



Low temperature sintered ZnTiO₃ dielectric ceramics with temperature coefficient of dielectric constant near zero

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Abstract

ZnTiO₃ compound is an attractive dielectric ceramics owing to its interesting dielectric properties in high frequency range ($\epsilon_r = 19$, $QXf = 30,000\text{GHz}$, $\tau_\epsilon \approx +120\text{ ppm/}^\circ\text{C}$). The structure, microstructure and dielectric properties of sintered ZnTiO₃, with a mixture of ZnO-B₂O₃ 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 (τ_ϵ). This parameter varies from positive to negative values with increasing the CuO content. The ZnTiO₃ composition sintered at 850°C with 5 wt.% ZnO-B₂O₃ glass phase and 2.2 wt.% CuO addition exhibits attractive dielectric properties ($\epsilon_r = 23$, $\tan \delta < 10^{-3}$ and a temperature coefficient of the dielectric constant near zero, $\tau_\epsilon = 3\text{ ppm/}^\circ\text{C}$) 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

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 ($\epsilon_r > 20$), a low dissipation factor ($\tan \delta < 10^{-3}$), a small temperature coefficient of the resonant frequency (τ_f) or a small temperature coefficient of the dielectric constant (τ_ϵ) [1,2] in high frequency range ($> 1\text{ MHz}$). 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 ZnTiO₃ ceramic has excellent dielectric properties ($\epsilon_r = 19$, $QXf = 30,000\text{ GHz}$, $\tau_\epsilon \approx +120\text{ ppm/}^\circ\text{C}$) and moreover, this is a promising candidate as

base material for low temperature sintering devices owing to its relatively low sintering temperature ($\sim 1150^\circ\text{C}$) without sintering aids. Kim *et al.* [4] have also investigated the low temperature sintering of ZnTiO₃-TiO₂ system using B₂O₃ addition with the aim to control τ_ϵ . 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)ZnTiO₃+xTiO₂ (where $\tau_\epsilon = +100$ for ZnTiO₃ [8] and $\tau_\epsilon = -500\text{ ppm/}^\circ\text{C}$ for TiO₂ [7]) 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 $\tau_{\epsilon 1}$, v_1 and $\tau_{\epsilon 2}$, v_2): $\tau_\epsilon = v_1 \tau_{\epsilon 1} + v_2 \tau_{\epsilon 2}$. Haga *et al.* [7] have shown that the temperature coefficient tuning of ZnTiO₃ + TiO₂ mixture is not trivial because of ZnTiO₃ decomposition at high temperature ($>945^\circ\text{C}$) into Zn₂TiO₄ + TiO₂. This leads to a very difficult control of ZnTiO₃/TiO₂ ratio at the end of the sintering stage.

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

In previous studies, CuO liquid phase is introduced as sintering aid to lower down the sintering temperature of several ceramics and obtain good dielectric properties [10–13]. Xing *et al.* [14] showed that the increase the quantity of the liquid phase sintering in ZnTiO_3 (ZT) ceramics, accelerate the decomposition of ZT to TiO_2 and Zn_2TiO_4 .

In this work, it is aimed to develop a new strategy for both lowering down the sintering temperature and controlling the permittivity temperature coefficient (τ_c) using appropriate additives. For this goal, the effect of a mixture of $\text{ZnO-B}_2\text{O}_3$ as glass phase additive on the decreased sintering temperature has been investigated. Moreover, the compound CuO has been also added in a view of controlling the temperature coefficient. 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 prepared. Specimens were then sintered at low temperature and characterised in terms of density, structure, microstructure and dielectric properties.

II. Experimental

ZnTiO_3 compound was prepared by solid state reaction between reagent graded precursors of ZnO and

Table 1. Symbol and the composition of the studied ceramics

Symbol for composition	ZnO-B ₂ O ₃ glass [wt.%]	CuO [wt.%]
ZT-ZB	5	0
ZT-ZB-0.5CuO	5	0.5
ZT-ZB-1CuO	5	1
ZT-ZB-2CuO	5	2
ZT-ZB-2.2CuO	5	2.2
ZT-ZB-2.3CuO	5	2.3
ZT-ZB-2.5CuO	5	2.5
ZT-ZB-3CuO	5	3
ZT-ZB-4CuO	5	4

TiO_2 (purity >99%). The precursors were appropriately weighted according to the Zn/Ti=1 molar ratio. Mixing 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 using zirconia balls in teflon jar for 3 hours. These conditions 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 ammoniac solution at pH=11 for 2 hours. 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 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-

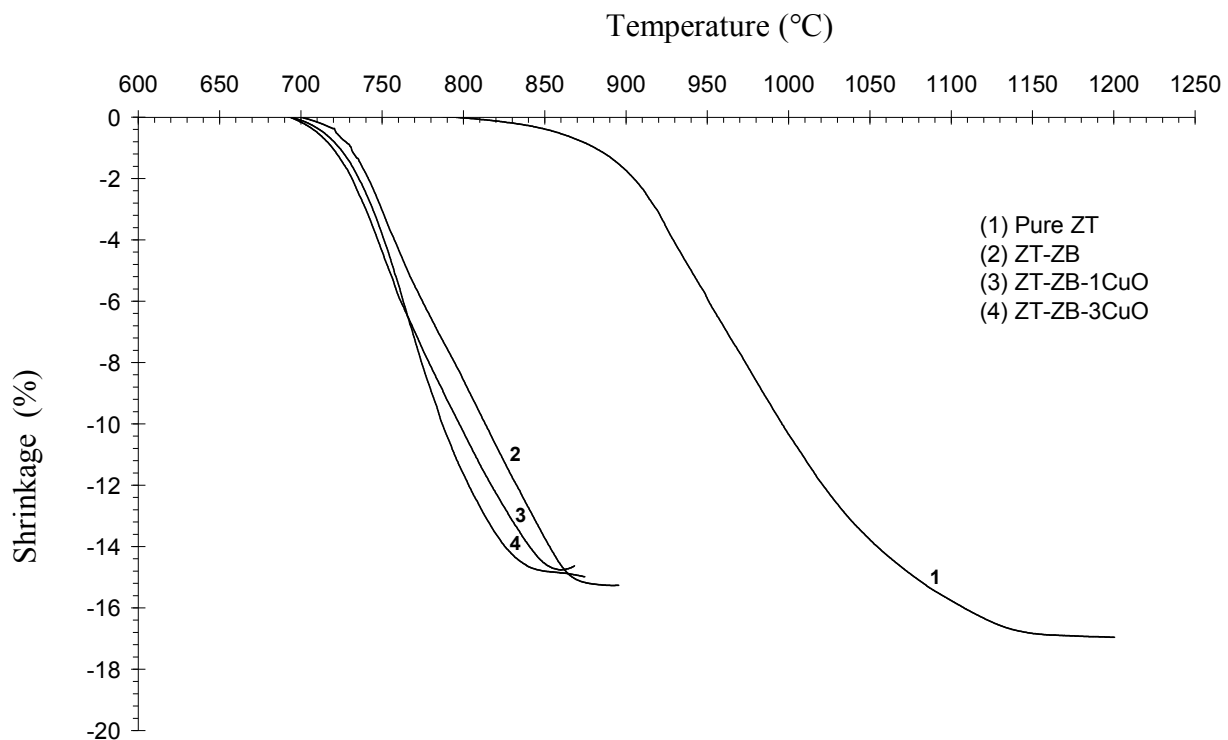


Figure 1. Shrinkage curves versus temperature

etary grinder for 45 minutes to obtain a fine powder. The mixture $\text{ZnTiO}_3 + 5 \text{ wt.}\% (\text{ZnO-B}_2\text{O}_3) \text{ glass} + x \text{ wt.}\% \text{ CuO}$ for $x=0, 0.5, 1, 2, 2.2, 2.3, 2.5, 3$ and 4 were prepared by mixing the powders in a planetary grinder for 45 minutes in absolute ethanol. Each formulation is named ZT-ZB- $x\text{CuO}$ (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°C to $+160^\circ\text{C}$. Crystallised phase composition has been identified by X-ray diffraction technique using the $\text{CuK}\alpha$ 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 ZnTiO_3 and $\text{Zn}_2\text{Ti}_3\text{O}_8$ phases. Reground 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 ZnTiO_3 based powders are given in Fig. 1. The temperature at which the maximum shrinkage is achieved for glass free 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 authorises a silver co-sintering. Fig. 2 shows the XRD patterns of ZT-ZB- $x\text{CuO}$ (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 ZnTiO_3 phase is the unique crystallised phase (Fig. 2a). This confirms that the addition of the glass phase favours the hexagonal ZnTiO_3 crystallisation as published elsewhere [9]. For $x = 0.5$ to $4 \text{ wt.}\%$, the sintered ceramics is multi-phased. The peaks of Zn_2TiO_4 and TiO_2 rutile phases were systematically observed showing that the ZnTiO_3 starts to decompose into the cubic Zn_2TiO_4 and TiO_2 at 850°C . This decomposition of 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 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 ZnTiO_3 phase decrease with increasing the CuO amount. In the same time, the characteristic peaks of the Zn_2TiO_4 and TiO_2 compounds strongly and simultaneously increase. This shows that the CuO addition enhances the formation of Zn_2TiO_4 and TiO_2 . Finally, when $x = 4 \text{ wt.}\%$, the hexagonal ZnTiO_3 phase has practically disappeared, Zn_2TiO_4 and TiO_2 being the major phases (Fig. 2c).

The bulk density of 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 $1\text{--}2 \mu\text{m}$. 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- $x\text{CuO}$ and Table 2 summarises the main dielectric

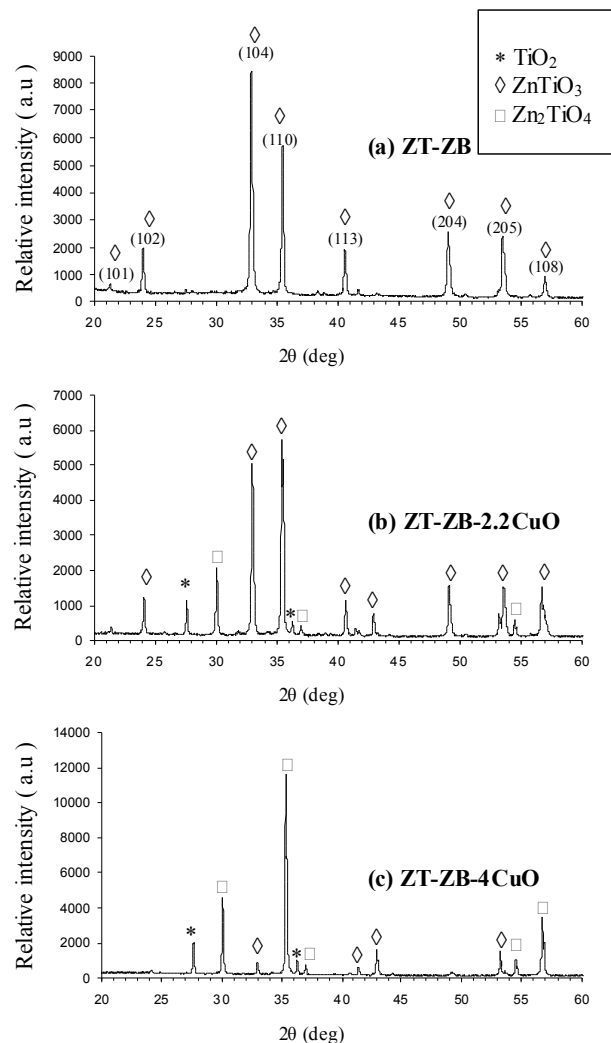


Figure 2. XRD patterns of ceramics sintered at 850°C : a) ZT-ZB, b) ZT-ZB-2.2 CuO and c) ZT-ZB-4 CuO

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

Sample	Sintering temperature [°C]	Relative density [%TD]	ϵ_r	$Tan \delta$	τ_c [ppm/°C]	ρ_i [$\Omega \cdot cm$]
ZT-ZB	850	95	20.5	$< 10^{-3}$	195	4.5×10^{14}
ZT-ZB-0.5CuO	850	95	20	$< 10^{-3}$	171	2.7×10^{11}
ZT-ZB-1CuO	850	97	20	$< 10^{-3}$	130	1.9×10^{10}
ZT-ZB-2CuO	850	95	23	$< 10^{-3}$	64	1.8×10^{10}
ZT-ZB-2.2CuO	850	98	23.5	$< 10^{-3}$	3	2.8×10^{10}
ZT-ZB-2.3CuO	850	97	24	$< 10^{-3}$	-20	5×10^{10}
ZT-ZB-2.5CuO	850	98	25	$< 10^{-3}$	-80	5.1×10^{10}
ZT-ZB-3CuO	850	93	25	$< 10^{-3}$	-83	9.8×10^9
ZT-ZB-4CuO	850	93	17	$< 10^{-3}$	-126	9.1×10^9

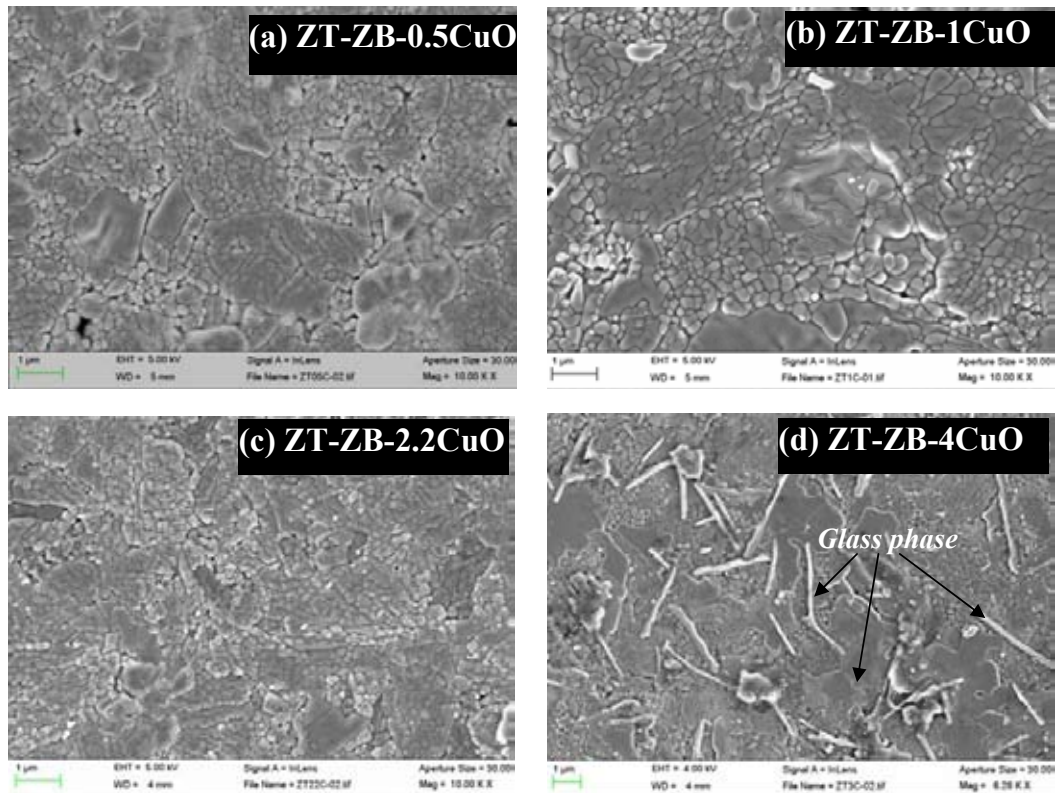


Figure 3. Scanning electron micrographs (SEM) of ceramics sintered at 850°C for 2h

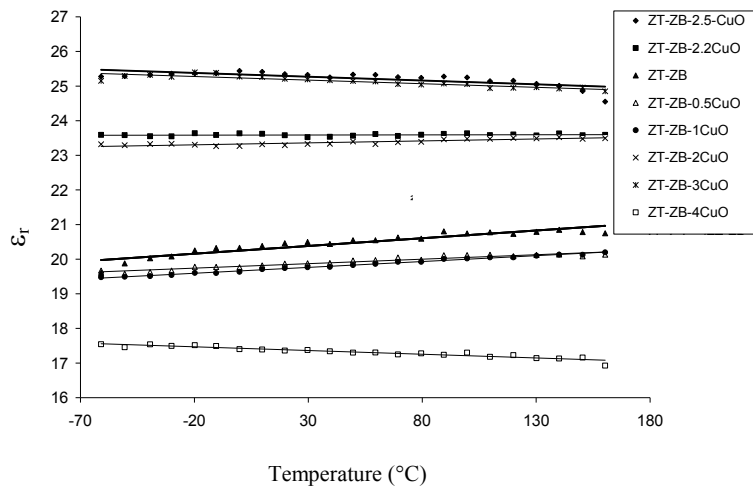


Figure 4. Dielectric characteristics of ceramics versus temperature at 1 MHz

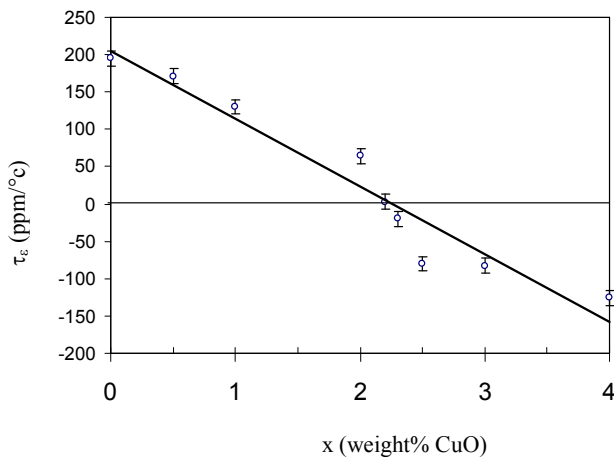


Figure 5. Temperature coefficient of dielectric constant (τ_{ϵ}) versus the CuO addition amount

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 ($\epsilon_r(\text{TiO}_2) \approx 100$) [4]. The dielectric losses are always lower than 10^{-3} . The dependence of τ_{ϵ} 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 τ_{ϵ} of TiO_2 ($\tau_{\epsilon}(\text{TiO}_2) < -500$ ppm/°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 τ_{ϵ} value which we obtained on ZT-ZB-2.2CuO sample sintered at 850°C which is $\tau_{\epsilon} = 3$ ppm/°C with a room temperature permittivity of around 23.

The resistivity of all composition is systematically higher than $10^{10} \Omega \cdot \text{cm}$. This value is convenient for most of the applications in dielectric devices (capacitors, LTCC, resonators, etc.). To show feasibility of

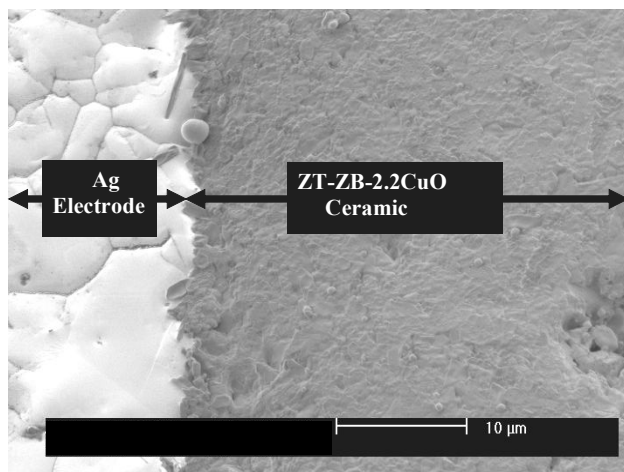


Figure 6. Scanning electron micrographs of ZT-ZB-2.2CuO samples co-fired with Ag at 850°C for 2 hours

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°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/°C and a loss factor lower than 10^{-3} .

IV. Conclusions

The effect of a mixture ($\text{ZnO-B}_2\text{O}_3$) 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 $\text{ZnTiO}_3 + 5 \text{ wt.}\% (\text{ZnO-B}_2\text{O}_3)$ formulation. The sintering temperature of the glass-added ZnTiO_3 samples is lowered down to 850°C compared to glass free compound which requires 1150°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 $\text{Zn}_2\text{TiO}_4 + \text{TiO}_2$ 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/°C with low loss factor ($< 10^{-3}$). Finally, a prototype of silver/ ZnTiO_3 based capacitor has been successfully sintered at 850°C from this composition exhibiting similar dielectric properties ($\tau_{\epsilon} = 1$ ppm/°C, $\epsilon_r = 24$ 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.

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