Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of the European Ceramic Society 25 (2005) 2763–2768

www.elsevier.com/locate/jeurceramsoc

Low temperature sintering of the binary complex perovskite oxides $x\mathrm{Ba}(\mathrm{Zn}_{1/3}\mathrm{Ta}_{2/3})\mathrm{O}_3 + (1-x)\mathrm{Ba}(\mathrm{Mg}_{1/3}\mathrm{Ta}_{2/3})\mathrm{O}_3$

F. Roulland, G. Allainmat, M. Pollet, S. Marinel*

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

Abstract

The interest for the complex perovskites oxides is known since several years. $\mathrm{Ba}(\mathrm{Zn}_{1/3}\mathrm{Ta}_{2/3})\mathrm{O}_3$ (BZT) and $\mathrm{Ba}(\mathrm{Mg}_{1/3}\mathrm{Ta}_{2/3})\mathrm{O}_3$ (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. 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). To lower the sintering temperature, a glass phase addition is performed on the complex formulations $x\mathrm{Ba}(\mathrm{Zn}_{1/3}\mathrm{Ta}_{2/3})\mathrm{O}_3 + (1-x)\mathrm{Ba}(\mathrm{Mg}_{1/3}\mathrm{Ta}_{2/3})\mathrm{O}_3$ (with $x = 0$, 1/3, 1/2, 2/3 and 1). These mixtures are envisaged to explore their dielectric properties. The sintering temperature lowering reached is higher than 400 °C when 10 molar% of borate oxide is added to the mixtures and their dielectric properties are very attractive ($\varepsilon = 25$ and $\tau_\varepsilon = -59$ ppm/°C for $x = 1/3$) for the fabrication of base metal electrodes multi layer ceramic capacitors (BME-MLCC).

Keywords: Dielectric properties; Sintering; Perovskites

1. Introduction

Complex perovskites oxides such as $\mathrm{BaZn}_{1/3}\mathrm{Ta}_{2/3}\mathrm{O}_3$ (BZT) and $\mathrm{BaMg}_{1/3}\mathrm{Ta}_{2/3}\mathrm{O}_3$ (BMT) are known to exhibit good dielectric properties.[1,2] They hence present medium permittivities (respectively $\varepsilon_{\mathrm{BZT}} = 30$ and $\varepsilon_{\mathrm{BMT}} = 25$), low dependences of permittivity versus temperature ($\tau_\varepsilon < 50$ ppm/°C), low losses factors ($Q > 1000$) in a large scale of frequency (1 kHz–10 GHz) and finally low temperature coefficients of the resonance frequency ($\tau_f < 5$ ppm/°C). These very attractive properties allow their uses in type I multilayer 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 ($\mathrm{B_2O_3}$) 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 1 MHz. It was also proved that the BMT samples are stables under reducing atmosphere (90% Ar/10% $\mathrm{H_2}$).[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 (xBZT + $(1-x)$BMT with $x = 0$, 1/3, 1/2, 2/3, 1) with addition of 10 molar% of $\mathrm{B_2O_3}$. For the rest of this work, we will use the following names: 30 for BZT only, 21 for 2/3 BZT + 1/3 BMT, 11 for 1/2 BZT + 1/2 BMT, 12 for 1/3 BZT + 2/3 BMT and 03 for BMT only.

2. Experimental procedure

$\mathrm{BaZn}_{1/3}\mathrm{Ta}_{2/3}\mathrm{O}_3$ (BZT) and $\mathrm{BaMg}_{1/3}\mathrm{Ta}_{2/3}\mathrm{O}_3$ (BMT) powders were prepared using commercial powders. $\mathrm{BaCO_3}$

---

* Corresponding author. Tel.: +33 2 31 45 26 30; fax: +33 2 31 95 16 00.
E-mail addresses: roulland@ismra.fr (F. Roulland), marinel@ensicaen.fr (S. Marinel).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.03.136

(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 2 h in a Teflon jar using 1 mm 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 h for BZT and 1300 °C for 2 h for BMT), these temperatures have been chosen according to a preliminary study.[9] The calcined powders obtained were re-milled for 1 h using the same process. The powder purity is systematically controlled by X-ray diffraction (XRD) using the Cu Kα X-ray radiation. Borate oxide (B_2O_3— Prolabo 98%) is then added to the xBZT + $(1-x)$BMT composition using a planetary grinder for 45 min in absolute ethanol. The mixtures obtained after drying are uniaxially pressed at 3880 kg into 8 mm diameter pellets. These discs are first sintered in air and then under argon + 1% H_2 moisture saturated atmosphere ($P(O_2) \ll 10^{-10}$ bar) 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 permittivity) were performed on discs with electrodes painted on each faces using an Indium Gallium eutectic (RLC bridges Fluke PM6306).

3. Results and discussion

The first part of this work is devoted to the study of the reference compounds, without glass phase addition. A dilatometric measurement was systematically performed on each of the five compositions (03, 12, 11, 21 and 30) and reported in Fig. 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] The temperatures corresponding to the end of the shrinkage for the three mixtures x $Ba(Zn_{1/3}Ta_{2/3})O_3 + (1-x)Ba(Mg_{1/3}Ta_{2/3})O_3$ are between the BZT one and the BZT one.

The dilatometric curves of the borate oxide added compounds are plotted in Fig. 2. The B_2O_3 additions are very efficient for all compositions as the ending shrinkage temperatures are lowered. The unitary compositions (03 and 30) can be sintered at 1200 °C. 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).

This could be very interesting in term 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 (1070 °C for 11, 12 and 21 and 1200 °C for 30 and 03). The thermal cycles slopes chosen are 200 °C/h. The samples 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 performed at 1 MHz and good dielectric properties are obtained (resumed in Table 1).

The permittivity monotonously decreases from 28.5 for the 30 compound to 25.2 for the 03 compound. The temperature coefficient has a similar behaviour (see Fig. 3). It is

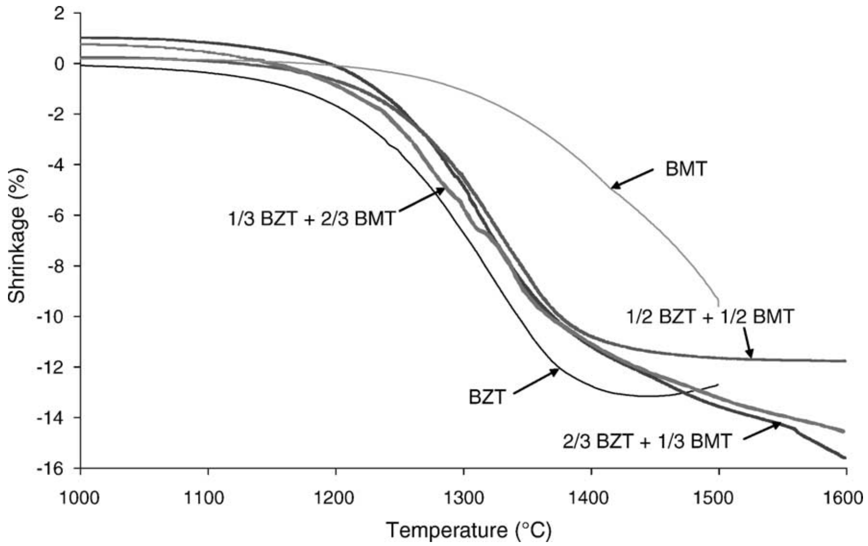

Fig. 1. Shrinkage curves of BZT/BMT mixtures samples vs. temperature.

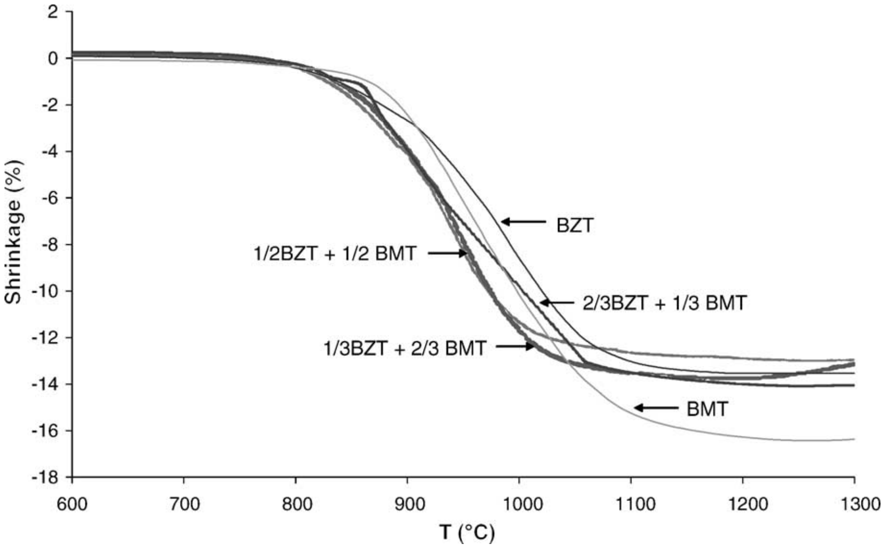

Fig. 2. Shrinkage curves of BZT/BMT mixtures samples with 10% B_2O_3 vs. temperature.

equal to −22 ppm/°C for the 30 composition, and increase in absolute value to reach −84 ppm/°C for the 03 one. The dielectric losses are very low for all the samples as they are lower than 10^{-3}.

The XRD characterisation performed on sintered samples previously crushed was performed. The 03 and the 30 compositions are single phase materials, exclusively composed by BZT and BMT respectively. The BZT and the BMT XRD diagrams are very close, so the XRD diagrams of the mixtures are very similar. It is hence difficult to conclude if the resulting samples are solid solutions or a mixture of BZT and BMT.

However, this hypothesis of the solid solution formation between BZT and BMT is reinforced by the EDS analysis: the

Table 1
Dielectric properties of binary samples with 10% B_2O_3 sintered in air

Nominal compound	Theoretical density (g/cm^3)	Relative density (% of theoretical one)	Epsilon	Temperature coefficient (ppm/°C)	tan δ
BZT + 10% B_2O_3 (30)	7.92	92	28.5	−22	<10^{-3}
2/3 BZT + 1/3 BMT + 10% B_2O_3 (21)	7.82	93	27.5	−43	<10^{-3}
1/2 BZT + 1/2 BMT + 10% B_2O_3 (11)	111	92	27.7	−50	<10^{-3}
1/3 BZT + 2/3 BMT + 10% B_2O_3 (12)	7.72	91	25.3	−60	<10^{-3}
BMT + 10% B_2O_3 (03)	7.63	92	25.2	−84	<10^{-3}

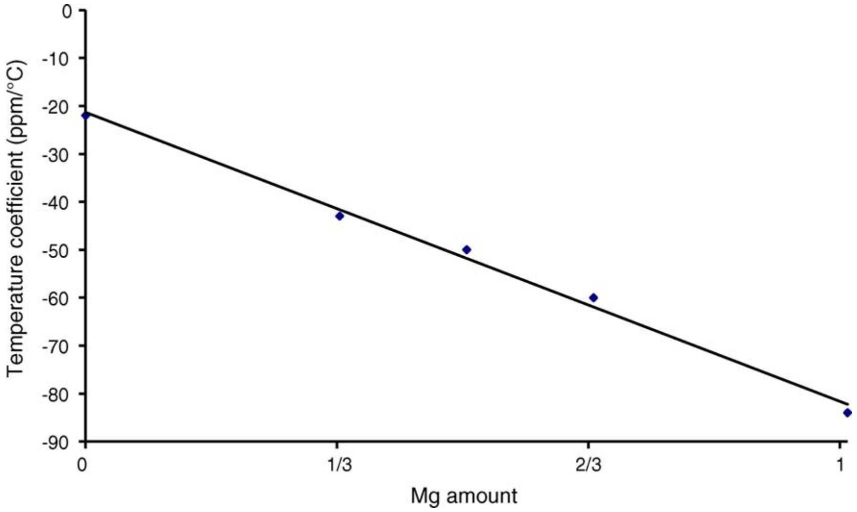

Fig. 3. Temperature coefficient evolution of air sintered samples vs. Mg amount.

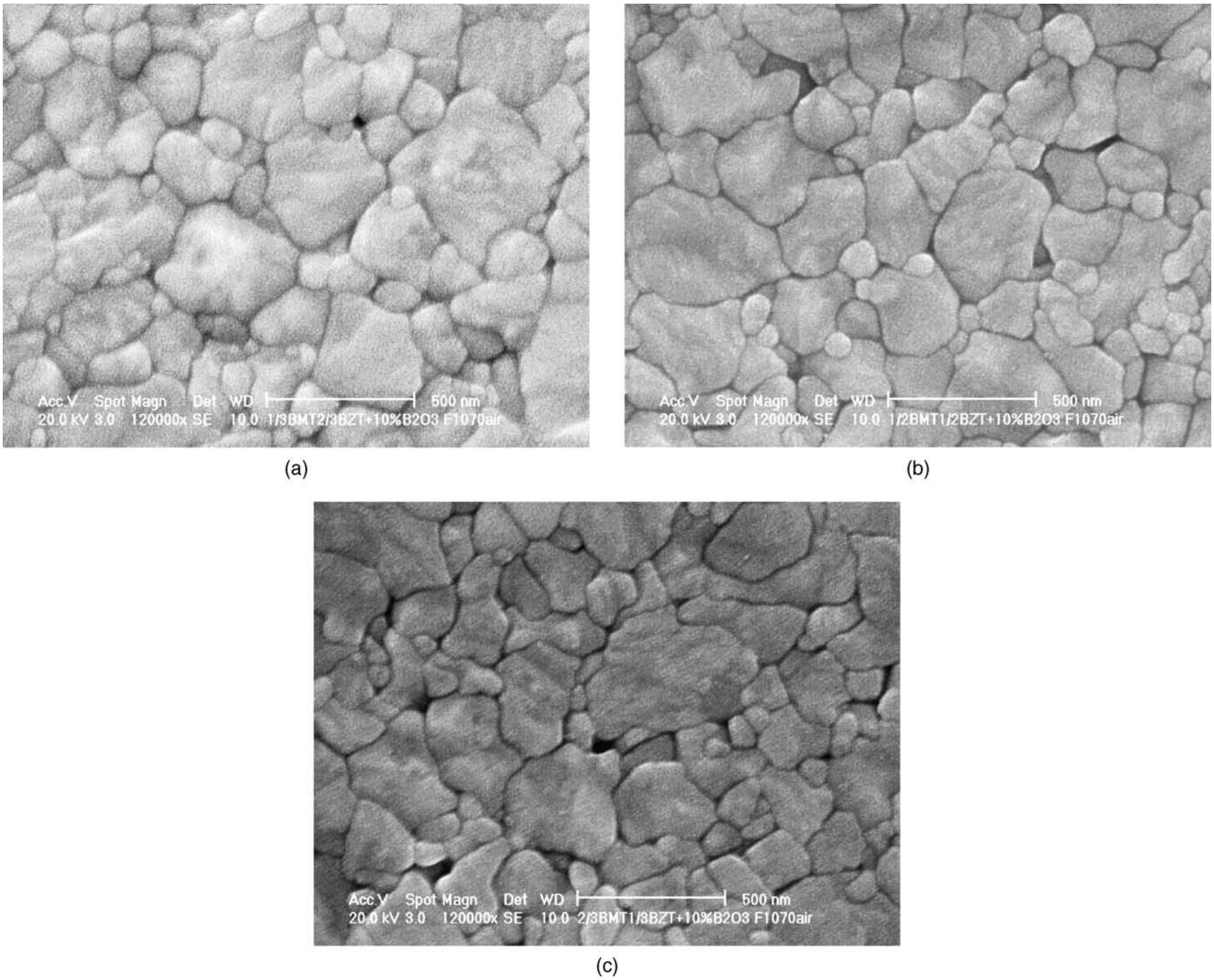

Fig. 4. (a) Scanning electron micrographs of the 21 sintered sample with 10% B_2O_3. (b) Scanning electron micrographs of the 11 sintered sample with 10% B_2O_3. (c) Scanning electron micrographs of the 12 sintered sample with 10% B_2O_3.

Mg and Zn amounts are very close to the theoretical values. The grain size is very small (close to 100 nm) which can be explained by the low sintering temperature (Fig. 4a–c).

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 (1200 °C for 30 and 03, and 1070 °C for 12, 11 and 21). The first statement is the densification lowering when the zinc proportion is increased (see Table 2). For the 30 compound, it is evidenced by XRD analysis (Fig. 5) that the cubic perovskite phase has totally disappeared and the $Ba_5Ta_4O_{15}$ phase is formed. Using the EDS analysis, a total zinc departure is observed[5] confirming the XRD patterns. This phenomenon is also observed on the mixtures especially for

Table 2
Dielectric properties of binary samples with 10% B_2O_3 sintered in reductive atmosphere

Nominal compound	Relative density (% of theoretical one)	Epsilon	Temperature coefficient (ppm/°C)	tan δ
BZT + 10% B_2O_3 (30)	70	15	−250	$<10^{-2}$
2/3 BZT + 1/3 BMT + 10% B_2O_3 (21)	77	17.5	−183	$<4\times10^{-3}$
1/2 BZT + 1/2 BMT + 10% B_2O_3 (11)	85	20.7	−164	$<3\times10^{-3}$
1/3 BZT + 2/3 BMT + 10% B_2O_3 (12)	88	21.9	−141	$<2\times10^{-3}$
BMT + 10% B_2O_3 (03)	89	25.6	−20	$<10^{-3}$

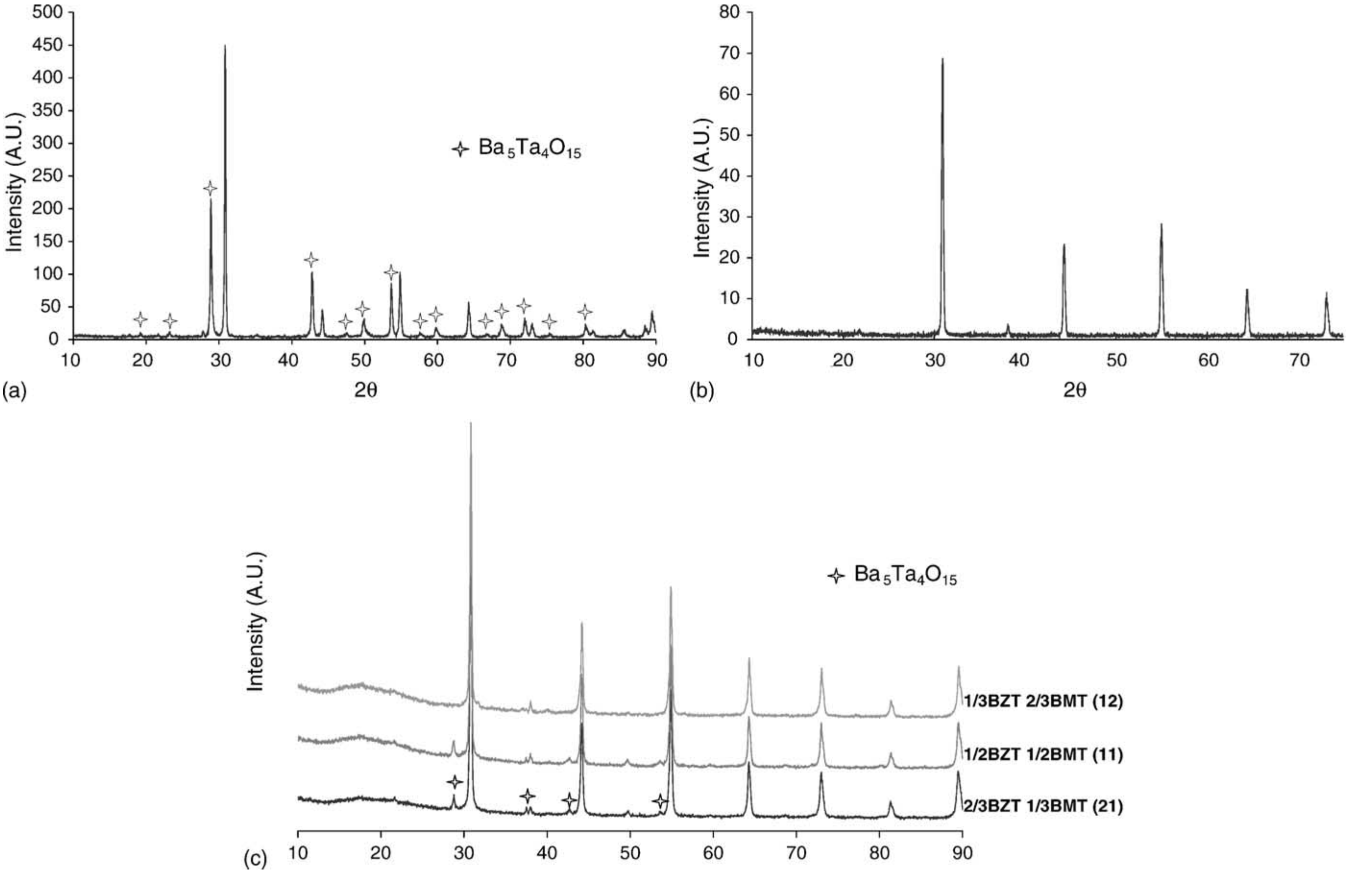

Fig. 5. X-ray diagrams of 30 (a), 03 (b) and 12, 11, 21 (c) samples with 10% B_2O_3 and 5% LiF sintered under reductive atmosphere.

the rich Zn ones (11 and 21 compounds). However the 03 and the 12 compounds are free of this secondary phase.

This phenomenon can partially 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 in Table 2. The main difference with the sintering under air concerns the permittivity and the temperature coefficient variations. The 03 and the 12 samples hence exhibit good dielectric properties. The permittivity regularly decreases from the 03 compound to the 30 one and in the same manner the temperature coefficient varies from −20 ppm/°C for the 03 composition to −250 ppm/°C for the 30 one. Dielectric losses are still low except for the 30 composition.

4. 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 allows a significant sintering temperature reduction reaching 300 °C for all the compounds. The 11 composition pellets sintered in air at 1070 °C during 2 h exhibit very good dielectric properties ($\varepsilon = 27.7$ and $\tau_\varepsilon = -50$ ppm/°C with low dielectric losses). It was also shown the linear dependences of the permittivity and the temperature coefficient with the Mg content. Moreover, the hypothesis of a solid solution between BZT and BMT has been reinforced by chemical analyses.

Under reductive atmosphere, the $Ba_5Ta_4O_{15}$ secondary phase has been detected due to the zinc departure. Nevertheless, the 12 sample keeps our attention since it exhibits satisfying dielectric properties ($d = 88\%$ of the theoretical one, $\varepsilon = 21.9$ and $\tau_\varepsilon = -141$ ppm/°C with low dielectric losses) measured on compounds which have been sintered at very low temperature (1070 °C).

Copper co-sintering tests have to be envisaged on low zinc content binary compounds (30 or 21 one) since the sintering temperature reached is lower than the copper melting point and they still have attractive dielectric properties. Nevertheless, the sintering temperature reached for this sample is very close to the copper melting point so further investigations have to be done to lower again this sintering temperature. The sintering atmosphere have to be also considered since the one used (argon + 1% H_2 moisture saturated atmosphere) is responsible of the zinc departure.

Acknowledgement

The authors acknowledge the Temex society for their collaboration in supporting this work.

References

1. Barber, D. J., Moilding, K. M. and Zhou, J., Structural order in $Ba(Zn_{1/3}Ta_{2/3})O_3$, $Ba(Zn_{1/3}Nb_{2/3})O_3$ and $Ba(Mg_{1/3}Ta_{2/3})O_3$ microwave dielectric ceramics. *J. Mater. Sci.*, 1997, **32**, 1531–1544.
2. Kawashima, S., Nishida, M., Ueda, I. and Ouchi, H., $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics with low dielectric loss at microwave frequencies. *J. Am. Ceram. Soc.*, 1983, **66**(6), 421–423.
3. Maoqiang, L., Synthesis of $Ba(Mg_{1/3}Ta_{2/3})O_3$ with complex perovskite structure. *Ferroelectrics*, 1997, **195**, 87–91.
4. Desu, S. B. and O'Bryan, H. M., Microwave loss quality of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics. *J. Am. Ceram. Soc.*, 1985, **68**(10), 546–551.
5. Kawashima, S., 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.*, 1993, **72**(5), 120–126.
6. Pollet, M., Marinel, S., Roulland, F. and Allainmat, G., Low temperature sintering of $B_2O_3/LiNO_3$ added $BaMg_{1/3}Ta_{2/3}O_3$ ceramics. *Mater. Sci. Eng. B*, 2003, **104**, 58–62.
7. Roulland, F., Marinel, S., Effects of glass phases additions and stoichiometry on the $Ba(Zn_{1/3}X_{2/3})O_3$ (X = Ta or Nb) sinterability and dielectric properties, in press.
8. Marinel, S., Pollet, M. and Allainmat, G., Effects of lithium salts additions on sintering temperature, cationic ordering and dielectric properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramic. *J. Mater. Sci.*, 2003, **38**, 1–6.
9. Roulland, F., Terras, R. and Marinel, S., Influence of both milling conditions and lithium salt addition on the sinterability of $Ba(Zn_{1/3}Ta_{2/3})O_3$. *Mater. Sci. Eng. B*, 2003, **104**(3), 156–162.