Ageing of (Pb, La)(Zr, Ti)O$_3$ ferroelectric ceramics and the space charge arising on hot poling

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Polarization–temperature diagrams of pyroelectric charge and the decrease of remanent polarization (P_R) at constant temperature are investigated in PLZT 8/65/35 ceramic samples. The arousal of space charge is shown to be unlike that of pyroelectric charge and highly dependent on poling temperature. This charge, measured by the thermally stimulated current in hot poled samples, obeys the dielectric discharge law $i = kt^{-n}$ and is also responsible for the recovery of P_R after the samples have been thermally depoled in part, in contrast with samples poled at room temperature. The evolution of P_R follows the law $-dP_R/P_R = A + B \ln t$ where the slope B decreases with poling temperature when the sign of P_R is that of the former polarization. The ageing behaviour is correlated with the space charge that arises on hot poling.

1. Introduction

Ageing is a well known phenomenon, observed in ferroelectric materials as a gradual decrease of several parameters dependent on the poling state. This effect was very soon detected in BaTiO$_3$ ceramics [1–3] and explained by stress relief mechanisms. Later, different authors studied ageing using different models, the main feature generally being the stabilization of ferroelectric domains [4, 5]. The appearance of an internal field due to impurities was proposed by Härdtl [6] and Okazaki *et al.* [7, 8], the latter describing a phenomenological model based on the appearance of a space charge located mainly on grain boundaries. It was stated that the stability of domain configuration might be ascribed to the segregation of impurities and vacancies into domains [9]. Recently, Borchhardt *et al.* [10] have interpreted the ageing of PLZT and strontium barium niobate (SBN) ceramics on the basis of a model of two levels of relaxation proposed by Reinecke *et al.* [11], assuming that ageing is a thermally activated change of the local configuration of ions to positions of thermal equilibrium corresponding to a certain temperature. In this study they mention the works of Schulze [12] and Smolensky [13] concerning the relaxor.

Commonly, in relation to ageing, evaluations are made of dielectric constant and piezoelectric parameters and, more recently, photovoltaic effect [14].

In this paper we report on polarization–temperature (P–T) diagrams and the temporal decrease of remanent polarization (P_R) at constant temperature in PLZT 8/65/35 samples. Space charge is shown to be present upon poling and the effect which it produces on P_R degredation is discussed.

2. Experimental results

2.1. Preparation of the sample

Among (Pb, La)(Zr, Ti)O$_3$ systems, usually referred to as PLZT, we are concerned with the composition 8/65/35 (8 being Lanthanum concentration in a material with a Zr/Ti ratio of 65/35) which has been obtained in our laboratories by means of a mixed oxide method, requiring calcination at 850° C. By isostatic pressing and sintering at atmospheric pressure at 1250° C, these ceramics have relative densities better than 97% and a grain size of 3 to 4 μm. Disc samples of 0.2 mm thickness and surface $S = 22$ mm^2 were prepared and gold electrodes evaporated onto them.
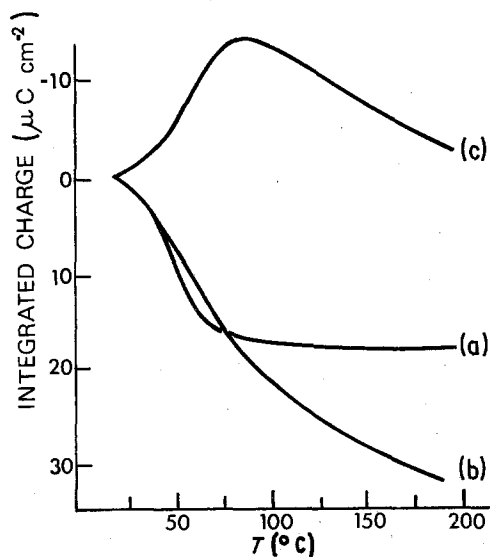
Thermally stimulated electric current is

Figure 1 P–T diagrams of PLZT. (a) Sample poled at 20°C. (b) Sample poled at 200°C. (c) Sample poled at 200°C, cooled to room temperature and then electrically switched.

accumulated and the total charge is registered as a function of temperature with an X–Y recorder. Hysteresis loops are traced at very low frequency $(1.2 \times 10^{-3} \, \text{Hz})$. The material has a remanent polarization $P = 21.5 \, \mu\text{C cm}^{-2}$, a coercive electric field $E = 4.5 \, \text{kV cm}^{-1}$ and a maximum of dielectric constant at $115°\text{C}$, which is considered the transition temperature T_{tr}.

2.2. P–T diagram
Initially, a PLZT sample poled at room tempera-

ture at $20 \, \text{kV cm}^{-1}$ was studied. After 4 h, according to the IRE standards [15], the charge released upon heating to $200°\text{C}$ has been integrated, giving curve 1a in Fig. 1, which shows saturation. If the sample is then cooled from $200°\text{C}$ to room temperature, no change is observed in the accumulated charge; that is, the sample returns to room temperature depoled. However, if instead of reaching $200°\text{C}$ at once, heating is carried out in steps, returning to room temperature each time, the curves shown in Fig. 2 are obtained. This means that there is some recovery of polarization, which is smaller as one approaches T_{tr}, and that when this temperature is exceeded the recovery is null.

Next, we poled another sample by applying a $20 \, \text{kV cm}^{-1}$ d.c. electric field at $200°\text{C}$ and letting the sample cool to room temperature before removing the field. A plot of charge released against temperature is shown in Figure 1b. No saturation appears now. However, as with the first sample, with successive heating and cooling cycles some polarization recovery at room temperature is obtained, as shown in Fig. 3. This recovery is greater than before, even after heating to $200°\text{C}$.

It is somewhat surprising that, in the case of hot poling, there are no signs of saturation of the integrated charge. In order to study this aspect further, a separate experiment was run in which the charge not only accumulated from room temperature to $200°\text{C}$, but after stabilizing at this temperature, continued to accumulate, attaining a value 10 times that corresponding to a process of cold poling. This phenomenon of accumulation of
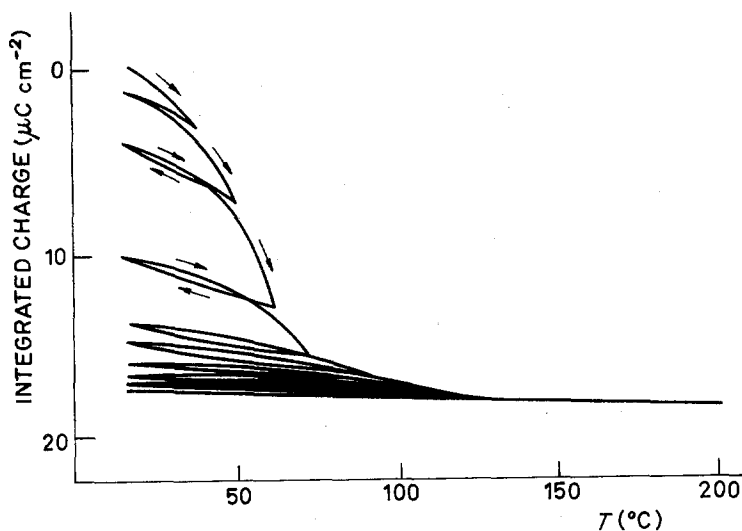

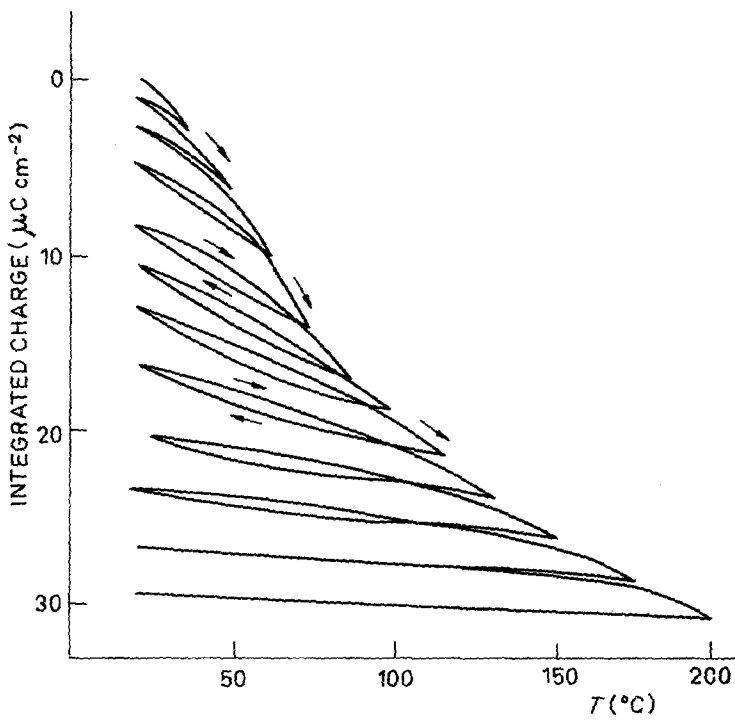*Figure 2* P–T diagram of PLZT poled at 20°C. Recovery of charge on cooling by steps of 12.5°C.

Figure 3 $P-T$ diagram of PLZT poled at $200°C$. Recovery of charge on cooling by steps of $12.5°C$.

"extra" charge is all the more manifest the greater the difference between T and T_{tr}. When the accumulation of charge is no longer measurable, returning to room temperature does not give rise to recovery.

Another sample, poled under the same conditions as the previous one, was afterwards subjected, at room temperature, to an electric field opposing polarization and sufficiently strong so as to invert the dipolar moment. Its $P-T$ diagram is shown in Fig. 4 (also curve 1c in Fig. 1). The beginning of the heating process, the signs of the liberated charge and its recovery by thermal cycles are opposite to those of the previous diagrams (as it should be due to the inversion of P_R); around $60°C$ recovery changes sign, and for a temperature higher than $80°C$ the sign of the liberated charge also changes. After that, the behaviour is that
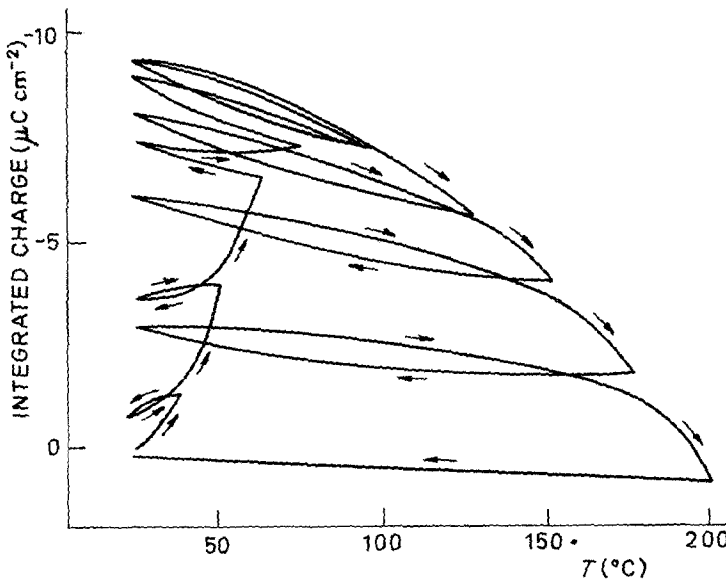

Figure 4 $P-T$ diagram of PLZT poled at $200°C$, cooled to room temperature and then electrically switched. Recovery of charge on cooling by steps of $12.5°C$.

of a hot-poled sample without further electric treatment.

2.3. Decay of extra current at constant temperature

In order to measure this extra charge adequately, as well as its behaviour time, we began with a sample polarized at sufficiently high temperature for the charge to be fairly large, and cooled down to room temperature while maintaining the applied field. Next, the sample was heated well above T_{tr}, to ensure that only the contribution of that charge existed, and maintained at a constant temperature $T > T_{tr}$ while measuring the discharge current. The initial current was the order of 10^{-8} to 10^{-9} A, slowly decreasing in time to values of between 10^{-11} and 10^{-12} A after 50 h. The decay of the discharge adjusts very precisely to the expression (Curie's law) [17]

$$dQ/dt = I = kt^{-n} \qquad (1)$$

where n depends on the measuring temperature and, with t in h, is equal to 0.723 for $T = 150°$C and 0.544 for $T = 200°$C; k depends on the heating rate from room temperature to the measuring temperature.

2.4. Degradation of P_R in hysteresis loops

The temporal variation of P_R has been studied from the hysteresis loop, always traced at room temperature. If the electric field is held at $E = 0$, a discharge is detected in the measuring integrator proportional to the spontaneous decrease of the P_R of the sample ($\overline{MM'}$ in Fig. 5).

For a virgin sample, the hysteresis loop is perfectly symmetrical. On samples which have previously been hot-polarized, loops appear slightly displaced in one of the directions of the electric fiel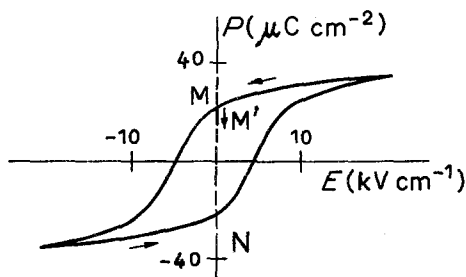d, indicating that an internal field has been generated that must be associated with the extra charge introduced during the poling process. This bias field depends on the number of hysteresis loops, due to their disturbing character. For the first loop, $E_{sp} = 1500$ V cm^{-1}, but this value reduces to less than half after ten loops, and is already repetitive.

The spontaneous decay of polarization fits very well to the known law

$$-\Delta P_R/P_R = A + B \ln t \qquad (2)$$

It should be noted that the poling process at room temperature is the hysteresis loop itself, and that its end is the beginning of the ageing of P_R. This makes it possible to determine with accuracy the logarithmic character of ageing by making measurements in the first minutes of the discharge.

Values of $A = 0.0426$ and $B = 0.170$, with t in min, are typical of a virgin PLZT sample for the two possible directions of polarization. In hot-poled PLZT samples, the coefficient B depends on the temperature of the previous poling (Fig. 6). Curve 6a refers to samples which maintain the sign of their polarization after describing a loop when they have been hot poled (point M in Fig. 5); the decrease in B means, in terms of ageing, that the degeneration of P_R in a sample poled at 150°C is 60% of that obtained when poling at room temperature. If P_R is placed in the opposite direction (point N in Fig. 5), B grows as the poling temperature increases (curve 6b), and the ageing increases considerably.

3. Discussion

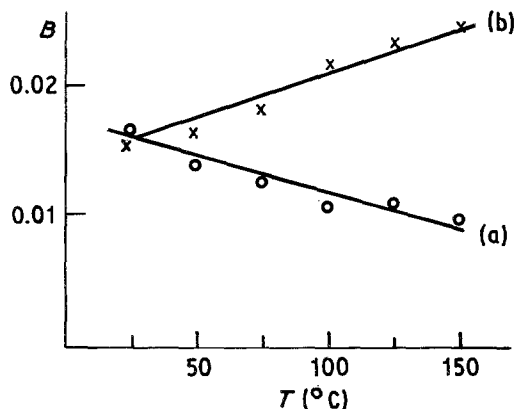The polarization process of a ferroelectric ceramic

Figure 6 Variation of coefficient B in hot-poled samples. (a) The sign of P_R through a hysteresis loop is the same after describing a loop. (b) The sign of P_R changes after describing one and a half loops.

Figure 5 Representative hysteresis loop of PLZT. $\overline{MM'}$ shows the time variation of P_R.

requires the application of strong electric fields over long time periods and a sufficiently high temperature [16] to allow the mobilization of local charges and the relaxation of internal stresses. Once the sample has been poled and maintained at room temperature, remanent polarization decreases with time [4] due to the stabilization of the domain structure, influenced by the evolution of the charge state of the sample, as discussed below.

3.1. Space charge
Different results, according to the poling process of the samples, show the existence of an electric charge of non-pyroelectric origin (Figs. 1 and 4) which is also thermically mobilized and has a double effect: on the one hand, to compensate the divergence of polarization, on other, to fix a given direction upon the polarization of the material.

An electric field, applied at room temperature, can invert the polarization of ferroelectric origin without sensibly affecting this extra charge, as shown in Fig. 4. The evolution of this charge at constant temperature obeys Curie's law of dielectric material due to the formation of a space charge [17].

The two types of charge coexist in the sample. Ferroelectric charge predominates at temperatures up to $60° C$ and space charge prevails over $80° C$. It may be inferred from the results of Fig. 4, taking into account the charge recovery loops upon lowering the temperature, that the space charge creates an electric field E_{sp} which can reorient the polarization to a certain degree.

3.2. Induced transition
The behaviour of polarization with temperature (Fig. 2) shows the existence of a phase transition induced by the poling electric field. This transition was detected by Keve and Annis [18] while studying a PLZT of the same composition as ours. The disappearance temperature of P_R around $60° C$ does not coincide with that of the peak of dielectric constant, $115° C$.

In Fig. 3 polarization of the hop-poled ceramics does not disappear at $60° C$, probably due to the existence of the field E_{sp} which causes the polarization to maintain itself up to higher temperatures, in a similar way as an external electric field, as is observed in [18]. Data from this reference are compared with those of the present work and it is concluded that the shift in the falling polarization

edge observed in $P-T$ diagrams is equivalent to that produced by an external electric field of $5 \, kV \, cm^{-1}$. The field E_{sp} due to the space charge in hot-poled PLZT ceramics is thus evaluated as about $5 \, kV \, cm^{-1}$; the discrepancy with the electric field obtained from displaced hysteresis loops may be due to the disturbing effect which is produced upon describing the loop.

3.3. Ageing
In Fig. 6a we can see that as the poling temperature increases, the coefficient B of the Equation 2 decreases at a rate of $-5 \times 10^{-3} °C^{-1}$. This shows that the internal field increases with poling temperature and maintains the polarization state in a more stable condition than poling at room temperature. When P_R has been inverted at room temperature, its ageing is more rapid and B increases as poling temperature increases (Fig. 6b) at a rate of $+7 \times 10^{-3} °C^{-1}$. The field E_{sp} now increases the ageing rate of P_R.

Okazaki and Nagata [7] have studied the poling—depoling process in PLZT and suggest that depoling is due to a space charge field which increases as P_R decreases. According to our results, the field E_{sp} is created during the poling process and disappears at a temperature higher than T_{tr}. This is not a depolarization field, like that of Okazaki, which should form at the cost of P_R, but rather similar to the fields produced by irradiation or impurities which fix polarization states.

4. Conclusions
In the poling process of a PLZT 8/65/35 ceramic, a space charge is induced, of internal origin, non-pyroelectric and susceptible to relief with temperature and time according to the equation of dielectric discharge. This space charge creates an electric field which fixes a polarization state, increasing or decreasing the ageing rate according to the direction of P, and affecting the polarization in the same way as an external field does. The induced phase transition has been confirmed by the polarization—temperature diagrams of samples poled at both room temperature and high temperatures ($\simeq 200° C$).

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