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EFFECTS OF THE SINTERING CONDITIONS ON THE DIELECTRIC CHARACTERISTICS OF 0.97BaTiO$_3$ – 0.03PbF$_2$ – 0.03LiF CERAMICS

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In the present work the influences of the sintering temperature and the sintering time on the dielectric properties of ceramics with composition (Ba,Pb)(Ti,Li)(O,F)$_3$ are examined . A mixture of 97mol. % $BaTiO_3$, 3mol. % PbF_2 and 3mol. % LiF is wet-ground then cold-pressed to pellets. These disks are sintered in air atmosphere at various temperatures during different sintering times. XRD analyses are performed on powder samples and the microstructure is investigated by SEM on fractured ceramics. Dielectric measurements are carried out as a function of temperature from 100K up to 473K in the frequency range 50Hz $\leq$ f $\leq$ 40 MHz. In any case , the triple substitution Ba – Pb , Ti – Li and O – F lowers simultaneously the ferroelectric Curie temperature T_C (70°C $\leq \Delta T_C \leq$ 140°C) and the relaxation frequency f_r of pure $BaTiO_3$ (f_r < 500MHz).

1. INTRODUCTION

The electronic industry is in expanding worldwide and the needs for dielectric ceramics become huger and huger . Among these materials, ABO_3 perovskites are very attractive due to their various applications such as capacitors, piezoelectric actuators, pyroelectric infrared detectors, electro-optical modulators …[1 - 3]. Most of dielectrics used as capacitors in integrated circuits are related to barium titanate $BaTiO_3$ [4]. Recently, additional interest has been shown in $BaTiO_3$ derived materials for the development of small size and high density FRAM comparable to DRAM [5 - 7].

In an earlier investigation we have studied the system $BaTiO_3$ – PbF_2 – LiF at 930°C. A new solid solution $Ba_{1-x}Pb_x(Ti_{1-x}Li_x)O_{3-3x}F_{3x}$ having the perovskite structure was obtained in the composition range $0 \leq x \leq 0.20$. The best dielectric performances were observed for x = 0.03 [8].

In the present work we shall examine the effects of the sintering parameters such as the sintering temperature (t_{sint}) and the sintering time (θ_{sint}) on the dielectric characteristics of ceramics with initial molar composition 0.97BaTiO$_3$ – 0.03PbF$_2$ – 0.03LiF . This sample is selected in the system $BaTiO_3$ – PbF_2 – LiF for its dielectric properties (high permittivity; low dielectric losses) and the value of T_C which is around room temperature, those make it interesting in the field of ferroelectric applications [8].

2. PREPARATIONS OF SAMPLES

2. 1. Powders preparation

Barium titanate $BaTiO_3$ with a Ba/Ti ratio close to 1 is previously synthesized at about 1100°C from $BaCO_3$ and TiO_2 powders of suprapur quality via the reaction:

$$BaCO_3 + TiO_2 \longrightarrow BaTiO_3 + CO_2$$

The intermediate compositions (Ba,Pb)(Ti,Li)$(O,F)_3$ are then prepared by interaction of PbF_2 and LiF on $BaTiO_3$:

$$0.97BaTiO_3 + 0.03PbF_2 + 0.03LiF \longrightarrow (Ba,Pb)(Ti,Li)(O,F)_3$$

The mixture of $BaTiO_3$, PbF_2 and LiF is homogenized and wet-ground in ethanol for 1h in air atmosphere. The obtained powder is then dried by heating in vacuum at 150°C for 2h in order to minimize the hydrolysis phenomenon during sintering.

2. 2. Ceramic preparation

The dried mixture with a starting composition of 97mol. % $BaTiO_3$, 3mol. % PbF_2 and 3mol. % LiF is shaped to discs of 13mm diameter and about 1 to 2mm thickness which are cold-pressed with latex as a binder under a pressure of 10^8 Pa. The pellets are then air-fired; the various parameters used in the sintering process are the following:

- heating and cooling rates: 200deg.h^{-1}
- sintering temperature (t_{sint}): 800°C , 900°C , 1000°C or 1100°C
- sintering time: 1h , 2h or 4h .

3. STRUCTURE AND MICROSTRUCTURE

3. 1. X-Ray diffraction study

The $BaTiO_3$ powder and (Ba,Pb)(Ti,Li)$(O,F)_3$ ceramics obtained are checked by XRD using monochromatic Cu $K_{\alpha 1}$ radiation (λ = 1.54051A) .

As a result, all the samples are single phases with a tetragonal or cubic perovskite structure (Table 1). The tetragonal lattice of pure $BaTiO_3$ becomes cubic when the ceramics are sintered at 900°C for 2h or 1000°C for 1 or 2h. On the other hand the symmetry remains tetragonal when the sintering is performed at 800°C for 2h, 1000°C for

4h or 1100°C for 2h. No Significant change is observed in the unit cell parameters of pure $BaTiO_3$ (a = 3.986Å; b = 4.026Å).

3. 2. Shrinkage and microstructure

Table 1 gives the shrinking coefficients $\Delta\Phi/\Phi$ on diameter vs. the temperature and time of sintering.

TABLE 1

Symmetry and shrinkage coefficients of $(Ba,Pb)(Ti,Li)(O,F)_3$ ceramics sintered in various conditions

Sample	A	B	C	D	E	F
t_{sint} (°C)	800	900	1000	1100	1000	1000
θ_{sint} (h)	2	2	2	2	1	4
$\Delta\Phi/\Phi$(%)	11.1	11.8	16.3	15.5	16.9	14.8
Symmetry	tetragonal	cubic	cubic	tetragonal	cubic	tetragonal

The ceramic microstructure is systematically investigated by scanning electron microscopy observations performed on fractured samples and using a JEOL apparatus, type JSM-840A. The operating voltage is 15kV.

Typical micrographs are depicted in Figure 1. No secondary phases are detected either in the grain boundaries or at the grain surface. This result is in good agreement with the XRD analysis.

As it may be seen in Figure 1, the ceramic grain size and shape are strongly influenced by the sintering temperature and the sintering time. With increasing t_{sint} or θ_{sint}, the grain size becomes coarse with the appearance of an intra-granular porosity in addition to the inter-granular one.The grain size is multiplied by approximately 10 when t_{sint} passes from 1000°C to 1100°C. The most regular and homogeneous grain morphology is observed on ceramic E sintered at 1000°C for 1h.

The intra-granular porosity is probably due to the volatilization of PbO resulting from a slight decomposition of the oxifluoride $(Ba,Pb)(Ti,Li)(O,F)_3$ when the heating temperature is too high or the heating time is too long.

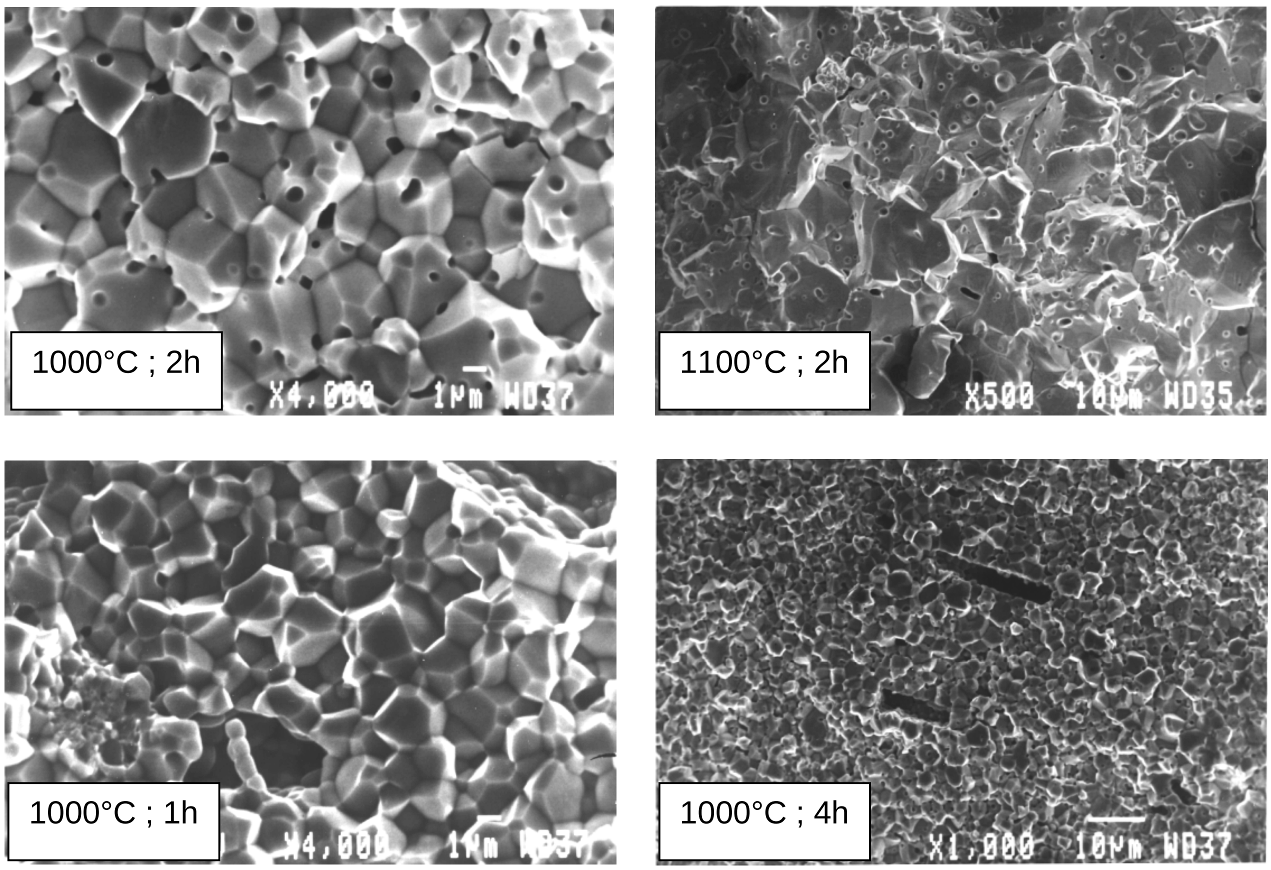

FIGURE 1

SEM micrographs of $(Ba,Pb)(Ti,Li)(O,F)_3$ ceramics sintered in various conditions

4. DIELECTRIC MEASUREMENTS

The ceramics are previously electroded by gold vapour deposition . The dielectric measurements are carried out under vacuum as a function of temperature using a WAYNE-KERR capacitance bridge and as a function of frequency using a HEWLETT PACKARD Impedance Analyzer HP4191A.

4. 1. Temperature dependence of the permittivity ε'_r and the dielectric losses $\tan\delta$

The real component of the dielectric permittivity ε'_r and the dielectric losses $\tan\delta$ are measured from 100K to 473K in the frequency range 50Hz – 10^5Hz.

Each ceramic exhibits a very broad maximum of the dielectric permittivity and a minimum of the loss factor at the ferroelectric temperature T_C. As example, Figure 2 shows the temperature dependence of ε'_r and $\tan\delta$ at 1 kHz for ceramic E sintered at 1000°C for 1h. The values of the permittivity and the dielectric losses at room temperature for this ceramic are respectively ε'_r (293K) ~ 7400 and $\tan\delta$ (293K) ~ 0.008.

The broadness of ε'_r peak is characteristic of a diffuse phase transition with local variation of composition either in the grain or from grain to grain. The dielectric characteristics are summarized in Table 2.

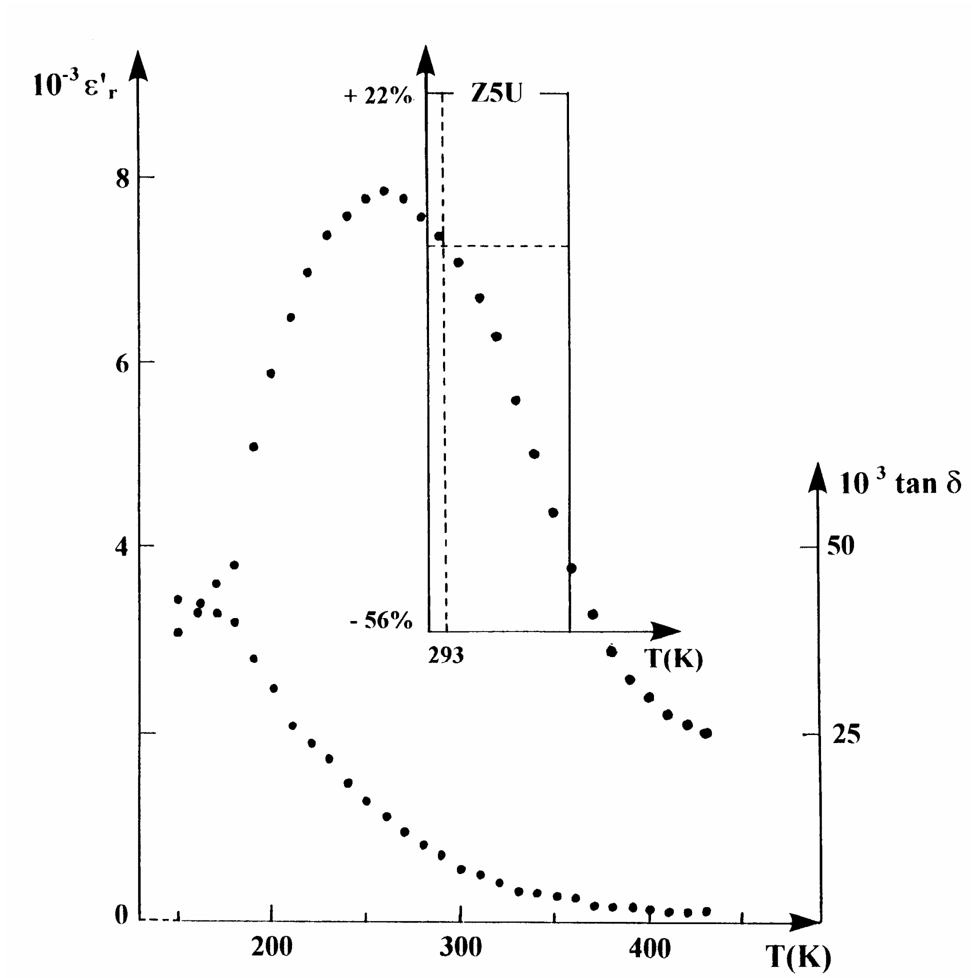

FIGURE 2

Variation with temperature of ε'_r and tanδ for sample E at 1 kHz

TABLE 2

Dielectric characteristics at 1kHz of $(Ba,Pb)(Ti,Li)(O,F)_3$ ceramics sintered in various conditions

Sample	A	B	C	D	E	F
T_C (K)	403	268	283	333	263	318
ε'_r (T_C)	1360	4100	7800	5900	7900	6700
tanδ (T_C)	0.002	0.010	0.010	0.005	0.012	0.007

An increase then a decrease is observed in the value of ε'_r with increasing t_{sint} whereas it decreases with θ_{sint}. These variations could be related to the densification mechanism and the ceramic microstructures. The sintering process is achieved at 1000°C after a holding time of 1h.

On the contrary, T_C decreases then increases with the temperature or the time of sintering. At 800°C the value of the ferroelectric Curie temperature is exactly the same than that of pure $BaTiO_3$ (T_C ~ 403K). From 900°C the value of T_C is much lower than 403K whatever the heating parameters (70°C $\leq \Delta T_C \leq$ 140°C). These results, which are especially ascribed to the double substitution O – F and Ba – Pb, agree quite well with our previous works on oxifluoride ceramics containing Pb [8, 9].

The optimal sintering conditions which lead to $(Ba,Pb)(Ti,Li)(O,F)_3$ ceramics with high density and good dielectric characteristics are the following : t_{sint} ~ 1000°C , θ_{sint} ~ 1h. The ε'_r – T curve of this ceramic shows a profile compatible with the Z5U class of capacitors whose requirements are $\Delta\varepsilon'_r / \varepsilon'_{r\ 293K} \leq +22\%$ at 283K and $\Delta\varepsilon'_r / \varepsilon'_{r\ 293K} \geq -56\%$ at 358K (Fig.2).

4. 2. Frequency dependence of the permittivities ε'_r and ε''_r

The complex impedance Z^* is measured as a function of frequency between 10^5Hz and $4x10^7$Hz at room temperature. The electrical data are converted into permittivity $\varepsilon^*_r = \varepsilon'_r - i\varepsilon''_r$ (ε'_r real component or dispersion, ε''_r imaginary part or absorption) using the relation :

$$\varepsilon^* = 1 / i\omega C_0 Z^*$$

where C_0 is the capacitance in vacuum [10] .

The frequency dependence of ε'_r and ε''_r for various sintering parameters is shown in Figures 3 and 4 using a logarithmic scale for f .The behavior of the complex permittivity with frequency is quite similar for all ceramics whichever the value of t_{sint} and θ_{sint} . Two domains can be observed: a low-frequency region where the permittivities are nearly frequency independent and a high frequency region where ε'_r decreases quickly whereas ε''_r rises toward a large maximum. These features are typical of dielectric relaxations. Unfortunately the curves are not complete because the setup used is limited in frequency to 40MHz. To have more details on this phenomenon, measurements at higher frequencies must be performed.

For ceramic E the peak of ε''_r appears at about 22MHZ which value is lower than that of pure $BaTiO_3$ (500MHz).

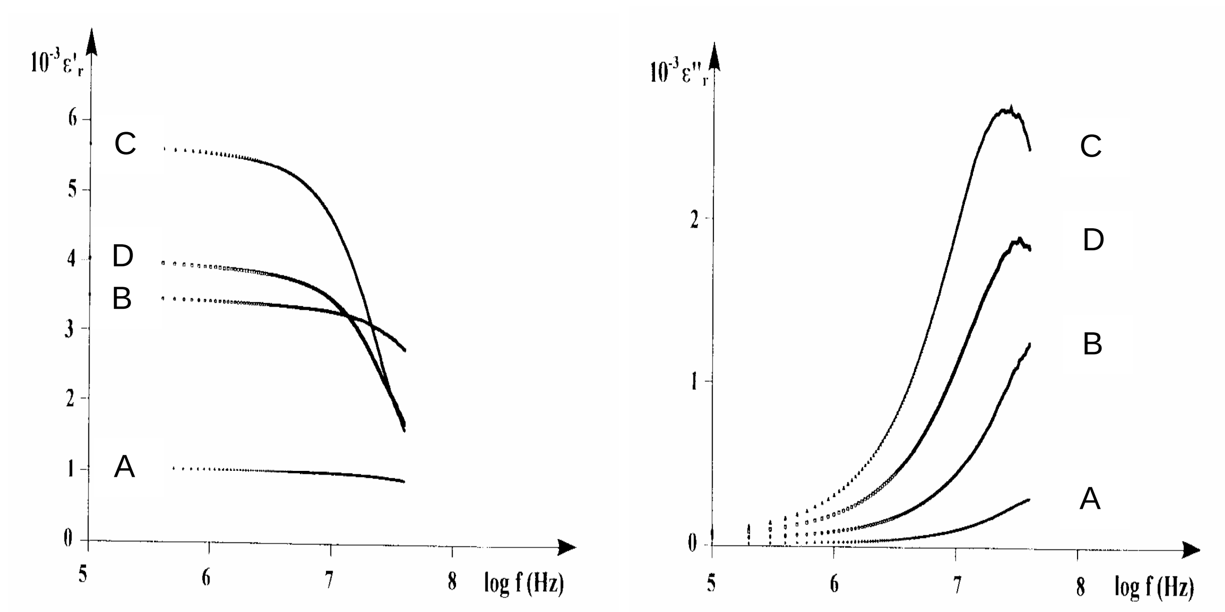

FIGURE 3

Frequency dependence of ε'_r and ε''_r for ceramics sintered 2h at various t_{sint} (A : 800°C ; B : 900°C ; C : 1000°C ; D : 1100°C)

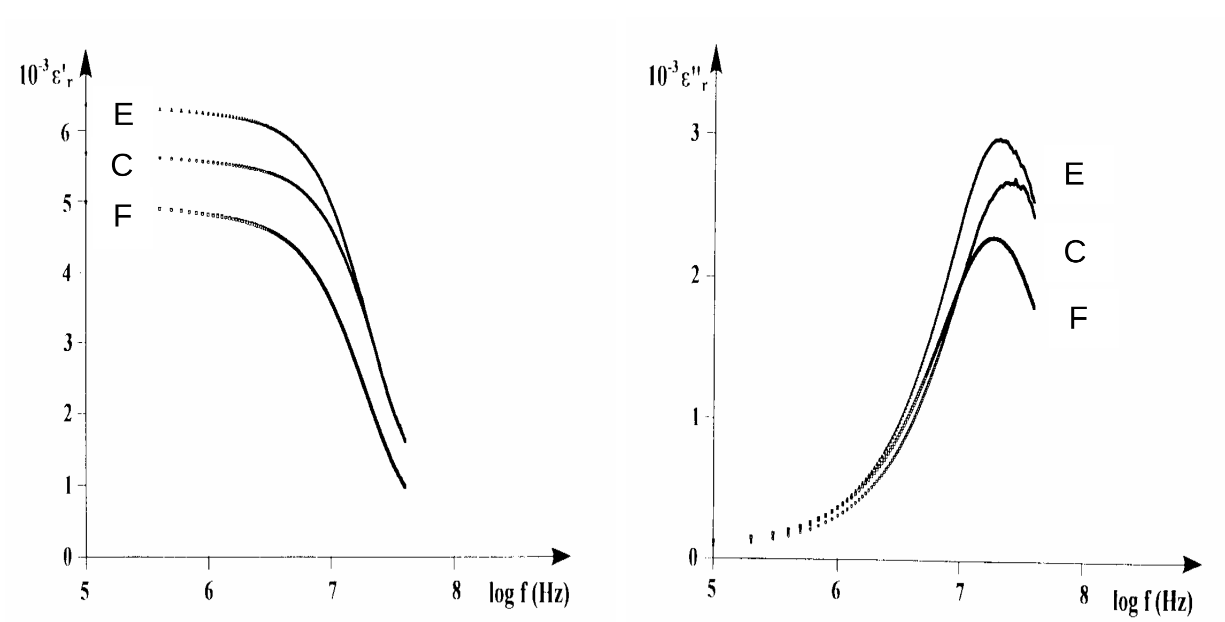

FIGURE 4

Variations of ε'_r and ε''_r with frequency for ceramics sintered at 1000°C for various θ_{sint} (C : 2h ; E : 1h ; F : 4h)

5. CONCLUSIONS

The influence of the temperature and the time of sintering on the dielectric response in $(Ba,Pb)(Ti,Li)(O,F)_3$ ceramics has been analyzed from 50Hz up to 40MHz .

At low frequencies, a diffuse ferroelectric phase transition is observed for each sample whatever the sintering conditions. The highest dielectric permittivity is obtained for a sintering at 1000°C for 1h. The corresponding ceramic is of substantial interest in the fabrication of Z5U capacitors.

At high frequencies, a dielectric relaxation appears in addition with the ferroelectric-paraelectric phase transition. For the investigations of this phenomenon, measurements will be performed beyond 40MHz.

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