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Modeling the paraelectric aging effect in the acceptor doped perovskite ferroelectrics: role of oxygen vacancy

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Abstract
The time dependence of physical properties in the paraelectric phase was probed recently in a
Mn^{3+} doped $(Ba_{0.8}Sr_{0.2})TiO_3$ ceramic, providing a simple situation (without spontaneous
polarization or domain walls) to quantify the role of the oxygen vacancy during aging. In the
present study, we propose a quantitative model for paraelectric aging to understand how the
distribution of the oxygen vacancy evolves with time and consequently influences the
dielectric response of the paraelectric phase. First, by comparing dielectric behavior of
paraelectric aging in a Mn^{3+} doped $(Ba_{0.75}Sr_{0.25})TiO_3$ ceramic and the dielectric tunable
effect, an internal bias field E_{in} related to the oxygen vacancy is shown to exist in the
paraelectric phase. Second, by introducing such a time dependent E_{in} in a Landau-type model,
we reproduce the dielectric response of Mn^{3+} doped $(Ba_{0.8}Sr_{0.2})TiO_3$ ceramic during
paraelectric aging. It is suggested that the increase of dielectric permittivity can be ascribed to
the decrease of E_{in} with time. The investigation of paraelectric aging is helpful for
understanding the role of the oxygen vacancy in influencing the physical properties of
ferroelectric materials.

(Some figures may appear in colour only in the online journal)

1. Introduction

Ferroelectric materials offer a wide range of properties
that make them attractive for a variety of microelectronic
applications [1–4]. Nevertheless, ferroelectric crystalline
solids invariably contain some lattice defects (dopant,
vacancy or impurity) [5]. Owing to such unwanted defects,
especially the mobile ones, several degradation challenges
arise, restricting technological applications of ferroelectric
materials [6–10]. The oxygen vacancy, as the most common
mobile defect, could induce time dependence (aging) or
cycling dependence (fatigue) of the ferroelectric, dielectric
and piezoelectric properties [6, 11–13]. It is thus important
to understand the role of oxygen vacancies in influencing the
properties of ferroelectric materials.

The ferroelectric aging effect, referring to a time
dependent change of physical properties, is one of the
most ineluctable obstacles to the reliability of ferroelectric
devices [12–15]. Practically, as time goes by, ferroelectric
aging manifests itself by shifting the typical ferroelectric
hysteresis loop along the field-axes or constricting its shape
into a double one (for poled or unpoled samples respectively),
whilst decreasing the dielectric and piezoelectric response [6].
Previous studies have shown that the existence of the
oxygen vacancy and its gradual ordering with time lead
to the aging effect, but the underlying mechanism is still
controversial [16–22]. Therefore, many researchers have

focused on these questions, including how the oxygen vacancy evolves during aging and how it influences the physical properties of ferroelectric materials [16–25].

Over decades several point defect related models were developed to identify the role of oxygen vacancies during ferroelectric aging in terms of space charge [19], reorientation of defect dipoles [24], charged oxygen vacancy trapping at domain walls [16] or the short range rearrangement of oxygen vacancies [18]. These models all argue that the oxygen vacancies reorder themselves within the ferroelectric materials, via either short range redistribution or long range migration. For a particular ferroelectric material in the ferroelectric phase, two relevant locations can be identified for the point defects to rearrange: the domain bulk and the domain wall. For instance, the domain wall models involve long range migration of oxygen vacancies to domain walls, while the short range rearrangement model requires the local reordering of oxygen vacancies in the domain bulk. However, all these models, involving the reordering of point defects in the two alternatives, encounter complications due to spontaneous polarization and discontinuity at domain walls when a quantitative interpretation is required. It is shown that the single domain state of the ferroelectric phase indeed undergoes aging, indicating that domain walls may be not the necessary condition for aging [11], whereas there still exists spontaneous polarization in the single domain state. Hence, a simple situation that excludes such complexities is expected to give us a chance to quantify the exact role of the oxygen vacancy during aging.

Practically, the ferroelectric aging effect can be 'erased' by experiencing the paraelectric phase, known as the thermally de-aging effect [22]. Recently, the time dependent change of properties in the paraelectric phase was probed, for previously ferroelectric aged materials only [26]. It is shown that the paraelectric phase undergoes a gradual increase in dielectric permittivity and decrease in dielectric loss with time; this is termed the 'paraelectric aging effect' [26]. As such a paraelectric aging effect is confirmed to exist only in acceptor doped (oxygen vacancy containing) samples, it is apparently related to the oxygen vacancy [26]. Since there are neither spontaneous polarization nor domain walls in the paraelectric phase, one may find that paraelectric aging indeed provides a simple situation for quantifying the time dependent behaviors that are related to the oxygen vacancy.

Therefore, in the present study, we are trying to provide a quantitative model for the paraelectric aging effect. Previous studies have shown that an internal bias field E_{in} is built up after ferroelectric aging [23, 24, 28]. Thus, first, by comparing the dielectric behaviors of paraelectric aging and the dielectric tunable effect, we show that such an E_{in} can be inherited in the paraelectric phase from the aged ferroelectric phase. Second, by introducing such an E_{in} into a Landau-type model, the dielectric response during paraelectric aging can be reproduced, and the results suggest that the increase of dielectric permittivity can be ascribed to the decrease of E_{in} with time. The present model demonstrates the phenomenology of paraelectric aging, and may be helpful for understanding the role of the oxygen vacancy in influencing the physical properties of ferroelectric materials.

2. Experimental procedures

The samples for proving the existence of an internal bias field in the paraelectric phase were Mn^{3+} doped $(Ba_{0.75}Sr_{0.25})(Ti_{1-x}Mn_x)O_{3-\delta}$ ceramics with x ranging from 0.000 to 0.010 (abbreviated as BST-xMn). All samples were prepared by a conventional solid-reaction method with starting chemicals of $BaCO_3$ (99.95%), $SrCO_3$ (99.9%), TiO_2 (99.9%) and Mn_2O_3 (99.9%). The calcining was performed at 1200 °C, and sintering was done at 1450 °C in air. Mn^{3+} was added as acceptor dopant so that the oxygen vacancies are simultaneously created by charge compensation. Sr^{2+} was added to lower the Curie temperature to about 48 °C, which is determined from the dielectric permittivity (ε) versus temperature (T) curves. All the samples in the ferroelectric phase are in a polydomain state. The ferroelectric aged sample was made by holding it at room temperature (RT) for one month to establish a well aged ferroelectric state. As the aging is a thermally activated process, higher temperature and longer time will promote the aging effect. Here we chose RT for convenience.

3. Experimental results

Here we are going to show that an internal bias field E_{in} indeed exists in the paraelectric phase, by means of the corresponding dielectric response. Previous studies have shown that the dielectric permittivity increases and dielectric loss decreases with aging time in the paraelectric phase of ferroelectric materials [26, 27]. Such a paraelectric aging effect occurs only when the paraelectric phase is formed from an *aged ferroelectric phase* through a reverse ferroelectric transition. Thus the paraelectric aging depends on the prior ferroelectric aging and is suggested to relate to a specific metastable 'microscopic state' of the paraelectric phase, immediately after the diffusionless ferro–para transition [14]. Such a specific microscopic state of the paraelectric phase is considered to inherit a certain ordering of the oxygen vacancy from the *aged ferroelectric phase* [14].

Numerous studies have shown that, after ferroelectric aging, the normal hysteresis loop is constricted into a double one (for the unpoled sample), and such aging behavior can be empirically interpreted by the building up of an internal bias field E_{in} with time from a fresh ferroelectric phase [28]. As paraelectric aging occurs just after the reverse phase transition from the *aged ferroelectric phase* and such a phase transition is time independent and diffusionless, one may thus suspect that the established E_{in} in the *aged ferroelectric phase* would be inherited in the paraelectric phase. Such an inherited E_{in} could influence the physical properties during the subsequent aging in the paraelectric phase.

In order to clarify the above suspicion, we compared the dielectric behavior of two kinds of paraelectric phase with different 'prior ferroelectric states' for the same Mn^{3+} doped BST sample. One is a paraelectric state formed from an *aged ferroelectric phase* (with E_{in} in the ferroelectric phase); the other is a paraelectric state formed from a *fresh ferroelectric phase* (without any E_{in} in the ferroelectric

phase). As shown in figure 1, the former shows a lower value of the dielectric permittivity compared with the latter. Such contrasting behavior reveals that a certain aftereffect was left from the *aged ferroelectric phase*, and the aftereffect somewhat lowers the dielectric permittivity in the paraelectric phase. From the literature, it is noticed that the external DC bias field lowers the dielectric permittivity of the paraelectric phase, which is known as the dielectric tunable effect [29–31]. Therefore, the aftereffect plays the same role as a bias field. It is known that an internal bias field E_{in} is built up after the prior ferroelectric aging and the evolution of E_{in} is always through diffusion. As the result, after a diffusionless phase transition to the paraelectric phase, such an E_{in} is inherited. It should also be noted that this E_{in} increases the Curie temperature (shown in figures 1(b) and (c)), being the same as the effect of an external DC bias field as well. Therefore, the role of the oxygen vacancy during paraelectric aging is equivalent to the existence of an E_{in} inherited from the aged ferroelectric phase. The comparison between the dielectric tunable effect and aging effect is just to show that employing the concept of an internal bias field can be an effective way to investigate the paraelectric aging effect. Because the existence of E_{in} lowers the dielectric permittivity, and the experimentally observed dielectric permittivity increases with time during paraelectric aging [26], it can be deduced that E_{in} could be gradually decreased during paraelectric aging. It should also be noted that with increasing defect (Mn^{3+}) concentration the two curves in figure 1 become more deviated from each other, as shown from figures 1(a) to (c). This indicates that high defect concentration will induce high internal bias field E_{in} in the material, and consequently has a more pronounced effect on the dielectric permittivity.

4. Modeling

In this section, we will formulate a phenomenological Landau-type model for the paraelectric aging effect. The above experimental study shows that the role of the oxygen vacancy during paraelectric aging can be considered to be equivalent to the existence of an internal bias field E_{in}. Now we are going to show how it affects the dielectric response of the paraelectric phase quantitatively. By introducing such an E_{in} coupled with an order parameter in a phenomenological Landau-type model, we show that the dielectric permittivity quadratically increases with decreasing internal bias field E_{in}, which is consistent with our experimental observation.

We consider the cubic paraelectric to tetragonal ferroelectric phase transition. In this case only the [001] component **P** of the polarization is involved, so the Landau expansion of the Gibbs free energy reads

$$F = F_{10} + \tfrac{1}{2}\alpha_0(T - T_0)P^2 + \tfrac{1}{2}\beta P^4 + \tfrac{1}{6}\gamma P^6, \quad (1)$$

where **P** is the order parameter, i.e. the spontaneous polarization; $\alpha_0(T - T_0)$ is a temperature dependent coefficient; β and γ are temperature independent coefficients. T is the temperature and T_0 is the phase transition temperature. An internal bias field E_{in} coupled to the order parameter **P**
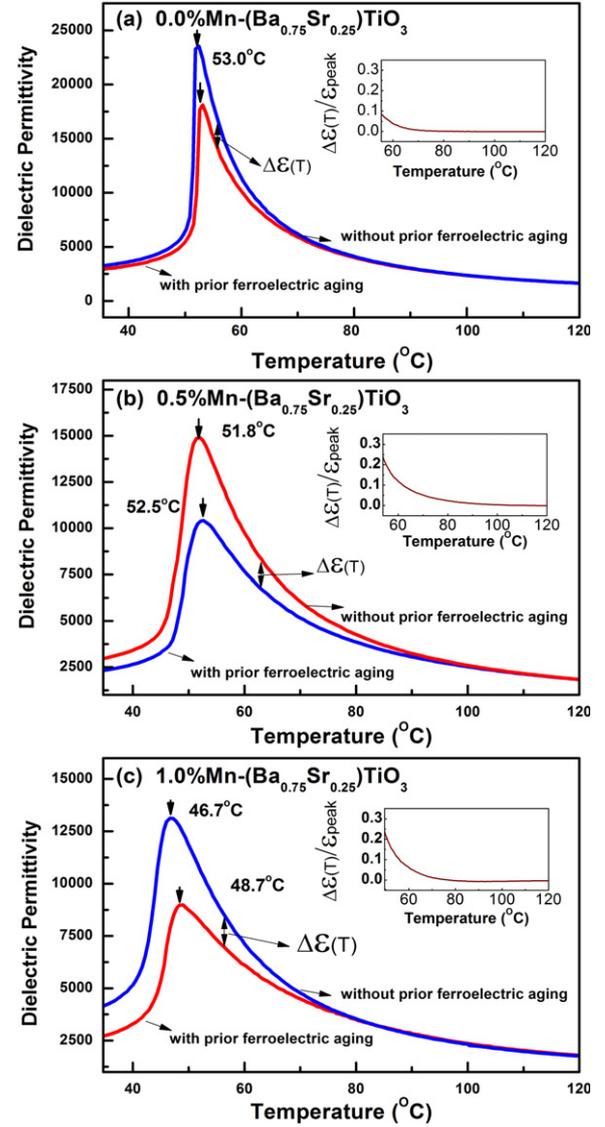

Figure 1. The dielectric permittivity as a function of temperature for Mn^{3+} doped $(Ba_{0.75}Sr_{0.25})(Ti_{1-x}Mn_x)O_{3-\delta}$. (a) $x = 0.000$, (b) $x = 0.005$, (c) $x = 0.010$. The lower curve corresponds to the one with prior ferroelectric aging, while the higher one corresponds to the one without prior ferroelectric aging, which is achieved by quenching the sample from high temperature above T_c. The inset shows the divergence of the two curves above the transition temperature ($\Delta\varepsilon$) as a function of temperature.

contributes to the free energy by $-E_{in}P$. In this case the total free energy is given by

$$F = F_{10} + \tfrac{1}{2}\alpha_0(T - T_0)P^2 + \tfrac{1}{4}\beta P^4 + \tfrac{1}{6}\gamma P^6 - E_{in}P. \quad (2)$$

In the present study, we will deal with the paraelectric phase, and hence the spontaneous polarization is zero, whereas a small polarization is induced due to the existence of an internal bias field E_{in}. Thus equation (2) is our thermodynamic model for describing the paraelectric aging process. We first determine the time dependence of E_{in}. The equilibrium of a system is given by the minimization of the free energy F (equation (2)) with respect to the order parameter,

i.e. $\frac{\partial F(P,T)}{\partial P} = 0$, thus

$$\alpha_0(T - T_0)P + \beta P^3 + \gamma P^5 - E_{in} = 0. \quad (3)$$

The P here, which is the P_D induced by the internal bias field E_{in}, is quite small compared to the spontaneous polarization P_S in the ferroelectric phase. Thus the high power terms (βP^3 and γP^5) in equation (3) can be ignored. Then the internal bias field E_{in} induced polarization P is given by

$$P = E_{in}/\alpha_0(T - T_0). \quad (4)$$

In the simplest approach, the temporal and spatial variations in polarizations are governed by the classical time dependent Ginzburg–Landau equation, i.e., $\tau \frac{\partial P}{\partial t} = -\kappa \frac{\partial F(P,T)}{\partial P}$. Combining equations (2) and (4), thus

$$\tau \frac{\partial E_{in}}{\partial t} = -\kappa \alpha_0^2 (T - T_0)^2 \frac{\partial F(P,T)}{\partial E_{in}} = \kappa \alpha_0 (T - T_0)E_{in}. \quad (5)$$

Since paraelectric aging is considered to correspond to the decrease of E_{in} with time, equation (5) must be resolved with the boundary conditions $E_{in}(0) = E^0$ and $E_{in}(\infty) = 0$. Thus the time dependence of E_{in} can be expressed as

$$E_{in} = E^0 \exp(-t/\tau_0), \quad (6)$$

which shows agreement with the experiment results in the literature [15, 17]. Thus E_{in} evolves as a classic Debye relaxation during paraelectric aging. Furthermore, the susceptibility of ferroelectrics is the second derivative of the free energy:

$$\frac{1}{\chi} = \frac{\partial^2 F}{\partial P^2} = \alpha_0(T - T_0) + 3\beta P^2 + 5\gamma P^4. \quad (7)$$

The high power term $5\gamma P^4$ in equation (7) can also be ignored for the same reason as before, so the dielectric permittivity in the paraelectric phase with E_{in} is given by

$$\chi = \frac{1}{\alpha_0(T - T_0)} \left[1 - \frac{3\beta E_{in}^2}{\alpha_0^3(T - T_0)^3 + 3\beta E_{in}^2} \right]. \quad (8)$$

From equation (8) we can easily see that the larger E_{in} the smaller the dielectric permittivity, when the fourth order coefficient β is positive [30, 31]. Therefore, with the decrease of E_{in} during paraelectric aging, the dielectric permittivity will gradually increase.

The $\frac{3\beta E_{in}^2}{\alpha_0^3(T-T_0)^3 + 3\beta E_{in}^2}$ term is the percentage increase in permittivity. The higher the aging temperature T, the smaller the relative change of permittivity. When the temperature is high enough, the change of permittivity will be nearly zero, as shown in figure 2. The relative change of dielectric permittivity ($\Delta\varepsilon$) versus temperature is shown in the inset of figure 2, which exhibits a similar tendency to the experimental results in the inset of figure 1. Combining equations (6) and (8), the dielectric permittivity versus aging time at different temperatures can be obtained. As shown in figure 3, the present model well fits the experimental data in [26] for various aging temperatures (90 °C, 100 °C, 110 °C, respectively).
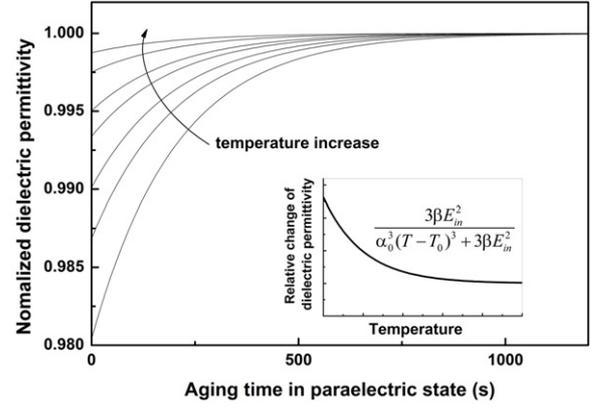

Figure 2. Simulated results that the dielectric permittivity increases with aging time at different aging temperatures in paraelectric state. The inset shows the relative change of permittivity ($\Delta\varepsilon$) as a function of temperature. The lower boundary of the temperature is the Curie temperature T_c, while the upper boundary is twice T_c.
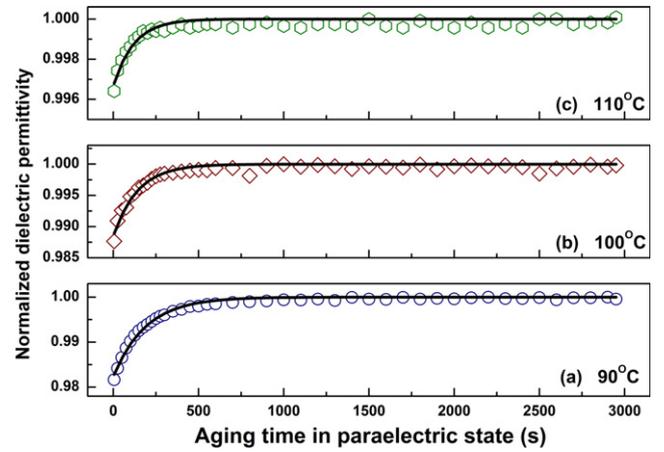

Figure 3. The experimental results that dielectric permittivity increases as a function of aging time at different temperatures (from [26]). The sample was aged in the ferroelectric phase for a week. Then the sample was up-quenched to the paraelectric phase and paraelectric aging started. The curves at different paraelectric aging temperatures can be well fitted by our relaxation function (equations (6) and (8)).

Therefore, by introducing an internal bias field to the above Landau-type model, the experimental results of paraelectric aging can be well reproduced. This phenomenological modeling quantitatively proves that the effect of the oxygen vacancy is equivalent to that of an internal bias field during paraelectric aging. It should be noted that our model is one dimensional and does not consider the gradient terms; thus, for a more accurate approach, the present model should be extended to two dimensional and include the gradient terms.

Now here arise the central questions: what is the atomic origin of the internal bias field E_{in} and how does the oxygen vacancy evolve during paraelectric aging? We notice that both the ferroelectric aging and paraelectric aging can be qualitatively understood by the symmetry conforming short range ordering (SC-SRO) principle of point defects [11, 26]. The main idea of the SC-SRO principle is that the short

range order symmetry of point defects follows the crystal symmetry when in equilibrium. (See [18] for a detailed explanation of the aging model.) One possible way to examine the SC-SRO principle at the atomic scale is to consider the Coulomb attractive force Q between the dopant and its surrounding oxygen vacancies (D^{3+}–V_O) [32, 33]. As shown in the literature [18], the parameter $P_i^{V_O}$, defined as the conditional probability of finding an oxygen vacancy in the O^{2-} site surrounding a dopant D^{3+}, can be used to describe the distribution of the oxygen vacancy. Before and after the diffusionless ferroelectric transition, the different crystal orientations are not equivalent and the distribution probabilities of oxygen vacancies at different crystal orientations are diverse. When more oxygen vacancies prefer one particular site, there will be more chance to find an oxygen vacancy at the site, so the conditional probability $P_i^{V_O}$ of that site will be larger. This gives rise to an unbalanced Coulomb force and may induce an internal bias field E_{in}. It should be also noted that defect doping will result in an internal stress field, mainly because the size of the dopant ion is always different from that of the host ion. A more complete atomic-level model for aging requires both internal electric field and internal stress field [34, 35].

5. Discussion and summary

In order to quantify the role of the oxygen vacancy in influencing the physical properties of ferroelectric materials, we choose a simple situation without spontaneous polarization or domain walls to present a quantitative model. The effect of oxygen vacancies on influencing the dielectric properties is equivalent to that of an internal bias field E_{in}. During paraelectric aging, the distribution of oxygen vacancies gradually varies to be homogeneous at different crystal orientations and correspondingly E_{in} is gradually decreased with time. However, the present Landau-type model does not take into account the domain wall effect, i.e. the interaction between oxygen vacancies and domain walls, which is also important in the ferroelectric phase. Therefore, the current internal bias field can be considered as a bulk driving force (in the domain bulk) for ferroelectric aging and further exploration on the domain boundary is still required. It is also noted that the aging effect in the present study is different from that in glassy systems. The former is due to the redistribution of mobile point defects through diffusion, while the latter is the slow dynamics of glass [36, 37].

In summary, by experimental results, we showed that an internal bias field E_{in} exists in the paraelectric phase. By introducing such a time dependent E_{in} coupled with the order parameter, we proposed a homogeneous Landau-type model to characterize the dielectric response change during paraelectric aging. It is suggested that paraelectric aging can be ascribed to the decrease of E_{in} with time. In order to understand the role of the oxygen vacancy during ferroelectric aging, except for considering such an E_{in} in the ferroelectric domain bulk, further studies on the interaction between the oxygen vacancy and the domain wall is also required.

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