound was prepared by solid state reaction using reagent grades powders of ZnO and $TiO_2$ (purity >99%). The precursors were appropriately weighted according to the $Zn/TiO_2 = 1$ molar ratio. Mixing was performed in an ammoniac solution at pH = 11 using zirconia balls in Teflon jar for 2 h. Resulting powder was subsequently dried at 120 °C under infra red lamps. The synthesis was done at 900 °C and 1000 °C.

The ZSB glass with the eutectic composition of 60% ZnO + 27% $B_2O_3$ + 13% $SiO_2$ (in mol.%) was prepared by mixing manually in an agate mortar the precursors. The powder was then melted at 1200 °C in a platinum crucible and quenched at room temperature in deionised water. The material was again manually crushed and used as sintering additive. Three formulations were prepared by mixing the sintering aids with the $ZnTiO_3$ powder for 2 h in absolute alcohol using ball milling in a Teflon jar:

(i) $ZnTiO_3$ + 15 mol.% ZSB, named ZNT–ZBS
(ii) $ZnTiO_3$ + 15 mol.% $B_2O_3$ crystallised, named ZNT–$B_2O_3$
(iii) $ZnTiO_3$ + 10 mol.% $B_2O_3$ + 5 mol.% LiF named ZNT–$B_2O_3$–LiF.

Purities of ZnO, LiF, $B_2O_3$, $TiO_2$ and $SiO_2$ are 99.995%, 99.95%, 98%, 99% and 99%, respectively. To prepare the disks, an organic binder (polyvinylic alcohol at 5%) was manually added to the powder. Disks having various dimensions, namely 8 mm in diameter, 2 mm thick and 24 mm in diameter, were prepared by uni-axial pressing at a load of about 2100 kgf. Green samples were finally sintered in air for 4 h in a tubular furnace at a dwell temperature determined by dilatometry. The sintered pellets were characterised in terms of density and dielectric properties, viz. dielectric constant and dissipation factor, using an LCR bridge (Fluke PM 6306). Insulation resistance was measured using a picoamperemeter (Sefelec DM500A). These measurements required electrodes to be painted on each disks face with an indium-gallium eutectic. Composition of the samples was performed by X-ray diffractometer (Philips X'Pert) using the Cu Kα radiation and the microstructures were investigated using scanning electron microscopy (SEM Philips XL'30).

## 3. Results and discussion

The synthesis of $ZnTiO_3$ as a single-phase is usually difficult due to the decomposition of $ZnTiO_3$ into $Zn_2TiO_4$ and $TiO_2$ phases above 945 °C [5,6]. XRD patterns (Fig. 1) performed on the powder synthesised at 1000 °C shows that the $Zn_2TiO_4$

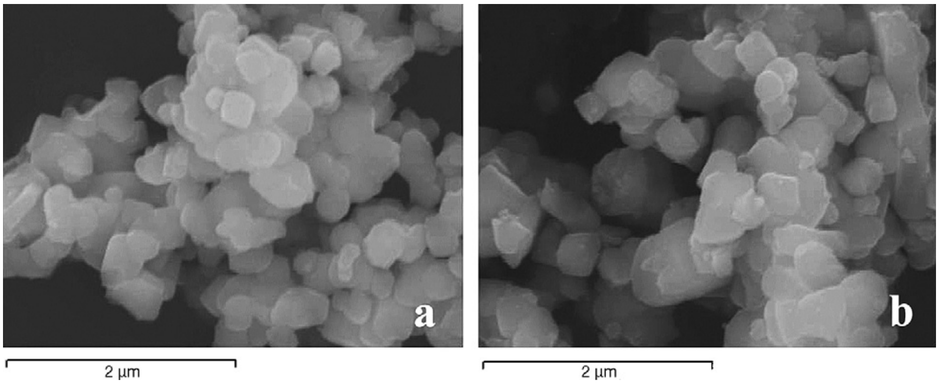
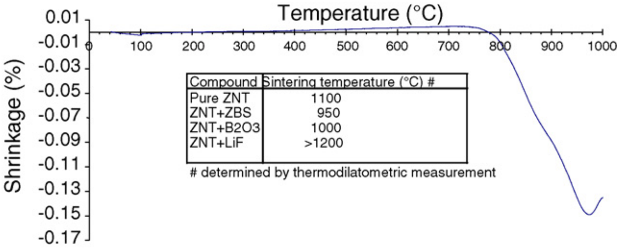


Fig. 2. Scanning electron micrographs (SEM) of $ZnTiO_3$ powders calcined at (a) 900 °C, and (b) 1000 °C.



| Compound | Sintering temperature (°C) # |
|---|---|
| Pure ZNT | 1100 |
| ZNT+ZBS | 950 |
| ZNT+B2O3 | 1000 |
| ZNT+LiF | >1200 |

# determined by thermodilatometric measurement

Fig. 3. Dilatometric curve of $ZnTiO_3$ + 15% ZBS compound.

phase is the majority phase. It is also observed the presence of the rutile $TiO_2$ and of the $Zn_2TiO_4$ phases. Thus, our results also show the identical features, which have been previously reported in literature. The XRD study performed on the powder synthesised at 900 °C clearly exhibits that the $ZnTiO_3$ phase is the majority phase. Furthermore, it shows the presence of $Zn_2Ti_3O_8$ and $ZnTiO_4$ as secondary phases. Moreover, at 900 °C, it is noticeable that the rutile $TiO_2$ phase is absent. Fig. 2 shows the representative SEM micrographs of $ZnTiO_3$ based powders calcined at different temperatures, i.e. 900 °C and 1000 °C. It can be observed that the powder's morphology is nearly spherical with a very narrow distribution centred at about 500 nm for the specimen synthesised at 900 °C. A slight grains growth is observed for the powder synthesised at 1000 °C in which the mean particle size is about 800 nm. In both cases, the powder should be very reactive because of their sub-micrometric size and their isotropic morphology. For the following, the 900 °C was systematically used for the synthesis for both aspect: a lower grain size and an higher $ZnTiO_3$ amount. Fig. 3 shows the dilatometric curve of the ZNT–ZBS sample. One can clearly evidence that this compound can be sintered at 950 °C. This temperature is the lowest sintering temperature we determine as indicated in the inset table. The ZNT–$B_2O_3$ can be sintered at 1000 °C whereas the ZNT–$B_2O_3$–LiF sample exhibits a maximum shrinkage at 1200 °C which is higher than the sintering temperature of the pure ZNT (1100 °C). This latter composition is consequently not interesting.

In a view of a silver co-sintering, all sintering aids added compounds have been sintered at 950 °C for 4 h in air in knowing that some of them should be not totally sintered (according to the thermo mechanical analysis (TMA)). After this sintering stage, the samples ZNT–ZBS, ZNT–$B_2O_3$ and ZNT–$B_2O_3$–LiF exhibit the respective density (in percentage of the theoretical) of 92%, 78% and 76%, which are in good agreement with TMA curves. The pure $ZnTiO_3$ ceramics sintered at 1100 °C has a density around 92% of the theoretical value. The theoretical value of the density has been chosen at 5.171 g/cm$^3$, i.e. the theoretical value for the $ZnTiO_3$ phase. SEM microstructures of the sintered samples are shown in Fig. 4. The pure $ZnTiO_3$ ceramics sintered at 1100 °C exhibits well dense microstructure with a mean grain size close to 10–15 μm. The ZBS added sample sintered at 950 °C is also dense with a smaller grain size (mean grain size lower than 10 μm). The other added samples ($B_2O_3$ and $B_2O_3$ + LiF) are porous in agreement with the too low chosen sintering temperature (950 °C instead of 1000 °C or 1200 °C, respectively).

Table 1 summarises the dielectric properties of our various compounds as well as their density. The variation in the microstructure and composition of these samples were clearly

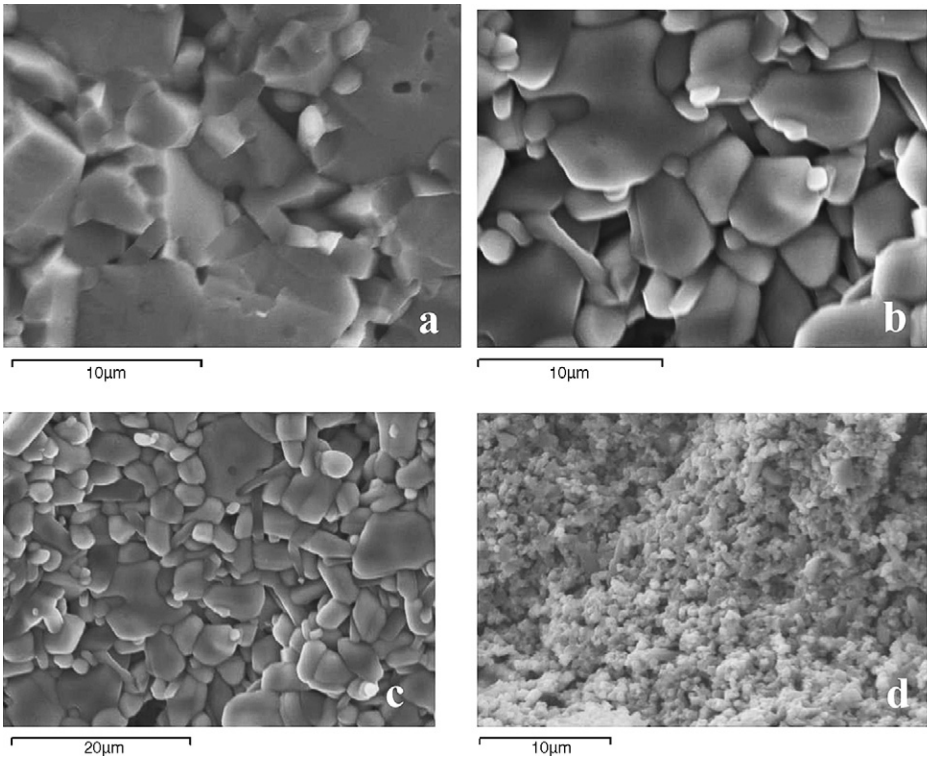


Fig. 4. (a) Scanning electron micrographs (SEM) of pure $ZnTiO_3$ ceramic sintered for 4 h at 1100 °C; SEM of (b) $ZnTiO_3$ + 15% ZSB, (c) $ZnTiO_3$ + 15% $B_2O_3$, (d) $ZnTiO_3$ + 10% $B_2O_3$ − 5% LiF ceramics sintered at 950 °C for 4 h.

Table 1
Dielectric properties of the sintered ceramics at 1 MHz

| Sample | Sintering temperature (°C) | Density in % of theoretical | $\varepsilon_r$ | $\tan(\delta)$ | $\tau_\varepsilon$ (ppm/°C) | $\log(\rho_I)$ (Ω cm) |
|---|---|---|---|---|---|---|
| $ZnTiO_3$ | 1100 | 92 | 30 | $<10^{-3}$ | −136 | 8.9 |
| $ZnTiO_3$ + 15% ZSB | 950 | 92 | 25 | $<10^{-3}$ | −158 | 11.3 |
| $ZnTiO_3$ + 15% $B_2O_3$ | 950 | 78 | 18 | $<10^{-3}$ | −152 | 7.8 |
| $ZnTiO_3$ + 10% $B_2O_3$ + 5% LiF | 950 | 76 | 16 | $<10^{-3}$ | −253 | 4.8 |

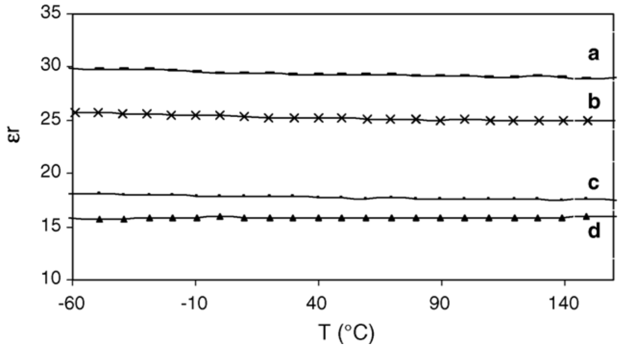


Fig. 5. Dielectric characteristics at 1 MHz of (a) pure $ZnTiO_3$; (b) $ZnTiO_3$ + 15% ZSB; (c) $ZnTiO_3$ + 15% $B_2O_3$ and (d) $ZnTiO_3$ + 15% ($B_2O_3$ + LiF).

reflected in their dielectric properties. As expected, the permittivity follows the density trend, higher the density higher the permittivity. The maximum permittivity is obtained for the pure compound ($\varepsilon_r = 30$) and the ZBS added sample also presents a satisfying relative dielectric constant of 25. These values are in good agreement with the published value, which is about 28 [5]. The average dielectric constant of $ZnTiO_3$, $Zn_2TiO_4$ and $TiO_2$ phases are 28, 21 and 110, respectively [5,7,8]. Consequently, as decomposition of $ZnTiO_3$ into $Zn_2TiO_4 + TiO_2$ occurs at high temperature (above 945 °C), the permittivity should increase with increasing sintering temperature considering the $TiO_2$ formation [8]. This could be explained the difference in permittivity values between the ZBS added sample sintered at 950 °C ($\varepsilon_r = 25$) and the pure compound sintered at 1100 °C ($\varepsilon_r = 30$) Moreover, for all samples, the temperature dependence of the dielectric constant is linear (Fig. 5). The pure compound exhibits a temperature coefficient of −136 ppm/°C whereas the ZBS added one has a coefficient of −158 ppm/°C. A well known equation [9] links the temperature coefficients of the dielectric constant ($\tau_\varepsilon$), the temperature coefficient of the resonant frequency ($\tau_f$) and the thermal expansion coefficient ($\alpha$): $\tau_f = (-1/2)\tau_\varepsilon - \alpha$. It is hence possible to evaluate the value of $\tau_f$ in considering that the value of $\alpha$ is around 10 ppm/°C, which was extracted from dilatometric curves. The $\tau_f$ factor should hence be in the range 70–100 ppm/°C for the pure ZNT and for the ZNT–ZBS samples. These values are convenient for some applications in dielectric devices.

## 4. Conclusion

The effects of glass phase ZnO–$B_2O_3$–$SiO_2$ (ZSB), $B_2O_3$ and $B_2O_3$ + LiF on the sintering behaviour and the dielectric properties of $ZnTiO_3$ based ceramic were investigated. $ZnTiO_3$ was synthesised by solid state reaction from ZnO and $TiO_2$. The dwell temperature has been chosen at 900 °C to reduce the decomposition of $ZnTiO_3$ into $Zn_2TiO_4 + TiO_2$. Although this precaution was taken, the final powder is composed of $ZnTiO_3$ with a mixture of $Zn_2TiO_4 + Zn_2Ti_3O_8$ as secondary phases but the absence of rutile $TiO_2$ was observed. Pure $ZnTiO_3$ based compound was sintered at 1100 °C for 4 h and pellet exhibit the expected dielectrics properties: $\varepsilon_{r(1\ \mathrm{MHz})} \approx 30$, $\tan(\delta_{(1\ \mathrm{MHz})}) < 10^{-3}$ and $|\tau_f|_{(1\ \mathrm{MHz})} < 100$ ppm/°C. The most interesting result is obtained for the ZBS added sample which is correctly sintered at 950 °C for 4 h. This material has a density of 92% of theoretical and has attractive properties: $\varepsilon_{r(1\ \mathrm{MHz})} \approx 25$, $\tan(\delta_{(1\ \mathrm{MHz})}) < 10^{-3}$, $|\tau_f|_{(1\ \mathrm{MHz})} < 100$ ppm/°C. These results make ZBS added $ZnTiO_3$ based formulation suitable for manufacturing low temperature co-fired ceramics.

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