Pb Mg1/3 Nb2/3 O3 (PMN) MULTILAYER CAPACITORS

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Résumé - Des condensateurs multicouches ont été réalisés à partir d'une chamotte 3 PbO - MgO - Nb_2O_5 dopée en oxyde de plomb, en utilisant comme électrode interne un alliage 70 Ag - 30 Pd. La nature et la répartition des phases dans les chips varient suivant l'importance du dopage en oxyde de plomb (6 - 8 % en poids) et les conditions de frittage (T_{Max} : 850°C - 1000°C, à l'air ou sous atmosphère controlée en plomb). On trouve, à travers une section d'un condensateur, une phase pyrochlore particulièrement développée en surface alors que la zone active est riche en phase perovskite associée éventuellement à une phase vitreuse à base d'oxyde de plomb, celle-ci abaissant la constante diélectrique du condensateur.

Abstract - Multilayer capacitors were made from a 3PbO - MgO - Nb_2O_5 mixing doped with lead oxide, and a 70 Ag - 30 Pd alloy as internal electrode. The phase nature and distribution in chips depend on the additions of lead oxide (6-8 wt %) and the sintering step (T_{Max} : 850 - 1000°C, in air or in a PbO controlled atmosphere). Through a chip cross section, one can note a pyrochlore type phase especially developped in the surface layer while the chip active area is essentially constituted of a perovskite type phase (PMN) and of an eventual glassy phase based on lead oxide, which strongly lowers the chip dielectric constant.

INTRODUCTION

Dielectric materials used for multilayer capacitors are usually alkali-earth titanates ($BaTiO_3$, $SrTiO_3$,...) which the firing temperature is near 1300°C. Since the usual ceramic multilayer capacitor process is characterized by a metal-ceramic cofiring step, the internal electrodes, used in this case, are necessary expensive alloys as for example Ag-Pd : 30 - 70 one.

Different possibilities can be considered to reduce the cost of multilayer ceramic capacitors :
- To lower the firing temperature of the dielectric materials such that high silver content alloys or base metals /1-4/ can be used as internal electrodes.
- To use a fabrication method of multilayer ceramic capacitors eliminating the metal-ceramic cofiring step such as the metal impregnation one. This method involves forming ceramic structures with porous layers which are then impregnated with inexpensive metal such as Pb, Sn or Ag /5,6/.

Among the low firing dielectric materials, the complex perovskite compounds $Pb(AB)O_3$ with A : Mg^{2+}, Fe^{3+}, Zn^{2+}, Ni^{2+} and B : Nb^{5+}, W^{6+}, Ta^{5+} are very promising. Fired at about 1000°C, they exhibit high dielectric constant (10.000) /7-11/.

However, previous studies on Pb $Mg_{1/3}$ $Nb_{2/3}$ O_3 compound (PMN) have shown that it is very difficult to get a pure perovskite phase /12-16/. The weak reactivity of the magnesium oxide associated with the high volatility of lead oxide leads to the formation of a pyrochlore phase (3 PbO 2 Nb_2O_5 type) preferentially located on the surface of samples and characterized by poor electric properties (low dielectric constant and resistivity, high dielectric losses). Recently, we have shown /17-19/ that an homogeneous distribution of pyrochlore and perovskite phases can be realized from the optimization of the firing step and that a control of lead oxide stoechiometry leads to the elimination of the pyrochlore phase. Consequently, the dielectric properties were notably improved : disk capacitors fired at 900°C exhibit at 20°C a high dielectric constant (12000) and resistivity (10^{12} Ω cm) associated with low dielectric losses (3 %).

This paper reports the dielectric properties of multilayer type capacitors corresponding to this system.

I - EXPERIMENTAL

Powders were prepared as follows : the reagent grade oxides of lead and niobium, and carbonate of magnesium* were milled, according to the lead magnesium niobate stoechiometry, in an attrition system for 1 hour using zirconia balls and acetone. The slurry was dried and calcined at 800°C for 2 hours. A lead oxide excess (Y : 6-8 wt %) was then added to the calcined product. After attrition milling for 2 hours, the average particle size of the powder is of a micron order with a specific surfaca equal to $4m^2/g$.

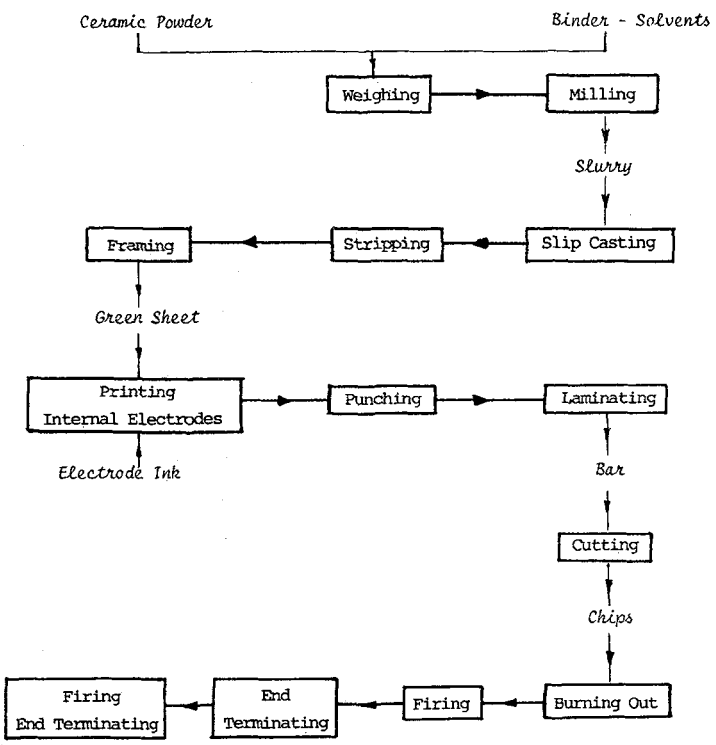


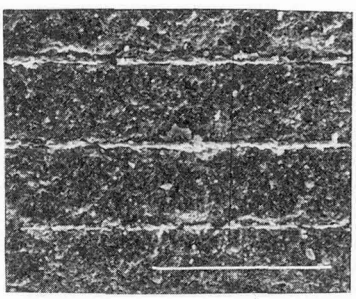
Fig. 1 Multilayer ceramic capacitors manufacturing process

*99,8 % PbO Merck-Darmstadt RFA

42,47 % MgO Merck-Darmstadt RFA

99,9 % Nb_2O_5 Merck-Darmstadt RFA

Multilayers capacitors were prepared by the process shown figure 1 : the film is formed by casting a slurry (Powder/Binder/Solvents : 56/10/34 wt %) on glass plate according to the doctor blade process (Cladan Caster Model 133) the green film, 40 µm thick, is then cut. The green sheets are screen printed with Ag/Pd : 70/30 electrodes. Ten printed sheets were then laminated in a single block which is cut into individual chips. After burning out, the chips are sintered according different methods (Maximum Temperature : from 850°C to 1000°C - Atmosphere PbO source or not). Figure 2 shows the typical layered structure of one chip capacitor observed by scanning electron micrograph.



(bar : 50 µm)
Fig. 2 Cross section of multilayer ceramic capacitor.

The following controls were achieved for the different chip capacitors.

- The losses of PbO oxide during sintering, from which one can deduce the residual lead oxide content (here after designated by PbO_{rsd}) that is to say the difference of lead oxide stoichiometry between the sintered material and the calcined product.
- The sintering shrinkage.
- The concentration of phases (pyrochlore and perovskite type) in samples.

Moreover dielectric constant and dissipation factor were measured at 1 KHz with 1V/rms from - 55°C to + 125°C using an automatic capacitance bridge. Insulation resistances were measured with a high resistance meter after applying 1 Vdc/µm for 1 min.

II - RESULTS (Table I)

N°	Y wt %	/ T_F /	Atm	wt % PbO_{rsd}	wt % PMN_A (1)	wt % PMN_S (2)	ΔL/L	ε_r	tg δ	ρ (Ω.cm)
(1)	8 %	/850°C/	in Air	+ 3 %	83 %	—	23 %	3127	2 %	2.10^8
(2)	—	/900°C/	———	+ 2 %	88 %	—	24 %	5780	1,5 %	3.10^{10}
(3)	—	/1000°C/	———	- 1 %	74 %	71 %	26 %	6350	1 %	$5,4\ 10^{11}$
(4)	6 %	/ ——/	———	+ 3 %	90 %	82 %	18 %	5354	6 %	8.10^9
(5)	7 %	/——/	———	- 1,3 %	77 %	14 %	28 %	7940	1 %	2.10^{11}
(6)	—	/——/	on $PbZrO_3$ Layer	- 0,5 %	87 %	36 %	30 %	10790	1,6 %	$2,5.10^{11}$
(7)	—	/——/	atm. powder ($PbZrO_3$)	+ 3,5 %	96 %	—	31 %	1094	3,8 %	———
(8)	—	/900°C/	———	+ 7 %	92 %	19 %	22 %	2430	4 %	2.10^{10}

Table I

Residual PbO oxide content, Perovskite content (1) Average (2) Surface, sintering Shrinkage and Electric characteristics of multilayer chips corresponding to Y wt % lead oxide additions to calcined product, sintered at T_F°C in different atmospheres.

. Volatilization mechanism of lead oxide and nature of phases.

- The volatilization of PbO increases with the PbO content added to the calcined product (samples (3) - (4) - (5)) and with the firing temperature (samples (1) - (2) (3)) but it can be reduce by using a PbO controlled atmosphere (samples (5) - (6) - (7)).

- The average perovskite content of samples depends on different parameters. In fact, given a residual lead oxide content (samples (1) - (4)) the firing temperature must be high enough to allow the synthesis of perovskite phase and in such a case, the average perovskite content increases with the residual lead oxide content (samples from (3) to (7). These results are in agreement with the formation mechanisms of perovskite phase proposed in previous studies /12/.

Moreover the volatilization of PbO leads to an inhomogeneous distribution of the residual lead oxide in samples and consequently to a gradient of perovskite phase which depends on the composition and the sintering conditions (Table I). So figure 3 shows the difference of microstructure between a surface layer (a) and on internal one (b) in a chip capacitor.

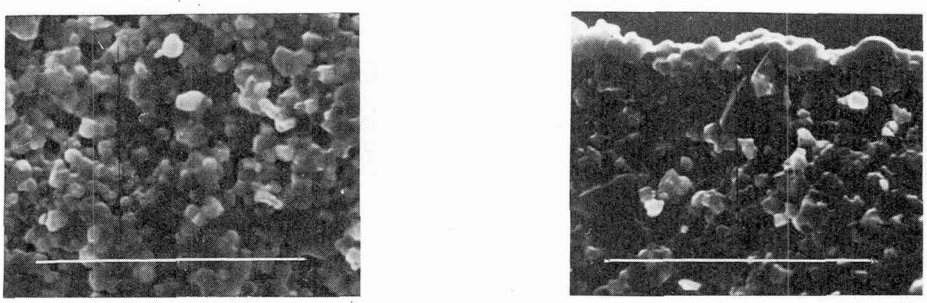


Fig. 3. Microstructure of a PMN multilayer ceramic fired at 1000°C.
a) in a ceramic layer b) at the surface (bar = 10 µm)

. Dielectric characteristics.

- As the dielectric constant is concerned, the average perovskite content appears less determining than the sintering shrinkage (samples (4) - (5)). Nevertheless, the type of phase gradient is crucial (samples (3) - (5)). In fact, for a same average perovskite content, the highest capacity corresponds to the strongest phase gradient because of the active area of a multilayer capacitor (figure 4).

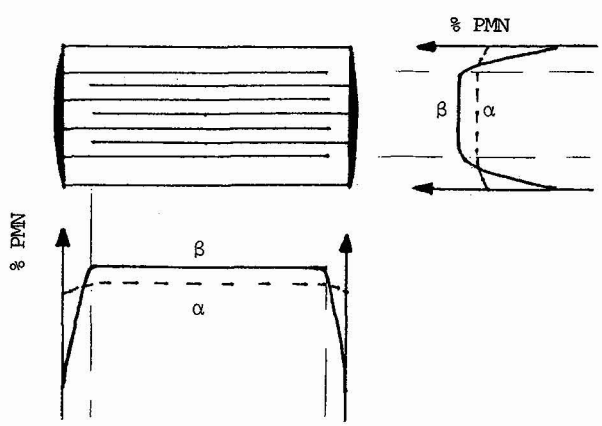


Fig. 4 : Example of two distributions of the perovskite phase, in a multilayer capacitor, corresponding to a same average perovskite content (the β distribution leads to a higher capacity than α one).

- For some samples, for instance (4) and (8), the dielectric constant variations cant'be explained through the previous parameters (perovskite content, phase gradient and sintering shrinkage). In fact, one can deduce from the values of lead oxide stoichiometry and PMN content in Table I that there is free lead oxide associated with PMN and pyrochlore phases in some sintered samples.Nevertheless, no lead oxide diffraction line appears on X-ray pattern, which only exhibit a broad diffuse peak towards small angles, suggesting that these samples contain a glassy phase based on lead oxide. Consequently, the low value of the dielectric constant for some samples can be due to a glassy phase gradient (similar to the PMN one).

CONCLUSION

The results show that the dielectric characteristics of multilayer capacitors can be improved according two ways.

- Either one keeps a phase gradient in the chips and one must adjust the lead oxide excess and the sintering step in order that there are the highest possible average perovskite content and densification rate, while avoiding the formation of a glassy phase due to a local lead oxide excess. Up to now, the best result is obtained for 7 % lead oxide excess and a sintering at 1000°C on a $PbZrO_3$ layer.

- Or one tries to eliminate the phase gradient : in such a case the two parameters : lead oxide excess/sintering step must define a pure perovskite supposing that there is no lead loss, which may be achieved by a sintering of samples in a powder with a lead oxide stoechiometry near the PMN one.

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