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2006 J. Phys.: Condens. Matter 18 4839

(http://iopscience.iop.org/0953-8984/18/20/008)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **18** (2006) 4839–4843 doi:10.1088/0953-8984/18/20/008

Negative longitudinal electrostriction in polycrystalline ferroelectrics: a nonlinear approach

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Received 23 September 2005, in final form 12 April 2006
Published 2 May 2006
Online at stacks.iop.org/JPhysCM/18/4839

Abstract
The longitudinal strains ξ_3 of initially unpoled polycrystalline (ceramic) ferroelectrics having different composition were measured as a function of the electric field strength E. The electric field dependences of the longitudinal piezoelectric coefficients $d_{33}(E)$ and longitudinal electrostriction coefficients $M_{33}(E)$ were calculated from the virgin $\xi_3(E)$ curves and analysed. It was shown that taking into account the polarization nonlinearity (that is, the dependence of dielectric susceptibility on E) leads to nonmonotonic field dependences $d_{33}(E)$ and $M_{33}(E)$. In a nonlinear system, the electrostrictive effect is due not only to polarization but also to the dependence of dielectric susceptibility on the electric field strength. The large magnitude of the dielectric susceptibility of soft and relaxor ferroelectric ceramics is responsible for the giant electrostriction being positive in low electric fields and negative in strong ones. The possibility of giant negative electrostriction existing has been found for the first time. In strong electric fields, the strain gain has a limitation because of the competition between the positive contribution of the piezoelectric effect and the negative contribution of electrostriction to the strain.

1. Introduction

Electrostriction is a universal property of solid and liquid dielectrics. It is usually considered that electrostriction is a consequence of the polarization of a substance [1, 2]. In normal dielectrics, which have a linear dependence of polarization $P = \varepsilon_0 \chi E$ on the electric field strength E ($\varepsilon_0 \chi = \mathrm{d}P/\mathrm{d}E$ is the dielectric susceptibility of a substance, ε_0 is the dielectric permittivity of vacuum), there takes place a quadratic P- or E-dependence of the strain ξ. In this case, the electrostriction coefficients are constant; that is, they are independent of the electric field strength.

However, in nonlinear systems, of which only polycrystalline ferroelectrics, namely ferroelectric ceramics, are considered in the present work, in sufficiently strong electric fields there occur domain-orientation processes related to domain switchings to the directions being nearest to that of the applied electric field when E increases and the recurrence of domains to

0953-8984/06/204839+05$30.00

the initial states when E decreases. The systems with such domain-orientation processes are nonlinear, and the important features of them are the phenomena of large electromechanical hysteresis in the dependence $\xi(E)$ and the nonmonotonic dependences of electromechanical coefficients on the electric field strength.

2. Basic aspects and formulae

In the following, we shall be interested only in the longitudinal electrostriction along direction 3 of the applied electric field E_3. The relative longitudinal strain ξ_3 is defined by the free energy, for which we shall use the usual expansion in powers of polarization and mechanical stresses [1, 2]. Then,

$$\xi_3 = Q_{33} P_3^2, \qquad Q_{33} = \frac{1}{2}\frac{\mathrm{d}^2\xi_3}{\mathrm{d}P_3^2}, \tag{1}$$

and the electrostriction is really defined by the polarization P_3 alone. The polarization-related longitudinal electrostriction coefficient $Q_{33} > 0$ and weakly depends [1] on temperature, polarization and the electric field strength.

However, in addition to equation (1), in a number of works (e.g., [3–6]) another definition of electrostriction is used when the strain is considered as a quadratic function not of the polarization P_3 but of the electric field strength E_3:

$$\xi_3 = M_{33} E_3^2, \qquad M_{33} = \frac{1}{2}\frac{\mathrm{d}^2\xi_3}{\mathrm{d}E_3^2} = Q_{33}(\varepsilon_0\chi)^2, \tag{2}$$

where M_{33} is the electric field-related longitudinal differential electrostriction coefficient. No attention is given, however, to the fact that the relations (2) are applicable only for linear systems for which the dielectric susceptibility $\varepsilon_0\chi = \varepsilon_0\chi_{33}$ shows no dependence on the electric field strength. In nonlinear systems, the domain-orientation processes drastically complicate the situation. It will be shown below that, as a result, the electric field dependences of the piezoelectric and electrostriction coefficients become nonlinear and nonmonotonic, and there arise large negative values of the differential electrostriction coefficient $M_{33} < 0$.

In previous works [7, 8], in the Preisach simulation of a converse piezoelectric effect in the prepoled ferroelectric ceramics we used the expansion of the function $\xi_3(E)$ in a power series near the point $E_3 = 0$ (a similar approach was used in [9] for the dependence of ξ_3 on the mechanical stress in the case of a direct piezoelectric effect). In the present work, the objects under study are initially unpoled ferroelectric ceramics, and the $\xi_3(E_3)$ function expansion in a power series is performed near each point of the virgin strain curve. In doing so, we cannot confine ourselves to a linear expansion term because, in low fields, the longitudinal piezoelectric coefficient of the unpoled ferroelectric ceramics $d_{33} \approx 0$, and, when d_{33} passes through the maximum, $M_{33} \approx 0$.

Therefore, in the following, we shall use and measure both the linear (the piezoelectric coefficient d_{33}) and quadratic (proportional to the electrostriction coefficient M_{33}) terms of the $\xi_3(E_3)$ function expansion in a power series of E_3 with the nonlinear dependence of polarization on the electric field strength taken into account [6, 10]. Polarization nonlinearity leads to the fact that both the longitudinal differential piezoelectric coefficient

$$d_{33} = \frac{\mathrm{d}\xi_3}{\mathrm{d}E_3} = 2Q_{33}P_3\frac{\mathrm{d}P_3}{\mathrm{d}E_3} = 2Q_{33}P_3\varepsilon_0\chi(E) \tag{3}$$

and the longitudinal differential electrostriction coefficient

$$M_{33} = \frac{1}{2}\frac{\mathrm{d}^2\xi_3}{\mathrm{d}E_3^2} = Q_{33}(\varepsilon_0\chi)^2 + Q_{33}P_3\frac{\mathrm{d}(\varepsilon_0\chi)}{\mathrm{d}E_3} \tag{4}$$

are functions of the electric field strength E_3.

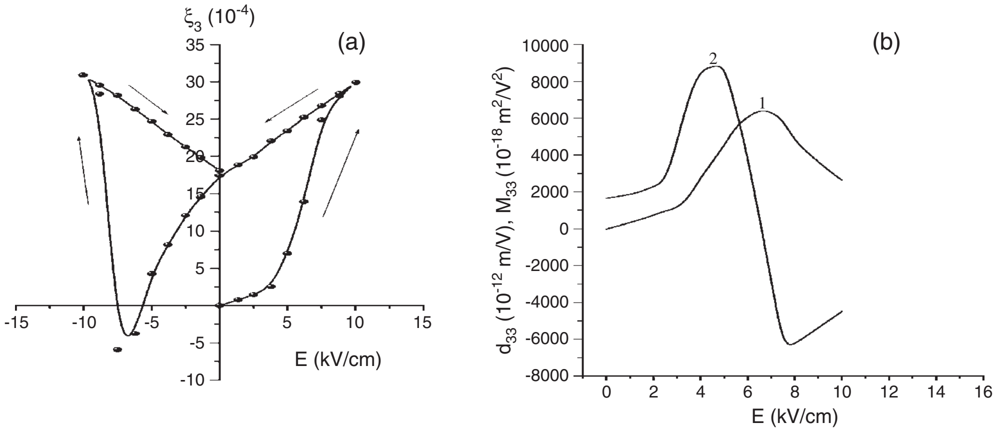

Figure 1. (a) The hysteresis behaviour of the strain ξ_3 versus the electric field E_3 in the soft ferroelectric PCR-7 ceramics at room temperature. (b) The converse differential piezoelectric coefficient d_{33} (curve 1) calculated from the virgin $\xi_3(E)$ curve and the differential electrostriction coefficient M_{33} (curve 2) obtained from the data (a).

Thus, in nonlinear approximation, owing to E-dependent domain-orientation processes, electrostriction originates not only from the polarization P_3 but also from the dielectric susceptibility $\varepsilon_0\chi$ and the dielectric nonlinearity $\mathrm{d}(\varepsilon_0\chi)/\mathrm{d}E_3 \neq 0$. As the dielectric susceptibility $\varepsilon_0\chi$ is always positive and the polarization P_3 increases monotonically with increase of E_3, the nonmonotonic dependence and even the change of the $M_{33}(E_3)$ sign are connected with the nonmonotonic E_3-dependence of the susceptibility $\varepsilon_0\chi$ and the change of the $\mathrm{d}(\varepsilon_0\chi)/\mathrm{d}E_3$ sign. Taking into account this dependence in equation (4) is the main distinction of our approach from the usually used [3–5] expressions (2). In the present work, we were not interested in d_{33} and M_{33} temperature behaviours; all our measurements were made at room temperature.

3. Experimental procedure

A specially designed stand was used to measure the longitudinal strain ξ_3 induced by the discretely increasing or discretely decreasing the electric field E_3 applied to samples of ferroelectric ceramics. The main stand element is a galvanomagnetic dilatometer with a digital indication of readings and the possibility of displaying them on a recorder and a computer. The stand provided the measurement of the relative strain to an accuracy of 10^{-5}. The successive differentiation of the experimental $\xi_3(E_3)$ curve over the electric field strength E_3 enabled one to obtain the $d_{33}(E_3)$ and $M_{33}(E_3)$ dependences in accordance with equations (3) and (4).

As the objects for study we have chosen two kinds of soft ferroelectric ceramics: PZT-type ceramics (PCR-7 [11]) and relaxor PMN–PT-type ceramics [12]. The samples of ferroelectric ceramics had a thickness of 1 mm and a diameter of 10 mm. The typical dependences $\xi_3(E_3)$ (electromechanical hysteresis loops at room temperature) and the electric field dependences $d_{33}(E_3)$ and $M_{33}(E_3)$ calculated from the virgin strain curve are shown in figures 1 and 2. (In [12] the dependences $\xi_3(E_3)$ of the PMN-type ferroelectric ceramics were measured for prepoled samples only.)

4. Results and discussion

The behaviour of the differential piezoelectric coefficient $d_{33}(E_3) = \mathrm{d}\xi_3/\mathrm{d}E_3$ calculated from the virgin strain curve by using equation (3) is not qualitatively different from that of the

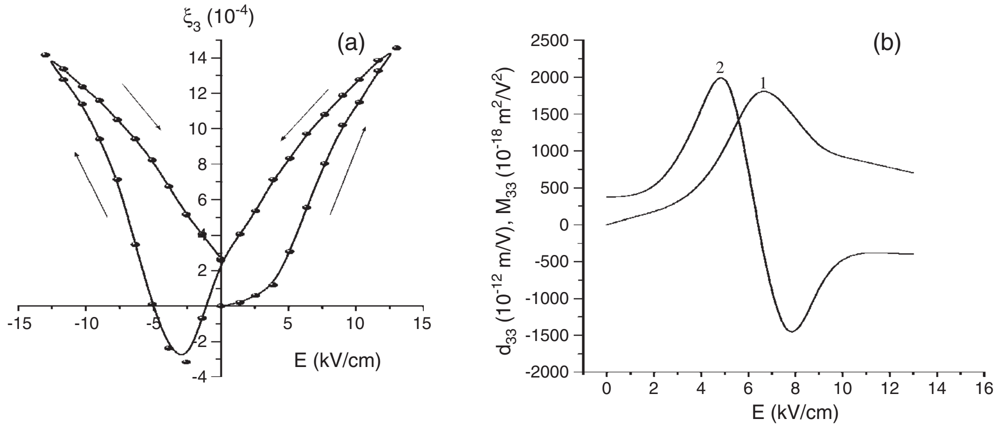

Figure 2. (a) The hysteresis behaviour of the strain ξ_3 versus the electric field E_3 in the relaxor ferroelectric 0.67 PMN–0.33 PT ceramics at room temperature. (b) The converse differential piezoelectric coefficient d_{33} (curve 1) calculated from the virgin $\xi_3(E)$ curve and the differential electrostriction coefficient M_{33} (curve 2) obtained from the data (a).

effective piezoelectric coefficient $d_{33}^{\text{eff}} = \xi_3/E_3$ [8]. Both the piezoelectric coefficients have specific maxima in strong electric fields, $E_3 = 4$–7 kV cm^{-1}, at which the domain-orientation processes are most intensive (any non-180° domain switchings contribute to the strains). In the absence of domain switchings the dielectric susceptibility $\varepsilon_0\chi$ does not depend on E_3 and, as is seen from equation (3), the dependence $d_{33}(E_3)$ is linear. The origin of $d_{33}(E_3)$ maxima is related to a nonuniform distribution of reoriented domains over the internal and coercive fields [8], but, at any electric field strength E_3, $d_{33} > 0$.

Extremes on the $M_{33}(E_3)$ curves are realized on the portions of steep growth and steep drop in $d_{33}(E_3)$ and correspond to the maximum rates of increasing or decreasing the intensity of non-180° domain-orientation processes. Of particular interest is a downward portion of the $d_{33}(E_3)$ curve in strong electric fields in which $\mathrm{d}(d_{33})/\mathrm{d}E \leqslant 0$ and the differential electrostriction coefficient $M_{33} \leqslant 0$. The reason for negative electrostriction is the following: in nonlinear dielectrics, in strong electric fields the dependence $P(E)$ is due not only to the change of the electric field strength E but also to the E-dependence of the dielectric susceptibility $\mathrm{d}P/\mathrm{d}E = \varepsilon_0\chi$ resulting from the rapid decrease of the number of reorientable domains and the saturation of the $\xi(E_3)$ curve. Thus, when the electric field strength E_3 increases, the longitudinal differential electrostriction coefficient M_{33} passes through the positive maximum, changes its sign, passes through the negative minimum and, with the further increase in E_3, increases monotonically. As far as we know, negative M_{33} values have not been discussed in the literature.

In low electric fields, the virgin strain curve shows that $d_{33} \approx 0$, $M_{33} > 0$, and the strain gain is of electrostrictive character. In strong fields, $M_{33} \leqslant 0$ and the strain gain (always positive) is defined, mainly, by the piezoelectric effect ($d_{33} > 0$), whereas the negative electrostriction ($M_{33} < 0$) results in the decrease of the strain gain. In order of magnitude, our d_{33} and M_{33} correspond to those measured in [10] where the maxima of d_{33} and negative M_{33} values were not revealed. A substantial difference in the electromechanical behaviour of the soft ferroelectric PZT-type ceramics (PCR) and the PMN–PT-type ones was not observed. Giant electrostriction is due to the great magnitude of dielectric susceptibility in soft and relaxor ferroelectric ceramics. As a result, the value of $|M_{33}| \approx 10^{-14}$ m^2 V^{-2} exceeds that for the normal ferroelectric ceramics by three orders of magnitude [13].

From the foregoing, it may be concluded that the behaviour of the electrostriction coefficients Q_{33} and M_{33} is very different because the electrostriction effect in a nonlinear system is due not only to polarization but also to the dependence of the dielectric susceptibility on the electric field strength. It is the competition between these two factors that leads to the unusual dependence $M_{33}(E_3)$ (figures 1, 2). In strong fields, the positive piezoelectric effect and the negative electrostriction make commensurable contributions to the magnitude of the ξ_3 strain gain: it is a manifestation of the effect of strain saturation. Such a behaviour is typical of nonlinear systems only; in linear systems, the dielectric susceptibility is independent of the electric field strength, $\mathrm{d}(\varepsilon_0\chi)/\mathrm{d}E = 0$ and $M_{33} > 0$; that is, the longitudinal electrostriction coefficient is always positive.

5. Conclusions

To summarize, it can be said that taking account of polarization nonlinearity leads to a nonmonotonic electric field dependence of the differential piezoelectric coefficient d_{33} and the differential electrostriction coefficient M_{33} calculated from the virgin strain curve. The great magnitude and the electric field dependence of the dielectric susceptibility are responsible for the giant electrostriction $M_{33} \approx 10^{-14}$ m^2 V^{-2} being positive in low electric fields and negative in strong ones. Giant negative electrostriction is observed not only in PMN–PT-type relaxor ferroelectrics but also in soft PZT-type ferroelectric ceramics (PCR).

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