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Effects of the sintering atmosphere on the $BaZn_{1/3}Ta_{2/3}O_3$ based Cu multilayer ceramic capacitors

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Abstract

Recent papers report that $BaZn_{1/3}Ta_{2/3}O_3$ (BZT) ceramic can be sintered at a temperature as low as 1050 °C owing to the use of flux agents like B_2O_3 + LiF combined with a slight non-stoichiometry, whereas its usual sintering temperature is 1400 °C. This low sintering temperature (below the Cu's melting point = 1083 °C) opens the route to fabricate copper based multilayer ceramic capacitors, in condition that a reductive atmosphere is used during the sintering. This paper presents the effect of three various sintering atmospheres (air, H_2 (1%) in N_2 and H_2 (1%) in Ar) on the stability and the dielectric properties of BZT. It is researched a suitable sintering atmosphere to prevent Cu from oxidation and to preserve the dielectric properties of BZT. Using the appropriate atmosphere, copper based multilayer ceramic capacitors, with attractive dielectric properties, have been successfully processed.

Keywords: Dielectric properties; Capacitors; Perovskites

1. Introduction

The dielectric $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) is a perovskite type material which exhibits attractive dielectric properties namely, a low losses factor ($\tan(\delta) < 10^{-3}$), a relatively high permittivity (ε_r around 30) and a low temperature coefficient of the permittivity at high frequencies (from MHz to GHz) ($|\tau_\varepsilon| < 100$ ppm/°C[1–4]). These properties make it attractive for fabricating type I multilayer chip capacitors. Nevertheless, BZT ceramic requires high temperature to be correctly sintered (1400 °C), forbidding the use of base metals as electrodes, viz. copper (melting point, m.p. = 1083 °C) and silver (m.p. = 961 °C). Recent papers have reported that BZT ceramic can be sintered at a temperature as low as 1050 °C owing to the use of B_2O_3 + LiF addition combined with a slight non-stoichiometry.[2,3] This result permits the co-sintering between the copper electrodes and the ceramic, providing the stability of the ceramic material during the high temperature treatment. This could open the route to fabricate Cu based multilayer ceramic capacitors. This type of components should be cheaper and more powerful than those co-sintered at high temperatures (>1400 °C) with expensive metals namely Pd, Pt. The aim of this work is to study the behavior of the pure BZT and the 'BZT + additives', for which sintering can be performed at 1050 °C, as a function of the employed atmosphere.

2. Experimental procedure

$Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba_{0.99}(Zn_{1/3}Ta_{2/3})O_{2.99}$ powders have been prepared by solid state reaction between $BaCO_3$ (Diopma 99.99%), ZnO (Cerac 99.995%) and Ta_2O_5 (HC Starck 99.9%). All conditions for the synthesis are summarized in the reference 3; in the same manner, the justification to synthesize the $Ba_{0.99}(Zn_{1/3}Ta_{2/3})O_{2.99}$ compound is also given in reference 3 as well as the powder characterization. It can be mentioned that the non-stoichiometry compound has a similar XRD pattern to that of the stoichiometric compound.[3] After the first thermal cycle, the powders have been reground for 45 min in an agate mortar using a planetary grinder in order to achieve a grain size of around one micrometer. For the non-stoichiometric compound, LiF (Prolabo 99%) and B_2O_3 (Prolabo >99%) have been also added according to the following nominal composition $Ba_{0.99}(Zn_{1/3}Ta_{2/3})O_{2.99}$ + 5 mol.% LiF + 10 mol.%. B_2O_3. This formulation named BZT_{LT}, can be sintered at 1050 °C according to our previous study.[3] Eight mm diameter and one mm thickness disks have been shaped using uniaxial pressing at 29 kN.

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Before pressing, an organic binder (polyvinyl alcohol) has been systematically added at around 3 wt% to improve the mechanical behavior of the green samples. Samples have been sintered in three various atmospheres. First, static air has been used as an oxidant atmosphere. Second, a flowing gas of H_2 (1%) in Ar moisture saturated and a flowing gas of H_2 (1%) in N_2 moisture saturated have been used as foaming atmosphere. Moisture saturated atmosphere is used to consume the CO_2 traces and P_{O_2} has been estimated using a zirconia sensor (Setnag). The sintering temperatures were 1400 and 1050° for, respectively, BZT and BZT_{LT}. The sintering time was systematically fixed at 2 h. Dielectrics properties (ε, tan(δ)) were measured at 1 MHz versus temperature (−60 °C/+180 °C) using a LCR bridge (Fluke PM6306) on disks of which each face has been previously covered by an In/Ga eutectic mixture to act as electrodes. Insulating resistivity has been measured using a picoamperemeter (Sefelec). Chemical and microstructural investigations of our samples have been carried out, respectively, by X-ray diffraction (Philips X'Pert, Cu Kα) and SEM observation (SEM Philips XL'30). Copper Based Multilayer ceramics capacitors prototypes have been fabricated by the TEMEX Company and their properties have been carefully examined.

3. Results and discussion

Table 1 summarizes the dielectric properties of the pellets depending of the various processing conditions. It is also indicated the oxygen partial pressure versus the atmosphere used.

3.1. Sintering in air

The first important point is that materials sintered in air (BZT or BZT_{LT}) exhibit the expected properties: density higher than 90% of the theoretical, a relative dielectric constant around 30, a low losses factor ($<10^{-3}$) and an insulating resistivity higher than 10^{11} Ω cm. Nevertheless, the compound sintered at low temperature (BZT_{LT}) has a slightly increased temperature coefficient (∼103 ppm/°C) compared to BZT (∼0 ppm/°C). The weight loss during sintering is about 3–3.5% which corresponds to the organic binder departure. The good stability of both compounds, when sintering is performed in air, has been obviously expected.

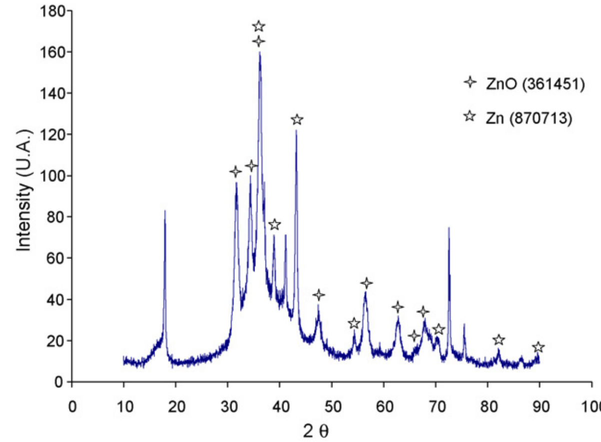

Fig. 1. XRD pattern of the powder which has been found at the cold zone of the furnace.

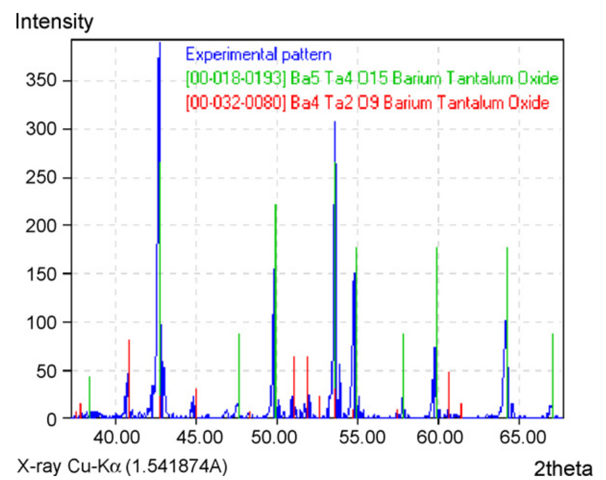

Fig. 2. XRD pattern of the BZT pellet sintered in Ar/H_2 reductive atmosphere.

3.2. Sintering of BZT in low oxygen partial pressure

A very high weight loss of nearly 10% during sintering in N_2/H_2 or Ar/H_2 is observed for BZT (Table 1). During sintering, a black powder has been deposited at the cold zone of the furnace (actually, at the extremities). XRD pattern of this powder (Fig. 1) has allowed to identify it as a mixture of zinc oxide (ZnO number PDF 361451) and metallic zinc (Zn PDF870713). Disks are finally not dense and are mainly composed by $Ba_5Ta_4O_{15}$

Table 1
Properties of the ceramics vs. the processing conditions

	Sintering conditions					Dielectrics properties (RT)			
	T (°C)	Atmosphere	P_{O_2}	Density (%)	$\Delta m/m$ (%)	ε_r	tan(δ)	τ_ε (ppm/°C)	log ρ_i (Ω cm)
BZT	1400	Air	2×10^{-1}	92.5	−3.5	31	$<10^{-3}$	0	15
		$N_2 + 1\%\ H_2$	10^{-10}	58	−9.5	24	10^{-2}	162	9
		$Ar + 1\%\ H_2$	$\ll10^{-10}$	57	−9.7	19	$<10^{-3}$	+140	9
BZT_{LT}	1050	Air	2×10^{-1}	90	−3	29	$<10^{-3}$	103	11.7
		$N_2 + 1\%\ H_2$	10^{-10}	90	−5	27	$<10^{-3}$	−40	13
		$Ar + 1\%\ H_2$	$\ll10^{-10}$	78	−9	20	$<10^{-3}$	−10	10.2

P_{O_2} is the partial pressure of oxygen; density is the apparent one, $\Delta m/m$ corresponds to the relative weight loss during sintering.