Low temperature sintering of the binary complex perovskite oxides $Ba(Zn_{1/3}Ta_{2/3})O_3$ + (1-x) $Ba(Mg_{1/3}Ta_{2/3})O_3$

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Abstract:

The interest for the complex perovskites oxides is known since several years. $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) and $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) have been broadly studied due to their attractive dielectric properties suitable for applications such as multilayer ceramic capacitors or hyperfrequency resonators. They hence exhibit at 1 MHz very low dielectric losses combined with a high relative dielectric constant which is stable with the temperature. Several complex formulations x $Ba(Zn_{1/3}Ta_{2/3})O_3$ + (1-x) $Ba(Mg_{1/3}Ta_{2/3})O_3$ (with x=0, 1/3, 1/2, 2/3 and 1) have been processed by conventional solid state method to investigate dielectric properties as a function of x. Unfortunately, these materials needs a too high temperature to reach a satisfying density. The BMT sintering temperature is indeed higher than 1500°C, which is too high to envisage a co-sintering with copper (T_f=1083°C) or nickel (T_f=1450°C). For this goal, a glass phase addition is performed on the complex formulations. The sintering temperature lowering reached is higher than 400°C when 10 molar % of borate oxide is added to the complex formulations and the dielectric properties of the solid solution obtained are very attractive (ε=25 and τ_ε=-59 ppm/°C for x=1/3) for the fabrication of Base Metal Electrodes Multi Layer Ceramic Capacitors (BME-MLCC).

Introduction

Complex perovskites oxides such as $BaZn_{1/3}Ta_{2/3}O_3$ (BZT) and $BaMg_{1/3}Ta_{2/3}O_3$ (BMT) are known to exhibit good dielectric properties[1,2]. They hence present medium permittivities (respectively ε_{BZT}=30 and ε_{BMT}=25), low dependences of permittivities versus temperature (τ_ε <50ppm/°C), low losses factors (Q>1000) in a large scale of frequency (1KHz – 10GHz) and finally low temperature coefficients of the resonance frequency (τ_f <5ppm/°C).

These very attractive properties allow their uses in type I multilayers capacitors (MLCC) or in high performance resonators. Unfortunately, very high temperatures (>1500°C) are required to obtain good densification and then to optimize properties[3,4]. Moreover, at high temperature zinc departure can be observed in BZT[5] involving a decrease of dielectric properties. So, several studies have been investigated in order to decrease the temperature of densification by addition of sintering aids (lithium compounds, glasses…). In previous works, the effect of boron oxide (B_2O_3) has been shown to significantly decrease the sintering temperature of BMT (by 400°C)[6] and BZT (by 350°C)[7] in air without altering dielectric properties at 1MHz. It was also proved that the BMT samples are stables under reducing atmosphere (90%Ar/10%H_2) [8]. The reducing atmosphere is of primary importance to envisage the manufacturing of Base Metal Electrodes – MLCC (BME-MLCC) by the co-sintering of the dielectric material with copper (Melting point = 1083°C) or nickel (Melting point = 1453°C) electrodes. This atmosphere is indeed necessary to avoid electrodes oxidation.

This work investigates different compositions mixing BZT and BMT (x BZT + (1-x) BMT with x = 0, 1/3, 1/2, 2/3, 1) with addition of 10 molar% of B_2O_3. For the rest of this work, we will use the following names: 03 for BZT only, 12 for 1/3 BZT + 2/3 BMT, 11 for ½ BZT + ½ BMT, 21 for 2/3 BZT + 1/3 BMT and 30 for BMT only.

Experimental procedure:

$BaZn_{1/3}Ta_{2/3}O_3$ (BZT) and $BaMg_{1/3}Ta_{2/3}O_3$ (BMT) powders were prepared using commercial powders. $BaCO_3$ (Diopma 99.99%), ZnO (Cerac 99.995%), Ta_2O_5 (Cerac 99.99%) and MgO (Cerac 99.95%) are weighted in appropriate proportions to synthesise both phases. Precursors were ball-milled for two hours in a teflon jar using 1mm diameter zircon balls in wet conditions. The liquid used for BMT is absolute ethanol while the one used for BZT is an ammoniac solution (pH=11). These conditions were determined by an electrophoretic zetametry study [9].

The mixture is subsequently dried under infrared lamps and calcined in air in a tubular furnace applying suitable temperature (1200°C for 1 hour for BZT and 1300°C for 2 hours for BMT), these temperatures have been chosen according to a preliminary study [9]. The calcined powders obtained were re-milled for 1 hour using the same process. The powder purity is systematically controlled by X-ray diffraction (XRD) using the K_α Cu X-ray radiation. Borate oxide (B_2O_3 – Prolabo 98%) is then added to the x BZT + (1-x) BMT composition using a

planetary grinder for 45 minutes in absolute ethanol. The mixtures obtained after drying are uniaxially pressed at 3880 kg into 12.6 mm diameter pellets. These discs are sintered in air in a tubular furnace at the appropriate temperature deduced by dilatometric measurements (TMA 92 Setaram). Sintered samples are characterised in terms of final density (apparent density) and phase content using an XRD diffractometer (Philips X'Pert). Microstructures were observed using a Scanning Electron Microscopy (SEM Philips XL'30) on samples previously polished and stripped off with an acid etching (HF/HNO_3 mixture). Dielectric properties (tan (δ) and permitivity) were performed on discs with electrodes painted on each faces using an Indium Gallium eutectic (RLC bridges Fluke PM6306).

Results and discussion:

The first part of this work is devoted to the reference compounds process, without glass phase additions to determine the efficiency of the future additions. A dilatometric measurement was systematically performed on each of the five compositions (03, 12, 11, 21 and 30) and reported on the figure 1. The end of the BMT shrinkage is not yet finished at 1500°C, whereas the BZT is totally densified for a temperature close to 1400°C. These temperatures are in good agreement with those mentioned in the literature [3,4]. If we now consider the behaviour of the binary compounds, we can see that the 11 one is very close to the BZT one. The shrinkage starts at 1100°C to be finished at 1400°C. The two other compositions (12 and 21) are comparable but they have a higher densification temperature. Moreover, the shrinkage proceeds in two steps. The first one is fast between 1100°C to 1380°C. The second one is slower until 1560°C.

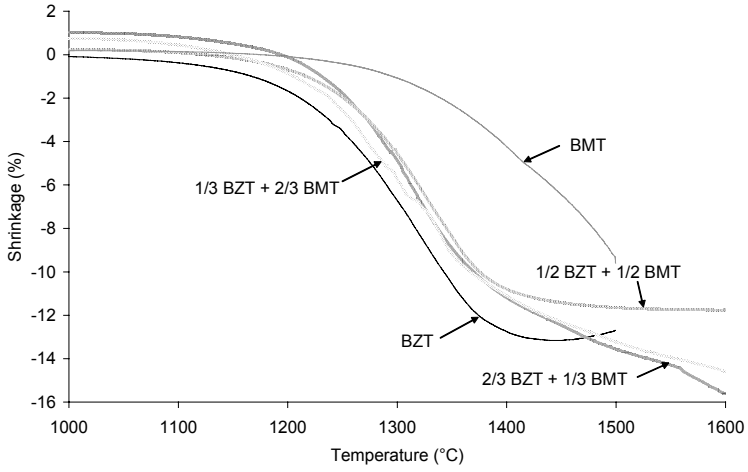

Figure 1

The borate oxide added compounds are now studied with the same protocol. The dilatometric curves are plotted on the figure 2. First, the B_2O_3 additions are very efficient for all compositions. All shrinkage temperatures are lowered. The unitary compositions (03 and 30) can be respectively sintered at 1150°C and 1200°C that is to say a remarkable 300°C sintering temperature lowering. The reduction is more spectacular on the binary compositions as the end of the shrinkage is obtained at 1070°C for the three compounds (12, 11 and 21).

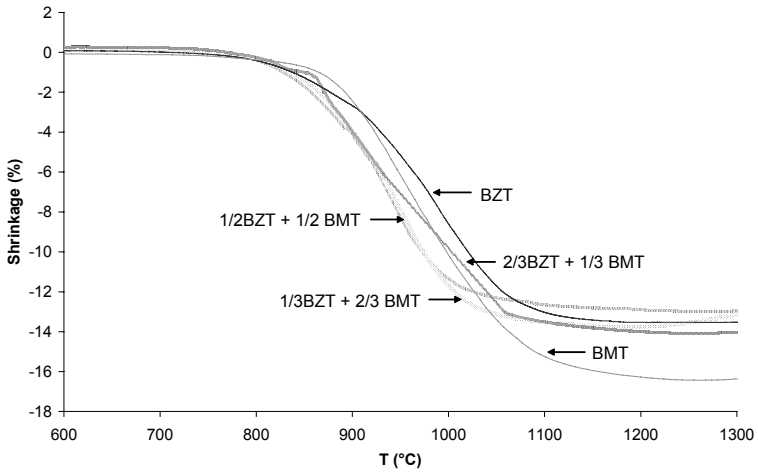

Figure 2

This could be very interesting in terms of sintering temperature as we can sinter our ceramics under the copper melting point (1083°C). Taking into account these results, several pellets of each composition are sintered in air in a tubular furnace at the well-fitted temperature. The thermal cycles slopes chosen are 200°C/h. The sintered pellets obtained are well-dense. Their densification are included in the range from 91 to 93% of the theoretical density calculated using the ratio between BMT and BZT. Their dielectric measurements were measured at 1 MHz and all the samples exhibit good dielectric properties which are resumed in the table 1.

Nominal compound	Theoretical density (g/cm^3)	Relative Density (% of theoretical one)	Epsilon	Temperature coefficient (ppm/°C)	Tan δ
BZT +10% B_2O_3 (03)	7.92	92	28.5	- 22	$< 10^{-3}$
2/3 BZT + 1/3 BMT +10% B_2O_3 (12)	7.82	93	27.5	- 43	$< 10^{-3}$
1/2 BZT + 1/2 BMT +10% B_2O_3 (11)	7.77	92	27.7	- 50	$< 10^{-3}$
1/3 BZT + 2/3 BMT +10% B_2O_3 (21)	7.72	91	25.3	- 60	$< 10^{-3}$
BMT +10% B_2O_3 (30)	7.63	92	25.2	- 84	$< 10^{-3}$

Table 1

We can see an evolution of the permittivity which regularly decreases from the 03 compound to the 30 one. The same phenomenon is remarkable considering the temperature coefficient which is equal to -22 ppm/°C for the 03 composition, and increase in absolute value to reach -84 ppm/°C for the 30 one. Moreover, the figure 3 shows a linear dependence of the temperature coefficient with the BMT proportion which wasn't evidenced for the permittivity. Concerning the last dielectric parameter measured, the dielectric losses are very low for all the samples as they are lower than 10^{-3}. The linear dependence of the temperature coefficient does not permit to conclude on a solid solution formation between BZT and BMT during the sintering step.

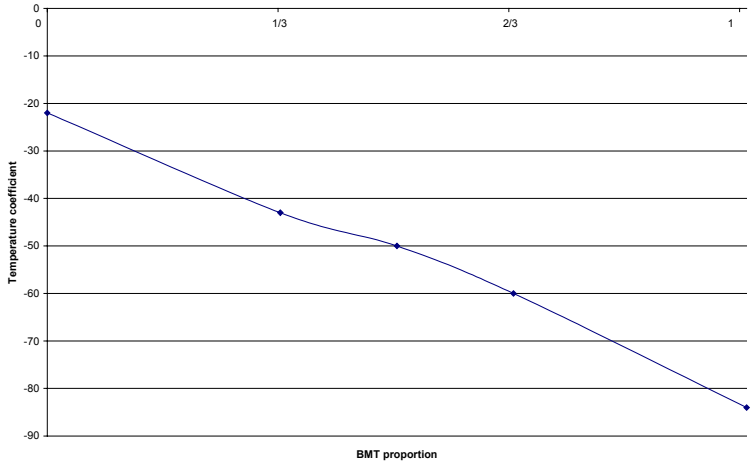

Figure 3

Nevertheless, the XRD characterisation performed on previously crushed samples was performed. On the first hand, the 03 and the 30 (unitary compositions) are single phase materials, exclusively composed by BZT or BMT respectively. the BZT and BMT phase. The three binary exhibits the same peaks than BZT or BMT phase as these two phases have nearly the same diffraction. The hypothesis of a solid solution is confirmed since the cell parameter continuously varies (refinement done using Jana 2000 [10]). The table 2 shows the perovskite cell parameter evolution versus the BMT proportion and the refinement parameters. Except the 21 composition which exhibits a too high cell parameter value, there is a regular increase of the perovskite cell parameter increasing from the 30 compound (4.092877 Å) to the 03 one (4.096422 Å). It is also noticeable that no secondary phase appears on diffraction diagrams for all compositions.

Compounds	BZT	2/3 BZT + 1/3 BMT	1/2 BZT + 1/2 BZT	1/3 BZT + 2/3 BMT	BMT
Cell parameter (10^{-10} m)	4.096422	4.095939	4.093896	4.098154	4.092877

Table 2

This hypothesis of the solid solution formation between BZT and BMT is confirmed by a SEM analysis. The EDS analysis prove the existence of a solid solution as the Mg and Zn contained in the grains are very close to the theoretical values calculated for each composition. If we now consider the grain size, it is very small due to the low sintering temperature. The average size is close to 100 nm illustrated by the SEM observation on the figure 4.

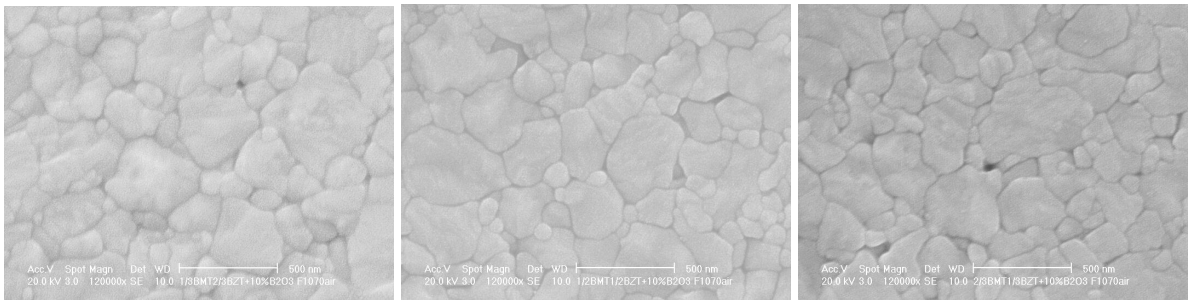

Figure 4

The last part of this study is devoted to the behaviour of the solid solution under reductive atmosphere. This condition is absolutely essential for the making of Base Metal Electrode Multi Layer Ceramic Capacitors. Several pellets of the five compounds were prepared and sintered under argon + 1% H_2 moisture saturated atmosphere. The sintering temperatures used are the same than under air (1150°C for 03, 1200°C for 30 and 1070°C for 12, 11 and 21). The first statement is the densification lowering when the zinc proportion is increased. This can be partially explained if we taking into account the XRD analysis. A secondary phase is detected which is identified as $Ba_5Ta_4O_{15}$ with a $Ba_3Zn_xMg_{1-x}Ta_2O_9$ solid solution. However the 30 compound is free of this secondary phase. This observation suggests that the $Ba_5Ta_4O_{15}$ is formed by the BZT decomposition according to the following equation:

$$BaZn_{1/3}Ta_{2/3}O_3 \rightarrow \frac{1}{3}ZnO + \frac{1}{6}(Ba_5Ta_4O_{15} + BaO)$$

This idea is confirmed by SEM observation combined with EDS analysis. Some porosity is present in our samples due to the zinc losses and the ratio between Ba and Ta

corresponds with the ratio which can be calculated in $Ba_5Ta_4O_{15}$. This phenomenon can explain the low density values calculated. These relative densities are hence calculated according to the pure BMT and BZT materials and does not take into account the secondary phase. The dielectric measurements on samples sintered under reductive atmosphere are collected on the table 3. The main difference with the sintering under air concerns the permittivity and temperature coefficient variations. Moreover, the 30 sample is the only one which exhibits good dielectric properties. Under reductive atmosphere, the permittivity regularly decreases from the 30 compound to the 03 one. The same phenomenon is remarkable considering the temperature coefficient which is equal to -20 ppm/°C for the 30 composition, and decrease to reach -250 ppm/°C for the 03 one. Nevertheless, a linear dependence can be extrapolated considering the theoretical Mg proportion of the different compositions. It is also remarkable that the dielectric losses become significant (10^{-2}) when we reach the 03 compound.

Nominal compound	Relative Density (% of theoretical one)	Epsilon	Temperature coefficient (ppm/°C)	Tan δ
BZT +10% B_2O_3 (03)	70	15	- 250	$< 10^{-2}$
2/3 BZT + 1/3 BMT +10% B_2O_3 (12)	77	17.5	- 183	$< 4.10^{-3}$
1/2 BZT + 1/2 BMT +10% B_2O_3 (11)	85	20.7	- 164	$< 3.10^{-3}$
1/3 BZT + 2/3 BMT +10% B_2O_3 (21)	88	21.9	- 141	$< 2.10^{-3}$
BMT +10% B_2O_3 (30)	89	25.6	- 20	$< 10^{-3}$

Table 3

Conclusions:

The sintering temperature lowering of the binary complex perovskite oxides $Ba(Zn_{1/3}Ta_{2/3})O_3$ + (1-x) $Ba(Mg_{1/3}Ta_{2/3})O_3$ has been investigated. First it was shown that a B_2O_3 addition authorises a significant sintering temperature reduction reaching 300°C in case of binary compounds (12, 11 and 21 ones). The pellets sintered in air at 1070°C during 2 hours exhibit very good dielectric properties (ε=27.7 and τ_ε=-50ppm/°C with no dielectric losses for the 11 compound) with a temperature coefficient which are linear dependant on the Mg content. Moreover, the existence of a solid solution between BZT and BMT has also been evidenced and a regular evolution of the perovskite cell parameter has been highlighted.

The effect of the reductive atmosphere has been also considered since it permits to envisage the making of copper BME-MLCC. The BZT behaviour under reductive atmosphere has influenced the samples properties. The formation of the $Ba_5Ta_4O_{15}$ secondary phase has hence been evidenced due to the zinc departure. A linear dependence of the dielectric properties with the Mg content was also remarkable. Copper co-sintering tests have to be envisaged on low zinc content binary compounds (21 or 30 ones) since the sintering temperature reached is lower than the copper melting point. Moreover, the good dielectric properties of these two samples (ε=21.9 and τ_ε=-141ppm/°C with low dielectric losses for the 21 compound) are suitable for the making of BME-MLCC.

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