



Effects of Glass Phase Additions and Stoichiometry on the $\text{Ba}(\text{Zn}_{1/3}\text{X}_{2/3})\text{O}_3$ ($X = \text{Ta}$ or Nb) Sinterability and Dielectric Properties

FRANÇOIS ROULLAND* & SYLVAIN MARINEL

Laboratoire CRISMAT UMR CNRS/ISMRA 6508, Université de Caen 6 Bd, Maréchal Juin, 14050 Caen cedex, France

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Abstract. $\text{Ba}(\text{Zn}_{1/3}\text{X}_{2/3})\text{O}_3$ materials where $X = \text{Ta}$ or Nb (respectively named BZT and BZN) exhibit attractive properties suitable for applications in type I Multi Layer Ceramics Capacitors (MLCC). Nevertheless, to produce such components using Base Metal Electrodes such as copper, a significant reduction of their sintering temperature is required. The aim of this work is first to study the effects of glass phases additions and secondly the stoichiometry influence on the sintering temperature of BZT and BZN. It is shown for example, that our materials can be sintered in air at a temperature lowered by 450°C when sintering agents (B_2O_3 with LiF) are combined with a slight non-stoichiometry. The sintered samples are characterised in terms of final density, microstructure and phase content and it was underlined that such modifications (additions and stoichiometry) does not affect the dielectric properties.

Keywords: ceramics, sintering, dielectric properties, glass phase, type I capacitors

Introduction

Complex perovskites $\text{Ba}(\text{Zn}_{1/3}\text{X}_{2/3})\text{O}_3$ where $X = \text{Ta}$ or Nb hold the attention of industrial company due to their attractive dielectric properties. These materials exhibit very low dielectric losses associated with a temperature stable permittivity and a high insulating resistivity that permits their use in type I capacitors. However, these two materials require a very high sintering temperature to reach a satisfactory density. It is indeed well established according to the literature that sintering temperatures higher than 1500 and 1350°C are needed respectively for the sintering of BZT [1] and BZN [2]. These temperatures are not suitable to manufacture Base Metal Electrodes Multilayer Ceramics Capacitors (BME-MLCC) where non-noble metals such as copper are used because of the low melting point of this metal (1083°C). For this reason the lowering of the sintering temperature by sintering agents additions is attractive. The effect of glass is known to reduce this temperature due to the presence of a liquid phase which can improve the species diffusion

[3]. Moreover lithium salts additions have been broadly studied in the case of BaTiO_3 and allow a significant reduction of the sintering temperature [4]. So in this work, the combined effect of these two agents has been considered. The second point which has focused our attention is the stoichiometry. The ABO_3 perovskites sinterability is well known to be sensitive to the stoichiometry [5]. Modifying the A/B ratio has a direct influence on the sinterability. In our perovskite, a deficiency in B site decreases the sinterability whereas a deficiency in A site increases the sinterability. The effect of a slight A site deficiency combined with the most efficient sintering agent has been also investigated in order to sinter such ceramics at very low temperature.

Experimental Procedure

$\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ and $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ nominal compounds were synthesised by an optimised solid state reaction [6] using high purity commercial powders. BaCO_3 (Diopma 99.99%), ZnO (Cerac 99.995%), Ta_2O_5 (Cerac 99.99%) and Nb_2O_5 (HC Starck 99.9%) were weighted in appropriate proportions and

*To whom all correspondence should be addressed. E-mail: roulland@ismra.fr

ball-milled in wet conditions (an NH_3 pH = 11 aqueous solution) during two hours using a Teflon jar (Netzsch 4V1M type) and 1 mm diameter zircon balls. The slurries obtained were dried under infrared lamps and manually ground before being calcined in air in a tubular furnace. The calcination cycle used was 1200°C during 1 h with 200°C/h slopes. An XRD analysis (Seifert XRD 3000P) was systematically performed to control the purity of the powders obtained. After the calcination step, BZT and BZN powders were re-milled by attrition for 1 h in NH_3 pH = 11 aqueous solution to recover a small grain size ($<1 \mu\text{m}$). The addition of sintering agents was subsequently performed using a planetary grinder for 45 min in alcoholic environment (absolute ethanol). The mixture obtained was dried and discs were uniaxially pressed into 8 mm diameter and 1 mm height using a 2870 kg load. Finally, the green samples were sintered in air in a tubular furnace with a well-controlled thermal cycle derived from a dilatometric measurement (TMA 92 Setaram).

The sintered discs obtained were characterised in terms of apparent final density, microstructure and dielectric properties. The samples were analysed on both the surface and the bulk using an XRD diffractometer (Philips X'Pert) and the microstructures were observed by Scanning Electron Microscopy (SEM Philips XL'30). The samples surfaces were previously polished and stripped off with a thermal etching to reveal the microstructure. The permittivity and the loss factor were measured using an LCR bridge (Fluke PM6306) on discs with electrodes painted on each face with an Indium-Gallium eutectic.

Results and Discussion

Effect of a Slight Non-Stoichiometry

In the $\text{ABB}'\text{O}_3$ perovskite structures, the A/B ratio can be modified by different ways. We can only change the B amount, only the B' amount, or finally change the $B + B'$ amount with B/B' constant. Precursors powders were weighted to precisely obtain a 1% deficiency in the A site. The compounds obtained were named $Z + 1$, $T + 1$ and $ZT + 1$ for BZT ones and $Z + 1$, $N + 1$ and $ZN + 1$ for BZN ones. The Z , T and ZT denominations mean that the 1% deficiency in the A site of BZT is obtained owing to an excess of Zn , Ta and $\text{Zn} + \text{Ta}$ respectively. The designations $Z + 1$, $N + 1$ and $ZN + 1$ have the same meaning in the case of BZN. Figure 1 shows the shrinkage of various BZT compounds versus the temperature and it can be seen that the non-stoichiometry does not modify the sinterability of our ceramics. The end of the shrinkage is always achieved around 1400°C . The phase content analysis shows that no secondary phase has appeared (see Fig. 2) and the cell parameter refined with Jana 2000 [7] is not modified (see Table 1) within the non-stoichiometry range investigated ($\leq 1\%$ deficiency in A site).

Effect of Glass Phases Additions on Stoichiometric Compounds

The effect of glass phases additions have been studied on the two stoichiometric compounds named BZT-0

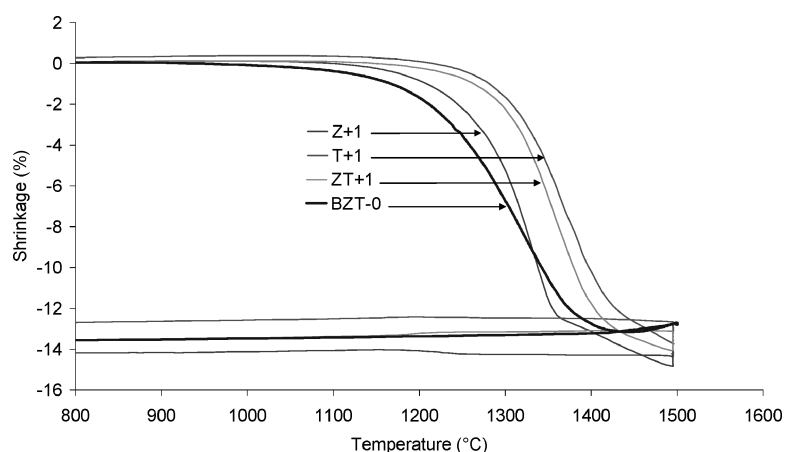


Fig. 1. Shrinkage curves of BZT-0 and non-stoichiometric BZT samples versus temperature.

Table 1. Cell parameter of BZT-0 and non stoichiometric BZT samples.

Compounds	BZT-0	Z + 1	T + 1	ZT + 1
Cell parameter (10^{-10} m)	4.09180 (± 0.00010)	4.09522 (± 0.00008)	4.09285 (± 0.000005)	4.09410 (± 0.00010)

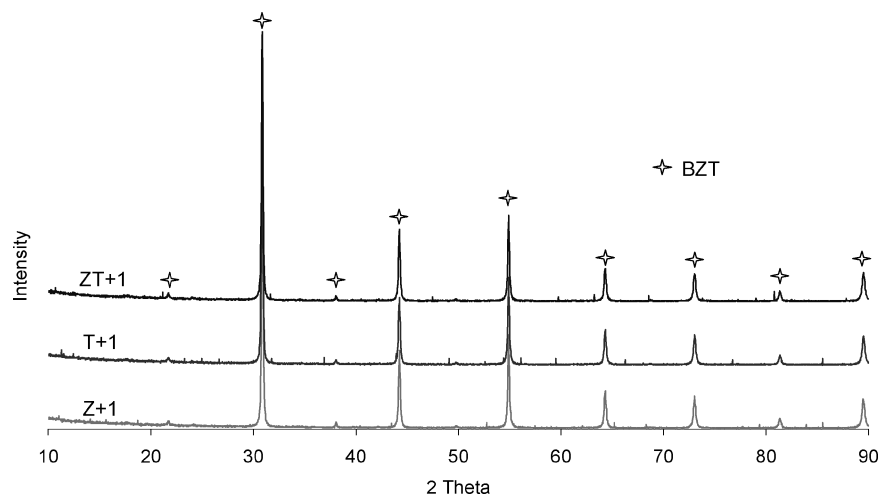


Fig. 2. X-ray Diagrams of BZT-0 and non-stoichiometric BZT samples.

and BZN-0. The two glass phases chosen are amorphous B_2O_3 and amorphous SiO_2 . First, an addition of 15 molar% of each glass system has been done. A dilatometric study is systematically performed on each mixture to observe the shrinkage as a function of the temperature. As we can see on the Fig. 3, a B_2O_3 addition is efficient for the lowering of the sintering temperature. It allows in both cases (BZT and BZN) a reduction of $300^\circ C$ of the sintering temperature with an acceptable final shrinkage value (13% for BZN sample and 15% for BZT one). If we now consider the SiO_2 additions, the results are more disappointing. The shrinkage of BZT-0 + 15% SiO_2 is complete at $1300^\circ C$ corresponding to a sintering temperature reduction of $200^\circ C$, with a final shrinkage value of 15% whereas the result for BZN-0 SiO_2 added is somewhat worse. The shrinkage proceeds in several steps as it can be seen on the derivative curve. Moreover, the strong shrinkage at $1400^\circ C$ combined with the sample deformation suggests that a fusion appears at this temperature.

A 10 molar% addition has been also tested on both BZT and BZN stoichiometric compounds to compare with the 15 mol% one. The dilatometric measurements shown in the Fig. 4 are similar between 10 and 15%

and these additions permit a sintering temperature reduction of $300^\circ C$. Nevertheless, the two compositions have been sintered to measure the properties of each one. Several pellets of each compound with the two B_2O_3 quantities have been sintered in air at $200^\circ C/h$ slopes. A 2 h dwell temperature was $1050^\circ C$ for BZN and $1200^\circ C$ for BZT. XRD analyses have been performed on each sintered sample obtained on both surface and bulk. In all cases, the ceramics are pure exhibiting only the BZT or the BZN perovskite phase. These X-ray diagrams are confirmed by a SEM analysis where no secondary phase is detected. The grain size for both compounds is very low (Fig. 5) and close to 100 nm which can be explained by the low sintering temperature. The dielectric measurements at 1 MHz are summarized in the Table 2 and for each material the results are very similar whatever the B_2O_3 quantity used (10% or 15%). For the BZT compounds, we have obtained good densities (92% of the theoretical one) and the basic material dielectric properties are not modified: ϵ_r is equal to 28.5 and 25.3 respectively for a 10% and a 15% B_2O_3 addition. The dielectric losses ($\tan \delta$) are less than 10^{-3} and the temperature coefficients of ϵ_r are negative and close to 0 (-22 ppm/ $^\circ C$ for 10% B_2O_3 and -28 ppm/ $^\circ C$ for 15% B_2O_3). The BZN

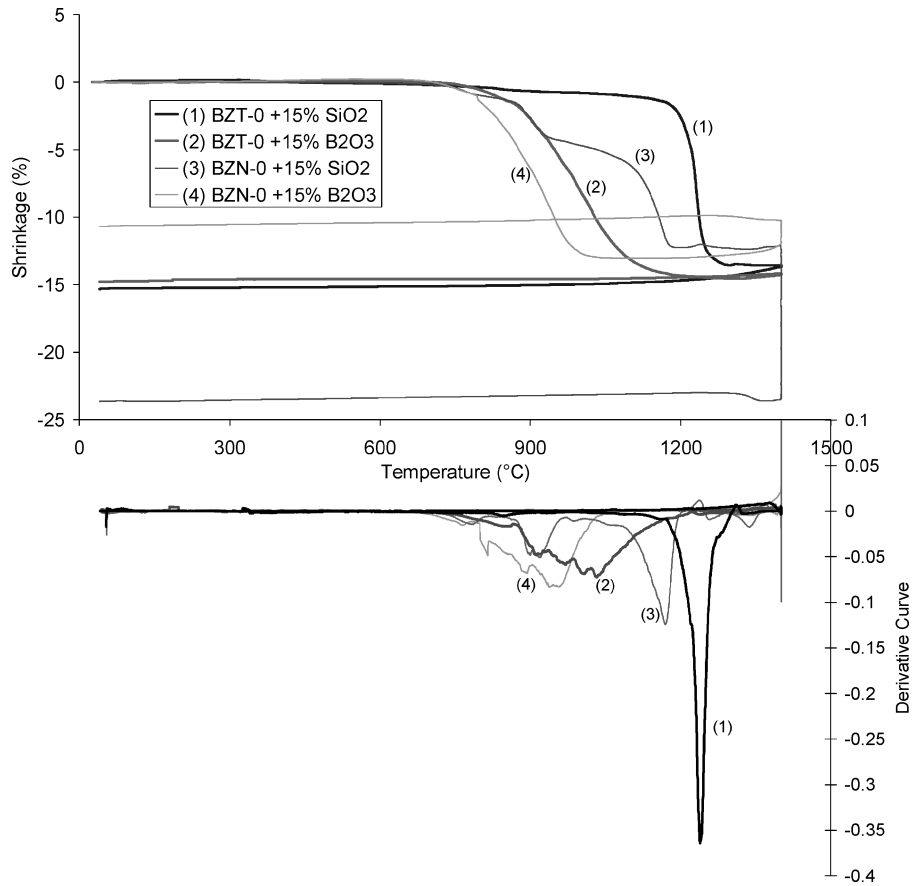


Fig. 3. Shrinkage curves and derivative curves of BZT-0/BZN-0 samples with 15% SiO₂ and B₂O₃ as a function of temperature.

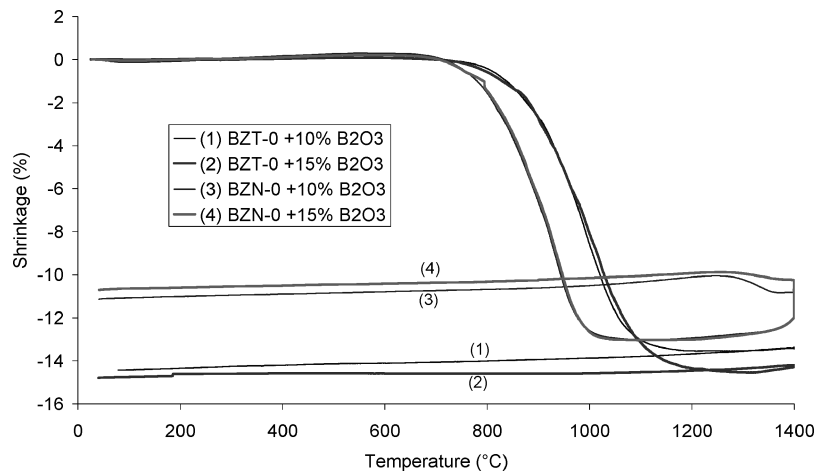
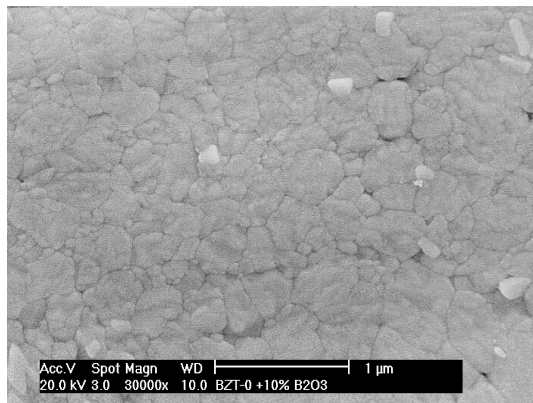


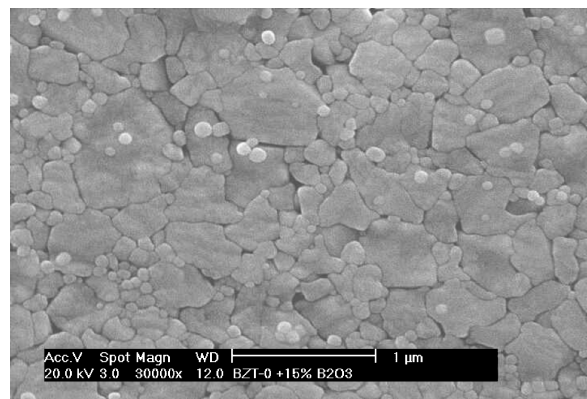
Fig. 4. Shrinkage curves of BZT-0/BZN-0 B₂O₃ added samples as a function of temperature.

Table 2. Dielectric properties of B₂O₃ added and B₂O₃ + LiF added BZT-0/BZN-0 sintered samples.

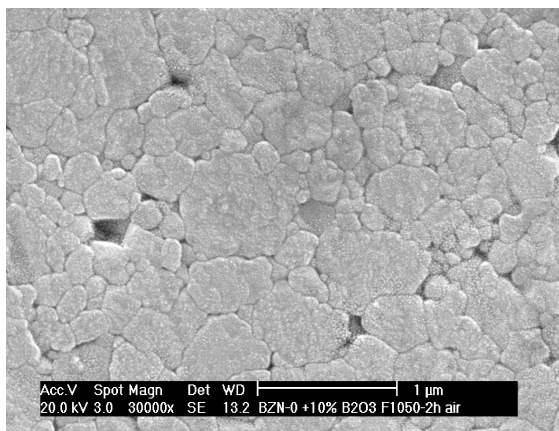
Nominal compound	Relative density (% of theoretical one)	Epsilon	Temperature coefficient (ppm/°C)	Tan δ	Resistivity ($\Omega \cdot \text{cm}$)
BZT-0 + 10% B ₂ O ₃	92	28.5	-22	$<10^{-3}$	$2.6 \cdot 10^{13}$
BZN-0 + 10% B ₂ O ₃	92	36.5	-74	$<10^{-3}$	$3.2 \cdot 10^{14}$
BZT-0 + 15% B ₂ O ₃	92	25.3	-28	$<10^{-3}$	$3.1 \cdot 10^{14}$
BZN-0 + 15% B ₂ O ₃	91	36.4	-74	$<10^{-3}$	$1.5 \cdot 10^{15}$
BZT-0 + 10% B ₂ O ₃ + 5% LiF	92	26.3	+73	$<10^{-3}$	$1.5 \cdot 10^{15}$
BZN-0 + 10% BaO ₃ + 5% LiF	91	36.9	+46	$<10^{-3}$	$1.3 \cdot 10^{14}$



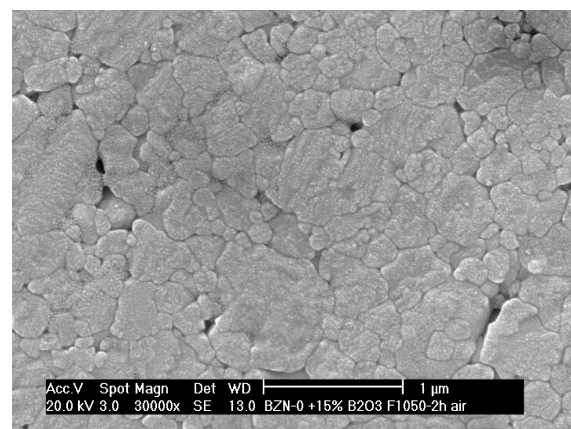
(a)



(b)



(c)



(d)

Fig. 5. Scanning electron micrographs of BZT-0/BZN-0 B₂O₃ added samples, (a) BZT-0 + 10% B₂O₃, (b) BZT-0 + 15% B₂O₃, (c) BZN-0 + 10% B₂O₃, (d) BZN-0 + 15% B₂O₃.

results confirm the fact that the amount of B₂O₃ added material does not modify the properties. In the case of a 10% B₂O₃ addition, we notice an ϵ_r equal to 36.5 with a negative temperature coefficient ($-74 \text{ ppm}/^\circ\text{C}$). For the 15% B₂O₃ addition, the permittivity is nearly the same ($\epsilon_r = 36.4$) with the same temperature coef-

ficient as the 10% added. The dielectric losses are still lower than 10^{-3} in each case.

The next part of the study was devoted to the investigation of the combination of the borate oxide additions with lithium fluoride additions to still lower the sintering temperature. As the results are similar between 10

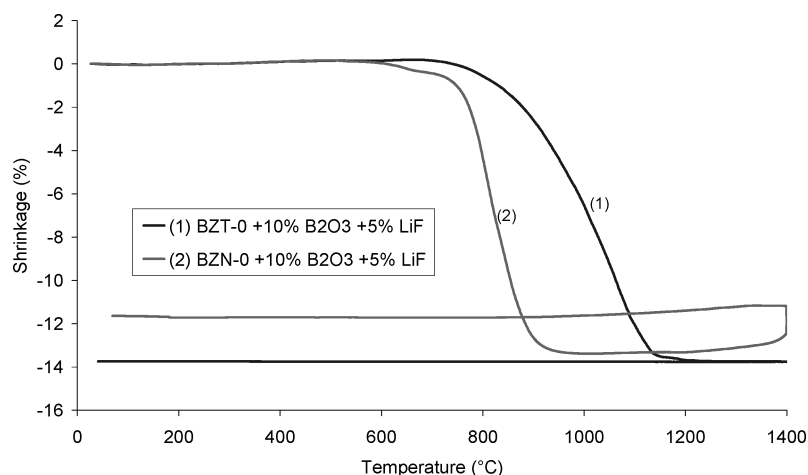


Fig. 6. Shrinkage curves of BZT-0/BZN-0 with 10% B_2O_3 and 5% LiF samples as a function of temperature.

and 15 molar% of B_2O_3 addition, it was decided to test only the amount of 10% in order to minimise the quantity of sintering agents added. A 10 mol% addition of B_2O_3 and a 5 mol% of LiF are done on BZT-0 and BZN-0 samples. As we can see on the dilatometric curves (Fig. 6), the sintering temperatures are still lowered by this combination. The shrinkage is totally achieved for a 1150°C temperature in case of BZT material, whereas a 1000°C temperature is enough for the BZN compound. Several pellets of BZT-0 + 10% B_2O_3 + 5% LiF and BZN-0 + 10% B_2O_3 + 5% LiF have been sintered to study their properties. The sintering is done in air with 200°C/h slopes at 1150°C for BZT and at 1000°C for BZN. All the samples are very well sintered with a final apparent density close to 92% of the theoretical one in both cases (BZT and BZN). The dielectric properties were measured at 1 MHz (see Table 2) and concerning BZT we found that its temperature coefficient becomes positive (+73 ppm/°C). The dielectric losses are still very low ($<10^{-3}$) and ϵ_r is equal to 26.3. For BZN, the LiF effect on τ_z is the same: it becomes positive (equal to +47 ppm/°C). The permittivity is the same as the previous compounds ($\epsilon_r = 36.3$) and the dielectric losses are still low ($<10^{-3}$). If we now consider the XRD analysis, only the BZT perovskite phase is observed in BZT-0 + 10% B_2O_3 + 5% LiF at the surface as well as at the bulk. On the other hand, a secondary phase is detected in BZN surface sample which disappears in the bulk. This secondary phase has been identified as zinc oxide. This one could not be detected with a SEM analysis. This remark confirms that this secondary phase is located only in the sample periphery since the sample

was polished before SEM observation. The grain size observed by SEM is still very low (≈ 100 nm).

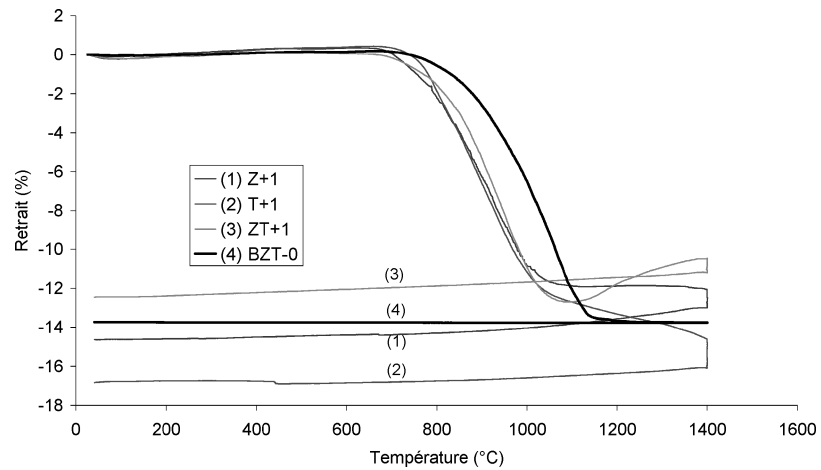
Combined Effects of Stoichiometry and Glass Phase Addition on the Sintering Temperature and the Dielectric Properties

Keeping in mind the copper melting point (1083°C), it is important to lower the BZT sintering temperature. For BZN, the objective of a sintering temperature lower than 1080°C is already achieved. So we have decided to test the most efficient sintering agent (10 mol% of B_2O_3 with 5 mol% of LiF) on each BZT non-stoichiometric compositions (Z + 1, T + 1, and ZT + 1). It has been observed that a combination of a slight non-stoichiometry with sintering agents addition can improve the sinterability. The nonstoichiometry improves the reactivity because vacancies are created in the structure. A dilatometric measurement is achieved on each mixture. We can see on the Fig. 7 that the origin of the non-stoichiometry have no influence on the shrinkage which starts at 700°C and finishes at 1050°C, which is lower than the melting point of copper. These latter results are very promising in terms of sintering temperature. The reduction is from 450°C considering the 1500°C sintering temperature mentioned in the literature [1].

Several pellets have been prepared (BZT Z + 1, T + 1 and ZT + 1 with a 10% B_2O_3 and 5% LiF addition) and sintered in air at 1050°C with a 2 h dwell and 200°C/h slopes. The final density reached is around

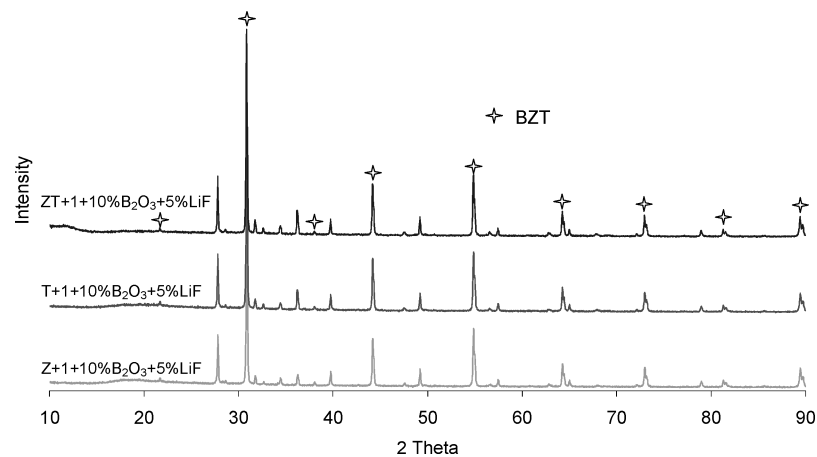
Table 3. Dielectric properties of non-stoichiometric BZT samples with 10% B₂O₃ and 5% LiF.

Nominal compound	Relative density (% of theoretical one)	Epsilon	Temperature coefficient (ppm/°C)	Tan δ	Resistivity ($\Omega \cdot \text{cm}$)
Z + 1 + 10% B ₂ O ₃ + 5% LiF	90	31.5	+98	$<10^{-3}$	$2.1 \cdot 10^{13}$
Z + 1 + 10% B ₂ O ₃ + 5% LiF	90	30.7	+107	$<10^{-3}$	$6.7 \cdot 10^{11}$
ZT + 1 + 10% B ₂ O ₃ + 5% LiF	90	29	+103	$<10^{-3}$	$5.8 \cdot 10^{11}$

Fig. 7. Shrinkage curves of BZT-0 and non stoichiometric BZT samples with 10% B₂O₃ and 5% LiF as a function of temperature.

90% for the three non-stoichiometric compounds and the dielectric properties at 1 MHz summarized in the Table 3 are very similar. The values observed for ϵ_r are close than the pure material ($\epsilon_r = 31.5$ for Z + 1, $\epsilon_r = 30.7$ for T + 1 and $\epsilon_r = 29$ for ZT + 1). The temperature coefficient is around 100 ppm/°C

($\tau_\epsilon = 98$ ppm/°C for Z + 1, $\tau_\epsilon = 107$ ppm/°C and $\tau_\epsilon = 103$ ppm/°C) and they exhibit dielectric losses lower than 10^{-3} . The phase content analysis performed by XRD reveals that no secondary phase is present on the samples bulks. In contrast, we can observe the same secondary peaks on all samples surfaces (Fig. 8).

Fig. 8. X-ray diagrams of non-stoichiometric BZT samples with 10% B₂O₃ and 5% LiF.

These secondary phases have not been yet identified. As we have said in the proceeding part, they could not be detected with a SEM analysis probably due to the polishing which removes the secondary phase from the surface, and the grain size observed is still very low (≈ 100 nm).

Conclusions

In our study, the lowering of the BZT and BZN sintering temperature has been investigated. The behaviour for this couple of material is quite similar. The best sintering agents combination is a mixture including 10 mol% of borate oxide and 5 mol% of lithium fluoride. Adding this proportion of agents to a stoichiometric material leads to a large lowering of the sintering temperature (350°C) without any modification of the main properties of the basic materials. The second aspect of this study was devoted to investigate the effect of the stoichiometry to be able to lower again the BZT sintering temperature. We saw that when 1% deficiency in A site is introduced in the added materials. This further lowered the sintering temperature by 100°C . We have also seen that the non-stoichiometry origin does not influence neither the sintering temperature nor the dielectric properties. These latest compounds seems to be very promising for manufacturing BME-MLCC since

we can sinter BZN as well as BZT at a temperature below the copper melting point. Further investigations are still in progress to determine an atmosphere which could be compatible for co-sintering our ceramics with copper electrodes.

Acknowledgment

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References

1. S. Kawashima, M. Nishida, I. Ueda, and H. Ouchi, *Journal Amer. Ceram. Soc.*, **66**(6), 421 (1983).
2. K.S. Hong, I.T. Kim, and C.D. Kim, *Journal Amer. Ceram. Soc.*, **79**(12), 3218 (1996).
3. C.L. Huang, M.H. Weng, C.T. Lion, and C.C. Wu, *Mat. Res. Bull.*, **35**, 2445 (2000).
4. J.M. Haussonne, G. Desgardin, P. Bajolet, and B. Raveau, *Journal Amer. Ceram. Soc.*, **66**(11), 801 (1983).
5. D.K. Lee, H.I. Yoo, *Sol. State Ionics*, **144**, 87 (2001).
6. F. Roulland, R. Terras, and S. Marinel, *Mat. Science Eng. B*, **104**(3), 156 (2003).
7. V. Petricek and M. Dusek, *Jana2000. The Crystallographic Computing System*, (Institute of Physics, Praha, Czech Republic, 2000).