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Lowering of $BaB'_{1/3}B''_{2/3}O_3$ complex perovskite sintering temperature by lithium salt additions

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Abstract

Complex perovskite materials with the formula $BaB'_{1/3}B''_{2/3}O_3$ have been broadly studied for their attractive dielectric properties. These materials exhibit a high relative dielectric constant and a very low dissipation factor. For example, the $BaMg_{1/3}Ta_{2/3}O_3$ material has a relative dielectric constant close to 26 with a dissipation factor lower than 10^{-4} at 1 MHz. These properties are very promising for applications such as hyper-frequency resonators or/and capacitors. Unfortunately, a high temperature is necessary to achieve a satisfying densification of this materials family (>1400 °C) whereas the lowering of this temperature is more and more crucial from the industrial point of view. In particular, the development of Base Metal Electrodes Multi-Layer Ceramic Capacitors (BME-MLCC) requires the sintering of dielectric materials at low temperatures (<1100 °C). The aim of the study is thus to lower the sintering temperature of these materials. For this goal, lithium salts (Li_2CO_3, LiF, $BaLiF_3$ and $LiNO_3$) have been tested as sintering agents to densify $BaZn_{1/3}Ta_{2/3}O_3$, $BaMg_{1/3}Ta_{2/3}O_3$ and $BaZn_{1/3}Nb_{2/3}O_3$ materials. It is shown, for example, that the $BaMg_{1/3}Ta_{2/3}O_3$ sintering temperature is lowered by 300 °C when 15 mol % of lithium nitrate is added without affecting the dielectric properties at 1 MHz. For the best sintering agents investigated and each studied materials, the ceramic is characterised in terms of final density, microstructure and dielectric properties and densification mechanisms are discussed.

Keywords: Dielectric properties; Perovskites; Sintering

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1. Introduction

Complex perovskites $BaB'_{1/3}B''_{2/3}O_3$ are very promising for electroceramics applications (ceramics capacitors or resonators) owing to their attractive properties. They hence exhibit a very low dissipation factor, a relatively temperature stable permitivity and a high insulation resistivity ($>10^{11}$ Ω cm). Unfortunately, these materials usually require high temperature to achieve a satisfying density (>92% of the theoretical one). The sintering temperatures of $BaZn_{1/3}Ta_{2/3}O_3$ (BZT),[1] $BaMg_{1/3}Ta_{2/3}O_3$ (BMT)[2] and $BaZn_{1/3}Nb_{2/3}O_3$ (BZN)[3] are indeed higher than 1500, 1550 and 1300 °C, respectively. Lowering these temperatures is of primary importance from a practical point of view since it could permit to co-sinter the dielectric with based metal (Ni or Cu) giving the opportunity to process Based Metal Electrodes Multilayer Ceramics Capacitors (BME MLCC). For this goal, the use of lithium salt additions as sintering agents has been investigated. It is well known that such additions are beneficial to reduce the sintering temperature of barium titanate.[4] The evoked phenomenon to interpret this sintering temperature lowering is the solid solution formation between LiF and $BaTiO_3$ as reported by Haussonne et al.[5] 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:

$$LiF \xrightarrow{BaTiO_3} Li_M^{3-} + F_o^{+} + 2V_o^{2+} + V_{Ba}^{2-}$$

The result is the formation of the solid formation expressed by $Ba^{2+}Li_x^{+}Ti_{1-x}^{4+}O_{3-2x}^{2-}F_x^{-}$. This mechanism explains the lowering of the sintering temperature owing to the vacancies creation which enhances the species diffusion. Taking into account that complex perovskites are iso-structural of $BaTiO_3$, the addition of LiF but, in general; of lithium salts have been tested to lower the sintering temperature of BZT, BZN and BMT.

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2. Experimental procedure

$BaB'_{1/3}B''_{2/3}O_3$ powders were prepared using commercial powders. $BaCO_3$ (Diopma 99.99%), ZnO (Cerac 99.995%), Ta_2O_5 (Cerac 99.99%), MgO (Cerac 99.95%) and Nb_2O_5 (HC Starck 99.9%) are weighted in appropriate proportions to synthesise $BaZn_{1/3}Ta_{2/3}O_3$ (BZT), $BaMg_{1/3}Ta_{2/3}O_3$ (BMT) and $BaZn_{1/3}Nb_{2/3}O_3$ (BZN). Precursor powders were ball-milled for 2 h in a teflon jar using 1 mm diameter zircon balls in wet conditions. The liquid used for BMT and BZN is absolute ethanol while the one used for BZT is an ammoniac solution (pH = 11). These conditions were determined by an electrophoretic zetametry study.

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 BZN; 1300 °C for 2 h for BMT), these temperature have been chosen according to a preliminary study.[6] 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 K_α Cu X ray radiation. Lithium salt is then added using a planetary grinder for 45 min 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 phases 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).

3. Results and discussion

3.1. Effect of lithium salts addition on stoichiometric compounds

First, the effect of the lithium salts on the three stoichiometric compounds named BZT-0, BZN-0 and BMT-0 have been studied. The four lithium salts (LiF, $BaLiF_3$, $LiNO_3$ and Li_2CO_3) are added in order to add the same Li^+ quantity whatever the lithium salt used. The lithium salt content introduced was calculated in respect to the addition of 15 mol % of Li^+ based on the dielectric molar content. A dilatometric study is systematically performed in order to observe the shrinkage as a function of temperature.

The shrinkage of BZT-0 is finished at 1400 °C and achieved 13.5% (Fig. 1). With $LiNO_3$ addition, the shrinkage is nearly finished at 1400 °C, but its value is low (about 12.5%). Li_2CO_3 addition is not favourable at all: the shrinkage starts later, is not finished at 1400 °C, and the final value is poor (about 9%). Finally, LiF and $BaLiF_3$ additions authorise a sintering temperature reduction of about 200 °C. In these cases the shrinkage is totally finished at 1200 °C.

It is noticeable that the BZN-0 can sinter at lower temperature than BZT-0 as shown on Fig. 2 (respectively 1350 and 1400 °C). Except for Li_2CO_3, the effect of the lithium salt additions on the sintering temperature is similar in both cases (BZT and BZN). LiF or $BaLiF_3$ compounds are the most efficient additions to lower the sintering temperature of BZN. They permit to achieve a sintering temperature of about 1150 °C. It is

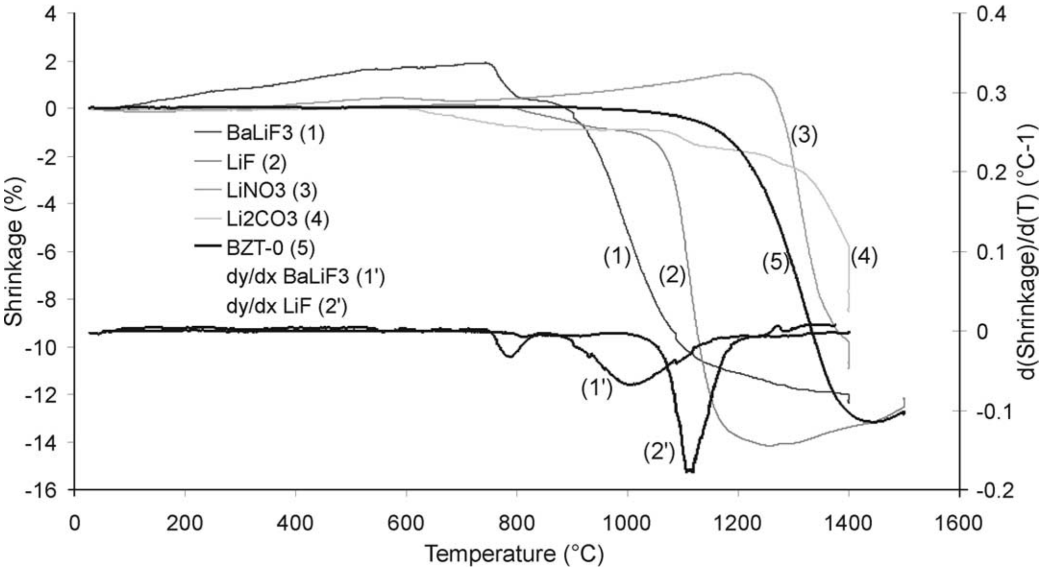

Fig. 1. Shrinkage curves and derivative shrinkage curves of BZT stoichiometric samples as a function of temperature.

evidenced that it appears, on the derivative shrinkage curves, maximums which can be explained by the melting of $BaLiF_3$ ($T_m = 850$ °C) and LiF ($T_m = 845$ °C). These are observed in BZN and BZT materials. For BZN, the Li_2CO_3 addition is beneficial since it permits to sinter the material at 1150 °C. However this sintering agent implies the carbonate departure during the high temperature stage which can be unfavourable for the densification. Due to that this agent was finally not chosen for the following studies.

The pure BMT material sinter at very high temperature (> 1500 °C) as it is usually mentioned in the literature[2] (see Fig. 3). The effects of the different lithium salt additions are in this case very different than those observed on BZN and BZT materials. $LiNO_3$ addition is the most efficient agent and permits to reach a sintering temperature of 1300 °C with a satisfying final shrinkage value (about 15%). The sintering of LiF added sample starts at low temperature (about 900 °C) but the shrinkage value is still too low even at 1300 °C (10%) due to the very low densification rate. Otherwise, although the shrinkage curves are very different, the addition of $BaLiF_3$ and Li_2CO_3 does not permit a significant sintering temperature lowering (this one is in both cases more than 1400 °C). Consequently the most efficient sintering agent investigated here for BMT material is $LiNO_3$.

Taking into account these results the chosen compositions are BMT + $LiNO_3$, BZT + $BaLiF_3$ and BZN + $BaLiF_3$. Several pellets of each one have been sintered and characterised by XRD on the bulk and on the sample surface. Results are summarised in Table 1 with the sintering temperature used. BZT and BZN are single-phase materials. There is no secondary phases as opposed to BMT. This one exhibits a secondary phase on its surface identified as $Ba_2Ta_5O_{15}$ whereas the bulk seems to be only composed of the cubic phase BMT. Nevertheless the presence of hexagonal surstructure peaks is clearly evidenced. Dielectric properties were measured at 1 MHz versus temperature (from −60 °C to 180 °C) on sintered samples. For BMT, the lithium salt addition does not alter the permittivity (ε_r equal to 25.4) as well as the temperature coefficient (τ_ε equal to −45 ppm/°C). On the contrary for BZT an BZN the $BaLiF_3$ added samples exhibit an higher ε_r than the undoped ones. Indeed the ε_r varies from 31.3 to 34 and from

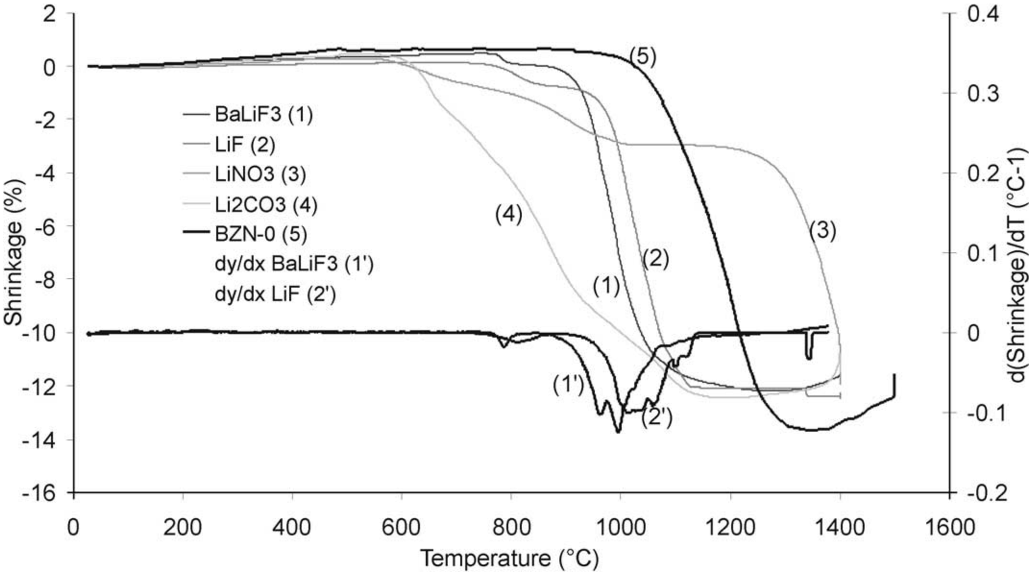

Fig. 2. Shrinkage curves and derivative shrinkage curves of BZN stoichiometric samples as a function of temperature.

Table 1
Results of XRD analyses for BZT/BZN/BMT sintered ceramics

	Surface	Bulk
BMT-0 + 15% $LiNO_3$ 1300 °C/2 h	BMT (cubic) + $Ba_3Ta_5O_{15}$	BMT (cubic) + hexagonal surstructure peaks
BZT-0 + 15% $BaLiF_3$ 1200 °C/2 h	BZT (cubic)	BZT (cubic)
BZN-0 + 15% $BaLiF_3$ 1150 °C/2 h	BZN (cubic)	BZN (cubic)
ZT-15 + 15% LiF 1050 °C/2 h	BZT (cubic) + unidentified phase	BZT (cubic)
ZN-15 + 15% LiF_3 1050 °C/2 h	BZN (cubic) + $Ba_4Nb_2O_9$	BZN (cubic)

25 to 48 respectively for BZT and BZN. Moreover in both cases the temperature coefficient is higher than 150 ppm/°C.

3.2. Influence linked to the non-stoichiometry

The effect of both non stoichiometry and lithium salts addition on the densification temperature of complex perovskite have also been investigated.[7] For BZT, considering only the sintering temperature, our best result is obtained for 15% Ba surstoichiometric compound doped with 15% molar LiF addition. This composition exhibits a very low sintering temperature as we can see in Fig. 4. The shrinkage starts at 600 °C, slows down at about 900 °C and saturates at 1280 °C. Taking into account this curve, BZT samples have been sintered at 1050 °C during 2 h. Ceramics obtained are dense (see Fig. 5) and X-ray analysis (Table 1) performed on the sintered pellets surface reveals BZT as majority phase with additional peaks not yet identified whereas the discs bulk are only composed of pure BZT phase. Finally we have practice dielectric measurements on this sample which show an ε_r equal to 35.5 at ambient temperature whereas the dissipation factors are smaller than 10^{-3}. Unfortunately the temperature coefficient τ_ε is damaged and reaches 495 ppm/°C.

For BZN, the most important sintering temperature reduction is also obtained when 15% molar Ba

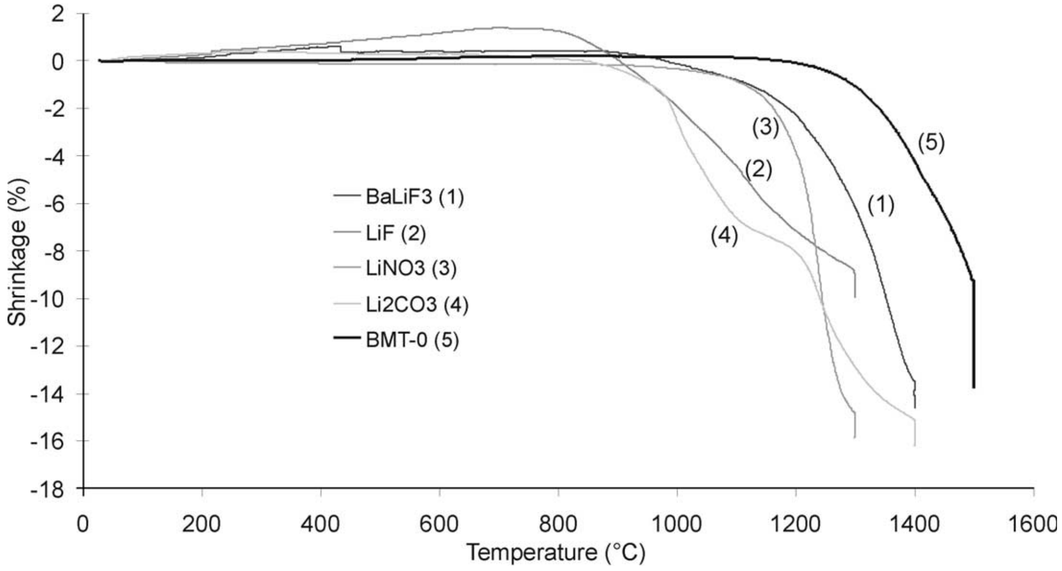

Fig. 3. Shrinkage curves of BMT stoichiometric samples as a function of temperature.

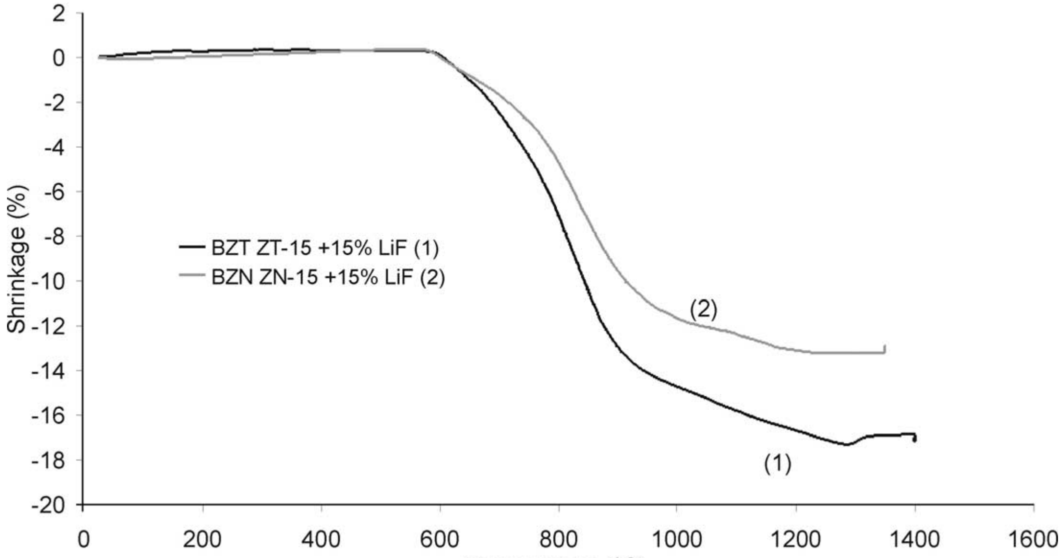

Fig. 4. Shrinkage curves of BZT/BZN non stoichiometric samples with 15% LiF salt as a function of temperature.

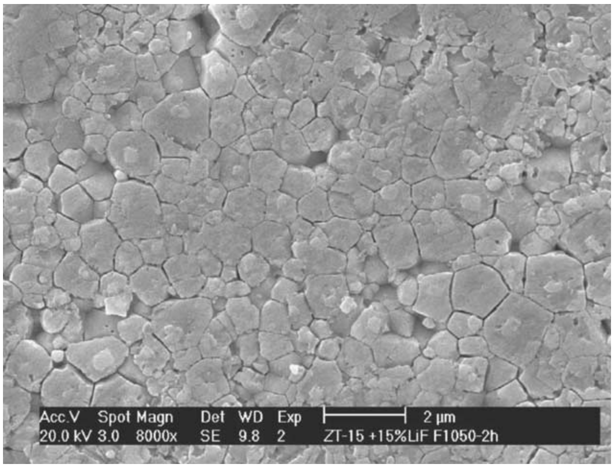

Fig. 5. Scanning electron micrograph of BZT nonstoichiometric sample with 15% LiF salt.

surstoichiometric BZN is used with an addition of 15% molar of LiF. This result is identical to the one observed for BZT material (see Fig. 4). Some discs shapes were pressed and sintered at 1050 °C for 2 h in air. As for the dielectric measurements, the doped samples have an ε_r at 25 °C equal to 50 whereas the temperature coefficient τ_ε is 290 ppm/°C and dissipation factors lower than 10^{-3}. The additions of LiF seem to increase dramatically τ_ε. XRD experiment performed on sintered pellets shows the presence of additional peaks in surfaces different from those of pure BZN. This secondary phase is identified as $Ba_4Nb_2O_9$ (Table 1).

4. Conclusions

In this study, the lowering of the sintering temperature of BZT, BZN and BMT ceramics using lithium salt additions has been investigated. The results for BZT and BZN materials are quite similar contrary to those observed for BMT. In the case of BZT and BZN, the $BaLiF_3$ sintering agent allows to reduce the sintering temperature of 200 °C. This sintering temperature lowering is still improved using barium surstoichiometric dielectric compounds doped with LiF, which permit to lower at least 300 °C of the sintering temperature. These results are consistent with the solid solution formation as already mentioned in the case of LiF doped $BaTiO_3$. Moreover, except for the temperature coefficient which is increased, the addition of lithium salts does not alter the dielectric properties (ε and tan δ). For BMT material, $LiNO_3$ addition is found to be the most efficient sintering agent investigated, it authorises a lowering of 250 °C of the sintering temperature without affecting dielectric properties. This preliminary study seems to be promising and further investigations are still in progress to achieve a sintering temperature lower than the copper melting temperature with satisfying electrical properties.

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