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Sintering of glass-added $BaZn_{1/3}Nb_{2/3}O_3$ ceramics

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Abstract

The complex perovskite oxide $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) has been studied for its attractive dielectric properties which place this material interesting for applications as multilayer ceramics capacitors or hyperfrequency resonators. This material is sinterable at low temperature with combined glass phase–lithium salt additions, and exhibits, at 1 MHz very low dielectric losses combined with relatively high dielectric constant and a good stability of this later versus temperature. The 2 wt.% of $ZnO–SiO_2–B_2O_3$ glass phase and 1 wt.% of LiF-added BZN sample sintered at 900 °C exhibits a relative density higher than 95% and attractive dielectric properties: a dielectric constant ε_r of 39, low dielectrics losses ($\tan(\delta) < 10^{-3}$) and a temperature coefficient of permittivity τ_ε of 45 ppm/°C^{-1}. The 2 wt.% $ZnO–SiO_2–B_2O_3$ glass phase and 1 wt.% of B_2O_3-added BZN sintered at 930 °C exhibits also attractive dielectric properties ($\varepsilon_r = 38$, $\tan(\delta) < 10^{-3}$) and it is more interesting in terms of temperature coefficient of the permittivity ($\tau_\varepsilon = -5$ ppm/°C). Their good dielectric properties and their compatibility with Ag electrodes, make these ceramics suitable for L.T.C.C applications.

Keywords: Dielectric properties; $Ba(Zn_{1/3}Nb_{2/3})O_3$; Glass phases; Low sintering temperature

1. Introduction

The low temperature co-fired ceramic (L.T.C.C) multilayer devices, composed of alternating dielectric and internal metallic electrode layers, have intensively aroused efforts from the ceramics community [1,2]. In these devices, the silver is commonly used as inner electrodes because of its high stability in high temperature (around 900 °C) in oxidant atmosphere. Moreover, the silver constitutes very good electrodes owing to both its high conductivity and relatively low cost. Of course, the drawback is the low melting point of silver, i.e. 961 °C, which imposes to develop high performance ceramics which can be sintered at low temperature, around 900 °C. It is well known that complex perovskite ceramics, having the general formula $Ba(B'_{1/3}B''_{2/3})O_3$ (B′ = Mg, Zn; B″ = Ta, Nb), exhibit very good microwave dielectric properties [3,4]. In particularly, the $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) ceramics have $\varepsilon_r = 41$, $Q = 5600$ at 10 GHz and $\tau_f = 28$ ppm/°C [5] that fit to the requirements for the LTCC and silver-based multilayer capacitors manufacturing. However, the BZN requires a sintering temperature higher than 1300 °C to achieve a satisfying density. Successful lowering of sintering temperature of BZN has been already reported by F. Roulland and S. Marinel [6]. In this paper, the authors report that dense stoichiometric BZN can be obtained at 950 °C owing to the addition of a mixture of B_2O_3 + LiF. This work is actually based on the addition of both a glass compound and a lithium salt as sintering agent. The low sintering temperature has permitted to co-sinter BZN + silver prototype exhibiting attractive dielectric properties. However, it is well admitted, in order to produce reliable components that the sintering temperature must be still decreased at around 900 °C because of the high diffusivity of silver. The purpose of our work is to investigate the system $ZnO–SiO_2–B_2O_3$ (ZSB) glass compound + lithium salt or B_2O_3 as sintering aid to allow BZN to be sintered at 900 °C without degrading its properties. The ZSB addition has been reported to be really efficient to decrease the sintering temperature of the dielectrics $(Zr,Sn)TiO_3$ or $BaZn_{1/3}Ta_{2/3}O_3$ [7,8]. This glass phase is well known to promote the densification of ceramics [9,10] and it is expected a similar behaviour for BZN.

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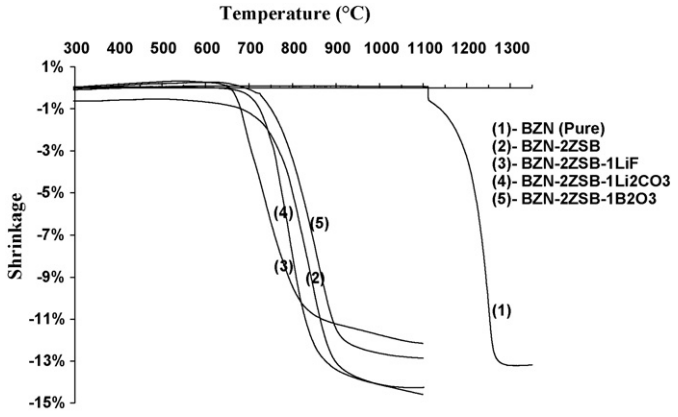

Fig. 1. Shrinkage curves vs. temperature.

2. Experimental procedure

The $Ba(Zn_{1/3}Nb_{2/3})O_3$ compound was prepared by solid state reaction using reagent grades powders of $BaCO_3$, ZnO and Nb_2O_5 (purity>99%). The precursors were appropriately weighted according to the $Ba(Zn_{1/3}Nb_{2/3})O_3$ stoichiometry. The mixing was performed in an ammoniac solution at pH 11 using zircon balls in a Teflon jar for 2 h. These conditions were found to be optimal to obtain very well-dispersed slurry [11]. The slurry was subsequently dried under infra-red lamps and the powder was manually reground and heat treated at 1100 °C for 2 h in air [6]. The powder was finally reground using the same process in ammoniac solution at pH 11 for 1 h.

For the glass preparation, the ZnO (crystallised, purity >99%), SiO_2 (amorphous, purity >99%) and the H_3BO_3 (amorphous, purity >99%) precursors were appropriately weighted according to the molar composition: 60% ZnO + 30% SiO_2 + 10% B_2O_3 and mixed in deionised water using zircon balls in a Teflon jar for 2 h. The mixtures were then melted at 1100 °C for 1 h in a platinum crucible and quenched at room temperature in deionised water. These glasses were grinded in a planetary grinder for 45 min to obtain a fine powder.

The $Ba(Zn_{1/3}Nb_{2/3})O_3$ + 2 wt.% ($ZnO–SiO_2–B_2O_3$) glass + 1 wt.% of X (with X = LiF, Li_2CO_3 or B_2O_3) mixtures were prepared by mixing in a planetary grinder for 45 min in absolute ethanol. To shape pellets, an organic binder (polyvinyl alcohol at 5 vol.%) was manually added to the powder and disks (8 or 6 mm in diameter, 2 mm thick) were shaped by uni-axial pressing at a load of about 2100 kg. The green samples were finally sintered in air in a tubular furnace for 2 h at dwell temperature determined by TMA (Thermo-Mechanical Analysis Setaram TMA 92), with heating and cooling rates of 150 °C/h. The density of the sintered samples were characterised using a He pycnometer (Accupyc 1330). The dielectric properties were determined versus temperature (from −60 to 160 °C) using a RLC bridge (PM6306). The crystallised phase composition has been identified by X-ray diffraction (XRD) technique using the Cu Kα X-ray radiation (Philips X' Pert) and the microstructures were observed using a scanning electron microscopy (SEM Philips XL'30).

3. Results and discussion

A dilatometric measurement was systematically performed on each composition. The thermomechanical curves are reported Fig. 1. The shrinkage of BZN without addition is completed at 1300 °C. The combination of the oxide or lithium salts and glass phases addition is known to form an eutectic which can increase the shrinkage rate [12]. The dilatometric curves clearly show that the sintering temperature decreases using this combination addition. The end of the shrinkage for the compositions BZN–2ZSB and BZN–2ZSB–$1B_2O_3$ is achieved at 930 °C. For BZN–2ZSB–1LiF and BZN–2ZSB–$1Li_2CO_3$ samples, the addition is more efficient, and the end of the shrinkage is obtained at 900 °C. These later additions make BZN sinterable under silver melting point.

Taking into account the dilatometric curves, pellets of each composition have been sintered in air. The XRD patterns

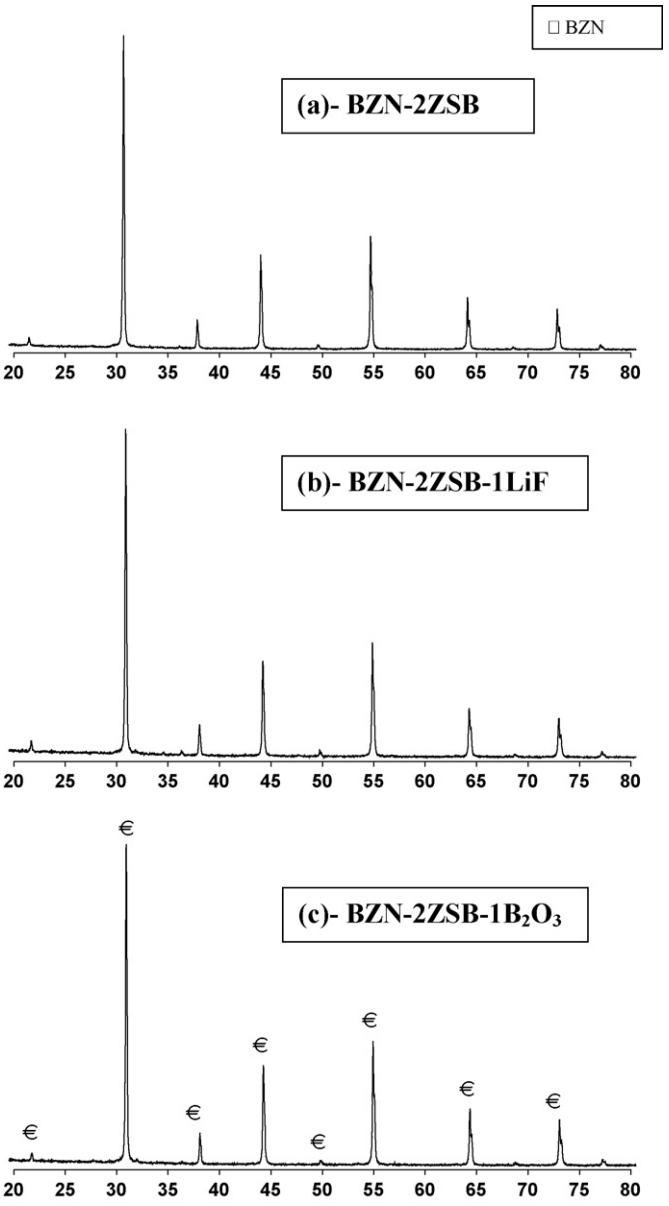

Fig. 2. XRD patterns of sintered samples.

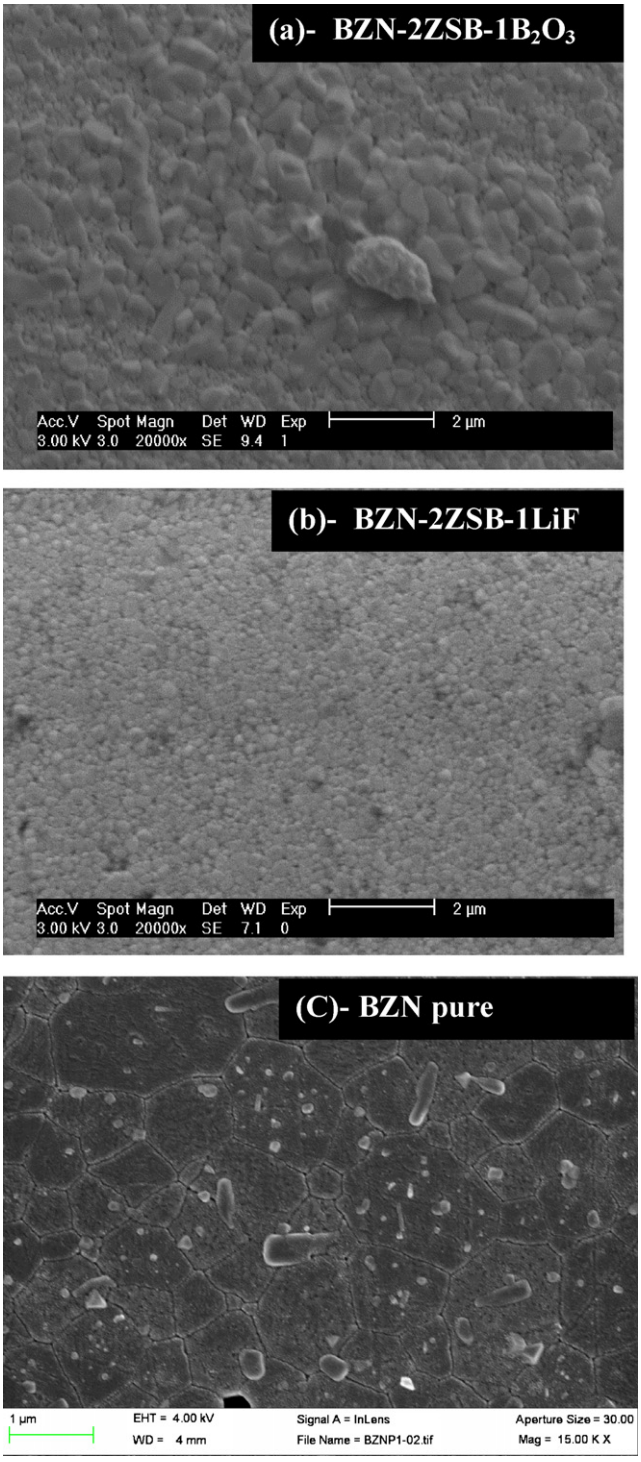

Fig. 3. Scanning electron micrographs (SEM) of sintered samples.

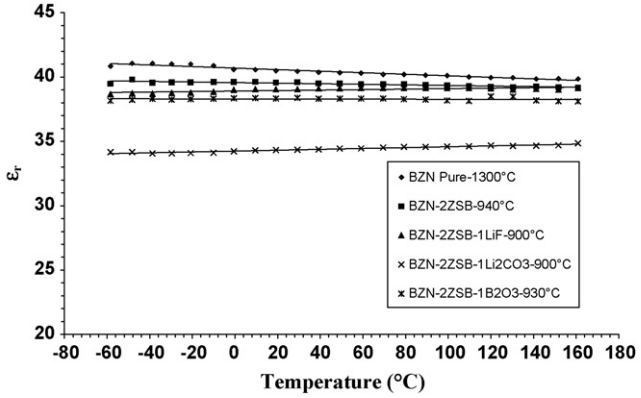

Fig. 4. Relative permittivity of the samples vs. temperature.

(Fig. 2), performed on crushed sintered samples, show that the ceramics compositions are single phase, exclusively composed by BZN perovskite phase without crystallised secondary phase.

Thanks to the 2ZSB-X additions, a relative density between 94% and 96% of the theoretical is obtained for all samples at a sintering temperature below 940 °C.

Fig. 3 shows SEM microstructure of the sintered samples. The ceramics with addition exhibit well dense microstructure in good agreement with the high relative density. The grain size are small, for both sample (mean grains size <500 nm) (Fig. 3(a) and (b)), which can be explained by the low sintering temperature. As a comparison, the grain size observed for BZN samples sintered at 1300 °C is around 1.5 μm (Fig. 3(c)).

The dielectric constant measured versus temperature curves for the sintered samples are plotted Fig. 4. Each sample exhibits a relative permittivity between 37 and 42. The temperature coefficient of the permittivity depended on the samples compositions. The pure BZN compound exhibits a negative temperature coefficient of the dielectric constant with a high value $\tau_\varepsilon = -148$ ppm/°C. However, the τ_ε value of BZN tends to increase as the oxide or salts lithium and glass phase is added, passing from negative to positive values (see Table 1). For the compositions BZN–2ZSB–1LiF and BZN–2ZSB–$1B_2O_3$, the materials exhibit very attractive dielectric properties, with a relative permittivity around 39 at room temperature, a temperature coefficient of 45 and −5 ppm/°C, respectively, and a loss factors lower than 10^{-3} at 1 MHz. The resistivities of these compositions are higher than 10^{13} Ω cm.

A prototype of silver/BZN-based capacitor has been designed using the ceramics with the composition of BZN–2ZSB–1LF. The sintering temperature was 900 °C for a dwell time of 2 h. Fig. 5 shows a SEM observation of a cross-section of this sample. No silver diffusion into the ceramic has occurred

Table 1
Dielectric properties and density of the sintered ceramics at 1 MHz

Samples	Sintering temperature (°C)	Relative density (%) of the theoretical	ε_r	tan(δ)	τ_ε (ppm/°C)	ρ_i (Ω cm)
Pure BZN	1300	97	40	$<10^{-3}$	−148	8.65×10^{12}
BZN–2ZSB	940	94	40		−55	7.48×10^{12}
BZN–2ZSB–1LiF	900	96	39		45	1.37×10^{13}
BZN–2ZSB–$1Li_2CO_3$	900	95	37		50	7.33×10^{11}
BZN–2ZSB–$1B_2O_3$	930	95	38		−5	5.30×10^{13}

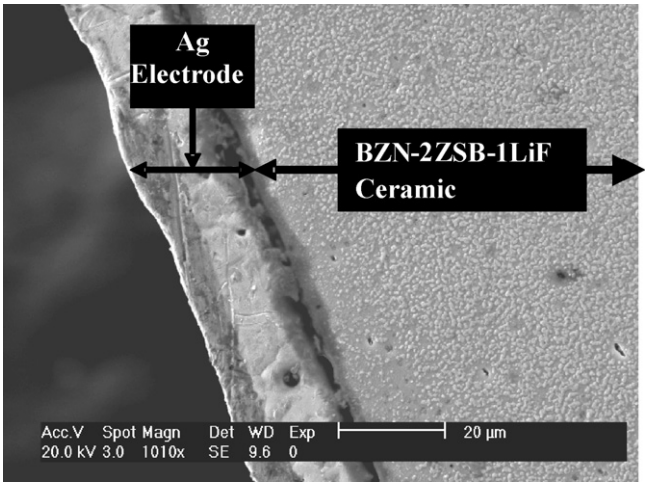

Fig. 5. Scanning electron micrographs of BZN–2ZSB–1LF samples co-fired with Ag at 900 °C for 2 h.

showing a satisfying compatibility between the electrode and the ceramic. This component exhibits very attractive dielectrics properties, i.e. a room temperature relative permittivity around 39, a permittivity temperature coefficient of 35 ppm/°C and a loss factor lower than 10^{-3} at 1 MHz. These properties make this formulation suitable to fabricate silver-based multilayer ceramic capacitors.

4. Conclusion

In this work, the lowering of the sintering temperature has been investigated by additions of oxide or lithium salts and glass phase in order to co-sinter BZN samples with silver electrodes. The sintered samples do not exhibit secondary phases and their properties are improved in comparison to the basic material. The best results are obtained for the additions of 2 wt.% $ZnO–SiO_2–B_2O_3$ + 1 wt.% LiF and 2 wt.% $ZnO–SiO_2–B_2O_3$ + 1 wt.% of B_2O_3. The sintered ceramics show a high density around 95–96% of the theoretical. The reported dielectric properties on these compounds, sintered respectively at 900 and 930 °C, exhibit a relative permittivity of 39 and 38, a temperature coefficient of the permittivity of 45 and −5 ppm/°C and dielectric losses lower than 10^{-3}. These good dielectric properties combined with the low sintering temperature make BZN based ceramic suitable for silver-based multilayer structure for L.T.C.C. applications.

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