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Ceramics International 32 (2006) 377–383

CERAMICS INTERNATIONAL

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# $Ba(Zn_{1/3}Nb_{2/3})O_3$ sintering temperature lowering for silver co-sintering applications

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Received 11 February 2005; received in revised form 14 March 2005; accepted 3 April 2005
Available online 25 May 2005

**Abstract**

The complex perovskite oxide $Ba(Zn_{1/3}Nb_{2/3})O_3$ have been broadly studied due to its attractive dielectric properties which place this material as a good candidate for manufacturing type I capacitors or hyperfrequency resonators. The development of Base Metal Electrodes Multi Layer Ceramic Capacitors (BME-MLCC) require a low sintering temperature to be co-sintered with a low cost metal such as copper or silver. Unfortunately, BZN requires a high temperature (1350 °C according to the literature) to reach a satisfactory density (>90% of the theoretical one). The aim of this work is to lower the BZN sintering temperature to allow a co-sintering with copper or silver electrodes. For this goal, different sintering agents (lithium salts and glass phases) have been tested on the nominal compound. It is shown that an addition of 10 molar% $B_2O_3$ combined with 5 molar% LiF authorises a sintering temperature lowering near to 350 °C. If a slight non-stoichiometry in A site is combined to these sintering agents, it is possible to reach a sintering temperature lower than 950 °C without affecting the basic material properties. For each composition obtained, the ceramic is characterised in terms of final density, microstructure and dielectric properties. The silver co-sintering is also performed.


*Keywords:* A. Sintering; D. Perovskites; E. Capacitors

## 1. Introduction

$Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) ceramic is very promising for electroceramics applications owing to their interesting dielectric properties. It can be used for example in applications, such as ceramics capacitors or hyperfrequency resonators. Their low dielectric losses, associated with a temperature stable permittivity and a high insulating resistivity, are compatible for manufacturing type I dielectric applications. Practically this ceramic needs a high sintering temperature to reach a satisfactory final density. The reported temperature is close to 1350 °C [1,2], that is too high to envisage a silver co-sintering ($T_{f(Ag)} = 961$ °C). For this reason, the lowering of the sintering temperature has been investigated. The effects of lithium salts are known to reduce the sintering temperature of $BaTiO_3$ relative phases [3,4]. These sintering agents can be tested with our material. Moreover, some glass phases additions can be used as sintering aids due to the presence of a liquid phase during sintering which can improve the species diffusion [5,6]. The combination of these two sintering agents has been also done with the aim to decrease the BZN sintering temperature below the silver melting point. Another parameter has been envisaged which is the stoichiometry. The effects of a slight non-stoichiometry are well known on the $ABO_3$ perovskites sinterability [7]. We have hence focused our attention on the silver co-sintering of the lowest sintering temperature composition. This point represents the final issue of our study because it could come out on silver-based MLCC manufacturing.

## 2. Experimental procedure

$Ba(Zn_{1/3}Nb_{2/3})O_3$ powders were synthesised using an optimised solid-state route [8]. High purity commercial powders ($BaCO_3$ Diopma 99.99%, ZnO Cerac 99.995% and

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0272-8842/$30.00 
doi:10.1016/j.ceramint.2005.04.002

$Nb_2O_5$ HC Starck 99.9%) are weighed in appropriate proportions according to the stoichiometric compound named BZN-0. The precursors were ball-milled for 2 h in a Teflon jar (Netzsch 4V1M type) using 1 mm diameter zircon balls in wet conditions (an $NH_3$ pH 11 aqueous solution). The homogeneous slurries obtained were subsequently dried under infrared lamps and calcined in air in a tubular furnace. The temperature used for the calcination was 1200 °C with a 1 h dwell and 200 °C/h slopes. An XRD analysis (Seifert XRD 3000P) is systematically performed on each sample to control its purity using the Kα Cu X-ray radiation. After the calcination, the powder was manually ground before re-milling by a 1 h attrition in $NH_3$ pH 11 aqueous solution to reach a fine diameter size (<1 μm). Sintering agents are then added using a planetary grinder for 45 min in alcoholic environment (absolute ethanol). The mixture obtained was dried and uniaxially pressed with a 2870 kg load into 8 mm diameter and 1 mm high pellets. These discs were sintered in air in a tubular furnace at the appropriate temperature deduced from a previous dilatometric study (TMA 92 Setaram). The ceramics obtained were characterised in terms of apparent final density and dielectric properties (relative permittivity, temperature coefficient and loss factor). These dielectric characterisations were done at 1 MHz in the range—60 °C/180 °C using an LCR bridge (Fluke PM 6306) on discs previously painted on each side with an indium–gallium eutectic for the contacts. A structural analysis was performed on both surface and bulk with an XRD diffractometer (Philips X'Pert), and the microstructure was 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.

## 3. Results and discussion

### 3.1. Effects of lithium salts additions on stoichiometric compounds

Firstly, the effect of several lithium salts on the stoichiometric compound named BZN-0 has been investigated. Four lithium salts (LiF, $BaLiF_3$, $LiNO_3$ and $Li_2CO_3$) have been chosen for their interesting well known effects on the sintering temperature lowering [9,10]. These lithium salts are added to obtain the same $Li^+$ quantity regardless of the lithium salt used. Hence, the lithium salt content introduced was calculated in respect to a 15 molar% of $Li^+$ addition. A dilatometric study is performed on each mixture obtained. It is noticeable on the dilatometric curves (Fig. 1) that LiF and $BaLiF_3$ are the most efficient sintering agents and allow a sintering temperature reduction near to 200 °C. The sintering temperature reached is about 1150 °C in both cases. The peaks which are evidenced at around 800 °C on the derivative curves can be correlated to the melting of $BaLiF_3$ and LiF which have very close melting points (850 and 845 °C, respectively). The $Li_2CO_3$ addition is also beneficial since it permits the sintering of the BZN-0 at the same temperature (1150 °C). However, this sintering agent implies the carbonate departure during the high temperature stage. This can be unfavourable for the process of our ceramics since its departure may produce cracks during the densification step. For this reason, the lithium carbonate was finally not chosen for the following studies. Finally, $LiNO_3$ have to be avoided since there is no gain in term of shrinkage temperature.

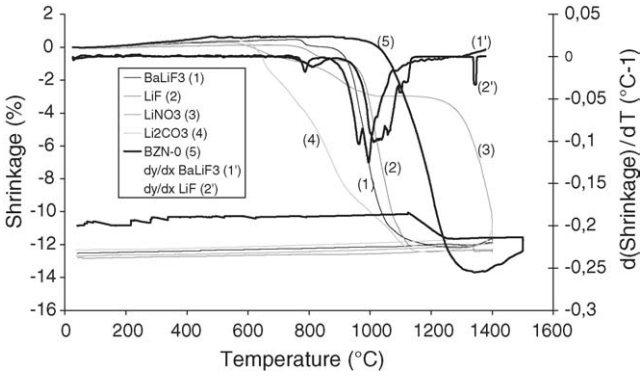


Fig. 1. Shrinkage curves and derivative shrinkage curves of lithium salts added BZN stoichiometric samples as a function of temperature.

Taking into account these results, several pellets of the LiF and $BaLiF_3$ added compounds have been sintered in air at 1150 °C during 2 h with 200 °C/h slopes. The pellets obtained with LiF are not as densified as expected (75% of the theoretical density), so this composition has not been kept for the following of the study. In contrast, the $BaLiF_3$ added samples are well dense (apparent density higher than 90% of the theoretical one) and are characterised by XRD on the bulk and on the sample surface. The samples bulks are BZN single-phase materials as well as the surface samples. Dielectric properties were measured at 1 MHz versus temperature (from −60 to 180 °C) on sintered samples. $BaLiF_3$ added samples exhibit a higher relative permittivity ($\varepsilon_r = 48$) than the undoped ones ($\varepsilon_r = 38$). The same phenomenon has already been observed on an adjoining material. The solid solution formation between LiF and $BaTiO_3$ as reported by Haussonne et al. [3] offer an explanation. Briefly, if we assume that $Li^+$ substitutes for $Ti^{4+}$ and $F^-$ enters in the anionic cell, the balance charge principle can easily explain the vacancies formation as given by the following equation:

$$LiF \xrightarrow{BaTiO_3} Li'''_{Ti} + F^{o}_{o} + 2V^{oo}_{o} + V''_{Ba} \quad (1)$$

The result of the Eq. (1) is the formation of the solid solution expressed by $Ba^{2+}_{1-x}Li^{+}_{x}Ti^{4+}_{1-x}O^{2-}_{3-3x}F^{-}_{x}$ and can be transposed to our material to propose an explanation for the difference of the permittivity observed. However, the temperature coefficient is altered with a value higher than 150 ppm/°C compared to the reference value (−50 ppm/°C).

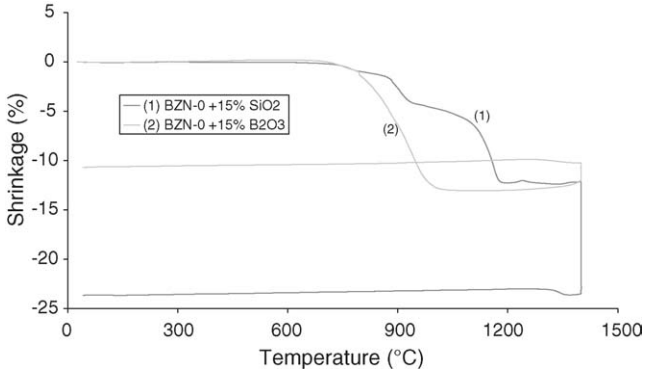


Fig. 2. Shrinkage curves of BZN-0 samples with 15% $SiO_2$ and $B_2O_3$ as a function of temperature.

### 3.2. Effects of glass phase additions on stoichiometric compounds

The effect of glass phase addition on the stoichiometric compound sinterability has been also explored. The two glass phase chosen are $B_2O_3$ and $SiO_2$. First, an addition of 15 molar% of each glass system has been done. A dilatometric study is performed to observe the shrinkage as a function of the temperature. As we can see in Fig. 2, a $B_2O_3$ addition appears to be efficient for the lowering of the sintering temperature. It allows a reduction of about 300 °C of the sintering temperature. If we now consider the $SiO_2$ addition, the result is more disappointing. The shrinkage proceeds in several steps, as can be seen on the derivative curve peaks. Moreover, the shrinkage falls down at 1400 °C that can probably reveals a partial melting of the sample.

Then the effect of $B_2O_3$ addition amount was investigated. Several molar% additions (5, 10 and 20%) have been tested on BZN-0 in comparison to the 15 molar% one. The dilatometric measurements shown in Fig. 3 clearly evidence that the 5 and 20% additions are not beneficial for the sinterability of our ceramic. The liquid phase generated by a 5% borate oxide addition is not enough to promote the diffusion. Concerning the 20% addition, the high shrinkage temperature can be explained by the formation of a secondary phase between $B_2O_3$ and ZnO [11]. Zinc oxide

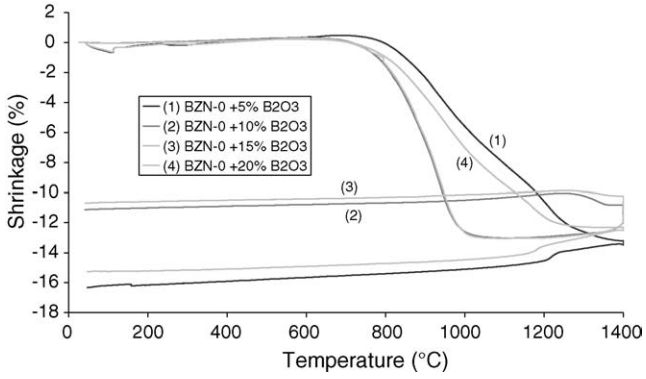


Fig. 3. Shrinkage curves of BZN-0 $B_2O_3$ added samples as a function of temperature.

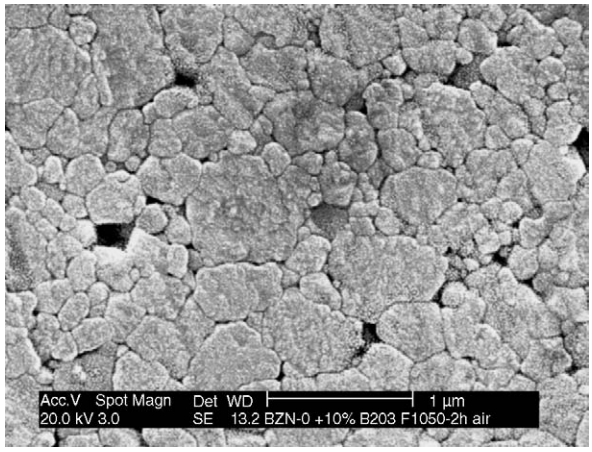


Fig. 4. Scanning electron micrographs of BZN-0 10% $B_2O_3$ added sample.

is known to be volatile in such compounds [12]. A secondary phase can be hence formed which slow down the densification. In contrast, the results for the 10 and 15% additions are similar in both cases and these additions amount permit a sintering temperature reduction of 300 °C. For the following, the two compositions have been sintered to measure the properties of each one. Several pellets of each composition with the two $B_2O_3$ additions quantities have been sintered in air with 200 °C/h slopes. The 2 h dwell temperature chosen is 1050 °C. An XRD analysis has been performed on each sintered sample on both surface and bulk. In all cases, the ceramics are pure exhibiting only the BZN perovskite phase. These X-ray diagrams are confirmed by a SEM analysis where no secondary phase is detected. In considering the grain size (Fig. 4), we notice a very small grain size for both samples (mean grains size <500 nm) which can be explained by the low sintering temperature. As a comparison, the grain size observed for BZN-0 samples sintered at 1350 °C is about 2 μm. The dielectric measurements at 1 MHz are summarised in Table 1 and for each material the results are very similar. We notice an $\varepsilon_r$ equal to 36.5 with a negative temperature coefficient (−74 ppm/°C). For the 15% $B_2O_3$ addition, the permittivity is nearly the same ($\varepsilon_r$ = 36.4) with the same temperature coefficient as the 10% one. The dielectric losses are still lower than $10^{-3}$.

### 3.3. Combined effects of glass phase and lithium salt addition

Keeping in mind that the main goal is the lowering of the sintering temperature, the combination of the borate oxide addition and the lithium fluoride addition has been performed. This mixture is known to form an eutectic phase which can increase the species diffusion [13,14]. As the results are similar regarding the 10 or 15 molar% of $B_2O_3$ addition, it was decided to keep the smallest amount to minimise the quantity of sintering agents added. A combination of a 10 molar% addition of $B_2O_3$ and a 5 molar% of LiF was performed on a BZN-0 sample. The

Table 1
Dielectric properties of $B_2O_3$ added and $B_2O_3$ + LiF added BZN-0 sintered samples

| Nominal compound | Relative density (% of theoretical one) | $\varepsilon$ | Temperature coefficient (ppm/°C) | tan $\delta$ | Resistivity ($\Omega$.cm) |
|---|---|---|---|---|---|
| BZN-0 + 10% $B_2O_3$ | 92 | 36.5 | −74 | $<10^{-3}$ | $3.2 \times 10^{14}$ |
| BZN-0 + 15% $B_2O_3$ | 91 | 36.4 | −74 | $<10^{-3}$ | $1.5 \times 10^{15}$ |
| BZN-0 + 10% $B_2O_3$ + 5% LiF | 91 | 36.9 | +46 | $<10^{-3}$ | $1.3 \times 10^{14}$ |

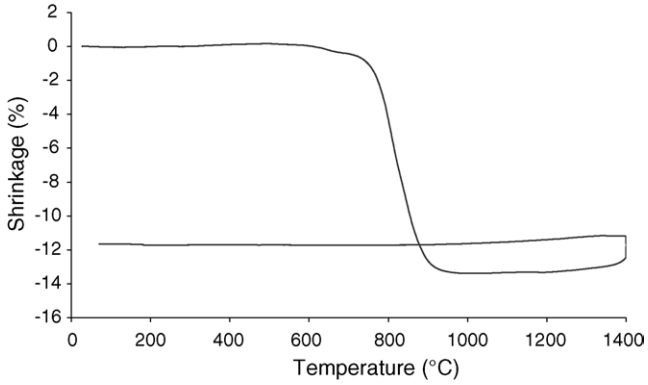


Fig. 5. Shrinkage curves of BZN-0 with 10% $B_2O_3$ and 5% LiF sample as a function of temperature.

dilatometric curve in Fig. 5 clearly shows that the sintering temperature still decreases using this combination. The shrinkage is indeed finished below 1000 °C. Several pellets of BZN-0 + 10% $B_2O_3$ + 5% LiF have been sintered in air with 200 °C/h slopes at 1000 °C to be characterised. All the samples exhibit good final apparent densities close to 92% of the theoretical one. The dielectric properties have been measured at 1 MHz (summarized in Table 1), and we can notice that the temperature coefficient becomes positive (equal to +47 ppm/°C) when referring to the non-lithium-added samples. The permittivity as well as the dielectric losses is not modified by the addition of these sintering agents ($\varepsilon_r = 36.3$ and $\tan\delta < 10^{-3}$). It is important to notice that a secondary phase, identified as zinc oxide, is detected

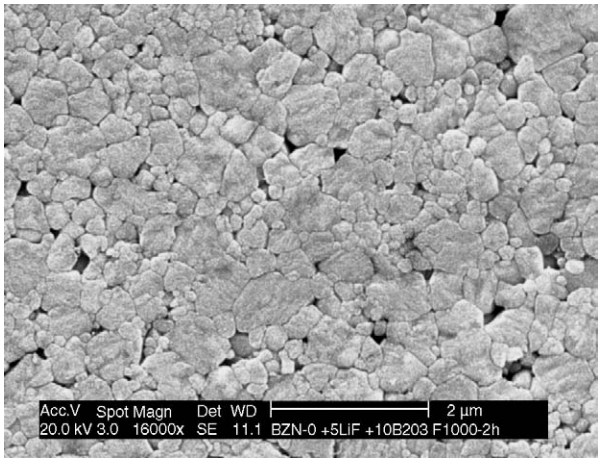


Fig. 6. Scanning electron micrographs of BZN-0 10% $B_2O_3$ and 5% LiF added sample section.

by XRD in the sample surface; whereas, it disappears in the bulk. But this impurity could not be detected with a SEM analysis, that suggesting that this secondary phase is only located in the sample periphery (the sample polishing was enough to remove it). This remark has been confirmed in observing by SEM a sample microstructure section (Fig. 6). The thickness of the zone where this secondary phase is located varies from 4 to 10 μm. The grain size is still very low (mean grains size <500 nm).

### 3.4. Combined effects of stoichiometry and sintering agents addition

Trying to decrease again the sintering temperature to below the silver melting point ($T_{f(Ag)} = 961$ °C), we decided to test several sintering agents additions (10 and 15 molar% $B_2O_3$ and 10 molar% $B_2O_3$ combined with 5 molar% LiF) on different BZN non-stoichiometric compositions. According to previous studies, it was demonstrated that a 1% deficiency in the A site is efficient to decrease the sintering temperature. The compounds obtained were named Z + 1, N + 1 and ZN + 1, with the abbreviations denoting the 1% deficiency in the A site of BZN due to an excess of Zn, Nb and Zn + Nb, respectively. Dilatometric measurements are performed on each one of the nine mixtures to observe the combined effect of the dopants and the stoichiometry. For 10 and 15% $B_2O_3$ additions, we can observe that the sinterability is increased but the origin of the non-stoichiometry seems to have no effect. As we can see in Fig. 7a and b, the end of the shrinkage is then reached at 950 °C, that is to say; a 100 °C improvement of the sintering temperature from the stoichiometric compound with the same sintering agents addition as a reference. The best results are obtained with the 10% $B_2O_3$ + 5% LiF added samples. Here again, the origin of the non-stoichiometry has no influence on the shrinkage which starts at 600 °C and finishes at a very low temperature close to 900 °C (Fig. 8). These last compositions are very promising as they become compatible with silver in terms of sintering temperature and its reduction is noteworthy of 450 °C.

Several pellets of each composition have been prepared. BZN Z + 1, N + 1 and ZN + 1 with a 10 or 15% $B_2O_3$ addition have been sintered in air at 1000 °C during 2 h with 200 °C/h slopes and the 10% $B_2O_3$ and 5% LiF added samples at 950 °C with the same cycle parameters. We first notice a good densification (between 92 and 93% of the theoretical density) for all compositions. If we look at the

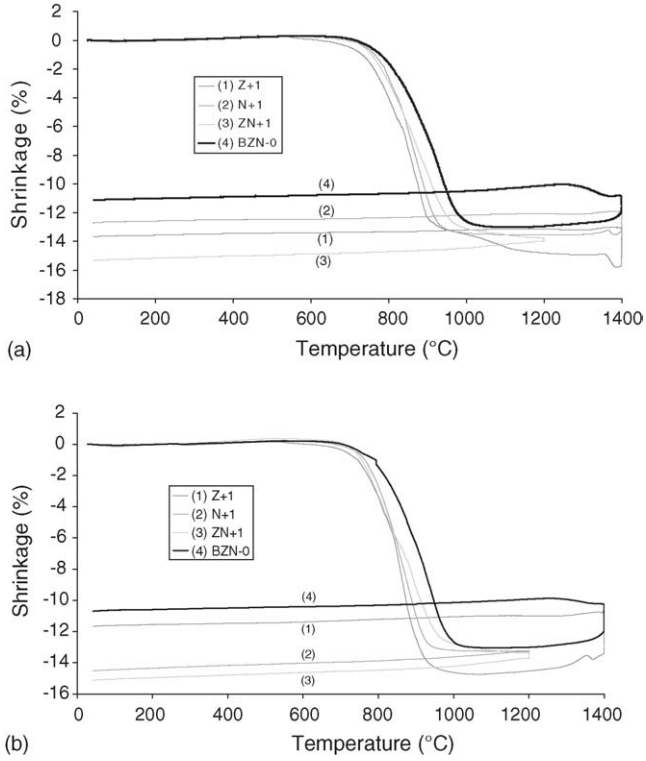


Fig. 7. Shrinkage curves of BZN non-stoichiometric samples as a function of temperature. (a) BZN non-stoichiometric samples + 10% $B_2O_3$. (b) BZT non-stoichiometric samples + 15% $B_2O_3$.

dielectric properties (see Table 2), the behaviour of the temperature coefficient is the same as those observed for the stoichiometric compounds. The temperature coefficient indeed becomes positive when LiF is added and the values reached for these 10% $B_2O_3$ + 5% LiF added samples are very attractive (42 ppm/°C for Z + 1, 53 ppm/°C for T + 1 and 37 ppm/°C for ZT + 1). For the other compounds (10 and 15% $B_2O_3$ added without LiF), neither the origin of the non-stoichiometry nor the amount of $B_2O_3$ addition have any influence on the temperature coefficient which is between −44 and −70 ppm/°C, and the dielectric losses are always lower than $10^{-3}$. However, two compounds need to be noted due to their low $\varepsilon_r$ value. ZN + 1 + 10% $B_2O_3$ and ZN + 1 + 10% $B_2O_3$ + 5% LiF actually exhibit a relative dielectric constant lower than 30 (27.2 and 29.6, respectively) which is not in good agreement with the other values observed (middle value close to 37). An XRD analysis has been systematically performed on both surface and bulk for each sample. The BZN perovskite phase is the unique phase which composed all bulk samples. The ZN + 1 surface samples added with $B_2O_3$ are also composed with the same BZN pure phase. In contrast, the Z + 1 and N + 1 exhibit some supplementary peaks which are not yet identified.

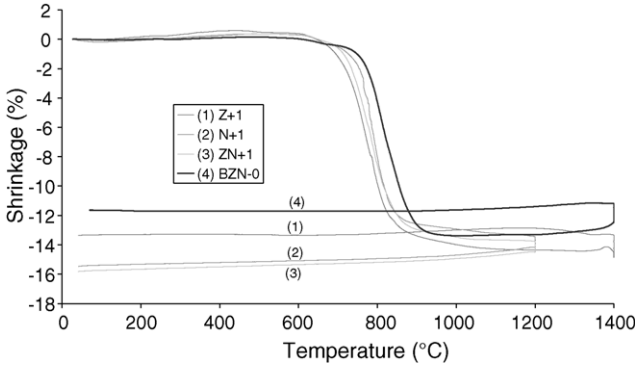


Fig. 8. Shrinkage curves of BZN non-stoichiometric samples with 10% $B_2O_3$ and 5% LiF as a function of temperature.

### 3.5. Properties of silver co-sintered samples

On the preceding part of our work, we have evidenced three compositions which can be sintered under 950 °C. Non-stoichiometric BZN samples with an addition of 10 molar% of $B_2O_3$ and 5 molar % of LiF are good candidates for a silver co-sintering ($T_f$ = 951 °C). Several samples of each non-stoichiometric composition (Z + 1, N + 1 and ZN + 1) with the sintering agents have been prepared and each pellet face has been painted with silver paste (H 29 541+). The samples obtained were co-sintered in air in a tubular furnace at 940 °C during 2 h with 200 °C/h slopes. The density of the ceramic is good (>90% of the theoretical one). The dielectric properties are still measured at 1 MHz between −60 and +180 °C. The ZN + 1 samples properties are very promising, with a high dielectric constant ($\varepsilon_r$ = 37.2) and good temperature stability ($\tau_\varepsilon$ = −42 ppm/°C). We can remark that the temperature coefficient ($\tau_\varepsilon$) becomes negative for all the samples when the silver

Table 2
Dielectric properties of $B_2O_3$ added and $B_2O_3$ + LiF added BZN non-stoichiometric sintered samples

| Nominal compound | Relative density (% of theoretical one) | $\varepsilon$ | Temperature coefficient (ppm/°C) | tan $\delta$ | Resistivity (Ω.cm) |
|---|---|---|---|---|---|
| Z + 1 + 10% $B_2O_3$ | 91.9 | 36.4 | −44 | $<10^{-3}$ | $3.8 \times 10^{12}$ |
| N + 1 + 10% $B_2O_3$ | 93.3 | 38.8 | −54 | $<10^{-3}$ | $3.5 \times 10^{14}$ |
| ZN + 1 + 10% $B_2O_3$ | 91.9 | 27.9 | −32 | $<10^{-3}$ | $1.6 \times 10^{13}$ |
| Z + 1 + 15% $B_2O_3$ | 92.6 | 37.4 | −59 | $<10^{-3}$ | $1.2 \times 10^{14}$ |
| N + 1 + 15% $B_2O_3$ | 93.3 | 39.1 | −59 | $<10^{-3}$ | $1.3 \times 10^{14}$ |
| ZN + 1 + 15% $B_2O_3$ | 92.8 | 38 | −68 | $<10^{-3}$ | $2.3 \times 10^{14}$ |
| Z + 1 + 10% $B_2O_3$ + 5% LiF | 92.7 | 33.3 | +42 | $<10^{-3}$ | $2.7 \times 10^{13}$ |
| N + 1 + 10% $B_2O_3$ + 5% LiF | 92.3 | 37.3 | +54 | $<10^{-3}$ | $2.4 \times 10^{14}$ |
| ZN + 1 + 10% $B_2O_3$ + 5% LiF | 89.2 | 28.5 | +14 | $<10^{-3}$ | $4.5 \times 10^{12}$ |

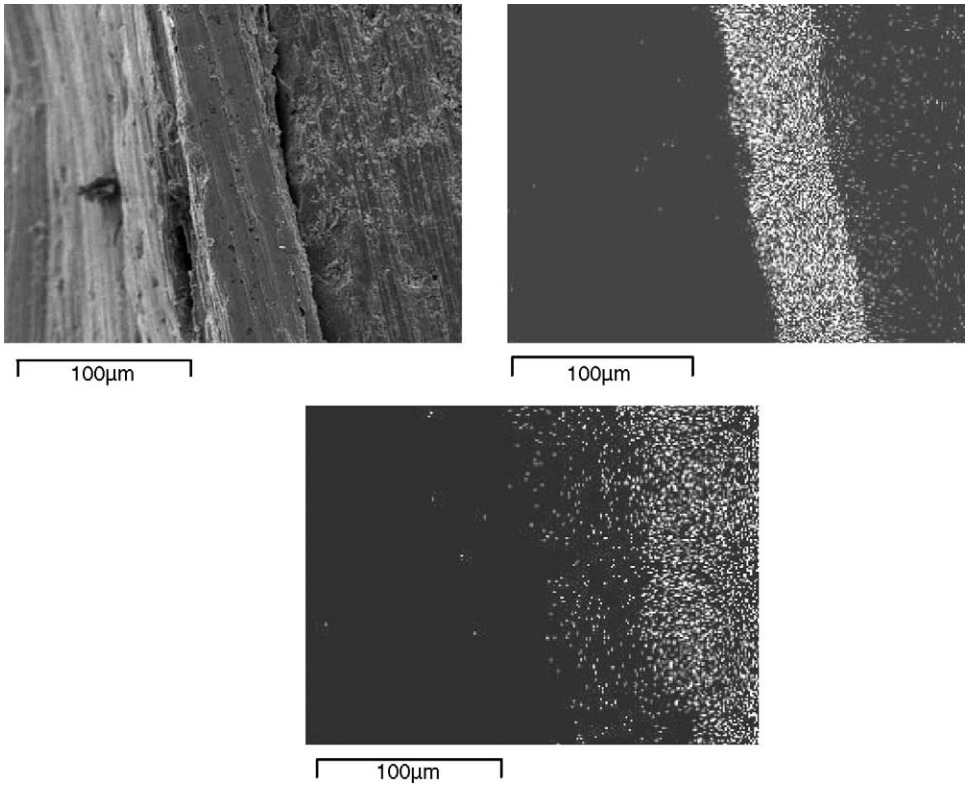


Fig. 9. Scanning electron micrographs of silver co-sintered BZN sample.

co-sintering is achieved. The two other compounds indeed exhibit a temperature coefficient equal to −35 and −18 ppm/°C for Z + 1 and N + 1, respectively. However, the values of relative permittivity are altered due to the density reached which are lower than 89% of the theoretical ones ($\varepsilon_{r(Z+1)} = 24.4$ and $\varepsilon_{r(N+1)} = 22.5$); whereas, the dielectric losses are not modified and still lower than $10^{-3}$. The phase content analysis shows that the BZN is the only phase present in our pellets and no silver diffusion was noticed on the SEM analyses presented in Fig. 9.

## 4. Conclusions

In this work, the lowering of the sintering temperature has been investigated to be able to co-sinter BZN based samples with silver electrodes. We have evidenced a lowering of the sintering temperature when some sintering aids (lithium salts or glass phases) are added to the BZN. The best results obtained are reached if 5 molar% of LiF are combined with 10 molar% of $B_2O_3$. The sintering temperature is then lowered by 350 °C without any modification of the dielectric material main properties. Another way to increase the sinterability has been explored which consists in a modification of the stoichiometry. We have succeeded in this way when 1% deficiency in A site is introduced in our material. An improvement of 100 °C is observed to finally reach a sintering temperature close to 900 °C which is suitable with a silver co-sintering. The last part of our study was to co-sinter some pellets to validate the silver co-sintering. The samples obtained are very promising to manufacture some BME-MLCC. These samples do not exhibit secondary phases and their properties are not altered if we refer to the basic material. A value of 37.2 was obtained for the permittivity and was found to be temperature stable ($\tau_\varepsilon = -42$ ppm/°C) with dielectric losses lower than $10^{-3}$. The atmosphere used is the air at a very low temperature which is very important from the industrial point of view.

Further investigations are still in progress to clarify the sintering mechanisms that occur and practically to be able to manufacture BZN based BME-MLCC.

## Acknowledgement

The authors want to acknowledge the TEMEX society for supporting this work.

## References

[1] I.T. Kim, K.S. Hong, S.J. Yoon, Effect of non-stoichiometry and chemical inhomogeneity on the order–disorder phase formation in the complex perovskite compounds of $Ba(Ni_{1/3}Nb_{2/3})O_3$ and $Ba(Zn_{1/3}Nb_{2/3})O_3$, J. Mat. Sci. 30 (1995) 514–521.

[2] J.K. Park, D.Y. Kim, Effect of grain size on diffusion-induced grain-boundary migration in $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramics, J. Am. Ceram. Soc. 79 (5) (1996) 1405–1408.

[3] J.M. Haussonne, G. Desgardin, Dielectric properties of barium titanate-based capacitors with lithium additions, Ceram. Trans. (1993) 155–166.
[4] L. Benziada, J. Ravez, Ferroelectric $BaTiO_3$ ceramics sintered at low temperature with the aid of a mixture of $CaF_2$ and LiF, J. Fluorine Chem. 73 (1995) 69–71.
[5] C.L. Huang, M.H. Weng, C.T. Lion, C.C. Wu, Low temperature sintering and microwave dielectric properties of $Ba_2Ti_9O_{20}$ ceramics using glass additions, Mat. Res. Bull. 35 (2000) 2445–2456.
[6] S.G. Lu, K.W. Kwok, H.L.W. Chan, C.L. Choy, Structural and electrical properties of $BaTi_4O_9$ microwave ceramics incorporated with glass phase, Mat. Sci. Eng. B 99 (2003) 491–494.
[7] D.K. Lee, H.I. Yoo, Oxygen nonstoichiometry of undoped $BaTiO_{3-\delta}$, Sol. State Ionics 144 (2001) 87–97.
[8] F. Roulland, R. Terras, S. Marinel, Influence of both milling conditions and lithium salt addition on the sinterability of $Ba(Zn_{1/3}Ta_{2/3})O_3$, Mat. Sci. Eng. B 104 (3) (2003) 156–162.
[9] J.M. Haussonne, G. Desgardin, P. Bajolet, B. Raveau, Barium titanate perovskite sintered with lithium fluoride, J. Am. Ceram. Soc. 66 (11) (1983) 801–807.
[10] M. Pollet, S. Marinel, G. Desgradin, $CaZrO_3$ a Ni-co-sinterable dielectric material for base metal-multilayer ceramic capacitor applications, J. Eur. Ceram. Soc. 24 (2004) 119–127.
[11] D.E. Harrison, F.A. Hummel, Phase equilibria and fluorescence in the system zinc oxide-boric oxide, J. Electrochem. Soc. 103 (9) (1956) 491–498.
[12] S. Kawashima, Influence of ZnO evaporation on microwave dielectric loss and sinterability of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics, Am. Ceram. Soc. Bull. 72 (5) (1993) 120–126.
[13] S.I. Berul, I.N. Nikonova, Reaction of boric anhydride with the fluorides of barium and lithium, Zh. Neorg. Khim. 11 (4) (1966) 910–915.
[14] M. Pollet, S. Marinel, F. Roulland, G. Allainmat, Low temperature sintering of $B_2O_3/LiNO_3$ added $BaMg_{1/3}Ta_{2/3}O_3$ ceramics, Mat. Sci. Eng. B 104 (2003) 58–62.