

Ba(Zn_{1/3}Nb_{2/3})O₃ sintering temperature lowering for silver co-sintering applications

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Abstract

The complex perovskite oxide Ba(Zn_{1/3}Nb_{2/3})O₃ 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% B₂O₃ 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.

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1. Introduction

Ba(Zn_{1/3}Nb_{2/3})O₃ (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 BaTiO₃ 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 ABO₃ 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})O₃ powders were synthesised using an optimised solid-state route [8]. High purity commercial powders (BaCO₃ Diopma 99.99%, ZnO Cerac 99.995% and

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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 4VIM 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 $\text{K}\alpha$ 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 ($<1 \mu\text{m}$). 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 $-60 \text{ }^\circ\text{C}/180 \text{ }^\circ\text{C}$ 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

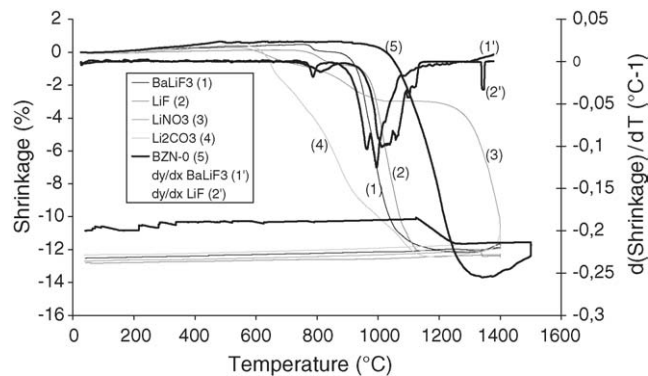
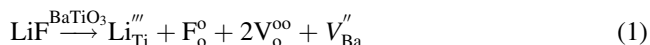


Fig. 1. Shrinkage curves and derivative shrinkage curves of lithium salts added BZN stoichiometric samples as a function of temperature.

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.

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 $180 \text{ }^\circ\text{C}$) on sintered samples. BaLiF_3 added samples exhibit a higher relative permittivity ($\epsilon_r = 48$) than the undoped ones ($\epsilon_r = 38$). 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:



The result of the Eq. (1) is the formation of the solid solution expressed by $\text{Ba}_{1-x}^{2+}\text{Li}_x^{+}\text{Ti}_{1-x}^{4+}\text{O}_{3-3x}^{2-}\text{F}_x^{-}$ 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 ($-50 \text{ ppm}/^\circ\text{C}$).

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