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1998 J. Phys.: Condens. Matter 10 9129

(http://iopscience.iop.org/0953-8984/10/40/016)

J. Phys.: Condens. Matter **10** (1998) 9129–9140. Printed in the UK   PII: S0953-8984(98)95822-2

Ageing of high field dielectric properties in $BaTiO_3$-based piezoceramics

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Received 10 July 1998

Abstract. The dielectric ageing characteristics of a commercial cobalt-doped $BaTiO_3$ ceramic have been determined over a range of applied field strengths (field amplitude E_0 from 0.1 to 2.0 kV mm^{-1}) and temperatures (30, 60, 80 °C). P–E (polarization–electric field) hysteresis data were obtained, from which the internal bias field E_i, polarization amplitude P_0 and the effective high field dielectric coefficients ε_r', ε_r'' and $\tan\delta$ were determined. Near-saturated P–E loops were obtained at high field levels ($E_0 = 2$ kV mm^{-1}); it was shown that E_i increased gradually during ageing to yield an ultimate value around 0.6 kV mm^{-1} after ageing for 17 h at 60 °C. The ultimate E_i value was reduced to approximately 0.4 kV mm^{-1} at a higher ageing temperature of 80 °C.

The P–E 'sub-loops' obtained for $E_0 < 0.5$ kV mm^{-1} showed a pronounced asymmetry and high loss at early ageing times, which were attributed to a combination of partial ferroelectric domain switching and domain wall vibration. These characteristics were effectively removed by domain stabilization during ageing, giving rise to a near-linear P–E relationship with apparently zero internal bias field at long ageing times. The effective dielectric coefficients ε_r', ε_r'' and $\tan\delta$ derived from these P–E data all reduced significantly during ageing, giving an almost loss-free dielectric response after ageing for 17 h. The dielectric behaviour at early ageing times was attributed to a combination of the intrinsic (ionic) response, ferroelectric domain wall vibration and partial domain switching. The two lossy domain-related polarization mechanisms were effectively 'frozen out' by domain stabilization processes during ageing, which enabled a quantitative determination of the three contributions to the complex permittivity ε_r^* at various ageing times, field amplitudes and temperatures.

1. Introduction

Changes in the dielectric properties of ferroelectric ceramics as a function of time after a thermal excursion above the Curie point or the application of a poling treatment are usually referred to as *ageing* phenomena. In early studies, these effects were attributed to a stress-induced *relaxation* of the ferroelectric domain structure to a more stable state [1–3]. During ageing, the low field dielectric permittivity was found to exhibit a logarithmic dependence on ageing time, while the high field P–E (polarization–electric field) loop of an unpoled specimen showed an increasing constriction. This phenomenon could be quantified in terms of the so-called *internal bias field* E_i, determined from the differentiated P–E loop or the I–E (current–field) curve. The value of E_i at a given ageing time represents the internal opposition to the reorientation of polarization away from the stabilized state and is therefore a measure of the degree of domain stabilization produced by the ageing process. In poled materials, E_i can be defined in terms of the shift of the P–E loop along the electric field axis, as shown in figure 1.

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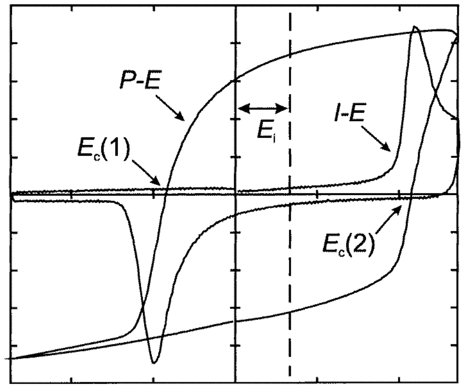


Figure 1. Illustration of I–E (current–field) and P–E (polarization–field) loops for poled acceptor-doped ferroelectric ceramic after ageing process, showing definition of *internal bias field* E_i.

In 1978, Hagemann discussed the ageing behaviour of a variety of acceptor-doped $BaTiO_3$ ceramics [4], concluding that the observed internal bias field and reduced loss at high field levels were most likely a result of ferroelectric domain wall stabilization processes, rather than the stress-induced domain rearrangement referred to by earlier authors [1–3]. According to Hagemann, the most likely mechanism for domain wall stabilization in acceptor-doped $BaTiO_3$ ceramics was the gradual reorientation of acceptor ion–oxygen vacancy associated defects (or 'defect dipoles') towards the local domain polarization. The formation of such defects in $BaTiO_3$ doped with divalent Co ions (for example) can be represented by the following equation, using the standard Kroger–Vink notation for point defects:

$$\mathrm{BaO} + \mathrm{CoO} \rightarrow \mathrm{Ba}_{Ba}^{x} + \mathrm{Co}_{Ti}'' + 2\mathrm{O}_{O}^{x} + \mathrm{V}_{O}^{\bullet\bullet}. \quad (1)$$

The basis for understanding such an ageing mechanism lies in the relatively high mobility of oxygen vacancies at temperatures close to ambient and the small diffusion distances involved in the exchange of the oxygen vacancy among adjacent sites in the perovskite crystal lattice. Similar conclusions regarding the ageing mechanism were reached by Lambeck and Jonker [5, 6], who reported changes in the ferroelectric domain wall mobility in Mn-doped $BaTiO_3$ single crystals, and by Carl and Hardtl [7], who studied the ageing and field-forced deageing characteristics of acceptor-doped PZT (lead zirconate titanate) ceramics.

In 1986, Dederichs and Arlt proposed a method by which the domain wall contributions to the dielectric properties could be determined, by measurement of the real and imaginary parts of the complex dielectric permittivity ε_r^* during ageing [8]. Their work demonstrated how the domain stabilization processes increasingly 'freeze out' the domain wall contributions to ε_r' and ε_r'' during ageing. Subsequently, Neumann and Arlt developed a quantitative model for the build-up of the internal bias field in acceptor-doped perovskite ferroelectrics, based on a defect dipole re-orientation process [9, 10]. Lohkamper *et al* demonstrated that this model could be used to provide a numerical description for the high field ageing and field-forced deageing behaviour, expressed in terms of the dependence of E_i on ageing (or deageing) time [11].

More recently, Robels and Arlt enhanced the model to provide a link between the increase of the internal bias field and the simultaneous reduction in low field dielectric permittivity and loss [12]. The oriented dipolar defects act to increase the domain wall force constant, thereby reducing the low field dielectric coefficients and establishing an internal bias field. According to their treatment, an inverse proportionality between the domain wall contribution to ε_r' (measured at low fields) and the internal bias field (measured at high fields) is predicted. The latter authors also provided experimental data to substantiate the results of their model.

In recent years, there has been an increasing diversification in the applications of piezoelectric materials, for example in areas such as ultrasonic motors, piezoelectric inkjet printheads and multilayer actuators [13]. In many of these applications, piezoelectric ceramics are being subjected to high levels of electric field and mechanical stress, under which their dielectric and piezoelectric properties are not well characterized or understood. Therefore, there is a need to provide both an improved description and a theoretical understanding of the behaviour of ferroelectric ceramics under high field conditions.

A previous publication described the variations in the dielectric properties of a commercial cobalt-doped $BaTiO_3$ ceramic as functions of field amplitude, ageing time and temperature [14]. In that work, two distinct ferroelectric domain-related polarization mechanisms were identified, which were attributed tentatively to reversible domain wall vibration and hysteretic domain switching. A procedure was proposed for determination of the intrinsic, domain wall vibration and domain switching contributions to the complex dielectric permittivity, based on the analysis of P–E hysteresis data. The present study was carried out in order to clarify the time dependence of the complex dielectric permittivity, measured at high electric field strengths, during ageing. The effect of temperature on the ageing characteristics was also evaluated.

2. Experimental procedures

The study was based on a commercial cobalt-doped $BaTiO_3$ piezoceramic, type PC3, manufactured by Morgan Matroc (Unilator Division, Ruabon, UK). Ceramic specimens were prepared by sintering pressed pellets at 1400 °C for 1.5 hours. Previous work established that the material had a tetragonally distorted perovskite type crystal structure with a c/a ratio of 1.007 and a Curie point of 100 °C. The grain size and relative density of the sintered ceramic were 4.1 μm and 94% respectively [14]. Conductive electrodes were applied to the ceramic specimens using a Ag-loaded paste (DuPont 7095) fired on at 550 °C. High field dielectric measurements were conducted using a computer-controlled system incorporating a custom-built current to voltage converter, as described previously [15]. Numerical integration of the measured current with respect to time yielded the polarization, thereby enabling determination of the P–E characteristics of the material.

Ageing experiments were carried out by first thermally deageing a specimen at 150 °C for 1 hour. Subsequently, it was transferred to a silicone oil bath, set to a temperature of 100 °C, and a continuous sinusoidal AC electric field was applied at an amplitude of 2 kV mm^{-1} and a frequency of 1 Hz. The oil bath was then cooled down to the required ageing temperature and allowed to stabilize for a period of at least 30 minutes. The ageing process was initiated by interrupting the continuous AC field and applying a single burst of two cycles at a field level of 2 kV mm^{-1}. This procedure acted to polarize the specimen in the negative sense, after which the resulting poled domain structure was progressively stabilized by the ageing processes.

At selected ageing times, single bursts of two sinusoidal electric field cycles were applied at successively increasing field levels of 0.1, 0.2, 0.3, 0.4, 0.5 and 2.0 kV mm^{-1}. The lower field levels ($E_0 = 0.1$ to 0.5 kV mm^{-1}, 20 Hz) were employed for measurement of the

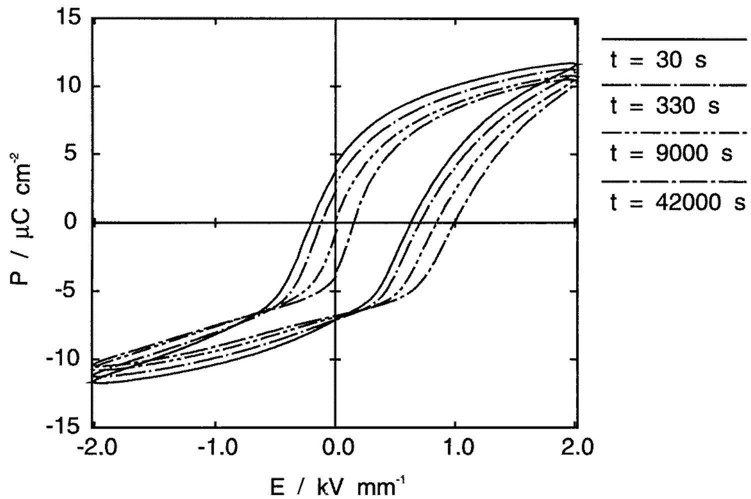


Figure 2. P–E hysteresis loops obtained during ageing of poled material at 60 °C (E_0 = 2 kV mm^{-1}).

high field dielectric properties, while the final high field pulse ($E_0 = 2.0$ kV mm^{-1}, 1 Hz) was used to establish the 'saturated' P–E characteristic. It was established that occasional measurements of this nature (separated by time intervals of the order of minutes or hours) did not disturb the ageing processes significantly.

3. Results

Measurement of the P–E hysteresis loops under an electric field amplitude of 2.0 kV mm^{-1} revealed high field ageing characteristics typical of acceptor-doped ferroelectrics, as shown in figure 2. The saturation and remanent polarization reduced gradually during ageing, while the P–E loops became shifted along the electric field axis, corresponding to an increasing internal bias field. The build-up of E_i during ageing at various temperatures is illustrated in figure 3. For this material, there was an initial rapid rise in E_i to give a value around 0.25 kV mm^{-1} at 30 and 60 °C. This was followed by a more gradual increase to yield an ultimate E_i value of approximately 0.6 kV mm^{-1} after ageing for 24 hours. Both the initial and the ultimate values of E_i were reduced significantly for a specimen aged at a higher temperature of 80 °C. The effect of temperature on the ultimate value of E_i was discussed previously in terms of a reduction in the splitting energy ΔW with increasing temperature [11]. ΔW represents the change in potential energy when an oxygen vacancy changes its position in the octahedron surrounding the acceptor ion [9].

It has been shown previously that the effective high field dielectric coefficients ε_r' and ε_r'' in cobalt-doped $BaTiO_3$ ceramics are reduced during ageing as a result of domain stabilization processes, as noted above [14]. This ageing effect can be demonstrated by examination of the P–E 'sub-loops' obtained during ageing at 60 °C, with a field amplitude of 0.5 kV mm^{-1} (figure 4). The reduction in the gradient of the curve and in the area of the P–E loop during ageing indicate reductions in the dielectric coefficients ε_r' and ε_r'' respectively. Furthermore, a gradual progression from a nonlinear and asymmetric hysteretic response to a near-linear reversible behaviour is evident in this figure, indicating a reduced degree of ferroelectric domain switching at longer ageing times.

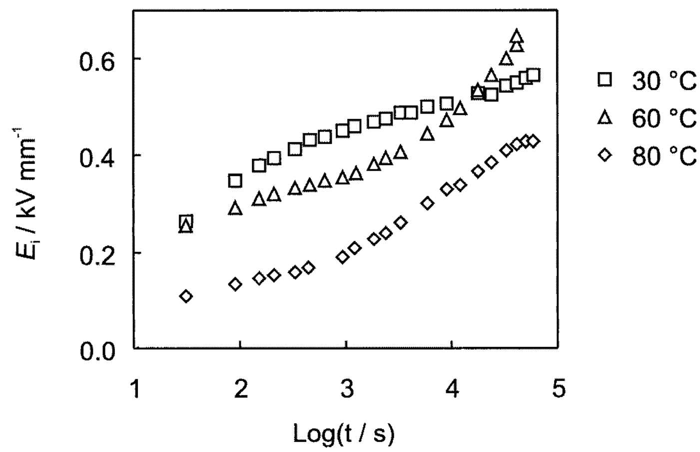


Figure 3. Build-up of internal bias field during ageing at various temperatures (E_0 = 2 kV mm^{-1}).

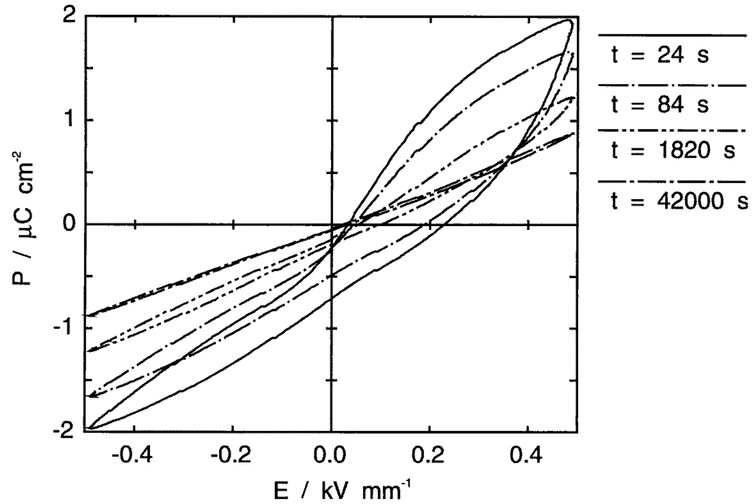


Figure 4. *P–E* hysteresis loops obtained during ageing of poled material at 60 °C (E_0 = 0.5 kV mm^{-1}).

These *P–E* loops, measured at field strengths below the coercive field, show some evidence of hysteretic domain switching and an internal bias field, as shown in figure 4. However, this characteristic was almost removed at long ageing times, as the domain stabilization process became more effective. A somewhat surprising result of this behaviour was a reduction in the measured value of E_i during ageing if the field amplitude was below 0.5 kV mm^{-1}, as shown in figure 5(a). It was shown previously that the apparent value of E_i increases significantly with field strength, reaching a constant value as the *P–E* loop approaches saturation [14, 16].

The apparent reduction in E_i during ageing for $E_0 < 0.5$ kV mm^{-1} can be understood by recognizing that the internal bias field represents an increase in the field required to reorient the polarization away from the stabilized state and a reduction in field required to

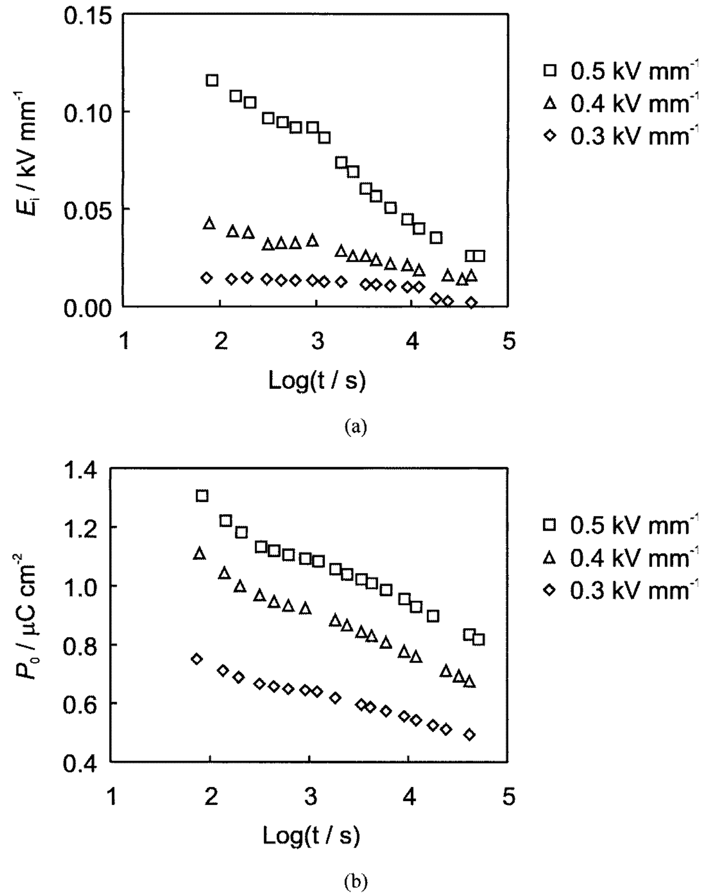
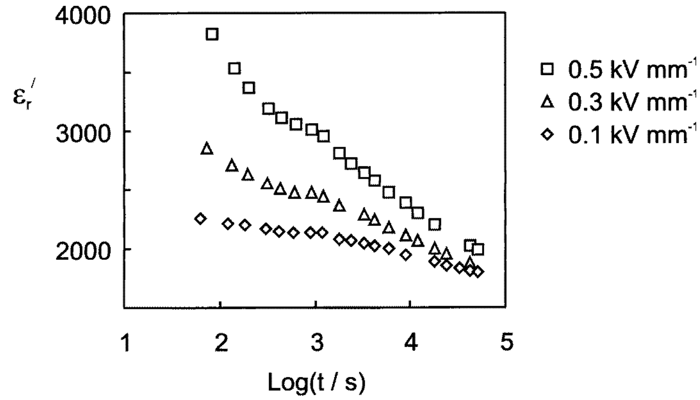


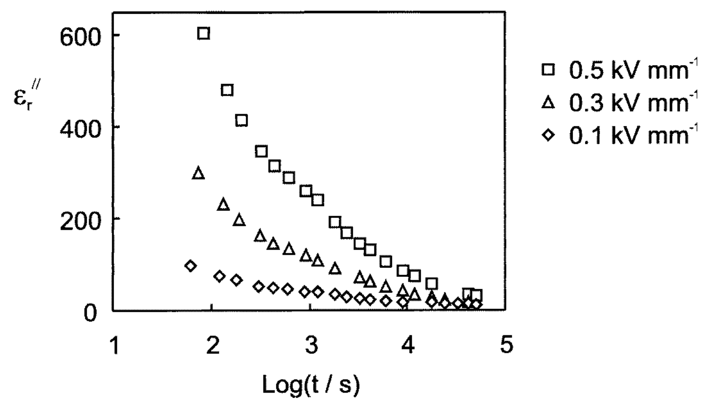
Figure 5. Variation of (a) apparent internal bias field E_i and (b) polarization amplitude P_0 measured at various intermediate field amplitudes during ageing at 60 °C.

reorient the domains back to the stable state. If the applied field strength is insufficient to induce any domain switching, then clearly the internal bias field will not be apparent. Thus, the tendency towards a near-linear P–E relationship with apparently zero internal bias field becomes more evident at longer ageing times and/or lower field strengths. This general trend is also reflected in the change in P_0, the amplitude of the polarization waveform, as a function of E_0 and ageing time, as shown in figure 5(b).

The dielectric coefficients obtained at various field amplitudes and ageing times during ageing at 60 °C are illustrated in figure 6. It is evident that both ε_r' and ε_r'' reduced significantly during ageing, with the change being more pronounced for high field amplitudes. For example, the ε_r' value measured at a field amplitude of 0.5 kV mm^{-1} reduced from 3820 to 1980 during ageing from 60 s to 17 hours, representing a reduction of approximately 50%. The reduction in loss was even more dramatic, with ε_r'' reducing by 95%, from 600 to 30, during the same ageing period. In terms of the loss tangent, $\tan\delta$ reduced from 0.158 to 0.015 at ageing times of 60 s and 17 hours respectively when measured at a field amplitude of 0.5 kV mm^{-1}. The equivalent $\tan\delta$ values were 0.043 and 0.006 respectively when measured at a field amplitude of 0.1 kV mm^{-1}.



(a) ε_r'



(b) ε_r''

Figure 6. Ageing of dielectric properties at 60 °C, measured at various intermediate field levels: (a) ε_r' and (b) ε_r''.

Previous authors have attributed such ageing effects in acceptor-doped ferroelectric ceramics to reductions in the domain wall contributions to ε_r' and ε_r'', as a result of domain stabilization processes [8, 12]. Similar observations were also made by Wu and Schulze [17], who studied the ageing of the high field dielectric coefficients in pure $BaTiO_3$ ceramics.

The ε_r' values obtained at 60 °C at various field amplitudes tend towards a common value close to 1800 at long ageing times. On the basis of previous work [8, 12], it can be concluded that this ultimate ε_r' value corresponds to the constant intrinsic ionic permittivity, while the pronounced reduction in ε_r' during ageing represents the 'freezing-out' of the domain wall contribution due to domain stabilization. Ageing of the imaginary part ε_r'' showed a broadly similar behaviour to that of ε_r', as shown in figure 6(b). However, in this case all of the ε_r'' values tended towards zero at long ageing times. Therefore, it can be concluded that the ultimate result of the ageing process is a dielectric response dominated by the loss-free ionic component of ε_r'.

Both the real and imaginary parts of the dielectric permittivity increased significantly on increasing the temperature, as shown in figure 7. Furthermore, the reductions in ε_r' and ε_r'' were larger at higher ageing temperatures, indicating an increase in the domain-related

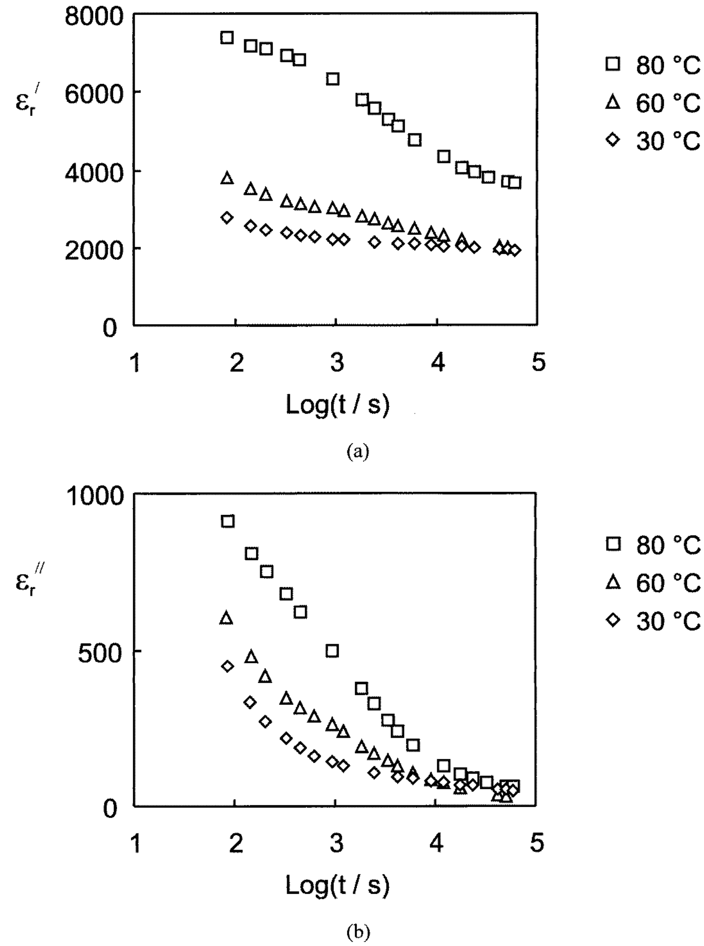


Figure 7. Ageing of dielectric properties at various temperatures, measured at 0.5 kV mm^{-1}: (a) ε_r' and (b) ε_r''.

contributions to the dielectric response at early ageing times. This is most likely due to an increase in the ferroelectric domain mobility on approaching the Curie point at 100 °C. The ε_r'' values were all close to zero at the end of the ageing period, although a small residual loss was present. The loss tangent, measured at a field amplitude of 0.5 kV mm^{-1}, reduced from 0.130 to 0.030 during ageing at 80 °C. It is clear from the changes in the P–E loops presented in figure 4 and the reductions in ε_r' and ε_r'' during ageing (figures 6 and 7) that the domain wall stabilization processes effectively remove the majority of the domain-related contributions to ε_r' and ε_r'' at each of the ageing temperatures.

4. Discussion

In earlier publications, several authors have utilized a plot of ε_r' against ε_r'' as a means of separating the domain-related contributions to the permittivity from the intrinsic ionic response [8, 12, 14]. A linear ε_r'–ε_r'' relationship is often observed, indicating a single lossy polarization mechanism, and extrapolation to zero loss yields the intrinsic ionic contribution to ε_r'. The changes in ε_r' during ageing can then be assigned to the lossy domain-related contributions. It is assumed that the measured ε_r'' values are due solely to a combination of domain wall vibration and domain switching.

Application of this procedure to the present results yields a nonlinear relationship, as shown in figure 8. Extrapolation to zero loss yields approximate ε_{ionic}' values of 1600, 1700 and 3000 at ageing temperatures of 30, 60 and 80 °C respectively. Furthermore, the curves obtained for different field amplitudes show a tendency to separate at early ageing times, which becomes more pronounced as the ageing temperature increases (compare figures 8(a) and 8(b)). This behaviour can be explained in terms of two distinct domain-related polarization mechanisms i.e. lossy domain wall vibration and hysteretic domain switching. The superposition of two separate ε_r'–ε_r'' plots, associated with these different lossy polarization mechanisms, could give rise to the nonlinear curves shown in figure 8. Examination of the P–E loops presented in figure 4 indicates that the hysteretic domain switching mechanism becomes more significant at high electric fields and/or short ageing times.

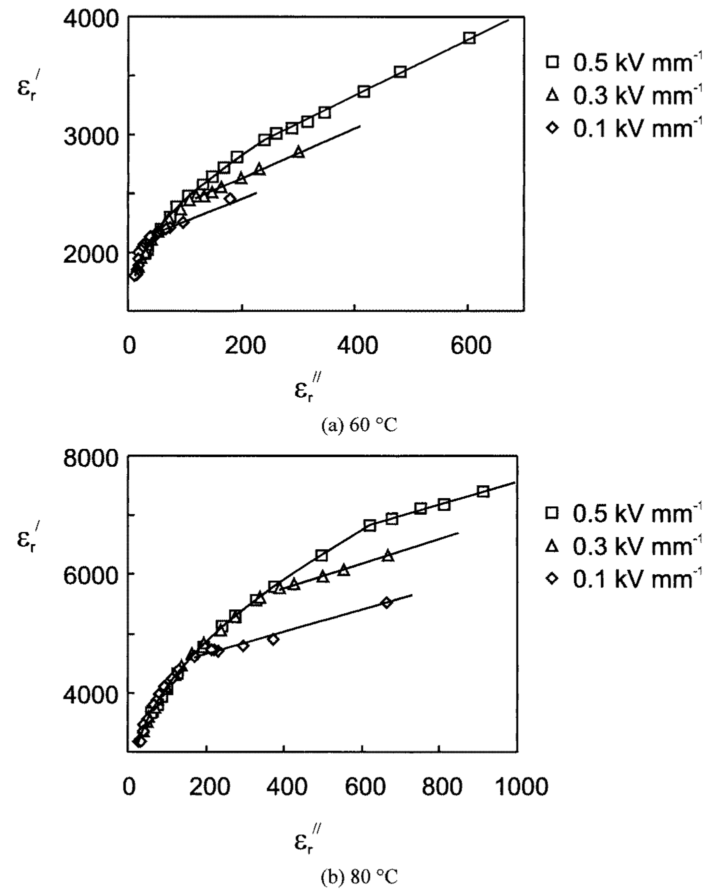


Figure 8. Plot of real against imaginary part of dielectric permittivity measured during ageing at temperatures of (a) 60 °C and (b) 80 °C; lines are for guidance only.

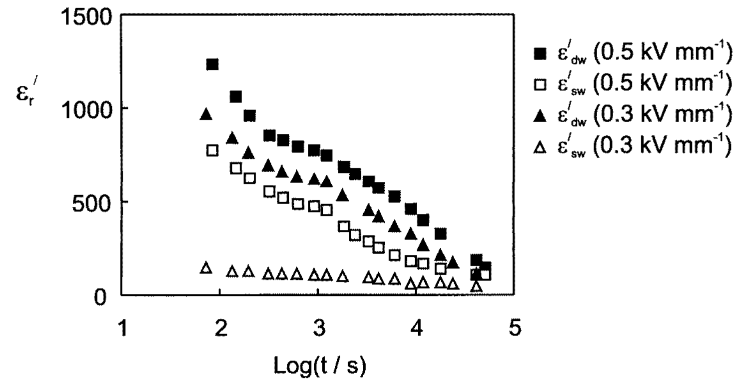


Figure 9. Reduction of ferroelectric domain contributions to dielectric permittivity during ageing at 60 °C, measured at various intermediate field amplitudes.

It is possible to estimate the magnitude of the domain wall vibration and domain switching contributions to the dielectric permittivity, ε'_{dw} and ε'_{sw}, by making the following assumptions:

(i) an electric field applied parallel to the stabilized polarization direction will induce only lossy domain wall vibration (i.e. no domain switching);

(ii) the contribution from domain wall vibration is independent of the sense of the applied field.

These assumptions would be invalid if some additional domain switching were to occur when the field was applied parallel to the stable polarization direction or if partial domain switching with the field in the opposite direction also led to a change in the contribution from domain wall vibration. Nevertheless, the strong asymmetry of the initial P–E loops shown in figure 4 suggest that these assumptions are valid to a certain extent and therefore that a reasonable estimation of ε'_{dw} and ε'_{sw} can be made. Further details of the procedures used for the separation of ε'_{ionic}, ε'_{dw} and ε'_{sw} were given in a previous publication [14].

For an ageing temperature of 60 °C, the results indicate that both domain wall vibration and domain switching contribute significantly to the dielectric response at a field strength of 0.5 kV mm^{-1}, as shown in figure 9. Both of these polarization mechanisms were effectively 'frozen out' by domain stabilization during ageing. The domain switching mechanism was less important for field amplitudes below 0.3 kV mm^{-1}, even at the beginning of the ageing period. The domain switching mechanism provided a larger contribution to the dielectric response at higher temperatures, as shown in figure 10. This can be explained in terms of a reduction in the coercive field on approaching the Curie point at 100 °C, with the result that partial domain switching occurs to a greater extent with increasing temperature.

The reduction in the gradient of the ε'_r–ε''_r curves at higher field levels and early ageing times (figure 8) can be correlated with an increase in the domain switching contribution (figures 9, 10), indicating that this is inherently a more lossy process than domain wall vibration, i.e. ε''_r increases more for a given contribution to ε'_r. Furthermore, the occurrence of partial domain switching at field levels below E_c could lead to depoling if the field was applied for a sufficiently long time, since field-forced deageing effects would inevitably cause a gradual increase in the degree of domain switching [16]. The long-term effects of cycling at field levels just below E_c have not been investigated in depth previously and represent an interesting topic for future studies.

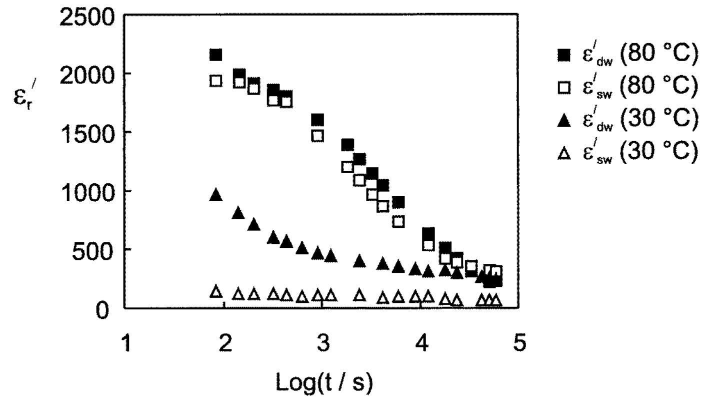


Figure 10. Reduction of ferroelectric domain contributions to dielectric permittivity during ageing at various temperatures, measured at 0.5 kV mm^{-1}.

5. Conclusions

Near-saturated P–E hysteresis loops, obtained at a field amplitude of 2 kV mm^{-1}, showed a pronounced shift along the electric field axis during ageing as a result of ferroelectric domain stabilization by dipolar defect associates. The corresponding values of the internal bias field E_i were found to increase gradually during ageing to yield an ultimate value of around 0.6 kV mm^{-1} after ageing for 17 h at 60 °C. The ultimate E_i value reduced to approximately 0.4 kV mm^{-1} at a higher ageing temperature of 80 °C. The P–E 'sub-loops' obtained at field levels below 0.5 kV mm^{-1} showed a certain degree of asymmetry and a high loss at early ageing times. These characteristics were effectively 'frozen out' during ageing to yield an almost linear and loss-free dielectric response. As a consequence, the apparent internal bias field measured at intermediate field levels below the coercive field seemed to reduce to zero during ageing. The effective dielectric coefficients ε_r', ε_r'' and $\tan\delta$ showed pronounced reductions during ageing as a result of the domain stabilization processes. Plotting the results on the complex permittivity plane yielded a nonlinear ε_r'–ε_r'' relationship, indicating contributions from two distinct domain-related polarization mechanisms i.e. ferroelectric domain wall vibration and domain switching. Extrapolation of the ε_r'–ε_r'' curves to zero loss yielded the intrinsic ionic permittivity values of approximately 1600, 1700 and 3000 at temperatures of 30, 60 and 80 °C respectively.

Acknowledgments

The authors would like to thank Morgan Matroc (Unilator Division, Ruabon, UK) for supplying the ceramic powder and Professor G Arlt for useful discussions. Dr Ben-Omran acknowledges the financial support of the Libyan Higher Education.

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