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Dielectric properties of $Ba(Mg,Zn)_{1/3}Nb_{2/3}O_3$ and effect of B_2O_3 and LiF addition

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Abstract

The dielectric and microwave properties of $(x)BaZn_{1/3}Nb_{2/3}O_3$–$(1-x)BaMg_{1/3}Nb_{2/3}O_3$ (BMZN) mixture were investigated. The complex perovskite-type ceramics $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) and $Ba(Mg_{1/3}Nb_{2/3})O_3$ (BMN) have a high dielectric constant ($\varepsilon_r = 39$ and 33, respectively), but while BZN has a relative low firing temperature (~1350 °C), BMN has a too high sintering temperature (>1500 °C) to make it attractive in some technological applications. Mixing these two dielectric ceramics in different proportions and adding some sintering agents (like glassy B_2O_3 and LiF) the sintering temperature can be decreased, and XRD patterns indicates the formation of a solid solution for all x values investigated. The dielectric properties are preserved or even improved for some specific combinations. For BMZN ($x = 1/4$), without any dopants, the Q_f factor is 76.7 THz for $f = 7.6$ GHz and the temperature coefficient of the resonant frequency τ_f is −4 ppm/°C, which is the best value for BMZN. These values make BMZN compounds suitable for microwave resonator applications.

We highlight in this paper that BMZN materials can be successfully sintered at low temperature (i.e. 940 °C), opening opportunities to manufacture base metal electrodes multilayer ceramic capacitors (BME-MLCC).

Keywords: BMZN; Perovskites; Dielectric properties; Capacitors

1. Introduction

Perovskite-type ceramics ABO_3 are largely used in the electronic industry. Among these materials, those of type $AB'_{1/3}B''_{2/3}O_3$, are particularly attractive for various applications such as microwave frequency resonators, multilayer ceramic capacitors (MLCC) or different type of detectors (thermal, pressure, vibration, radiation, etc.). These complex perovskites are particularly studied because they often exhibit very low dielectric losses. The hard competition between the companies involved in this field keeps indeed scientific research in a very intense activity. One of the main goal from the industry point of view is to lower the cost of some electronic devices by replacing the expensive noble metal electrodes (Pt, Pd) by cheaper base metal electrodes (BME) (like Cu, Ni, Ag) [1–3]. This substitution could be possible if we succeed (i) to lower the sintering temperature (T_s) below the melting point of BME (1083 °C, Cu; 961 °C, Ag); and (ii) to control the stability of the dielectric compound in reductive atmosphere [4] to avoid the BME oxidation.

Regarding the sintering temperature diminution, the most common way to achieve this is the use of sintering aids. The materials tested on this purpose are the glassy B_2O_3 compound and the lithium fluoride LiF. The literature is rich in studies devoted to lower the sintering temperature using various additives (LiO_2, $LiNO_3$, SiO_2, MgO) [5,6].

$BaMg_{1/3}Nb_{2/3}O_3$ (BMN) is one of the perovskite-type ceramic which has interesting properties ($\varepsilon_r = 32$, $\tau_f = 33$ ppm/°C, $Q_f = 56$ THz at 10 GHz) but because of its high T_s (>1500 °C) [1] it is less used than $BaZn_{1/3}Nb_{2/3}O_3$ (BZN), which exhibits a lower T_s (1350 °C) and similar dielectric properties ($\varepsilon_r = 41$, $\tau_f = 30$ ppm/°C, $Q_f = 54$ THz at 10 GHz) [1].

This paper is devoted to investigate the dielectric and microwave properties of BMN–BZN mixture, and the effect of sintering aids like B_2O_3 and LiF on the sintering temperature and dielectric properties of this system. The formation of the $Ba_3Mg_{1-x}Zn_xNb_2O_9$ solid solution is also discussed.

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2. Experimental procedure

Ceramic samples of composition $Ba_3(Mg_{1-x}Zn_{1-x})$-Nb_2O_9 (BMZN) with $x = 0$, 0.25, 0.5, 0.75, 1, were prepared via a conventional solid-state reaction method, using reagent grade carbonates and oxides: $BaCO_3$ (Diopma, 99.99%), MgO (Cerac, 99.95%), ZnO (Cerac 99.995%), Nb_2O_3 (HC Starck 99.9%). The materials were weighted in the appropriate molar ratio and mixed into an ammoniac solution (pH 11) by attrition milling for 2 h, using 1 mm diameter ZrO_2 balls in a teflon jar. The powders were then dried and calcinated at a temperature of 1200 °C for 1 h in air, using a 200 K/h heating/cooling rate.

After a manual de-agglomeration in an agate mortar, two batches of BMZN samples were synthesised: the first without any additives and the second with adding 10 M% of B_2O_3 (Prolabo, 99.93%) and 5 M% of LiF (Prolabo, 99%). Before pressing in pellets the powders were reground during 1 h, in the same manner as before calcination. The dried powders were subsequently axially pressed in cylindrical pellets of about 2–3 mm in height and of about 6 mm in diameter for dilatometric measurements and of about 8 mm in diameter for sintering. An organic binder (Rhodoviol^{TM}) was added to the powders before shaping.

The thermal treatments were performed in a tubular furnace (PYROX) under air atmosphere. The pellets were sintered during 2 h following the same thermal cycle as for the calcination, the temperature of the dwell ranging from 1500 to 940 °C.

Dilatometric measurements were carried out in air atmospheres using a Setaram TMA dilatometer. During the experiments a slight load of 1 g is applied on the pellets to allow the measurement. All samples were heated and cooled with 200 K/h ramp, the dwell time being 2 h.

The crystalline structures of the samples were examined through X-ray powder diffraction using either a Rikagu diffractometer (Cu Kα radiation) or with a Philips X'Pert (Cu Kα radiation).

For electrical measurements the discs were painted on both sides with In–Ga eutectic paste. The dielectric characteristics [ε, tg(δ)] versus temperature were acquired with a FLUCKE 6306 LCR-meter at 1 MHz and 1 V in the range of −60–180 °C. The electric insulating resistance was measured using a SEFELEC DM500H megohmmeter and the microwave frequency measurements were performed using a cavity method.

3. Results and discussions

3.1. Study of BMN–BZN solid solution

The diffraction pattern of BMZN powders calcinated for 1 h at 1200 °C, depicted in Fig. 1, highlights that all the peaks in pure BMN ($x = 0$) can be indexed with a cubic structure ($Pm\bar{3}m$) with a cell parameter $a = 4.08712$ Å. No tendency

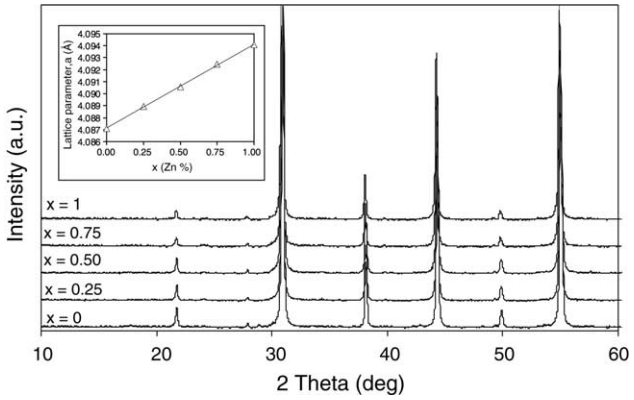

Fig. 1. XRD patterns and lattice parameter evolution vs. Zn content in $(1-x)$BMN–(x)BZN calcinated powders.

of superstructure formation can be observed, thus we have a disordered type perovskite-like structure. As well known, the so-called disordered behaviour comes from the randomly arrangement of B-type cations in this ABO_3-type perovskite structure (Mg and Nb in this case), which are positioned in the volume centre of oxygen octahedrons.

Increasing the Zn content in BMZN, no significant modification in the XRD pattern is evidenced. Nevertheless, the lattice parameter monotonously varies from 4.08712(4) Å for BMN to 4.09408(4) Å for BZN, suggesting the formation of a total solid solution (see Fig. 1). The ionic radii $^{VI}R_{Mg^{2+}} = 0.720$ Å and $^{VI}R_{Zn^{2+}} = 0.745$ Å, easily explain the lattice parameter increasing.

The maximum densification of BMN (about 95% of the theoretical density) is achieved at relative high temperature (i.e. 1500 °C) as it can be observed on the dilatometric curve (see Fig. 2). Although for $Ba(Mg, Zn)_{1/3}Nb_{2/3}O_3$ the sintering is lower than 1500 °C (about 1350 °C for BZN), we decided to sinter all $Ba_3Mg_{1-x}Zn_xNb_2O_9$ samples (with x ranging from 0 to 1) at 1500 °C in air, to have a set of reference.

For the sintered pellets, XRD patterns performed on both the sample surface and in the bulk are shown on the Fig. 3. Some modifications can be evidenced as the Zn content in-

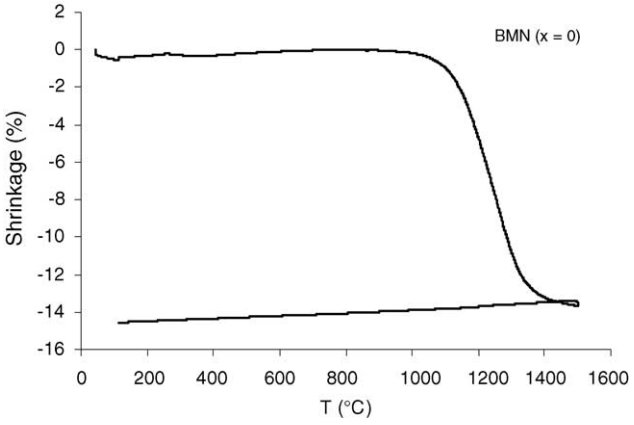

Fig. 2. Shrinkage curve of BMN sample as a function of temperature.

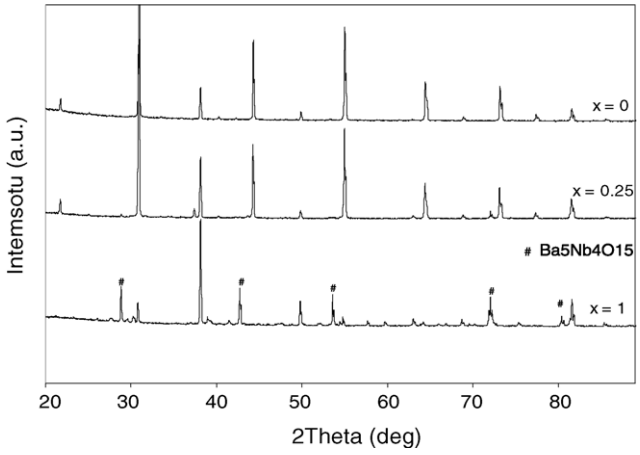

Fig. 3. XRD patterns on the surface and in the bulk of $(1-x)$BMN–(x)BZN sintered pellets.

creases in the BMZN material. In BZN ($x = 1$), for example, on the pellet's surface a Ba–Nb binary oxide phase is detected and could be identified as $Ba_5Nb_4O_{15}$ (PDF #14-0028) while the bulk sample is only constituted of the BZN material. This behaviour can be connected with the departure of the Zn from the sample surface, caused by the high T_s.[7] Contrariwise the $x = 0$ sample has the same XRD pattern (pure BMN) in the bulk as well on the surface. For intermediate value of x, a mixture between $Ba_5Nb_4O_{15}$ and BMZN is also observed on the surface of the pellet, the $Ba_5Nb_4O_{15}$ content decreasing as the Zn content decreases.

Dielectric measurements performed on BMZN sintered pellets show that the dielectric properties continuously vary versus x (Fig. 4). The dielectric constant ε varies almost linearly from $\varepsilon_r = 33$, which is characteristic to BMN, to $\varepsilon_r = 39$ characteristic to BZN. The losses factors ($tg(\delta) = 1/Q$) are 0 in the range of errors for all the samples and the insulating resistivity is high for all x values ($>10^{12}\ \Omega$ cm) with a value particularly high for $x \leq 0.25$ ($>10^{14}\ \Omega$ cm) (see Table 1).

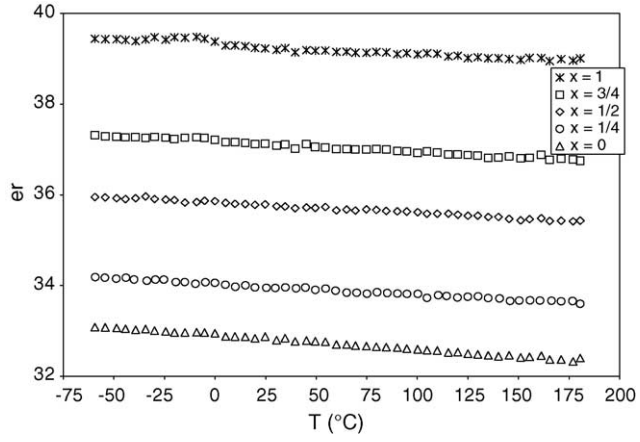

Fig. 4. Dielectric constant vs. temperature of BMZN ($x = 0$–1) pellets measured at 1 MHz.

Table 1
Dielectric and electric measurements for BMZN + 0 samples

x	ε_{r25} (±3)	τ_ε (ppm/K)	tg(δ)	log ρ (Ω cm) (±1)
0.00	33.0	−98		14.7
0.25	34.1	−70		14.7
0.50	35.9	−64	$<10^{-3}$	13.2
0.75	37.2	−65		14.3
1.00	39.4	−59		12.0

The hyperfrequency characteristics of BMZN samples are summarised in Fig. 5. As it can notice, while the ε_r and τ_f slightly vary, the Q_f factor has an interesting evolution. It is relatively high for $x = 0$ (63.7 THz), increases for $x = 0.25$ (76.7 THz) and then drastically decreases (<16 THz) for $x \geq 0.5$. The highest Q_f values are obtained on $x = 0.25$ compound.

3.2. Lowering of the sintering temperature of BMZN

In order to decrease the sintering temperature T_s of BMZN solid solutions, the effect of some additives has been tested. From the dilatometric curves it has been found that, by adding 10 M% of B_2O_3 and 5 M% LiF [6,8] the T_s will decrease appreciably (see Fig. 6). The sintering temperatures that have

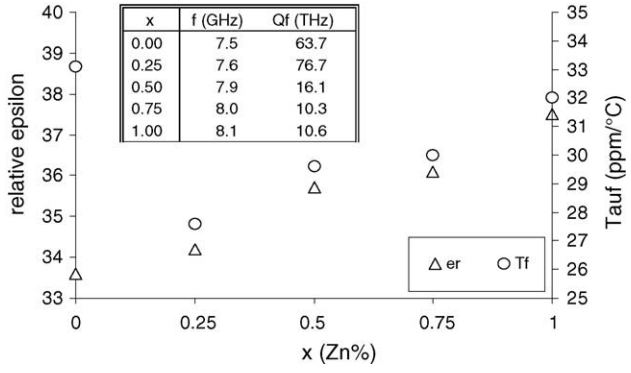

Fig. 5. The dielectric properties vs. Zn content (x) in BMZN sintered samples measured in high frequency.

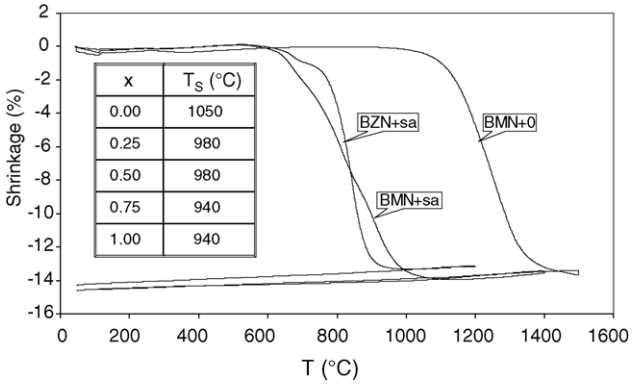

Fig. 6. The effect of the sintering aids on the shrinkage curves vs. temperature in BMZN compounds. The chosen sintering temperatures decreases as Zn content (x) increases.

Table 2
Electric measurements for BMZN + sa samples

x	ε_{r25} (±1)	τ_ε (ppm/K)	tg(δ)	log ρ (Ω cm) (±1)
0.00	28.5	−77		15.4
0.25	30.8	−62		15.4
0.50	23.1	−52	$<10^{-3}$	12.1
0.75	33.26	+21		12.7
1.00	24.77	+37		12.2

been used for the treatment of these pellets for all x values are presented on the table included in Fig. 6.

It can also be noticed by adding the sintering aids the crystalline lattice of BMZN solid solutions will preserve the cubic ordered structure. No binary Ba–Nb secondary phase can be detected on the pellets surface, proving that the T_S diminution avoid the Zn departure from the structure.

The dielectric measurements of BMZN + sa pellets are summarised in Table 2. It can notice that the dielectric properties are more or less affected, depending on Zn content and on T_s. The remarkable result is that the temperature coefficient τ_ε varies from negative values ($\tau_\varepsilon = -77$ ppm/°C) to positive one ($\tau_\varepsilon = +37$ ppm/°C) with x, allowing to adjust this coefficient to zero. This gives the possibility to process NPO (negative positive zero) dielectric.

4. Conclusions

Mixing the two dielectric ceramics $(1-x)$BMN–(x)BZN a cubic, disordered type perovskite-like structure solid solution is obtained after the calcination. The high temperature sintering enhance the Zn departure from the structure, evidenced by secondary phase apparition. This departure is more evident on the surface of the pellets while in the bulk is limited. Increasing x from 0 to 0.25 the Q_f factor is improved from 63.7 to 76.7 THz. A further increase of Zn content will decrease rapidly this factor. The sintering agent addition (B_2O_3 and LiF) and consequently the T_s reduction does not affect the dielectric properties especially for BMZN with $x = 0.25$. It can be noticed that all the parameters preserve almost the same values as in the sample without additions. With their Q_f factor of about 80 GHz the BMZN $x = 0.25$ could be suitable for some resonator applications. It was also evidenced that the τ_ε coefficient is tuneable to zero by adjusting the x value for the low sintering temperature compositions.

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