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Low temperature sintering of $ZnTiO_3/TiO_2$ based dielectric with controlled temperature coefficient

A. Chaouchi [a,b], S. Marinel [a,*], M. Aliouat [b], S. d'Astorg [a]

[a] *Laboratoire CRISMAT, UMR 6508 CNRS/ENSICAEN, 6 Bd Maréchal Juin, 14050 Caen cedex, France*
[b] *Laboratoire de Chimie Appliquée et Génie Chimique, Université de Tizi-Ouzou Mouloud Mammeri, Algeria*

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Abstract

Structure, microstructure and dielectric properties of $ZnTiO_3$ and rutile TiO_2 mixtures ($ZnTiO_3 + xTiO_2$ with $x = 0$, 0.02, 0.05, 0.1, 0.15 and 0.2) sintered using $ZnO–B_2O_3$ glass phase (5 wt.% added) as sintering aid have been investigated. For all compounds, the sintering temperature achieves 900 °C. The X-ray diffraction patterns indicate for $x = 0.1$ that the material is composed by three phases identified as $ZnTiO_3$ hexagonal, TiO_2 rutile and ZnO. The presence of ZnO is explained by the introduction of Ti into Zn site to form the $(Zn_{1-x}Ti_x)TiO_{3+x}$ solid solution in resulting the departure of ZnO from the $ZnTiO_3$ structure. The $ZnTiO_3 + 0.15TiO_2$ composition sintered at 900 °C with glass addition exhibits attractive dielectrics properties ($\varepsilon_r = 23$, $\tan(\delta) < 10^{-3}$ and a temperature coefficient of the dielectric constant near zero ($\tau_\varepsilon = 0$ ppm/°C)) at 1 MHz. It is also shown that the introduction of TiO_2 allows to tune the temperature coefficient of the permittivity. All these properties lead this system compatible to manufacture silver based electrodes multilayer dielectrics devices.

Keywords: Perovskite; Dielectric properties; Capacitors; $ZnTiO_3$; TiO_2; Sintering

1. Introduction

The rapid development of the wireless communication implies to design new ceramics sinterable at low temperature, e.g. at around 900 °C and exhibiting good dielectric properties. This low sintering temperature is of primary importance to produce silver co-sintering devices such as silver based multilayer ceramic capacitors or hybrid circuits.[1,2] The required specifications in term of dielectrics properties are a high dielectric constant ($\varepsilon_r > 20$), a high quality factor ($Q > 10{,}000$) which corresponds to a low dielectric loss ($\tan(\delta) = 1/Q$) and a temperature coefficient of the permittivity close to zero ppm/°C. Two temperature coefficients are commonly used; the first one is the temperature coefficient of the resonant frequency (τ_f) and the second one is the temperature coefficient of the permittivity (τ_ε). The two both coefficients are linked by the well-known relation $\tau_f = (-1/2)\tau_\varepsilon + \alpha$ in which α is the thermal expansion coefficient.[3] The control of one coefficient means that the second one is also tuned. All these requirements must be fulfilled at high frequency range (from MHz to GHz) that will allow to produce more performer and more miniaturized electronic devices needed in the telecommunication system. Golovchanski et al.[4] reported that $ZnTiO_3$ ceramic is a promising microwave dielectric material because it only requires a sintering temperature of about 1100 °C in the absence of sintering additives and exhibits attractive dielectrics properties ($\varepsilon_r = 19$, $QXf = 30{,}000$ GHz, $\tau_\varepsilon \cong +120$ ppm/°C). In a recent paper,[5] the glass phase addition on $ZnTiO_3$ phase has been carefully examined in terms of sinterability and dielectric properties. It was precisely shown that the formulation $ZnTiO_3 + 5$ wt.% of $(ZnO–B_2O_3)$ could be sintered at 900 °C. The resulting sintered samples exhibit attractive dielectric properties at high frequency range, e.g. a relative permittivity around 22 and low dielectric losses ($\tan(\delta) < 10^{-3}$). However, the τ_ε value has been measured to be higher than +100 ppm/°C on this sample. The difficulty in controlling the temperature coefficient stands in the presence of secondary phases, as Zn_2TiO_4 and TiO_2. It is indeed well established that Zn_2TiO_4 and TiO_2 phases are stable at high temperature leading very difficult the obtaining of $ZnTiO_3$ as single phase.[6] One strategy developed for controlling the temperature coefficient is to

* Corresponding author. Tel.: +33 2 31 45 13 69; fax: +33 2 31 95 16 00.
E-mail address: sylvain.marinel@ensicaen.fr (S. Marinel).

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add a compound with a very high value of the temperature coefficient with an opposite sign. Haga et al.[7] have studied the mixture $(1-x)$ $ZnTiO_3$ ($\tau_\varepsilon \cong +100$)[8] $+ xTiO_2$ ($\tau_\varepsilon \cong -500$ ppm/°C)[9] to tailor the temperature coefficient according to the well-known mixing rule. This rule links the resulting temperature coefficient (τ_ε) of a composite versus the temperature coefficients of the compounds belonging to the material and characterised by their volume fractions (respectively $\tau_{\varepsilon 1}$, ν_1 and $\tau_{\varepsilon 2}$, ν_2): $\tau_\varepsilon = \nu_1\tau_{\varepsilon 1} + \nu_2\tau_{\varepsilon 2}$. Haga et al. have shown that the temperature coefficient tuning of $ZnTiO_3 + xTiO_2$ mixture is not trivial because of $ZnTiO_3$ decomposition at high temperature (>945 °C) into $Zn_2TiO_4 + TiO_2$. This leads very difficult the control of $ZnTiO_3/TiO_2$ ratio at the end of the sintering stage. In this context, the purpose of our work is to investigate the dependence of τ_ε versus x in the system $ZnTiO_3 + xTiO_2 + 5$ wt.% ($ZnO–B_2O_3$) glass phases. The low temperature sintering (900 °C), obtained via the glass phase addition, should permit to avoid the $ZnTiO_3$ decomposition, resulting in a better control of the $ZnTiO_3/TiO_2$ ratio. Hence, a control of the temperature coefficient could be expected. Practically, various compounds consisting in a $ZnTiO_3 + xTiO_2 + 5$ wt.% ($ZnO–B_2O_3$) mixture with $x = 0$, 0.02, 0.05, 0.1, 0.15, and 0.2 have been prepared. Specimens were sintered at 900 °C and characterised in terms of structure, microstructure, density and dielectric properties.

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 equimolar ratio. The mixing was performed in ammoniac solution at pH 11 using zircon balls in a Teflon jar for 3 h. These conditions were found to be optimal to obtain a very well-dispersed slurry.[10,11] The slurry was subsequently dried and the powder was manually reground and heat treated at 800 °C for 2 h in air. The powder was finally reground using the same process than before in ammoniac solution at pH 11 for 2 h. For the glass preparation, the ZnO (crystallised, purity >99%) and the 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 mixtures were then melted at 1100 °C for 1 h in a platinum crucible and quenched at room temperature in deionised water. These glasses were grinded in a planetary grinder for 45 min in order to obtain a fine powder. The mixtures $ZnTiO_3 + 5$ wt.% ($ZnO–B_2O_3$) glass $+ xTiO_2$ for $x = 0$, 0.02, 0.05, 0.1, 0.15, and 0.2 were prepared by mixing the powders in a planetary grinder for 45 min in absolute ethanol. Each formulation is named ZT–ZB–xT, the x value being the TiO_2 molar content introduced per mol of $ZnTiO_3$ (see Table 1). To manufacture the pellets, an organic binder (Polyvinyl alcohol at 5 vol.%) was manually added to the powder and disks (8 or 6 mm in diameter, 2 mm in thickness) were shaped by uni-axial pressing at a load of about 2100 kg. The green 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 density of the pellets were characterised using a He pycnometer (Accupyc 1330). In-Ga electrodes were manually deposited on each face of the disks and the dielectric properties versus temperature (from −60 to 160 °C) were determined using a RLC bridge (PM6306) at 1 MHz. The crystallised phase composition has been identified by X-ray diffraction (XRD) technique using the Cu Kα radiation (Philips X' Pert) and the microstructures were observed using a Scanning Electron Microscopy (SEM Philips XL'30).

Table 1
Table depicting the symbol and the composition of the studied ceramics

$ZnTiO_3$ (mol)	$ZnO–B_2O_3$ glass (wt.%)	TiO_2 (mol)	Composition name
1	5	0	ZT–ZB
		0.02	ZT–ZB–0.02T
		0.05	ZT–ZB–0.05T
		0.1	ZT–ZB–0.1T
		0.15	ZT–ZB–0.15T
		0.2	ZT–ZB–0.2T

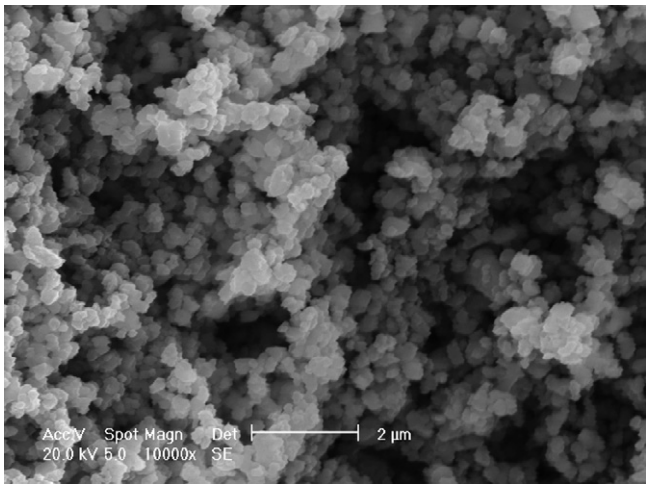

Fig. 1. Scanning electron micrographs (SEM) of powders $ZnTiO_3$ calcined at 800 °C.

3. Results and discussion

After the calcination step at 800 °C, the powder is mainly composed by $ZnTiO_3$ and $Zn_2Ti_3O_8$ phases. Takai et al.[12] have indeed reported that pure $ZnTiO_3$ phase is very difficult to

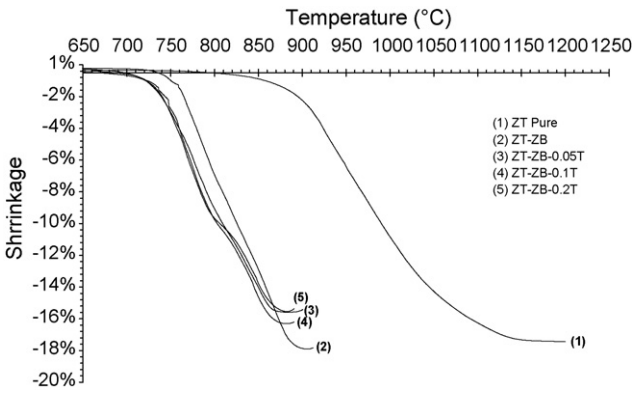

Fig. 2. Shrinkage curves vs. temperature.

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

Sample	Sintering temperature	Relative density	ε_r	Tan(δ)	τ_ε (ppm/°C)
ZT–ZB	900 °C	96	20	$<10^{-3}$	149
ZT–ZB–0.02T		96	22		72
ZT–ZB–0.05T		96.5	24		93
ZT–ZB–0.1T		95.5	22		−13
ZT–ZB–0.15T		98	23		0
ZT–ZB–0.2T		97	27		−55

synthesise. After the grinding process, $ZnTiO_3$ based powder presents a very fine microstructure and a very narrow distribution of grains size centred at around 400 nm (Fig. 1). The shrinkage versus temperature curves of the $ZnTiO_3$ based powder, with and without glass phase addition, are given in Fig. 2. The temperature of the maximum shrinkage is around 1150 °C for the glass free compound whereas the glass phase added sample could be sintered at around 900 °C. This temperature has a very attractive practical aspect since it authorises a silver co-sintering. As it can be easily observed in Fig. 2, the introduction of rutile TiO_2 has not significantly modified the TMA curves. Hence all compositions (from $x = 0$ to 0.2) have been sintered at 900 °C allowing to achieve, for all specimens, a relative density higher than 95% of

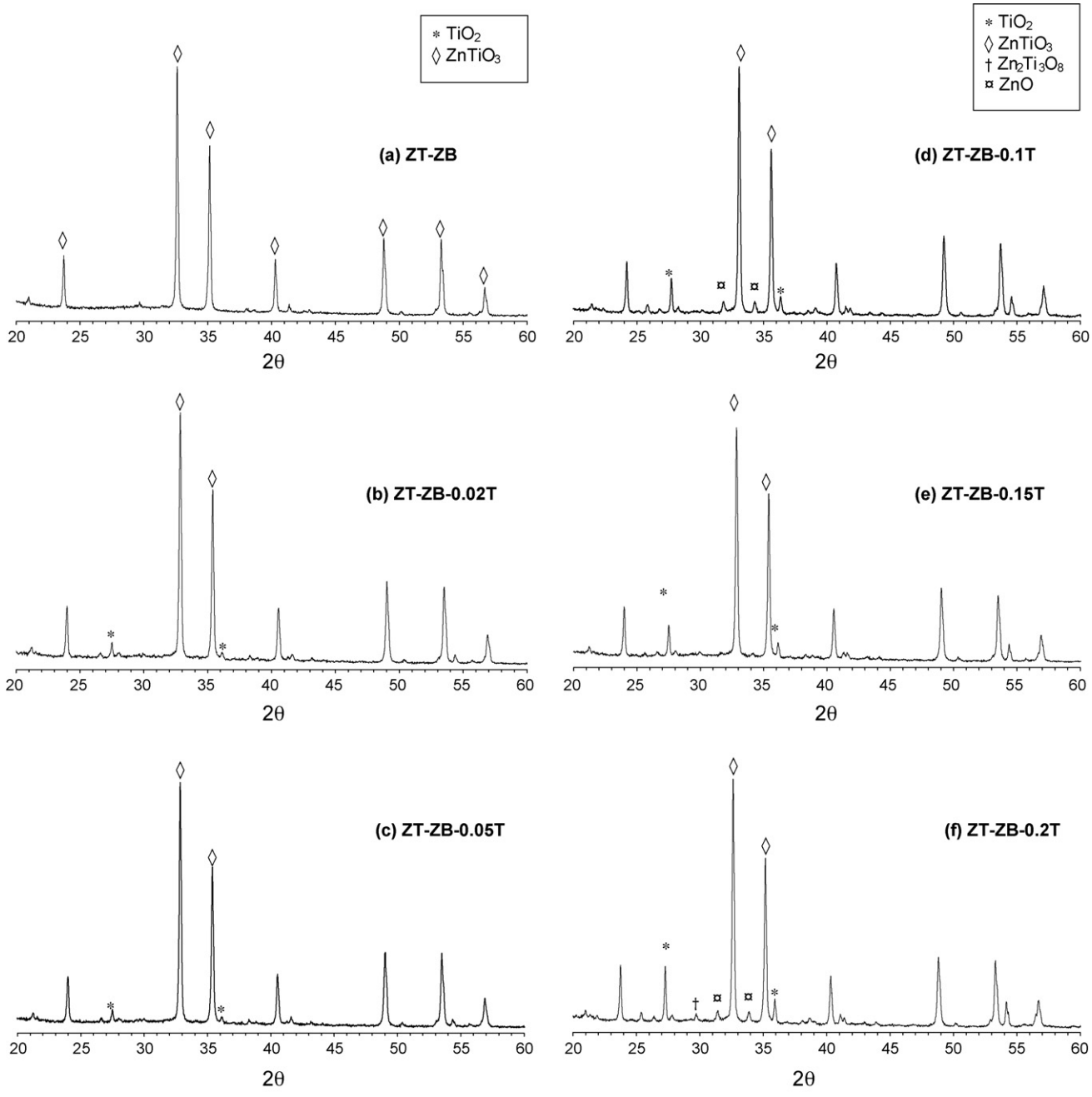

Fig. 3. XRD patterns of ceramics sintered at 900 °C.

the theoretical value (see Table 2). It must be mentioned that the theoretical density was determined by calculating the mean theoretical density of the mixture '$ZnTiO_3 + xTiO_2$' for each x value. Fig. 3 shows the XRD patterns of the various compounds as a function of x. It is important to mention that XRD patterns were recorded from powders coming from sintered specimens; that is the most convenient way to get information from the global composition of the materials. For $x = 0$, the XRD pattern indicates that the hexagonal $ZnTiO_3$ phase is the unique crystallised phase (Fig. 3(a)). This result evidences that the addition of the glass phase promotes the hexagonal $ZnTiO_3$ crystallisation as it has been previously published.[5] For ZT–ZB–xT samples with $x = 0.02$ and 0.05, XRD patterns indicate only the presence of $ZnTiO_3 + TiO_2$ (Fig. 3(b) and (c)). For $x = 0.1$ (Fig. 3(d)), the $ZnTiO_3$, TiO_2 and ZnO phases are clearly observable. The ZnO apparition could be explained by a substitution mechanism ($Zn \Leftrightarrow Ti$) already evoked by the group of Kim et al.[13] in the Zn_2TiO_4 crystal. In this oxide, Ti^{4+} occupies both sites, i.e. the octahedral and the tetrahedral sites and they discussed about the electronic transport properties of the $Zn_{2-2x}Ti_{1+x}O_4$ solid solution. In the $ZnTiO_3$ system, the structure is quite different: Zn^{2+} and Ti^{4+} occupy, respectively the tetrahedral and octahedral sites and, in this environment, their ionic radii are nearly identical, respectively 0.600 and 0.605 Å.[14] It is admitted that Ti^{4+} can substitute Zn^{2+} into the tetrahedral site implying the formation of the $(Zn_{1-x}Ti_x)TiO_{3+x}$ solid solution. This mechanism is assumed to occur when there is an excess of TiO_2. The consequence is that some ZnO is rejected from $ZnTiO_3$ as it can be described by the following equation:

$$ZnTiO_3 + xTiO_2 \rightarrow (Zn_{1-x}Ti_x)TiO_{3+x} + xZnO$$

It is suggested that the presence of the glass phase could promote the formation of $(Zn_{1-x}Ti_x)TiO_{3+x}$ due to the increase of the atomic diffusion. To confirm this assumption, the refinement of the diffraction patterns has been performed and the cell volume of the hexagonal $ZnTiO_3$ phase has been determined versus x. Fig. 4 shows the variation of the cell volume against the TiO_2 content (x). From $x = 0$ to $x = 5\%$, the cell volume of the $ZnTiO_3$ continuously increases which suggests the partial introduction of Ti into the Zn site as described above (the Ti^{4+} ion having an ionic radii higher than Zn^{2+} one). The XRD pattern of the ZT–ZB–0.15T powder (Fig. 3(e)) is quite different since the ZnO phase has disappeared. A possible explanation is that the excess of ZnO rejected from $ZnTiO_3$ to form $(Zn_{1-x}Ti_x)TiO_{3+x}$ has reacted with the excess of TiO_2 to form $ZnTiO_3$ again. This is probably due to the large amount of TiO_2 introduced in this compound. The decreasing of the cell volume accounts for this phenomena (Fig. 4). It can be also mentioned that this

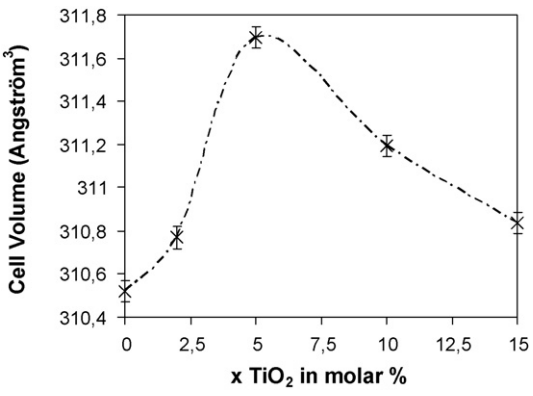

Fig. 4. Variation of the cell volume vs. the TiO_2 addition.

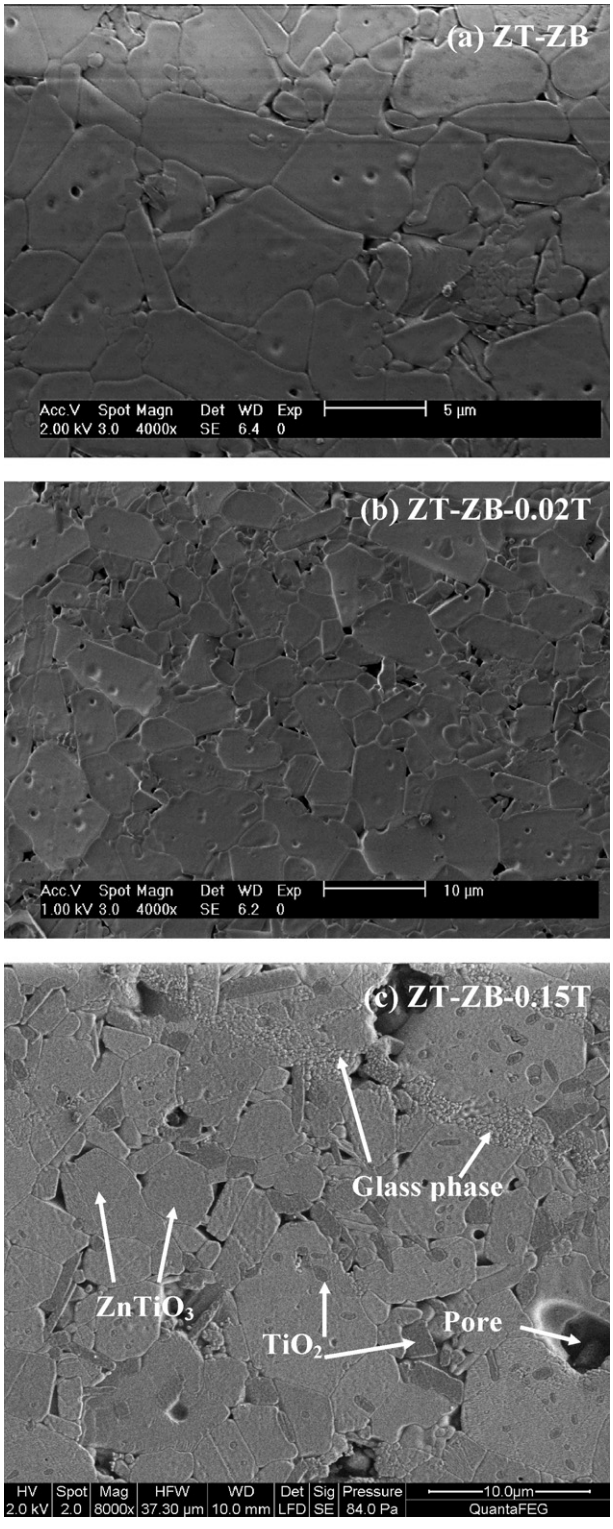

Fig. 5. Scanning electron micrographs of ceramics sintered at 900 °C.

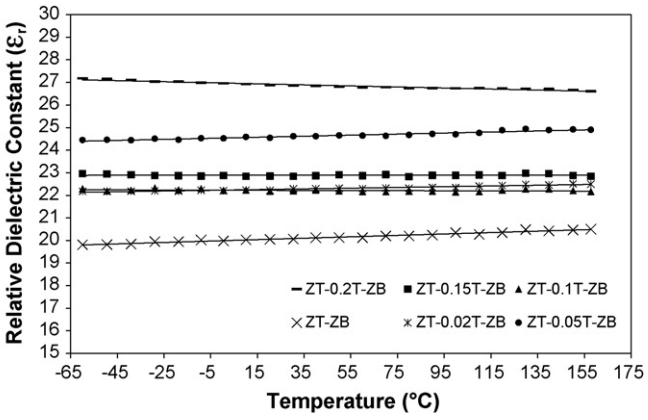

Fig. 6. Relative permittivity of ceramics vs. temperature at 1 MHz.

phenomena has probably begun for a TiO_2 amount lower than 15%, since for $x = 10\%$, the cell volume has started to decrease. For $x = 0.2$, the XRD pattern (Fig. 3(f)) indicates the presence of four main phases: $ZnTiO_3$, ZnO, $Zn_2Ti_3O_8$ and TiO_2. The system is becoming so complex that no value of '$ZnTiO_3$' cell parameters has been accurately obtained. The very large amount of TiO_2 essentially conducts to the formation of a multi-phase ceramic. This investigation unambiguously shows the complex chemistry of the $ZnTiO_3$/TiO_2 system.

The microstructures of ceramics are shown in Fig. 5. The ZT–ZB compound (Fig. 5(a)) is well dense beside the presence of some intra granular pores. The grains are elongated which is a typical feature of $ZnTiO_3$ (see also Fig. 5(b)). When TiO_2 is added in a large amount (for example ZT–ZB–0.15T), the microstructure is much more heterogeneous (Fig. 5(c)). The EDS system has permitted to discriminate phases visible on the SEM micrographs. Typical grains of $ZnTiO_3$ are easily found, the TiO_2 grains have a cubic shape with a grain size around 3–5 μm and the glass phase is randomly distributed at the grain boundaries (Fig. 5(c)).

The dielectric constant versus temperature curves for the system ZT–ZB–xT are plotted in Fig. 6. The first observation is that the higher the TiO_2 content, the higher the relative permittivity. This is due to the high value of TiO_2's permittivity ($\varepsilon_r \cong 100$).[9] Nevertheless, there is not a linear dependence of ε_r versus x; this could be related to the reactivity between the TiO_2 and $ZnTiO_3$ phases as previously discussed. The dependence of τ_ε versus x is also not linear (Fig. 7), probably due to the same reason (reactivity in the system $ZnTiO_3$–TiO_2). However, the τ_ε value tends to decrease as the TiO_2 content increases passing from positive to negative values. In the range $0.1 < x < 0.15$, the temperature coefficient is lower than 10 ppm/°C in absolute value. This range of x values corresponds to the domain where ZnO preferentially reacts with TiO_2 to form $ZnTiO_3$, leading to the presence of mainly $ZnTiO_3 + TiO_2$. This binary mixture leads to a better control of the τ_ε parameter. Even though the $ZnTiO_3$–TiO_2 chemistry is complex, these results are, from a practical aspect, very interesting to process high temperature stable capacitors with silver electrodes. A prototype of silver/$ZnTiO_3$ based capacitor has been designed from the composition ZT–ZB–0.15T. The sintering temperature was 900 °C for a dwell time of 2 h. Fig. 8 shows a SEM observation of a cross section of this sample. No silver diffusion into the ceramic has occurred showing a satisfying compatibility between the electrode and the ceramic. This component exhibits very attractive dielectrics properties, i.e. a room temperature relative permittivity around 24, a permittivity temperature coefficient of 3 ppm/°C and a loss factor lower than 10^{-3} at 1 MHz.

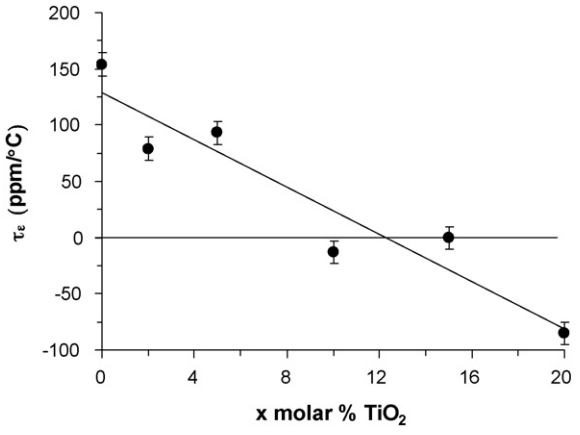

Fig. 7. Temperature coefficient of the permittivity versus the TiO_2 addition amount in the system ZT–ZB–xT.

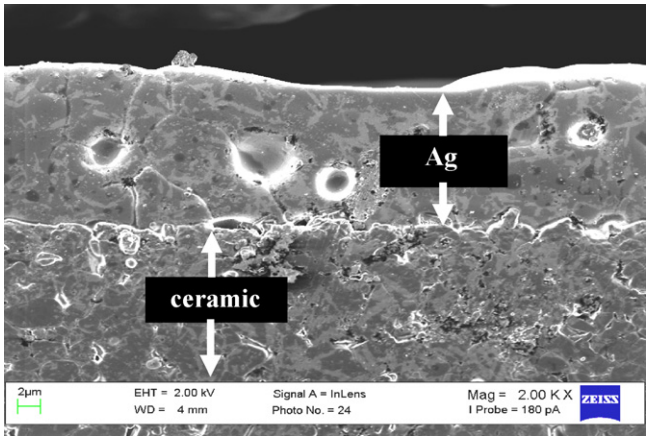

Fig. 8. Scanning electron micrographs of ZT–ZB–0.15T samples co-fired with Ag at 900 °C for 2 h.

4. Conclusion

The structure, microstructure and dielectric properties of the $ZnTiO_3$ (hexagonal) + TiO_2 (rutile) system have been investigated. Low temperature sintering has been allowed by the addition of ZnO–B_2O_3 glass phase. The $ZnTiO_3$ based material was sintered at 900 °C adding 5 wt.% of glass phase. Otherwise, the introduction of TiO_2 does not modify the TMA curves. Usual densities of 95–96% of the theoretical are routinely obtained in these sintering conditions. The composition of the ceramics analysed by X-ray diffraction technique clearly shows the complexity of the $ZnTiO_3$–$xTiO_2$ system. For $x = 0.1$, a peak characteristic of ZnO is clearly identified suggesting that the Ti^{4+} for Zn^{2+} substitution is effective to form the $(Zn_{1-x}Ti_x)TiO_{3+x}$ solid solution. At higher TiO_2 content ($x = 0.15$), the excess of titanium oxide tends to react with ZnO to form again $ZnTiO_3$

and at very high TiO_2 content ($x = 0.2$), a multi-phases material is obtained (presence of $ZnTiO_3$, ZnO, $Zn_2Ti_3O_8$ and TiO_2). It is clearly evidenced that the temperature coefficient of the permittivity highly depends on the x content. The τ_ε value tends to decrease as the TiO_2 content increases passing from positive to negative values. In the range $0.10 < x < 0.15$, the temperature coefficient is lower than 10 ppm/°C in absolute value which is very interesting from a practical aspect. All the other properties are maintained (loss factor, permittivity). A prototype of silver/$ZnTiO_3$ based capacitor has been designed from the composition ZT–ZB–0.15T which exhibits very attractive dielectric properties, i.e. a temperature coefficient close to zero ($\tau_\varepsilon = 3$ ppm/°C), $\varepsilon = 24$ and $\tan(\delta) < 10^{-3}$ at 1 MHz. These properties make this formulation suitable to fabricate silver based multilayer ceramic capacitors.

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