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Low sintering temperature of $(Zn_{0.65}Mg_{0.35})TiO_3$–$xCaTiO_3$-based dielectric with controlled temperature coefficient

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Abstract

$(Zn_{0.65}Mg_{0.35})TiO_3$–$xCaTiO_3$-based dielectric ceramics sintered at low temperature thanks to $ZnO–B_2O_3$ glass phase addition are investigated. The effects of such additions on the dilatometric curves, the microstructure, the phase composition and the dielectric properties have been carefully examined. It is shown that the sintering temperature is significantly lowered to 930 °C by the addition of 2 wt.% of $ZnO–B_2O_3$ glass phase. The temperature coefficient of permittivity (τ_ε) could be controlled by varying the $CaTiO_3$ content and lead to near zero τ_ε value. As an optimal composition, $(Zn_{0.65}Mg_{0.35})TiO_3 + 7\%CaTiO_3$, co-sinterable with silver electrodes at 930 °C, exhibits at 1 MHz, a relative permittivity of $\varepsilon_r = 21$, a temperature coefficient of the permittivity τ_ε of −4 ppm/°C and low dielectric losses ($\tan(\delta) < 10^{-3}$). These interesting properties make this system promising to manufacture Ag-based electrodes multilayer dielectric devices.

Keywords: A. Sintering; C. Dielectric properties; E. Capacitors

1. Introduction

The rapid progress in mobile and satellite communications implies the need to design new dielectric system with high performances. That means having materials with low dielectric losses, high permittivity and stable temperature coefficient of the resonance frequency (τ_f). Many dielectric materials have been developed and modified for this goal [1,2]. For most of these applications, the multilayer structure, with metallic and ceramic layers, is used and hence, the main difficulty is to control the co-sintering stage. This processing step means that the sintering temperature has to be lower than the electrodes melting point and has to be high enough to obtain well-dense ceramic. As silver electrodes are generally used, the co-sintering ceramic-metal must be performed at around 900 °C, far enough below the silver melting point (961 °C). As the usual dielectric materials need high temperature to be well sintered (>1100 °C), the lowering of this temperature is one essential condition to envisage the dielectric-metal co-sintering. Adding sintering aids like low-temperature softening glasses, optimizing the chemical processing, and reducing the particle size of the starting materials are three of the most commonly used methods to reduce the sintering temperature of ceramics. Among these methods, the addition of glass phase, inducing sintering in presence of a liquid phase, is well known for its efficiency [3–12] and its low cost. $ZnTiO_3$ exhibits interesting dielectric properties [13]. Moreover, $ZnTiO_3$ can be sintered at low temperature (<950 °C) owing to the addition of $ZnO–B_2O_3$ glass phase [14]. In this case, the glass phase addition allows to decrease the sintering temperature without degrading the dielectric properties. It has been also evidenced that the $(Zn,Mg)TiO_3$ system exhibits attractive properties [15]. As an example, the $(Zn_{0.65}Mg_{0.35})TiO_3$ solid solution, sintered at 1100 °C, has a dielectric constant of 20, a quality factor Q of 15,000 at 10 GHz, and a temperature coefficient of the resonant frequency of −75 ppm/°C [15]. It is hence evidenced that the drawback of this material is its too high temperature coefficient for NPO type applications. It must be kept in mind that τ_f is related to the thermal expansion coefficient, α, and the temperature coefficient of permittivity, τ_ε, as follows: $\tau_f = -(1/2)\tau_\varepsilon + \alpha$. Since $\alpha\psi$ for microwave ceramics is known to be around 10 ppm/°C, the τ_ε coefficient of $(Zn_{0.65}Mg_{0.35})TiO_3$ is around 150 ppm/°C which forbids the use of such material in

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Table 1
The symbol and the composition of the studied ceramics.

$Zn_{0.65}Mg_{0.35}TiO_3$ (mol)	$ZnO–B_2O_3$ glass (wt.%)	$CaTiO_3$ (mol)	Symbol of composition
1	2	0	ZMT–ZB
		0.02	ZT–ZB–02CT
		0.05	ZT–ZB–05CT
		0.07	ZT–ZB–07CT
		0.1	ZT–ZB–1CT

NPO type capacitors leading the need to tailor this coefficient. It is well established, according to the mixing rule [16], that the temperature coefficient τ_ε of a mixture is given by $\tau_\varepsilon = \nu_1 \tau_{\varepsilon 1} + \nu_2 \tau_{\varepsilon 2}$, where $\tau_{\varepsilon 1}$, $\tau_{\varepsilon 2}$, ν_1 and ν_2 are, respectively the two temperature coefficients and the two volume fractions of the two mixed materials. To tailor the τ_ε temperature coefficient to 0 ppm/°C by this way, two kinds of dielectrics have to be used, exhibiting positive and negative temperature coefficients, respectively. $CaTiO_3$ is a well-known dielectric, exhibiting a relative permittivity of 170, a quality factor of 3600 at 7 GHz, and a temperature coefficient of the resonant frequency of +800 ppm/°C [17] or a temperature coefficient of the relative permittivity close to −1600 ppm/°C. $(Zn_{0.65}Mg_{0.35})TiO_3$ and $CaTiO_3$ actually exhibit temperature coefficients with opposite signs.

The purpose of this work is consequently to study composites, based on these both phases, $(Zn_{0.65}Mg_{0.35})TiO_3$ and $CaTiO_3$. Many volume ratio are investigated, corresponding to $(Zn_{0.65}Mg_{0.35})TiO_3$–$x CaTiO_3$ (with $x = 0$, 0.02, 0.05, 0.07 and 0.1) with $ZnO–B_2O_3$ glass addition as sintering aid. The crystalline phases, the microstructure and the dielectric properties of these ceramics are reported. The dielectric properties have been measured in the MHz range, that is convenient for type I multilayer ceramics capacitors applications.

2. Experimental procedure

$(Zn_{0.65}Mg_{0.35})TiO_3$ and $CaTiO_3$ powders were prepared by solid-state reaction, using reagent grades powders of ZnO, TiO_2 and MgO and CaO (purity >99%). The precursors were appropriately mixed according to the desired stoichiometry of each compound. The milled powders, having the nominal compositions $(Zn_{0.65}Mg_{0.35})TiO_3$ and $CaTiO_3$, were dried and then heat treated at 800 and 1100 °C for 2 h, respectively, with heating and cooling rates of 150 °C^{-1}. These thermal cycle treatments have been chosen according to the previous papers [14,18]. For the glass preparation, the ZnO (crystallised, purity >99%) and H_3BO_3 (amorphous, purity >99%) precursors were appropriately weighted in equimolar ratio and mixed in deionised water using zircon balls in a Teflon jar for 2 h. The mixture was then melted at 1100 °C for 1 h in a platinum crucible and quenched at room temperature in deionised water. This glass was grinded in a planetary grinder for 45 min to obtain fine powder. The $(Zn_{0.65}Mg_{0.35})TiO_3$ + 2 wt.% ($ZnO–B_2O_3$) glass + $x CaTiO_3$ (for $x = 0$, 0.02, 0.05, 0.07, 0.1) mixtures were prepared by mixing the powders in a planetary grinder for 45 min in absolute ethanol. The symbols of each composition were reported in Table 1. To manufacture disks, organic binder (PVA, 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 with a load of 2100 kg. Samples were finally sintered in air, in a tubular furnace for 2 h at a dwell temperature determined by TMA (Thermo-Mechanical analysis Setaram TMA 92), with heating and cooling rates of 150 °C/h. The sintered pellets were characterised in terms of density using an He pycnometer (Accupyc 1330) and dielectric properties using a RLC bridge (PM6306) at 1 MHz. Dependence of the dielectric properties versus temperature has been determined from −60 to +160 °C. Crystallised phase composition has been identified by X-ray diffraction technique using the Cu Kα copper X-ray radiation (Philips X'Pert) and microstructures were observed using a scanning electron microscopy (SEM Philips XL'30).

3. Results and discussion

Fig. 1 shows the thermo-mechanical analyses of the ZMT–ZB–xCT compounds. It firstly evidenced that the ZMT compound can be sintered at 930 °C, thanks to glass phase

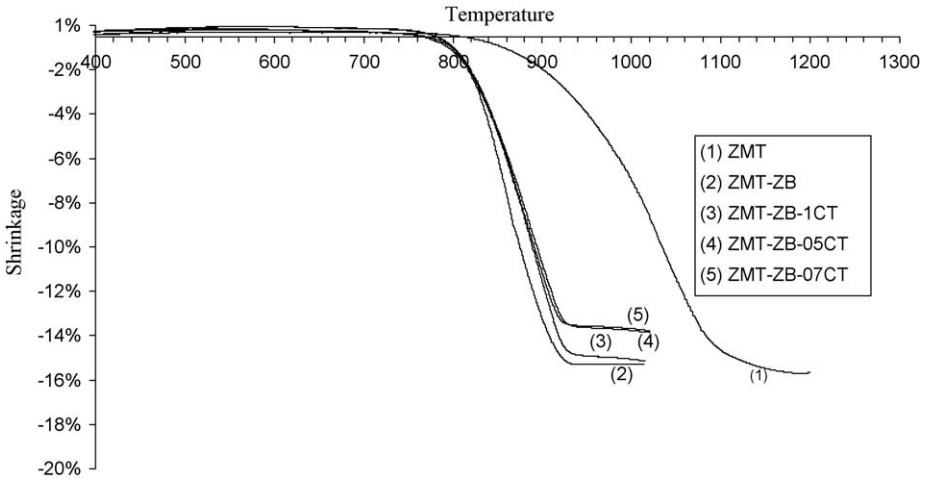

Fig. 1. Shrinkage curves versus temperature.

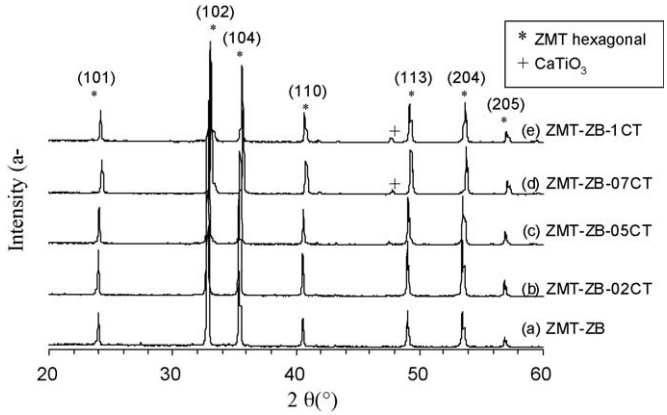

Fig. 2. XRD patterns of ceramics sintered at 930 °C.

addition, whereas the pure one has to be sintered at 1180 °C. The introduction of $CaTiO_3$ did not significantly influence the TMA curves. Regarding these analyses, all samples have been sintered at 930 °C. This temperature is really attractive since it authorises silver co-sintering. The XRD patterns of ZMT–ZB–*x*CT ceramics sintered at 930 °C show that the hexagonal ZMT phase is well preserved after sintering, even in the presence of $CaTiO_3$ and whatever the investigated $CaTiO_3$ content (see Fig. 2). The $CaTiO_3$ perovskite is clearly identified for ZMT–ZB–05CT (Fig. 2(c)) and the peak intensity gradually increases when $CaTiO_3$ content increases (Fig. 2(d) and (e)). It is clear that none of the secondary phase is detected showing that the two compounds ($(Zn_{0.65}Mg_{0.35})TiO_3$ and $CaTiO_3$) do not react together during the high temperature stage. The low sintering temperature used also prevents the material from the formation of other secondary phases such as $MgTi_2O_5$ or $(Mg,Zn)_2TiO_4$ as often observed in this system [19]. Fig. 3 shows SEM pictures of ZMT-based ceramics sintered at 930 °C. A remarkable difference has been observed from the bulk and the surface observation. The surface microstructure is homogeneous and the average grain size is about 5 μm (Fig. 3(c) and (d)). For the bulk, the liquid phase sintering effect is clearly observed in the grain morphology: the ceramics reveal a relatively dense microstructure with a large grain size distribution (Fig. 3(a) and (b)). Fig. 4 and Table 2 show the dielectric properties of the ZMT–ZB–*x*CT samples (co-sintered with silver electrodes at 930 °C). The samples density is always higher than 94% of the theoretical (Table 2). Fig. 4 highlights the linear dependence of the relative permittivity versus temperature. Moreover, the temperature dependence of the dielectric constant (τ_ε) of ZMT–ZB–*x*CT decreases with increasing $CaTiO_3$ content, passing from positive to negative values for $x > 7\%$ as shown in Fig. 5.

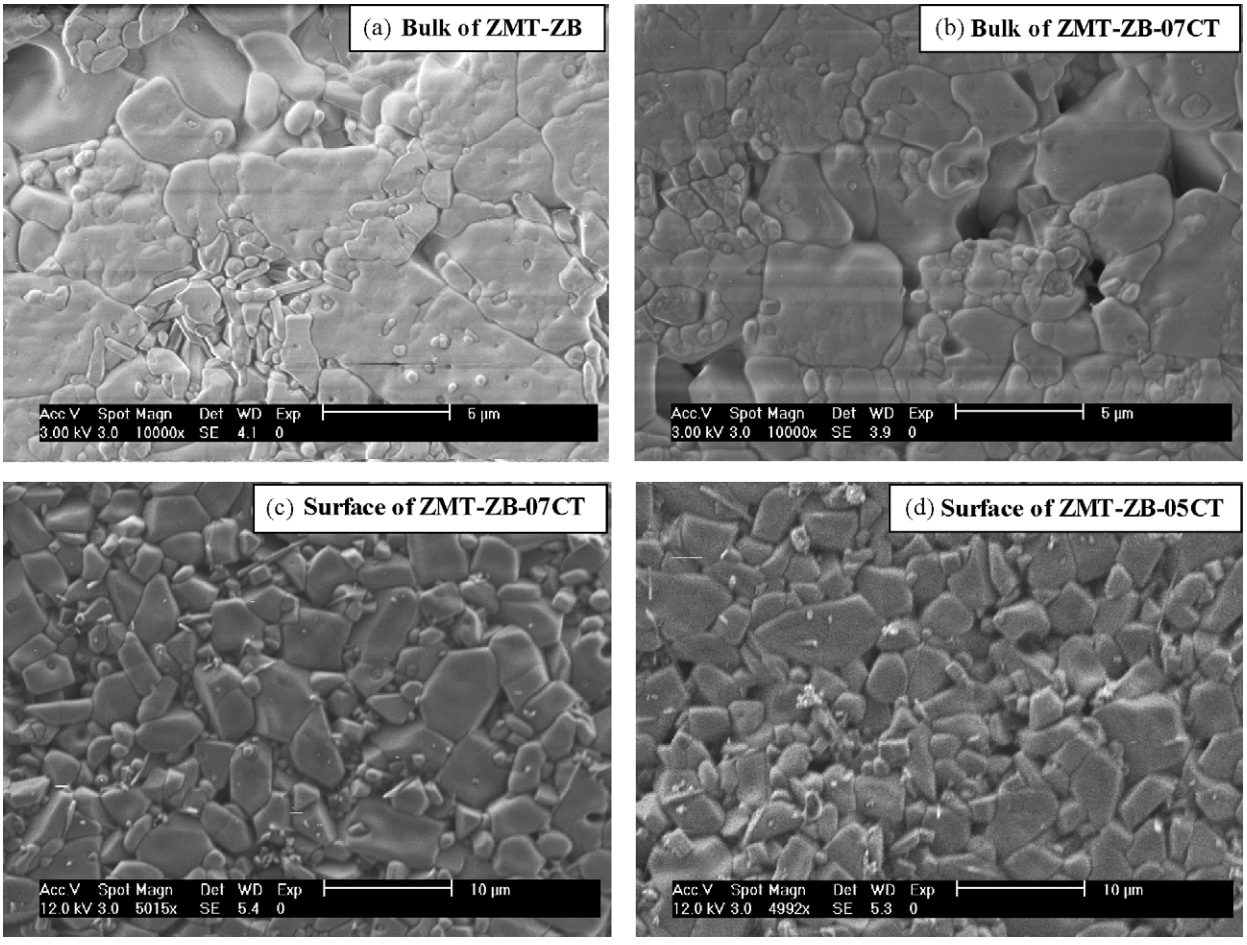

Fig. 3. Scanning electron micrographs (SEM) of ceramics sintered at 930 °C for 2 h.

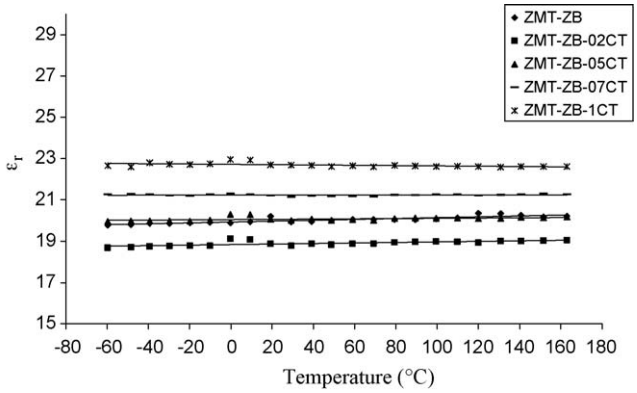

Fig. 4. Dielectric characteristics of ceramics co-fired with Ag at 930 °C versus temperature at 1 MHz.

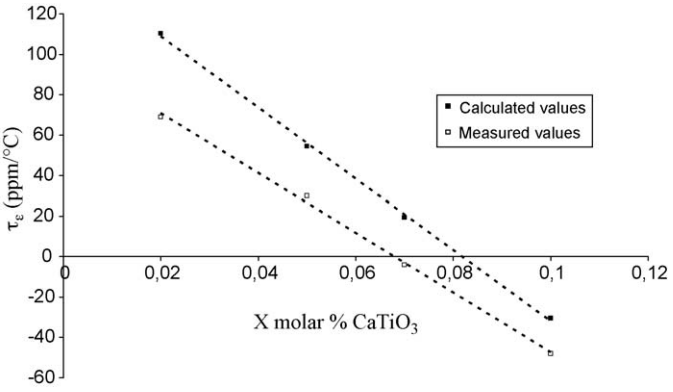

Fig. 5. Temperature coefficient of dielectric constant (τ_ε) of ZMT–ZB–xCT composition sintered at 930 °C versus the x addition amount.

This behaviour has been already evidenced on τ_f in the GHz region for a similar system [19]. In Fig. 5, it is also plotted the calculated value of (τ_ε), determined by the mixing rule $\tau_\varepsilon = \nu_1\tau_{\varepsilon 1} + \nu_2\tau_{\varepsilon 2}$, with ($\tau_{\varepsilon 1}$, ν_1) and ($\tau_{\varepsilon 2}$, ν_2) corresponding, respectively to the ZMT and CT phases. Both calculated and measured τ_ε values linearly decrease by increasing the $CaTiO_3$ amount but the measured values are lower than the theoretical ones. To explain this slight difference, several assumptions can be proposed. Firstly, heterogeneous distribution of Ca, Zn and Ti atoms in the polycrystalline microstructure may affect the dielectric properties of the ZMT–ZB–xCT mixture and hence the temperature coefficient. This point has been already evoked by Ramirez et al. [20] when they studied the frequency dependence on the dielectric properties of $Ca_2Cu_2Ti_4O_{12}$. Secondly, microstructure defects which could not easily observed by SEM, such as phase separation or segregation, may also affect the dielectric behaviour of such compound [20]. Thirdly, the addition of a glass phase, as a sintering aid, should be considered as a third phase which may affect the temperature dependence of the permittivity [21–23]. All these parameters should be taken into consideration to understand the shift between calculated and measured values of τ_ε. Nevertheless, from the technological aspect, it is shown that the temperature coefficient of ZMT can be controlled owing to the addition of $CaTiO_3$ and a temperature coefficient of the permittivity close to zero is obtained when the CT amount is around 7 mol%. A prototype of silver/ZMT–ZB–07CT-based capacitor has been fabricated, with a sintering temperature of 930 °C. Fig. 6 shows a SEM observation of a cross-section of this sample. No silver diffusion into the ceramic has occurred, showing the good

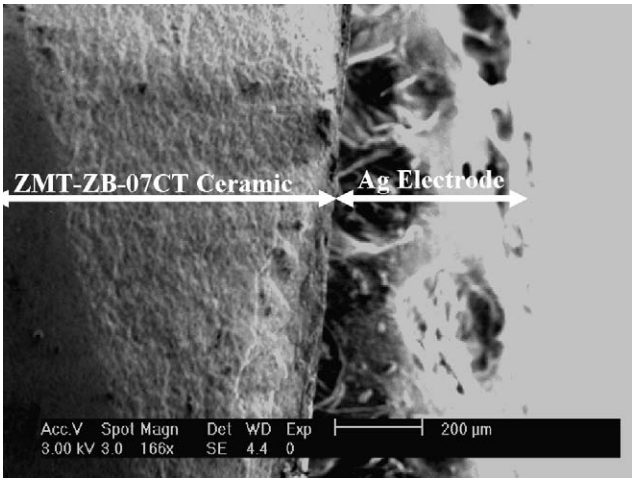

Fig. 6. Scanning electron micrographs of ZMT–ZB–07CT samples co-fired with Ag at 930 °C for 2 h.

compatibility between both materials. This ZMT–ZB–07CT component exhibits very attractive dielectrics properties, i.e. a low-temperature coefficient of permittivity $\tau_\varepsilon = -4$ ppm/°C with $\varepsilon_r = 21$, $\tan(\delta) < 10^{-3}$ and $\rho > 10^{14}\ \Omega$ cm.

4. Conclusion

The structure, microstructure and dielectric properties of $(Zn_{0.65}Mg_{0.35})TiO_3 + xCaTiO_3$ (with $x = 0, 0.02, 0.05, 0.07, 0.1$) ceramics sintered at low temperature with $ZnO–B_2O_3$ glass phase were investigated. From the dilatometric studies, it was shown that the sintering temperature was lowered to 930 °C owing to the

Table 2
Dielectric properties and density of the sintered ceramics at 1 MHz.

Sample	Sintering temperature	Density in % of theoretical	ε_r	Tan(δ)	τ_ε (ppm/°C)	Mean grains size (μm) (from SEM)
ZMT–ZB	930 °C	95	20	$<10^{-3}$	105	5
ZT–ZB–02CT	930 °C	94	19		69	4
ZT–ZB–05CT	930 °C	94.15	20		30	3.5
ZT–ZB–07CT	930 °C	94.9	21		−4	3
ZT–ZB–1CT	930 °C	96.27	23		−48	2.5

addition of 2 wt.% of $ZnO–B_2O_3$ glass phase. It has been shown that the sintered samples contained both ZMT and CT phases, without other crystallised secondary phase. In quite agreement with the mixing rule, the permittivity temperature coefficient of the mixture linearly varies with the $CaTiO_3$ content from positive to negative values, passing from zero for the ZMT–ZB–07CT compound. A prototype, based on this formulation, co-fired with silver electrodes at 930 °C, exhibits low-temperature coefficient of the dielectric constant $\tau_\varepsilon = -4$ ppm/°C, $\varepsilon_r = 21$, $\tan(\delta) < 10^{-3}$ and $\rho > 10^{14}\ \Omega$ cm. These properties make this formulation suitable for silver-based multilayer ceramic capacitors manufacturing.

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