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A polycrystal hysteresis model based on the Landau theory for ferroelectric ceramics

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Most key elements of ferroelectric properties are defined through the hysteresis loops. For polycrystalline ceramics, each grain exhibits a specific loop and contributes to the ferroelectric ceramic's one. The resulting hysteresis loop is influenced both by the frequency and temperature. In this paper, we propose a polycrystal hysteresis model describing the hysteresis in ferroelectric materials as a function of the temperature and frequency. This model, based on the Landau phenomenological thermodynamic potential theory, allows determining the behaviors of ceramics. This theory differs from the classical phenomenological ones : it is a macroscopic -based thermodynamic approach and it can provide the evolution of polarization state, and other coefficients as a function of electric field, temperature and frequency simultaneously. The proposed model is developed, discussed, and compared with experimental piezoelectric characterizations on a PZT based piezoelectric transducer ceramic. Hysteresis loop comparisons between modeling and experimental data are given and are shown to be in good agreement with the polarization versus electric field and temperature. It is interesting to note that the model developed in this paper could also predict the dielectric constant (ε_{33}) as a function of the electric field using a simple P(E) measurement.

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1. Introduction

Piezoelectric ceramics are commonly used in numerous piezoelectric actuators and sensors [1-3]. Most ferroelectric materials behave as piezoelectric for low driving levels. Increasing levels (electric field, temperature or stress) lead to a depoling resulting in dielectric and piezoelectric performances degradation. It is usually considered that this latter phenomenon is due to the irreversible domain wall motion as well as nucleation and growth of domains with new orientations [4-8]. The resulting nonlinear and hysteretic nature of piezoelectric materials induces a power limitation for heavy duty transducers or a lack of controllability for positioners. Consequently a nonlinear modeling including hysteresis appears to be a key issue to get a good understanding of transducers behavior.

Some of the applications, such as those in space, involve environments where the electric field and temperature varies over a wide range. It is therefore necessary to characterize the behavior of these ceramics over a wide range of possible operating electric fields and temperatures. Electric field and temperature variations will result in significant nonlinear behavior of the material's coefficients and will therefore affect its overall performance [9-13]. This nonlinearity occurs due to the material composition, dopants and internal defects, microstructure and is dependent on the magnitude of the temperature or electric field variations. Aside from the hysteresis and nonlinearity discussed above, ceramics are also useful in many applications to enhance the pyroelectric and electrocaloric effects of piezoelectric materials used for energy harvesting and refrigeration [14-18]. In general to understand these observations, we recall that the piezoelectric effect includes both intrinsic and extrinsic contributions, as discussed by Damjanovic [19] and Zhang et al. [20]. The polarization P will be equal to $P=P_{int}+P_{ext}$ where d_{int} is the intrinsic or the single-domain response and d_{ext} is the extrinsic or domain walls and other defects response which involves irreversible domain wall motion. In previous work [16], the depolarization process with temperature was shown to be due to due to the decrease of the dipole moment induced by the variation of unit cell parameters (intrinsic effect). Domain switching (extrinsic effect) occurs only near the Curie temperature and is responsible for the hysteretic behavior of polarization with temperature. Under an electric field, the depolarization of the sample is mainly due to domain switching [21].

Several microscopic and macroscopic models have been proposed in the literature for understanding the hysteretic behavior of various materials [22-26]. However, the majority of these models are purely electrical or thermal. It is consequently difficult to correlate the results to both solicitations (the electric field and temperature simultaneously) in order to obtain a clear physical understanding.

In order to solve this problem, we propose a model in this paper. This model accurately simulates the process of polarization reversal and allows describing the P–E loops of a polycrystalline system, this model being based on the modification of Landau-type phenomenological theory. This model enables to express the polarization as a function of temperature and electric field. The model was validated experimentally for different frequencies.

In the second part of this study, the proposed model was used to predict, starting from measurements at several temperatures, the dielectric coefficient values as a function of electric field intensities.

Comparisons simulation/experimentations made on soft $Pb_{0.95}La_{0.05}Zr_{0.45}Ti_{0.45}O_3$ piezoelectric ceramic.

2. Hysteresis loop modeling based on the theory of Landau Devonshire

This model is based on the phenomenological theory of Landau - Devonshire aimed to describe the order – disorder transitions, ignoring the specifics of the particular system considered [27-28]. This theory has been applied for the first time by Devonshire on $BaTiO_3$. First, this work is focused on the ferroelectric behavior only and dissipation of energy during the polarization will be introduced later. The dissipation term can be modeled as a modified equivalent circuit. Figure 1 shows this equivalent circuit for which a resistance is added in series to the perfect ferroelectric ones. Usually, the structure is considered parallel to the piezoelectric ceramics, but this structure does not explain the non-reversal of polarization observed on some ceramics. To model the energy dissipation, we introduce a term $\tau\frac{dP}{dt}$ taking into account the variation of polarization with the electric field, with τ: the dissipative coefficient.

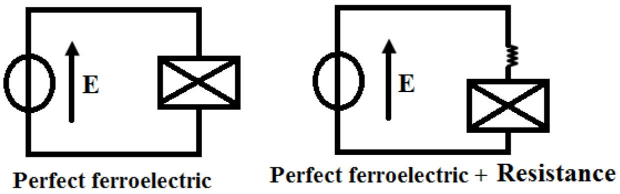

Fig. 1. Schematic model.

A crystalline solid can be characterized thermodynamically by its internal energy U. The free energy F can be expressed in terms of internal energy U as follows.

$F = U - \theta S - \sigma\varepsilon$ with

θ: temperature

S: entropy

σ: Stress

ε: Deformation

According to the theory of Landau - Devonshire, the differential internal energy U can be expressed by:

$$dU = T\,dS + EdP + \sigma d\varepsilon$$

where E is the electric field and P the polarization.

We can also express dF (differential free energy) from the Helmholtz free energy (F = U-TS) and the differential of internal energy. The differential free energy can then be written as:

$$dF = -SdT + EdP + \varepsilon d\sigma$$

Assuming that the effects associated to the transition depend mainly on the polarization, we therefore developed the free energy (second order transition) power of P near the transition temperature θ_C. The free energy of ferroelectric ceramics, determined at constant stress, depends on the temperature and polarization. It is expressed by:

$$F(P,\theta) = F_0(\theta) + \frac{AP^2}{2} + \frac{BP^4}{4} \qquad (1)$$

A and B are two variables depending on the temperature.

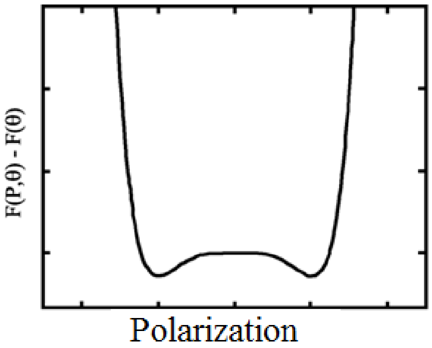

Fig. 2. Landau Devonshire energy vs. polarization

This function presents two minima which correspond to energetically stable states of polarization (Figure 2). Indeed stability imposes $\frac{\partial^2 F}{\partial P^2} >> 0$. $A = a(\theta - \theta_C)$ with a> 0 and B> 0 as to be chosen in such a way that the solution for $(\theta < \theta_C)$ is $P \neq 0$. The equation becomes:

$$F(E,\theta) = F_0(\theta) + \frac{a(\theta-\theta_C)P^2}{2} + \frac{BP^4}{4} \qquad (2)$$

with: θ and θ_c corresponding respectively to working and transition temperatures.

Since E=dF/dP, we can write:

$$E = \left.\frac{\partial F}{\partial P}\right|_{\theta} = a(\theta-\theta_C)P + BP^3 \qquad (3)$$

P_r corresponds to the minimum of the function F(P, θ) to E = 0. Therefore, the remanent polarization is the solution of the equation $a(\theta-\theta_C)P + BP^3 = 0$.

To solve this equation, 3 solutions are possible:

P_r=0 (non polarized materials), and $P_r = \pm\sqrt{\frac{a(\theta_C-\theta)}{B}}$ (ferroelectric material).

The coercive field corresponds to $\frac{\partial P}{\partial E} \to \infty$ when $E \to E_C$ either $E_C = \frac{2}{3\sqrt{3}} \times \frac{\left[a(\theta-\theta_C)\right]^{3/2}}{B^{1/2}}$.

Assuming $\alpha = a(\theta-\theta_C)$ therefore $P_r = \pm\frac{\alpha^{1/2}}{B^{1/2}}$ et $E_C = \frac{2}{3\sqrt{3}} \times \frac{\alpha^{3/2}}{B^{1/2}}$. Equation 3 can then be written as follows:

$$E = \frac{3\sqrt{3}}{2} \times \frac{P}{P_r} \times E_c \times \left(\frac{P^2}{P_r^2} - 1\right) \tag{4}$$

Taking into account the constant (P_r and E_C) defined previously, the polarization can be plotted as a function of electric field using equation 4 (Fig. 3). In the region (b - e), shown in dotted line, the value of ε is negative because $\frac{\partial P}{\partial E} < 0$.

Such value has no physical meaning (ε<0) and the stability conditions are not respected. Consequently the polarization does not follow this path but for specific value of electric field it passes directly (jump polarization) from b to c and from e to f respectively.

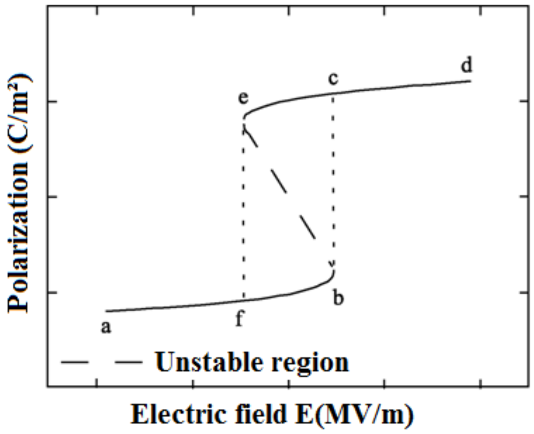

Fig. 3. Polarization vs. electric field: the polarization describes the cycle (a–f–b–c–d–c–e–f–a), (b – e) unstable region.

In order to model the hysteresis loop and improve the results found with Equation 4, the resistance R was added corresponding to a dissipated energy during polarization.

$$E = \tau\frac{\partial P}{\partial t} + \frac{3\sqrt{3}}{2}\frac{P}{P_r}E_c\left(\frac{P^2}{P_r^2} - 1\right) \tag{5}$$

The resistance R placed in series with the ferroelectric allows to introduce the effects of frequency in the model. The losses term $\tau\frac{dP}{dt}$ allows dissipating the energy by friction of domain walls.

In order to highlight this phenomenon, we performed numerical simulations for different frequencies. The figure 4 presents the simulation results obtained for several frequencies and the experimental results obtained on the PZT ceramics. For low frequencies (50 mHz), the cycle is symmetric and the value of the coercive field is close to the experimental one. When the frequency increases, the term $\tau\frac{dP}{dt}$ becomes more important and this is observed in the hysteresis loop by an increase of the coercive field. For high frequencies, the cycle is not symmetrical and the polarization does not saturate. A part of energy is dissipated in the resistance and consequently the effective applied field decreases. Then, the applied electric field has to be increased to return the polarization, but without exceeding the breakdown voltage of the ceramics. The non-reversal of polarization is determined by the value of $\tau\frac{dP}{dt}$ parameter for soft ceramics, the value of $\tau\frac{dP}{dt}$ must be low because we can polarize at relatively high frequencies. It is the reverse for hard ceramics.

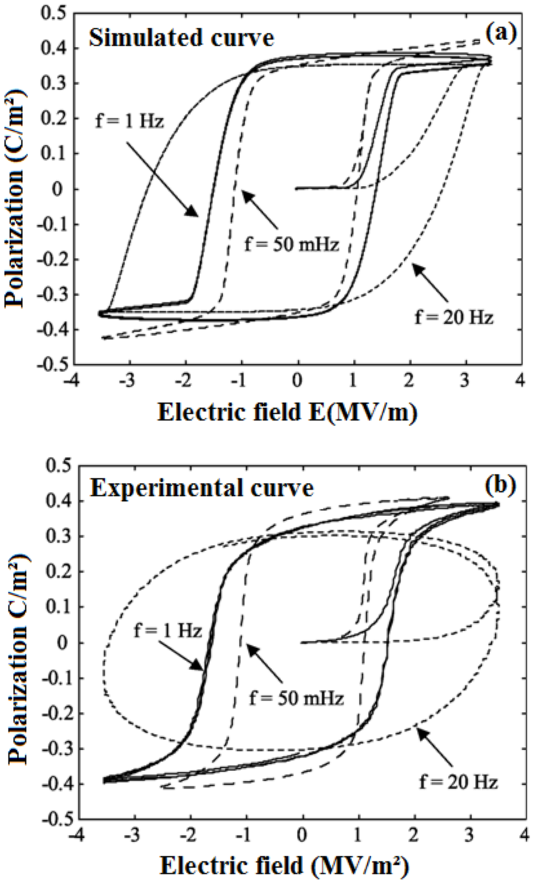

Fig. 4. Comparison between experimental and simulation results for the P/E cycle: (a) simulation, (b) experimental

According to physical analogy of equation 5, a ferroelectric material is equivalent to the perfect ferroelectric one in series with a resistance. It seems interesting to observe the influence of polarization (P) and the electric field E on E_f (electric field on the perfect ferroelectric) noted over time.

In this case:

$$E_f = E - \tau \frac{\partial P}{\partial t}$$

Figs. 5a,b,c show the evolution of E, E_f and P at 0.05, 0.5 and 5Hz respectively. At low frequency, the electric field (E_f) at the terminals of ferroelectric cycle decrease below the coercive field (Ec = 0.8 MV / m) and therefore we can reverse the polarization. By increasing the frequency (or the value), the field on the ferroelectric becomes very asymmetric. The minimum value of E_f is less than the coercive field and therefore cannot reverse the polarization. At high frequency, it becomes impossible to reverse the polarization for the negative field.

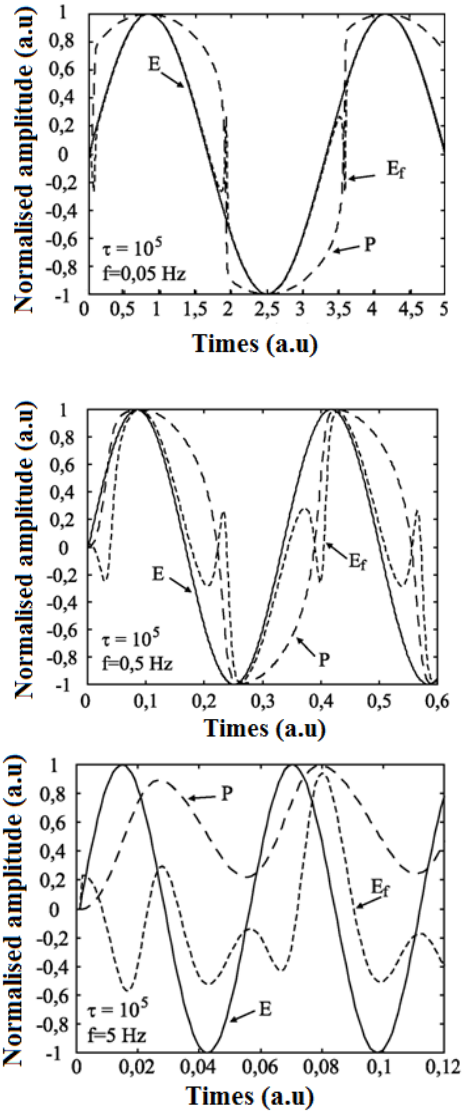

Fig. 5. Evolution of E, E_f and P for different frequencies.

Considering that the model is representative of the experimental reality, we can find a physical reason for the term of dissipation $\tau \frac{\partial P}{\partial t}$:

The term dissipation of energy can be attributed to:

➢ A “dielectric viscosity”. All the elementary polarizations (domains) do not switch simultaneously leading in a macroscopic delay.

➢ A significant resistance at the grain boundaries or domain walls (domain/domain). In fact, this model (ferroelectric perfect +resistance) is equivalent to a series of grains or domains (Fig. 6).

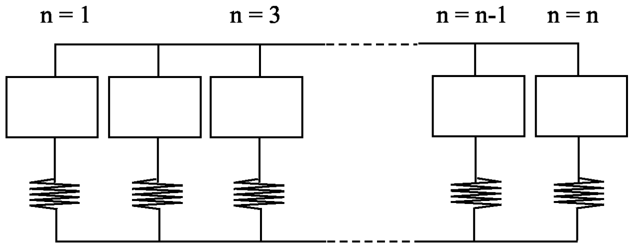

Fig. 6. Schematic structure of model

3. Temperature effects

The remanent polarization of a piezoelectric ceramic decreases with temperature and vanishes above a temperature θ_c called Curie temperature. Experimentally this diminution leads to a progressive decrease of coercive field with temperature. This characteristic is introduced into the model via the coercive field Ec.

The coercive fields vs. temperature follows a Curie-Weiss law. as defined by the:

$$E_C = \frac{2}{3\sqrt{3}} \times \frac{\left[a(\theta-\theta_C)\right]^{3/2}}{B^{1/2}}$$

Where E_c^0 is the value of coercive field for $\theta = 0$ and θ_c is the Curie temperature of the material. It is then possible to calculate the remanent polarization (P_r) at a given temperature and to draw it as a function of θ (Fig. 7). Figure 7 shows a good correlation between the experimental and theoretical curves. This good agreement confirms the legitimacy of the proposed model. A ferroelectric-paraelectric transition is also observed at Curie temperature (200 ° C in our case) (Pr = 0).

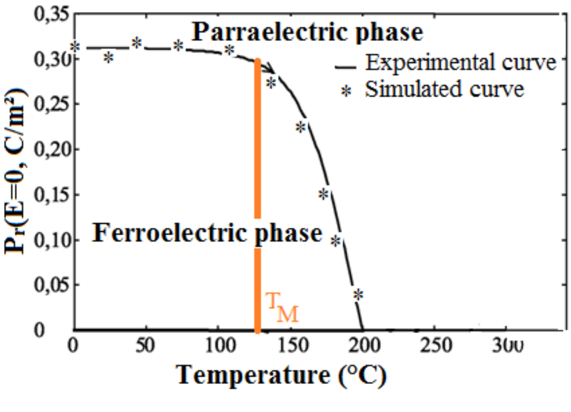

Fig. 7. Evolution of P_r as a function of temperature

Then, the polarization remains constant (P = 0) when the temperature drops below the Curie temperature. This phenomenon is characteristic of piezoelectric ceramics because of their polycristallinity. Indeed, the orientation of domains below the Curie temperature is random. The sum of the spontaneous polarizations of each domain is therefore zero. It is interesting to note that for pure electric measurements, the presented model made it possible to determine the maximum temperature for practical use (T_M) (cf. Figure 7). It indicates that the working temperature should not exceed 150°C. This value corresponds to the maximum of temperature before observing a dramatic decrease of piezoelectric properties.

4. Prediction of dielectric constant

After introducing the effects of electric field and temperature, it remains to determine the dielectric, piezoelectric and pyroelectric coefficients depending on temperature and electric field from the proposed model. For that, one should start by following piezoelectric constrictive equations, restricting to one dimension. These equations can be formulated with the temperature and the electric field as independent variables, thus giving:

$$dD = \varepsilon_{33}^{T} dE + p\,d\theta \tag{6}$$

$$D = \varepsilon_0 E + P \tag{7}$$

where D, P, E, θ and p correspond tot the electric displacement, the polarization, the electric field, the temperature and the pyroelectric coefficient, respectively.

Since the polarization is large enough compared to $\varepsilon_0 E$, $P >> \varepsilon_0 E$, then D can be considered equivalent to P.

The coefficients are defined as:

$$\frac{dP(E,\theta_0)}{dE} = \varepsilon_{33}^{\theta}$$

and

$$\frac{dP(E_0,\theta)}{d\theta} = p \tag{8}$$

This model based on the resistance/ ferroelectric can simulate the behavior of a ceramic whatever the initial polarization and regardless of the applied electric field. The simulation results show the way for more general simulations. We can for example apply a static electric field (E_{stat}) and superpose it an sinusoidal electric field. The comparison between the experimental curve and theoretical curve is shown in Figure. We observed that the two relative permittivities (experimental and simulation) vary similarly during a cycle of electric field. Such a good agreement between simulation and experiment proved that the proposed model allows to predict the dielectric constant (ε_{33}) under electric field using only electric measurements P(E).

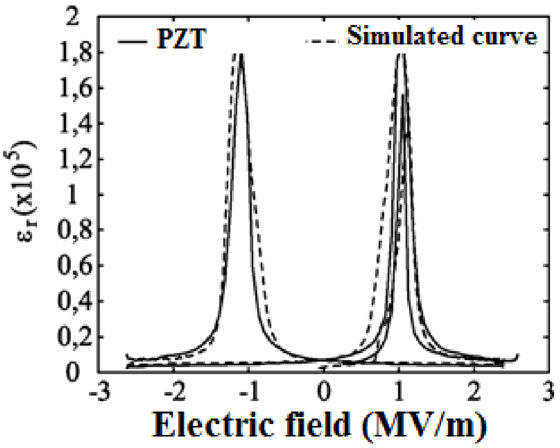

Fig. 8. Evolution of the relative permittivity as a function of the E

5. Conclusions

In summary, an extensive model based on Landau-type phenomenological theory for polycrystallined ferroelectrics is proposed by summing the free energies of the domains. Using this model, polarization hysteresis loops of a PZT ceramic can be well simulated with or without energy dissipation. Unlike previous models, our model can accurately predict the coercive fields and remanent polarization values at any electric fields, temperatures and frequencies by using fewer parameters. The resulting nonlinear and hysteretic nature of piezoelectric materials induces a power limitation for heavy duty transducers or a lack of controllability for positioners. Consequently, a nonlinear modeling allows us to understand transducers behaviors and to determine limits of use.

The proposed model was also used to predict the values of dielectric constant (ε_{33}), and the results of such a prediction were compared to experimental data. A good agreement was found between simulation and experiments, proving that the model made it possible to predict the dielectric constant (ε_{33}) variations, under electric field by using only P(E) cycle.

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