RELAXATION AND RESONANCE PHENOMENA: INVESTIGATIONS IN NEW OXIFLUORIDE CERAMICS

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New oxifluoride ceramics have been obtained by air-firing cold-pressed pellets with various composition (1-x)$ATiO_3$ + xMF_2 + xLiF (A=Sr, Ba ; M=Ca, Pb). The complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ was measured as a function of temperature (150 K $\leq T \leq$ 450 K) and frequency (20 Hz $\leq f \leq 10^9$ Hz). Different dielectric behaviors were observed for these ceramics. For $Sr_{1-x}M_x(Ti_{1-x}Li_x)O_{3-3x}F_{3x}$ phases, no transition point was found in the temperature range investigated while for $Ba_{1-x}M_x(Ti_{1-x}Li_x)O_{3-3x}F_{3x}$ ceramics a diffuse phase transition occurred from the ferroelectric tetragonal structure to a paraelectric cubic one. At high frequencies, a resonance phenomenon was observed for $SrTiO_3$ derived ceramics whereas a dielectric relaxation was obtained for $BaTiO_3$ related materials.

I - INTRODUCTION

Non-conducting ceramics are of increasing importance as the electronic industry is in expanding worldwide. Dielectric ceramics are mainly used as capacitors in integrated circuits and as electrical insulators [1, 2]. The capacitors take up most of the area in modern memories chips [3]. Requirement of greater speed data transmission and dielectric resonators have prompted the investigations in crystalline materials at higher and higher frequencies. During the last decade, relaxation and resonance phenomena in the gigahertz region have attracted considerable attention both from theoretical and experimental points of view [4 – 6].

In previous works, we studied the systems $BaTiO_3 – MF_2$ – LiF and $SrTiO_3 – MF_2$ – LiF (M = Ca, Pb) and several solid solutions with general formula $A_{1-x}M_x(Ti_{1-x}Li_x)O_{3-3x}F_{3x}$ were obtained [7 – 9]. The purpose of this study is to investigate the relaxation and the resonance phenomena in these new compounds.

II - THEORY

II. 1 Polarization in dielectric materials

A dielectric material can react to an electric field by four mechanisms of polarization characterized by an electronic polarizability α_e, an ionic or atomic polarizability α_i, an orientation or dipole polarizability α_d and a space-charge or interfacial polarizability α_s. The total polarizability α of the dielectric may be written as the sum of the four terms: $\boldsymbol{\alpha = \alpha_e + \alpha_i + \alpha_d + \alpha_s}$. The total polarization can be represented as the sum: $\mathbf{P = P_e + P_i + P_d + P_s = \alpha E}$

The contributions of these various polarizations in the dielectric permittivity are frequency dependent. The electron polarization P_e which is common to all materials contributes at very high frequencies (> 10^{10} Hz). The ionic polarization process P_i appears at frequencies up to the infrared region of the spectra while the dipole P_d and space charge P_s polarizations participate only at lower frequencies.

II. 2 Dielectric relaxation and resonance

Resonances are involved by the electronic polarization whereas space charges and dipoles are responsible of dielectric relaxations. The behavior of the complex permittivity as a function of frequency is quite different for a resonance and a relaxation. These two phenomena are characterized by a strong frequency dispersion of the dielectric response.

For relaxations, ε' decreases slightly with the frequency increasing. Beyond the relaxation frequency f_r, ε' decreases quickly whereas ε" traverses a very huge maximum. The peculiarity of a relaxation is that the peak of ε" is much broader than for a resonance.

The resonances occur in the microwave range. Their characteristic features are that ε' rises hyperbolically from the low frequency value to a maximum then dips to a minimum with negatives values and a sharpness in the dielectric absorption ε".

II. 3 Theoretical models

To explain the high frequency dispersion in dielectrics, several concepts have been elucidated and various models have been proposed to describe the processes. Some of them are well fitted by experimental materials while others do not lead to agreement with experiments.

For the study of dielectric relaxations, the Debye equation is by far the most useful model as well as the simplest one .The Debye law is in good agreement with insulating materials with negligible or small electrical conductivity. In practice, the behavior of most dielectric materials deviates from the Debye response and is often described by modified expressions. Among the modified equations, the most important are the Cole-Cole and the Davidson-Cole laws.

II. 4 Equivalent electrical circuits

Some passive networks are mathematically analogous with some dielectric materials. A dielectric obeying the Debye equations with a single relaxation time may be represented either by a capacitor C_s in serie with a resistance R_s or by a parallel combination of a capacitance C_p and a resistance R_p.

The simplest appropriate circuit to describe the process of resonance at optical frequencies will be a combination of an inductance L, a capacitance C and a resistance R, all in series.

III - EXPERIMENTS

III. 1 Preparations

Powders of $SrCO_3$, $BaCO_3$, TiO_2, CaF_2, PbF_2 and LiF were used to prepare the ceramics. Stoichiometric $SrTiO_3$ and $BaTiO_3$ were previously synthesized by heating an equimolar mixture of $SrCO_3$ and TiO_2 or $BaCO_3$ and TiO_2 at 1373K in air atmosphere:

$$SrCO_3 + TiO_2 \rightarrow SrTiO_3 + CO_2 \quad ; \quad BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2$$

Various compositions were then prepared from strontium titanate or barium titanate powder and the fluoride mixture (CaF_2+LiF) or (PbF_2+LiF). Cold-pressed pellets of 13mm diameter and about 1mm thickness were fabricated by pressing the mixtures $(1-x)ATiO_3+x(MF_2+LiF)$, A=Sr, Ba, M=Ca, Pb under a pressure of 10^8 Pa then air-fired .

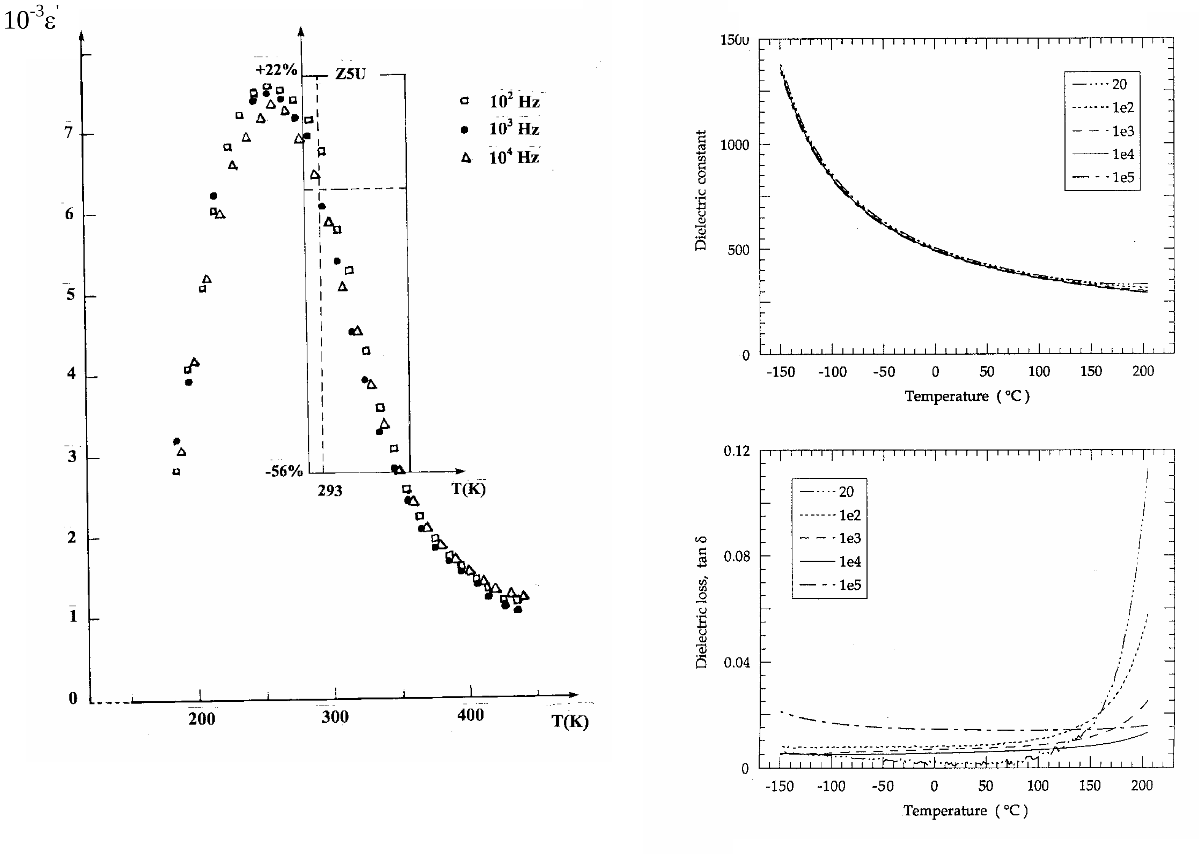
The circular faces of the ceramics thus obtained were polished and electroded by gold vapor deposition for dielectric measurements.

III. 2 Dielectric study as a function of temperature

The real component ε' of the dielectric permittivity and the dielectric loss factor tanδ were measured from 100 K to 473 K in the frequency range 20 Hz – 10^5 Hz. The measurements were performed under vacuum or in nitrogen gas N_2.

For $Sr_{1-x}M_x(Ti_{1-x}Li_x)O_{3-3x}F_{3x}$ phases no transition peak was found in the temperature range investigated. On the other hand a diffuse phase transition occurred from the ferroelectric tetragonal structure to the paraelectric cubic one in $Ba_{1-x}M_x(Ti_{1-x}li_x)O_{3-3x}F_{3x}$ ceramics. As examples, Fig.1 shows the temperature dependence of the dielectric constant and the dielectric losses for ceramics corresponding to compositions $Sr_{0.97}Pb_{0.03}(Ti_{0.97}Li_{0.03})O_{2.91}F_{0.09}$ and $Ba_{0.97}Pb_{0.03}(Ti_{0.97}Li_{0.03})O_{2.91}F_{0.09}$. The first one was sintered at 1223 K while the sintering temperature was 1273 K for the second one, the sintering time being 2 hours for the two ceramics.

$Ba_{0.97}Pb_{0.03}(Ti_{0.97}Li_{0.03})O_{2.91}F_{0.09}$ $Sr_{0.97}Pb_{0.03}(Ti_{0.97}Li_{0.03})O_{2.91}F_{0.09}$



$Sr_{0.97}Pb_{0.03}(Ti_{0.97}Li_{0.03})O_{2.91}F_{0.09}$

Fig. 1
Temperature dependence of *the dielectric permittivity and the dielectric losses.*

III. 3 Dielectric measurements as a function of frequency

The complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ was measured in the frequency range 20 Hz – 10^9 Hz. The behavior of the two kind ceramics with frequency was quite different. A resonance phenomenon was observed for $SrTiO_3$ derived ceramics in the range $2.x.10^8$ Hz – $5x10^8$ Hz whereas a dielectric relaxation was obtained for $BaTiO_3$ related materials in the range $9x10^6$ – $3x10^7$ Hz. The values of the resonance frequency or the relaxation frequency in these new oxifluoride ceramics are much lower than that of $SrTiO_3$ ($f_{r1} = 3x10^{12}$ Hz, $f_{r2} = 1.65x10^{13}$ Hz) or $BaTiO_3$ ($f_r = 5x10^8$ Hz). The room temperature frequency dependence of ε' and ε" for ceramics $Sr_{0.97}Pb_{0.03}(Ti_{0.97}Li_{0.03})O_{2.91}F_{0.09}$ and $Ba_{0.97}Pb_{0.03}(Ti_{0.97}Li_{0.03})O_{2.91}F_{0.09}$ is given , as example, in Fig. 2

In Fig.2 we have also plotted ε"(f) versus ε'(f) at 300 K for ceramic $Ba_{0.97}Pb_{0.03}(Ti_{0.97}Li_{0.03})O_{2.91}F_{0.09}$. The Argand diagram is a semi-circle and is consistent with a Debye-type process.

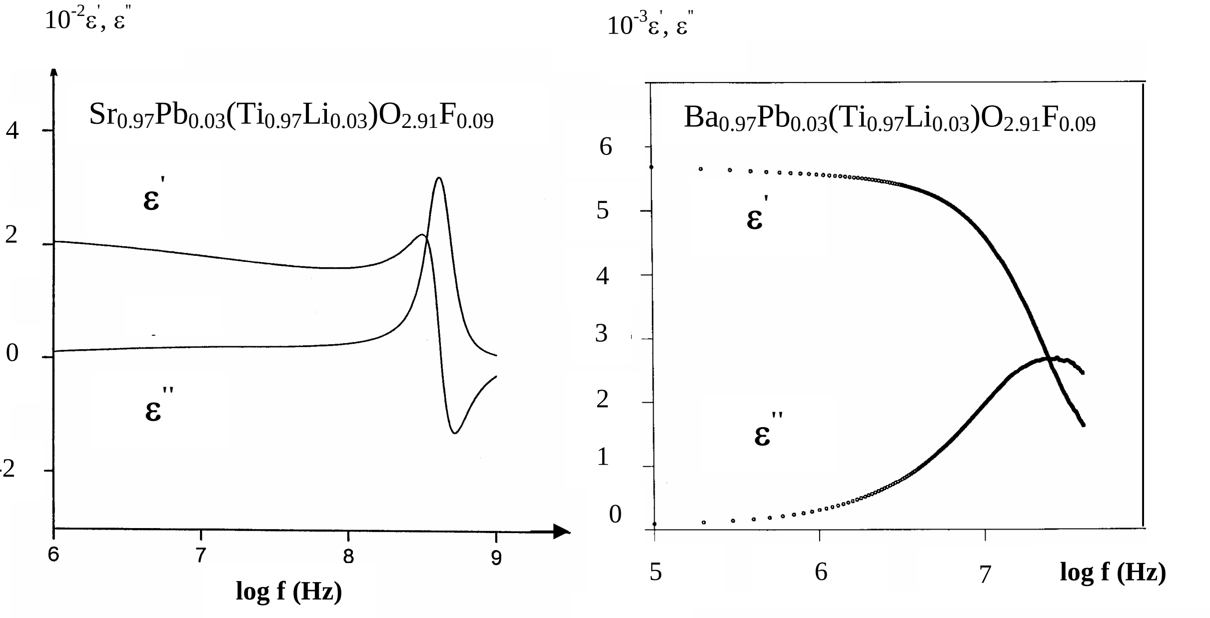
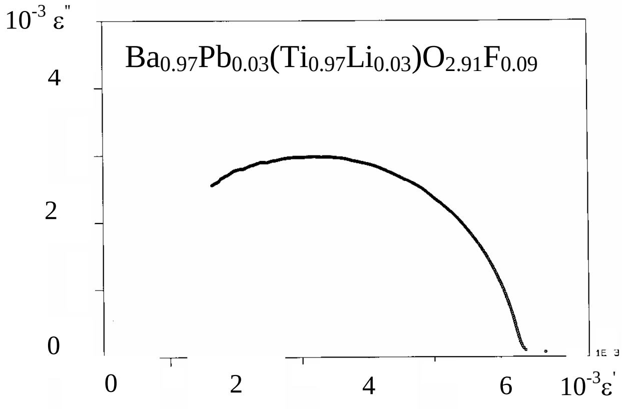


Fig. 2:
Dispersion and absorption versus frequency for ceramics $Sr_{0.97}Pb_{0.03}(Ti_{0.97}Li_{0.03})O_{2.91}F_{0.09}$ and $Ba_{0.97}Pb_{0.03}(Ti_{0.97}Li_{0.03})O_{2.91}F_{0.09}$.
Argand diagram for ceramic $Ba_{0.97}Pb_{0.03}(Ti_{0.97}Li_{0.03})O_{2.91}F_{0.09}$.



IV - CONCLUSION

New oxifluoride ceramics with formula $A_{1-x}M_x(Ti_{1-x}Li_x)O_{3-3x}F_{3x}$, A=Sr or Ba and M=Ca or Pb have been obtained at low temperature thanks to the mixture MF_2+LiF.The dielectric measurements have shown a resonance phenomenon for $SrTiO_3$ derived ceramics and a dielectric relaxation for $BaTiO_3$ related compounds. The resonance frequency of $SrTiO_3$ and the relaxation frequency of $BaTiO_3$ are strongly lowered by the triple substitution M – A, Li – Ti and F – O. The $Sr_{1-x}M_x(Ti_{1-x}Li_x)O_{3-3x}F_{3x}$ phases could find an application in the fabrication of resonators whereas $Ba_{1-x}M_x(Ti_{1-x}Li_x)O_{3-3x}F_{3x}$ materials could be used as dielectric for Z5U multilayer capacitors at low frequencies or as absorbent for electromagnetic waves at high frequencies.

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