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Study of the behaviour of the dielectric constant in Cu,Fe:BaTiO$_3$

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Abstract: In this work we study the behaviour of the dielectric constant of BaTiO$_3$ single crystals doped with Cu and Fe for different ion percentages, particularly, the influence of these heterovalent substitutions on the ferroelectric-paraelectric phase transition whose temperature is found at T_c=120 °C for pure samples. The dielectric constant ε in terms of temperature shows that the Curie temperature decreases when the quantity of impurities increases and presents a broadening and flattering of the maximum of $\varepsilon(T)$ within higher values, with the transition becoming more and more diffuse. It is interesting to have a material with very high permittivity (high-k) because of its capacity to store an important quantity of electric charges. The ε anisotropy and the Curie-Weiss law are also verified with a good ratio between the slopes of $\varepsilon^{-1}(T)$ from both sides of the transition, leading to a Curie constant: C=13×10^4 K for BaTiO$_3$:1.6%Fe in the polar phase. BaTiO$_3$ is a displacive ferroelectric going through a first-order phase transition. The substitutions have an effect on the dynamics of the perovskite lattice. They induce charges transfer to Ti and a diminution of elastic forces in BaTiO$_3$. Then we discuss the fact that the maximum of permittivity does not depend on the phase transition but on the nature of the material.

Key words: Phase transition, Ferroelectric BaTiO$_3$, Remeika single crystals, Dielectric constant, Curie constant
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INTRODUCTION

The unusual dielectric properties of barium titanate make this ferroelectric compound at the ambient temperature a significant material for electrical engineering. Moreover, its photorefractive character is very useful in nonlinear optics for holographic storage (Mathey *et al.*, 1998).

Indeed, the best-known perovskites of the ABO$_3$ type, BaTiO$_3$, SrTiO$_3$ and CaTiO$_3$ intervene in the manufacture of multi-layer capacitors, thermistors and also transducers for their piezoelectricity (Akira *et al.*, 1991).

Because of their strong permittivity and weak dielectric losses, ferroelectric materials are promising for microwave applications, such as capacities with strong permittivity, accordable filters and resonators, and modulators of frequency. So the great variation of the dielectric permittivity at ambient temperature is an important characteristic.

The reliability, the effectiveness and the improvement of these components are related to the structure and the microstructure of the thin layers ferroelectric materials (Khalal *et al.*, 1999a).

THEORETICAL AND EXPERIMENTAL ASPECTS

In order to account for the macroscopic phenomena of the discontinuity of the polarization, for a first-order ferroelectric, free energy $F(P)$ is expressed by Devonshire (1949) as

$$F = \alpha P^2/2 + \beta P^4/4 + \gamma P^6/6,$$
$$\alpha = A(T - T_0),\ \ \beta = B,\ \ \gamma = C,$$

where A and γ are positive constants, β is a negative constant and P is the polarization.

This expression is supposed to be valid in the ferroelectric and paraelectric phases (a case of low structural distortions). The assumptions on the coefficients involve the possibility for $F(P)$ to have two equal minima for $P=P_S$ spontaneous polarization, on both sides of a third extremum $P=0$, which can also be a minimum according to the considered interval of temperature (Ouedraogo, 2002).

In the case of a ferroelectric, the dielectric susceptibility $\chi>>1$ and the permittivity ε practically merges with the susceptibility χ:

$$\varepsilon \approx \chi,$$

$$\frac{1}{\varepsilon_0\chi}=\left(\frac{\mathrm{d}E}{\mathrm{d}P}\right)_{\mathrm{T}}, \quad \frac{1}{\varepsilon_0\chi}=A(T-T_0)+3BP^2+5CP^4.$$

We get the solutions near the transition from expression of P_S replaced inside:

$$\frac{1}{\varepsilon_0\chi}=-4A(T-T_0)+\frac{B^2}{C}\left(1-\frac{4AC}{B^2}\right)(T-T_0)^{1/2}+\frac{B^2}{C},$$

$$\text{for } T<T_0<T_c, \quad 1/(\varepsilon\chi)=-2A(T-T_0),$$

$$\text{for } T_c<T, \quad 1/(\varepsilon\chi)=A(T-T_0),$$

where T_c (the Curie temperature) is the temperature of the phase transition. The following properties were thus established:

(1) On both sides of T_c, the variations of the reverse of susceptibility are linear with slopes in a 2:1 ratio in absolute value.

(2) In the theory of the catastrophe of polarization, ε becomes infinite, corresponding to a finished value of polarization in the absence of applied field. When T_0 is at the top of the transition, the permittivity ε follows the Curie-Weiss law: $C/(T-T_c)$.

The studied single crystals were obtained from the Dielectrics Laboratory of the University of Dijon which was formed by the method of KF flow (Remeika, 1954). Crystallization was made during the cooling of a molten mixture of barium carbonate ($BaCO_3$) and titanium oxide (TiO_2) in a bath of potassium fluoride (KF). They have the shape of triangular thin blades whose thickness varies between 60 m and 150 m according to the rate of doping. Known as butterfly wings, they have a surface area of about 0.5 cm^2 and the ferroelectric axis "*c*" is generally perpendicular to the large face.

The samples doped with copper and iron look yellow, which become darker with increasing the percentages of impurities. Doping is carried out during the growth of crystallization. For doping with copper, $Cu(NO_3)_2{\cdot}3H_2O$ is added and then TiO_2 subtracted, whereas doping with iron, Fe_2O_3 is added and then TiO_2 subtracted. The operation is controlled at the end by spectrophotometric dosage.

Iron penetrates the samples more easily than copper, which explains why in the samples doped with iron, the atomic percentages are 4 to 5 times those of copper-doped samples.

The entire measurements of permittivity and thermo-currents are developed in the laboratory. The dielectric constants include: (1) A bridge of capacity of the type 1613-A; (2) An audio-frequency oscillator of the type 1311-A; (3) A granted amplifier and a detector of zero type 1232-A.

Two very thin electrodes in silver painting are deposited on the crystal. The cooling of the oven is achieved by means (electric floodgates) of a temperature regulated cold nitrogen jet directed onto the tube of a steel cell, on which the sample is located. The temperature is measured by means of a chromel-alumel thermocouple within the tube at 4 mm from the sample. The temperature accuracy is then about 0.5 °C.

RESULTS AND DISCUSSION

The permittivity ε is defined in weak field. The samples made of monodomain "*c*" by a field E=500 V/cm, are then assembled according to one of the directions "*a*" or "*c*" for measurement.

Let T_M be the temperature to the maximum of ε corresponding to the passage of the quadratic structure to cubic symmetry.

For two pure crystals taken from the same bath and assembled according to "*a*" and "*c*" axes, we find equal values, close to T_c=120 °C (Fig.1) and an anisotropy of ε. The curve ε_a is located at the top of ε_c in ferroelectric phase, as observed in paraelectric phase (Fig.2). Nevertheless, the ratio of the values of the permittivity decreases from 16 at the ambient temperature to 2 at the transition temperature, with the lowest of only 1.1 in the non-polar phase (Table 1).

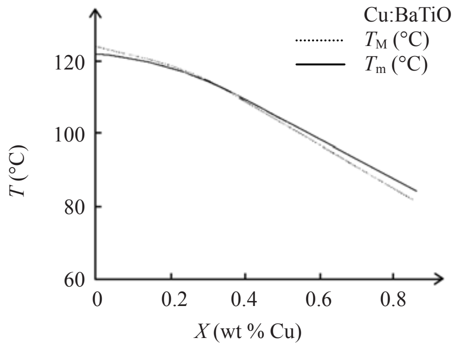

Fig.1 T_M: Temperature of the maximum of dielectric constant (ε'); T_m: Temperature of the maximum of thermo-current (i_P)

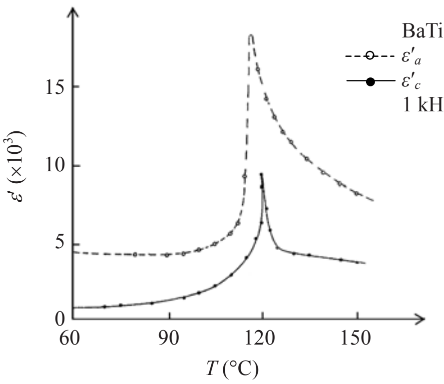

Fig.2 Anisotropy of dielectric constant

Table 1 Dielectric constants ε_a and ε_c

Phase		ε_a	ε_c	$\varepsilon_a/\varepsilon_c$
Ferroelectric	T=25 °C	5000	300	16
	T=90 °C	4000	1000	4
Paraelectric	T_c=120 °C	19000	8600	2.3
	T=150 °C	4000	3500	1.1

The variations of $\varepsilon^{-1}(T)$ have different slopes in the two phases with a discontinuity for T_M from which the Curie constant (C) is derived.

According to Matthias and von Hippel (1948), the permittivity of an obviously non pure crystal (T_c between 80 °C and 90 °C) reached 1700 at 20 °C in the direction perpendicular to the polar axis whereas it was only 150 in the direction of the polarization.

Merz (1951) had later found that for very thin crystals with a single field a factor $\varepsilon_a/\varepsilon_c$=20 and had noted that this factor disappeared with the transition at Curie point (120 °C).

Thus, the anisotropy is the largest in the field of the ambient temperatures.

For the Cu-doped crystals, T_M decreases according to the concentration as shown in Fig.1, with a less acute maximum but larger amplitude.

The temperature for the maximum permittivity practically merges with that of the maximum of thermo-current i_p. We find T_{max}≈T_M.

ΔT, calculated from the difference between the temperatures T_M for the pure crystal and for the doped crystals, varies linearly with the percentage of Cu (Ouedraogo, 2002).

Only with Fe-doping, the maximum of ε decreases for strong doping with the percentage of iron (Figs.3 and 4).

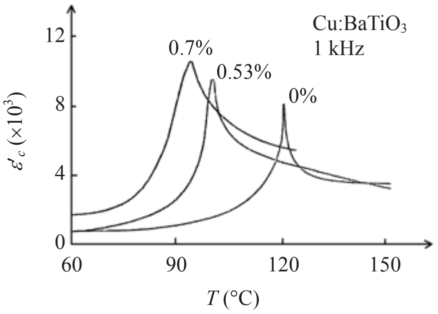

Fig.3 Dielectric constant of Cu:BaTiO3

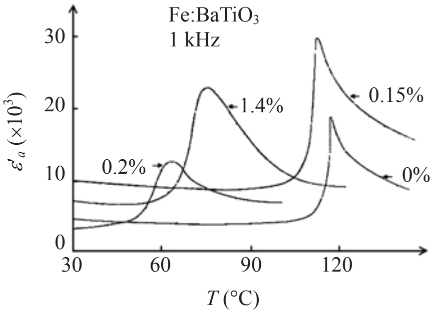

Fig.4 Dielectric constant of Fe:BaTiO3

A broadening and flattering of the maximum of $\varepsilon(T)$ and a shift of the Curie temperature T_c have also been observed in Fe-doped $BaTiO_3$ ceramics (Knauer, 1979). Similar effects also exist in the potassium tantalite niobate (Abdulraheem *et al.*, 2006) and in several oxides with perovskite structure: Nb:$KTaO_3$, Cu,La:$PbTiO_3$ (Bidault *et al.*, 1995).

From $1/\varepsilon_a(T)$ curves, we find out the Curie constants of 13×10^4 K in ferroelectric phase and 25×10^4 K in paraelectric, i.e., a ratio of 2 for 1.6% Fe (Fig.5).

It is possible to remove the phase transition for strong concentrations in the case of the La:$BaTiO_3$, The effect of La was observed by Raman diffusion,

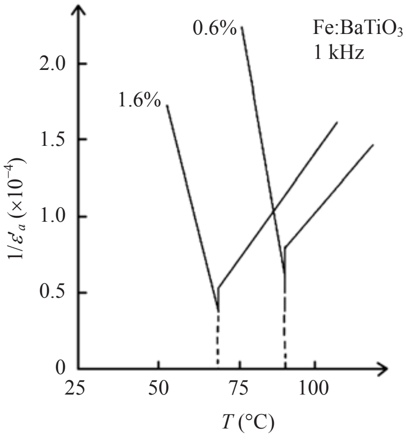

Fig.5 Inverse of dielectric constant of Fe:$BaTiO_3$

for which an additional mode appears with an increase of the intensity with the rate of La (Kchikech *et al.*, 1993). They confirmed the increase in conductivity under reducing treatment due to the exponential increase in Cu^{2+} defects. Substitution induces a transfer of charges of oxygen towards titanium (partial reduction of titanium) (Khalal *et al.*, 1999a).

Chen *et al.*(1999) also concluded that Cu doping might be responsible for the metallic behaviour observed in Cu-doped $BaTiO_3$.

There is thus an influence of heterovalent substitutions on the dynamics of the lattice and conduction in perovskites (Khalal *et al.*, 1999b).

We suppose that for high percentages of copper, the Cu^{2+} ion is in site Ti^{4+}, which results in a very marked Jahn-Teller effect with a distortion of the lattice (Choi *et al.*, 1999).

For high concentrations, the disorder increases by doping, giving a decrease in the activation energy W. In reduced crystals, W drops to zero when the conductivity increases. This could be understood on the basis of correlated electron hopping or of band broadening (Chanussot and Ouedraogo, 1981).

Displacements of ions represent a particular mode of vibration. In the Cochran theory of the soft mode, this mode is linked to the order parameter which is T_{1u} in $BaTiO_3$, a representation inducing a polarization. The cancellation of an eigen frequency of vibration of the solid at temperature T_c corresponds to the disappearance of the force of recall to which the atoms are subjected, their displacements are not deadened any more and the solid becomes “soft”, i.e. unstable for this mode. A stability can be found only when the system is passing to a new phase.

The existence of the soft mode is the characteristic of structural transitions (Papon *et al.*, 1999). In the case of $BaTiO_3$ the transition is displacive because spontaneous polarization has a discontinuity.

In any case, the various models must take into account the modifications in the couplings between electrons and vibrations, if it is supposed that the ion doping is placed in titanium position, changing the symmetry of the position and the couplings (Ouedraogo and Chanussot, 1998) and thus affecting the properties of $BaTiO_3$ (Tsygankov and Safonov, 2002).

In a view of miniaturization in microelectronics, perovskite materials with very high permittivity are interesting candidates to replace dielectrics currently used in the development of Metal/Insulator/Metal (MIM) capacitors. High dielectric constant porcelain composition contains mainly $BaTiO_3$, but also contains by weight, 1 to 5% of $LaTiO_3$ and 2 to 5% of Ta_2O_5 providing a high dielectric constant of at least 3000. The maximum of ε is found with grains of about 700 nm when $BaTiO_3$ is quadratic, i.e. ferroelectric, and is thus not derived from the phase transition quadratic-cubic (Bernaben, 1996).

The origin and the microstructure of the material are important in the dielectric behaviour of barium titanate. T_c and ε decrease with the size of the grains when the diffusivity increases until it disappears for grains of about 100 nm.

CONCLUSION

$BaTiO_3$ materials have been developed for dielectric applications for a long time, with various substitutional ions used for Ba^{2+} and Ti^{4+} to miniaturize the capacitors with large capacitance.

The temperature T_M of the maximum of the dielectric permittivity ε is a good experimental approach of T_c, the Curie temperature.

The cubic-quadratic transition of $BaTiO_3$ is influenced by Cu and Fe doping; T_M decreases and the transition becomes more diffuse for high rates of doping agents. The transition could disappear for very important quantities of defects, such as Cu, Fe, La and Co.

The variations of $\varepsilon^{-1}(T)$ are in agreement with the thermodynamic approach for a first-order transition, with the Curie constants doubling when the system passes from the ferroelectric phase to the paraelectric phase in $BaTiO_3$. These dielectric properties of barium titanate could be affected by many different parameters, such as temperature, ambience, coating process, grain size, etc. (Guillan, 2005; CIRIMAT, 2005)

In a previous study (Ouedraogo *et al.*, 1978), we considered that, by the theory of groups, by using broken symmetries (Boccara, 1981), the Ti^{4+} ion jumped from the center of octahedral TiO_6 (symmetry O_h) on a forth-order axis (symmetry C_{4v}), then on a second-order axis (symmetry C_{2v}), and finally on a third-order axis (symmetry C_{3v}), thus causing a lowering of the symmetry (Merz, 1949). This made it possible to find various phases of $BaTiO_3$.

Taking now the polarization P associated with the vectorial representation T_{1u} of the group O_h of the cube as the order parameter (the Landau theory), we notice that it has a discontinuity at the point of transition which was then known to be of the first-order (Ouedraogo, 2002; 2003). That is the case with $BaTiO_3$, a displacive ferroelectric at room temperature.

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