Journal of the European Ceramic Society 20 (2000) 2705–2711

www.elsevier.com/locate/jeurceramsoc

Degradation of PZT-4D hard piezoceramics under moderate heating

M. Algueró *, F. Guiu, M.J. Reece

Department of Materials, Queen Mary and Westfield College, University of London, Mile End Road, London E1 4NS, UK

Abstract

The changes produced in the dielectric permittivity, the transverse piezoelectric coefficient, the k_{31} coupling factor, the s_{11}^E elastic compliance and the mechanical quality factor of PZT-4D hard piezoceramics by heating have been investigated. The ceramics were then repoled, and the reversible and irreversible components of the changes quantified. The results showed that depolarisation began at 150°C. A high level of poling was retained even after heating at 300°C ($d_{31} = -83 \times 10^{-12}$ C N^{-1} and $k_{31} = 0.225$), only 20°C below the transition temperature. However, a significant irreversible degradation of the mechanical quality factor, Q_m, occurred at a temperature as low as 100°C. Experiments on thinned specimens showed that the degradation of Q_m took place in the Ag doped layer produced by the electrodes. Indentation surface cracks were also introduced into the ceramics to investigate the behaviour of cracks during the thermal treatments. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Actuators; Degradation; Piezoelectric properties; PZT

1. Introduction

Piezoelectric ceramics are well known to be liable to heat to temperatures well above 100°C under the increasing electric fields used to drive them in devices. This particularly applies to piezoelectric ceramics driven by high frequency unipolar electric fields,[1] such as those used for high speed impact printer heads (field >1 kV mm^{-1}, printing speed $\sim$3 kHz).[2] It also applies to piezoceramics driven by bipolar fields at the mechanical resonance frequency ($\sim$kHz), such as those used for high power ultrasonic motors.[3] The origin of this phenomenon has already been studied. Zheng et al.[4] have stated that for lead zirconate titanate (PZT) based multilayered actuators in the free stress state, it is mostly linked to the dielectric hysteretic losses, though they pointed out that under an external stress, mechanical losses might also be significant.

Self-heating may be detrimental to a device performance in many ways and would affect the piezoelectric active element through two mechanisms: depolarisation, which manifests itself as a degradation of the relevant piezoelectric parameters, and is reversible by repoling the piezoceramic; and irreversible degradation. As an example of the latter, clusters of microcracks have been shown to appear in PZT-8 hard piezoceramics during electric cycling at the resonance frequency as a consequence of the element heating. These microcracks were able to interact with pre-existing surface cracks leading to their growth and the failure of the element .[5] Efforts to reduce these non-desired effects have focused on two approaches: the development of novel driving techniques that reduce heating, such as the antiresonance driving for ultrasonic motors,[6] and the tailoring of processing. The latter aims to reduce dielectric losses, to increase the stability of polarisation and to increase the resistance to cracking. For instance, it is well known that acceptor doping of PZT reduces the dielectric hysteretic losses.[7] It is also known that hot poling increases the stability of the electrical polarisation.[8] Much might be gained from the characterisation and understanding of these degradation phenomena in commercial piezoceramics. This would lead to the definition of the limiting operation conditions. Also, the introduction of actuators in more severe environments, such as engines, is an area in which increasing effort is being put.[9] The study of the behaviour of existing piezoceramics at temperatures above room temperature and the mechanisms underlying their thermal degradation would assist the development of actuators for such high temperature applications.

---

* Corresponding author. Tel.: +44-171-975-5555 ext. 4792; fax: +44-181-981-9804.

E-mail address: m.alguero@qmu.ac.uk (M. Algueró).

PII: S0955-2219(00)00221-1

PZT-4D hard piezoceramics (Navy Type I) are a lead zirconate titanate high power material capable of producing large mechanical drive amplitudes while maintaining low mechanical and dielectric losses. They are suited for ultrasonic cleaning, sonar and other high power acoustic radiation applications.[10] We present here an investigation of the thermal degradation of a ceramic of this type. The changes of the room temperature (RT) relative dielectric permittivity (ε_{33}), transverse piezoelectric coefficient (d_{31}), coupling factor (k_{31}), compliance ($s^{E}{}_{11}$) and mechanical quality factor (Q_{m}) after thermal treatments at increasing temperatures (from 100 to 350°C, which is above the transition temperature at 320°C[10]) have been measured. After each specific thermal treatment, the ceramics were repoled and the reversible and irreversible components of the changes obtained. Care was taken to account for ageing effects, which would have confused the measurement of relative property changes. Indentation surface cracks were introduced into the as-received specimens and their evolution during the treatments monitored.

The starting state of the material was "as received", in which the ceramic was already Ag electroded and poled by the supplier. The material had a brownish colour in the centre, but a black layer around 0.5 mm thick next to the Ag electrodes. Thinning experiments were performed on selected specimens to work out any possible role played by this layer on the thermal degradation.

2. Experimental procedures

The ceramics were provided by Morgan Matroc Transducers Division (Southampton, UK) as poled electroded plates (25.4×25.4×5.25 mm). Results shown here correspond to four different plates from the same batch. Catalogue values[10] for the five electromechanical properties to be monitored during the experiments are given in Table 1. The plates were cut into bars of 25.4×5×5.25 mm, which are suitable sizes for the measurement of the d_{31} piezoelectric coefficient and related parameters by the resonance technique. One 25.4×5 mm face was polished with 1 μm diamond paste, and a set of nine Vicker's indentations with loads of 2.5, 5 and 10 kg (three of each) were placed on the surface. The indents were located so that the cracks, emanating from the corners of the indentation impressions, were parallel and perpendicular to the electrodes.

The thermal treatments were accomplished in a conventional furnace at 100, 150, 200, 250, 300 and 350°C at a rate of 5°C min^{-1}. The ceramics were held at the treatment temperature for 30 min, and then allowed to cool down in the furnace after switching it off. The ageing behaviour of the electromechanical properties of the heat treated ceramics was then measured over a period of 10 days.[11] The ceramics were then repoled in an oil bath at 100°C with an electric field of 3 kV mm^{-1}, which had been found to be the most efficient field for poling in a previous investigation.[12] They were held at these conditions for 30 min and then allowed to cool down to 30°C with the field maintained on. The ageing behaviour of the electromechanical properties of the repoled ceramics was then measured over a period of 40 days.[11]

The ε_{33} dielectric permittivity at RT and 1 kHz was measured with a LCR meter and the electric admittance modulus spectrum was measured with a circuit analogous to that described in Ref. 13 The d_{31}, k_{31}, $s^{E}{}_{11}$ and mechanical quality factor, Q_{m}, were evaluated from the positions of the maximum and minimum of the admittance modulus, and the value of the modulus at the maximum.[13] We are aware that an error is committed when the maximum and minimum of the admittance modulus are used instead of the maxima of the conductance and resistance, respectively.[14] However, this error has been shown to be small when the figure of merit M, whose definition is given in Eq. (1), is well above of 3.[15]

$$M = \frac{|A|_{mx}}{2\pi f_m C} \tag{1}$$

where $|A|_{mx}$ is the maximum of the admittance modulus, f_m the frequency of the maximum, and C the capacitance at 1 kHz. The lowest figure of merit found in this research was 27. Therefore, significant errors in our measurements are not expected.

The size and length of the indentation impression and the cracks were recorded with an optical microscope before and after the thermal treatments and after repoling. From these measurements, the initial Vicker's hardness and toughness of the ceramic, and any crack

Table 1
Macroscopic parameters for the PZT-4D hard piezoceramics

	ε_{33}	d_{31} ($\times 10^{-12}$ C N^{-1})	k_{31}	s^{E}_{11} ($\times 10^{-12}$ m^2 N^{-1})	Q_{m}
Catalogue	1300	−135	0.325	13.3	600
As received	1041±11	−94±2	0.287±0.005	11.72±0.02	973±57
Repoled	1043±43	−100±5	0.31±0.02	11.91±0.08	697±41

growth occurring during the treatments were measured. Additional new sets of indents were put into some selected bars after the thermal treatment, and after the repoling step. This was done to monitor possible changes of the Vicker's hardness and toughness with the treatments.

Two thinning experiments on specimens were performed to investigate the possible role played by the black layer next to the electrodes:

— The Ag electrodes and a ~1 mm layer of adjacent ceramic were removed from an as-received bar, completely removing the black areas. Then, Au electrodes were sputtered on the new surfaces and the electromechanical properties of the ceramic were measured. After this, the ceramic was thermally treated at 350°C and repoled, and again its properties were measured.

— Two bars, an as-received bar and one which had been thermally depoled at 350°C and subsequently repoled, were thinned in steps from one side. An Au electrode was deposited after each thinning step, and the properties measured.

Scanning electron microscopy (JEOL JSM-6300 microscope) and energy dispersive X-ray spectroscopy (Link system) were used to investigate any microstructural or compositional difference between the centre of the ceramic and the layer next to the electrode, and to monitor any change occurring during the thermal treatments. No difference existed between the two areas within the sensitivity of the techniques, and no change occurred during the treatments either.

3. Results and discussion

The properties of the as-received material are given in Table 1. Ageing effects were observed after all of the thermal treatments and after all of the repoling steps. As an example, the time evolution of the d_{31} piezoelectric coefficient and the s_{11}^{E} compliance for a ceramic after a thermal treatment at 100°C, and after its subsequent repoling, is shown in Fig. 1. This time evolution presents a linear behaviour with log time after the treatment, which is well known to occur in acceptor doped piezoceramics.[16]

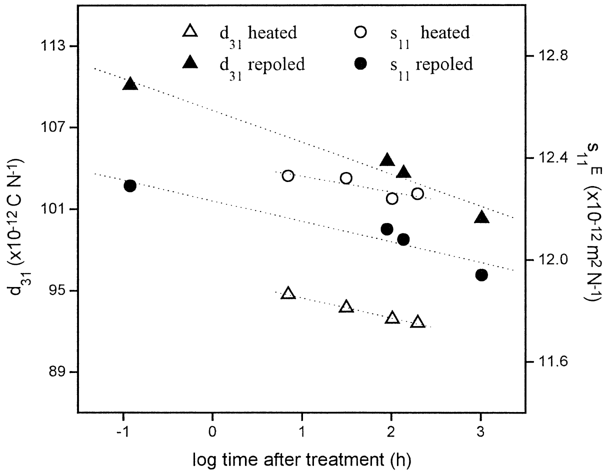

Fig. 1. Time evolution of the d_{31} piezoelectric coefficient and the $s^{E}{}_{11}$ compliance after a thermal treatment at 100°C and the subsequent repoling step.

The changes of the electromechanical properties, expressed as % of the as-received values (Table 1), produced following the thermal treatments and following the repoling step are shown in Fig. 2. The values quoted correspond to those measured after ageing for 1000 h. When not available, the parameter was extrapolated making use of the linear fitting shown in Fig. 1.

The treatment at 100°C hardly affected the ε_{33} dielectric permittivity, the d_{31} piezoelectric coefficient, the k_{31} coupling factor, and the $s^{E}{}_{11}$ compliance (after ageing

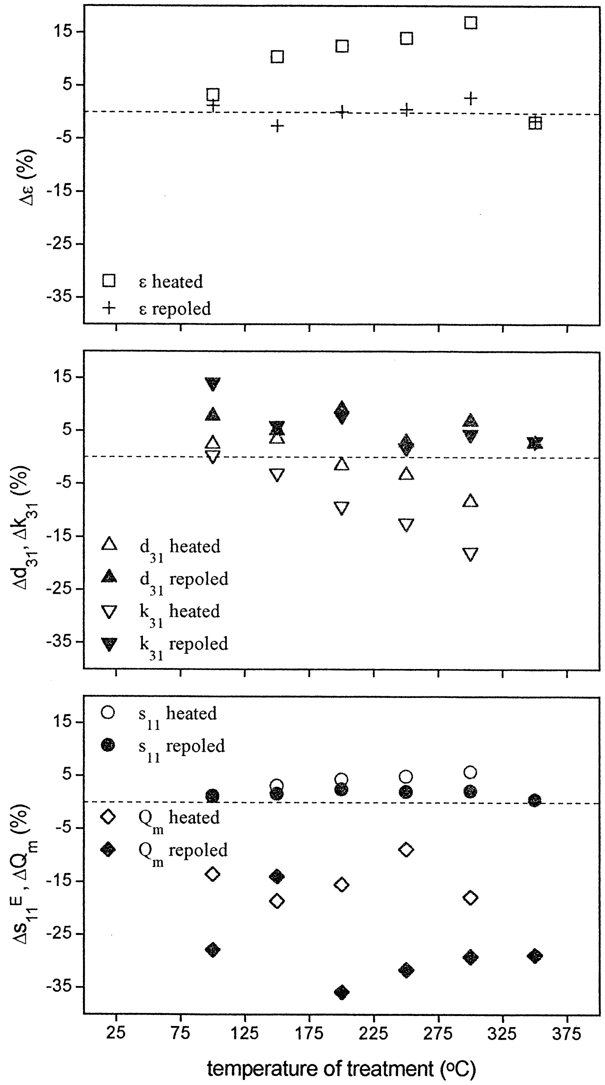

Fig. 2. Percentage change relative to as-received material in the electromechanical properties of PZT-4D piezoceramics after a thermal treatment at different temperatures and ageing, and after a subsequent repoling step and ageing (1000 h). Error bars are not included because they are smaller than the symbols themselves.

for 1000 h, see Fig. 2). However, the mechanical quality factor, Q_m, decreased significantly, ~15%. The treatment at 150°C increased the permittivity by a ~10%, and to a lesser extent the compliance and the d_{31} piezoelectric coefficient. It slightly decreased the coupling factor, and had the same effect on the mechanical quality factor as the treatment at 100°C. Treatments between 200 and 300°C caused ε_{33} and $s^E{}_{11}$ to increase with temperature, by up to ~17 and ~6%, respectively; while d_{31} and k_{31} decreased by up to ~8 and ~18%, respectively. Q_m decreased by ~15% independent on the treatment temperature. The treatment at 350°C did not alter the initial room temperature value of ε_{33}. On the other hand, the remaining admittance resonance was so weak that reliable values for any of the related parameters could not be obtained, though both d_{31} and k_{31} can be assumed to have dropped to very low values.

The repoling after thermal treatment step mostly recovered ε_{33}, d_{31}, k_{31} and $s^E{}_{11}$ (after ageing for 1000 h, see Fig. 2) to their as-received values underlining the reversible character of most of the changes. The final values for d_{31}, k_{31} and $s^E{}_{11}$ were slightly higher than the as received ones, 6, 6 and 2%, respectively. However, Q_m was not recovered, but further decreased, reaching a value 30% lower than for the as received material. Average values after repoling and ageing for the five properties are given in Table 1.

The fact that the values for the ε_{33} and s^E_{11} coefficients hardly increased and that the values for d_{31} and k_{31} did not decrease after the treatment at 100°C and ageing strongly suggests that the polarisation of the ceramics is not affected by a treatment at this temperature. On the other hand, their trends with increasing temperature in the range 150–300°C are consistent with an increasing disorientation of the ferroelectric domains (depolarisation). ε_{33} and s^E_{11} increased because of the depolarisation process, reflecting the dielectric and elastic anisotropies of the single crystal coefficients (ε_{11}, $s^E{}_{33} > \varepsilon_{33}$, $s^E{}_{11}$).[17] d_{31} and k_{31}decreased. The reversibility of the properties after repoling supports this interpretation. It is remarkable that a significant fraction of the polarisation seems to remain after the thermal treatment at 300°C, which is only 20°C below the temperature of the ferroelectric–paraelectric transition. This is manifested by the still high piezoelectric coefficient and coupling factor, -83×10^{-12} C N^{-1} and 0.225. It is necessary to heat the ceramic well above the transition temperature, to 350°C, to depole it and even then, a weak piezoelectric activity is still observed.

There have been also observed irreversible changes during heating, which already occur at 100°C, a very moderate increase of d_{31}, k_{31} and s^E_{11}, and a significant decrease of the mechanical quality factor. Results from the thinning experiments give some insight into this behaviour. The measurements from the experiment involving the removal of ~1 mm at each electrode are shown in Table 2. The ε_{33}, d_{31}, k_{31} and s^E_{11} coefficients were higher for the thinned specimen than for the material with electrodes (see Table 1), but the Q_m was much smaller. The Q_m of the thinned specimen did not show any degradation after being thermally treated at 350°C and subsequent repoled (after ageing for 1000 h). Therefore, the degradation of Q_m seems to take place in the layer next to the electrodes, which has initially different properties than the centre of the ceramic. The results of the progressive thinning experiment on the as-received and depoled and repoled bars are shown in Fig. 3 for the s^E_{11} compliance and the mechanical quality factor. The changes of the parameters as a function of the thickness removed are given as % of the values for the non-thinned specimens. The piezoelectric parameters are not presented but followed the same trend as the compliance. The mechanical quality factor noticeably decreased after removing a layer of 0.25 mm, while s^E_{11}, d_{31} and k_{31} increased. Both the decrease in Q_m and the increase in the other three parameters became more significant after removing 1.25 mm. The coefficients then remained essentially constant with further reduction in specimen thickness up to 3.25 mm. Further thinning caused the fracture of the as-received specimen. The depoled and repoled specimen did not fracture but its parameters showed an anomalous decrease. After having removed a total layer thickness of 4.75 mm, the admittance resonance became so weak that the coefficients could not been inferred. The behaviour of the specimens up until 3.25 mm is consistent with the results in Tables 1 and 2, which suggest that the properties and behaviour of the surface/electrode layer is very different from the interior of the sample. The decrease of all parameters with further thinning is indicative of the depoled and repoled specimen being mechanically damaged, probably in the form of microcracks.

Ag diffusion from the electrodes to the ceramic is known to occur in PZT during the sintering of the electrodes at temperatures ranging between 500 and 850°C. Ag was found to penetrate more than 1 mm into the ceramic in a typical electrode sintering preparation, and

Table 2
Macroscopic parameters for the PZT-4D hard piezoceramics after removing the original electrodes and a 1 mm thick layer of ceramic

	ε_{33}	d_{31} ($\times10^{-12}$ C N^{-1})	k_{31}	$s^E{}_{11}$ ($\times10^{-12}$ m^2 N^{-1})	Q_m
As received	1199	−113	0.313	12.26	498
Repoled	1163	−110	0.311	12.21	497

reached a concentration up to 0.2% in diffusion saturation experiments.[18] It was mostly located at the grain boundaries, though its solution into the perovskite structure could not be ruled out.[18] Ag^{1+} substitutes for Pb^{2+} in PLZT, and its solubility is around 4 mol%.[19] Its solubility has also been studied in PMN-PT and found to be 0.7 mol.%.[20] Above 0.7 mol.% Ag concentration the PMN-PT ceramics blackened. For both cases, the Ag doping reduced significantly the dielectric permittivity. It seems reasonable to accept that some Ag has diffused into our PZT-4D ceramics, which would explain the black colour of the layer next to the electrodes, though below the sensitivity of the EDXS (~1%). Ag is an acceptor dopant. Therefore, it would cause the formation of oxygen vacancies, which may associate with it to form complexes with a dipolar momentum. These complexes are capable of aligning themselves with the spontaneous polarisation within each domain, limiting domain wall mobility.[16] As a consequence, the domain wall contribution to the electromechanical properties, which add to the single crystal one,[21] would be reduced. This is consistent with the behaviour of the layer next to the electrodes. Therefore, it seems reasonable to assume that some Ag has dissolved into the perovskite. However, we have to keep in mind that the PZT-4D composition already has an acceptor dopant, so the nature of the defect complexes may be rather complicated, perhaps involving two types of metallic cations and oxygen vacancies. Within this scheme, we could understand the irreversible changes observed at 100°C as due to the dissociation at that

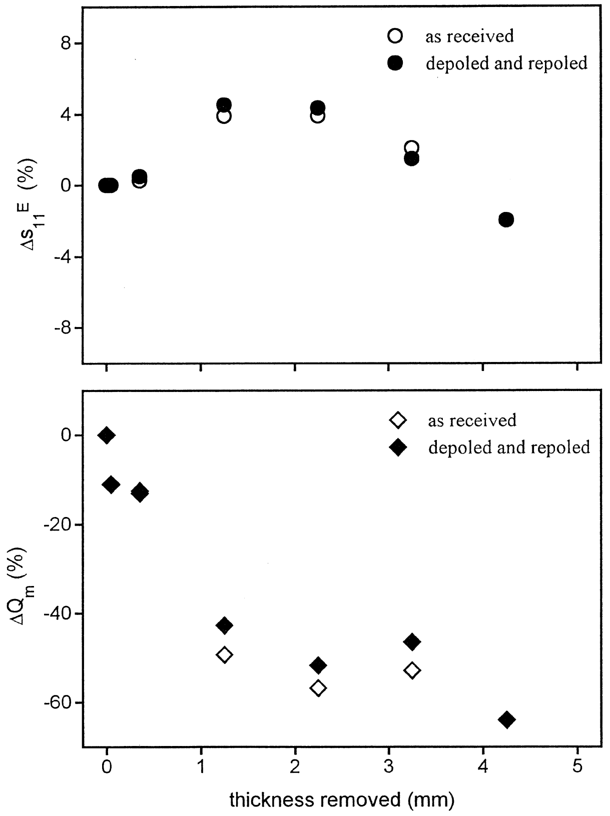

Fig. 3. Percentage change in the s^{E}_{11} compliance and in the mechanical quality factor of an as-received PZT-4D piezoceramic specimen and of a depoled and repoled specimen with the thickness of material removed from one of their Ag electrodes. Error bars are not included because they are smaller than the symbols themselves.

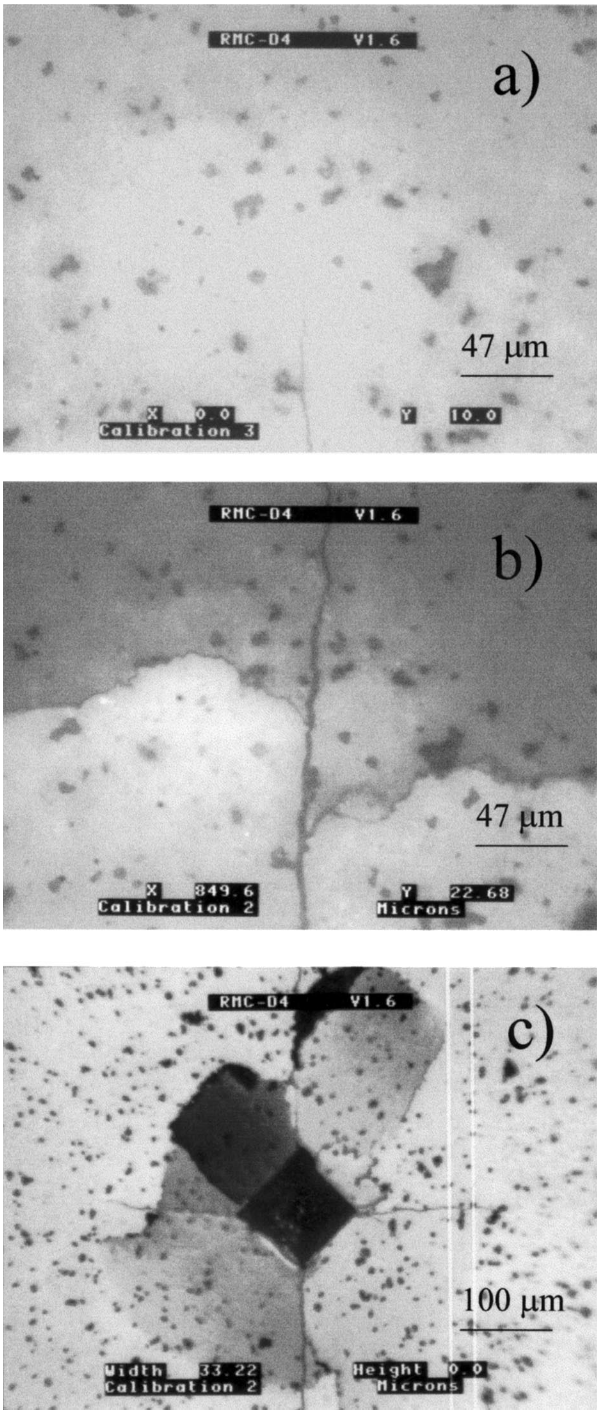

Fig. 4. Vicker's indentation crack in a PZT-4D piezoceramic: (a) before; and (b) after a thermal treatment at 350°C. (c) Indentation impression after a thermal treatment at 350°C showing extensive chipping.

temperature of such defect complexes involving Ag^+. Actually, the observation of ageing effects after the treatment at 100°C, which is known to hardly depole the ceramic, is most probably related to the dissociation of these defects and their subsequent reassociation once the ceramic is cooled down. The fact that the as-received properties cannot be fully recovered indicates that the reassociation of all the initial defects is not possible, at least on the scale of time in which the experiments were done. Measurements after 6 months have shown that the mechanical quality factor is still lower than the as-received one.

The length of Vicker's indentation cracks was highly anisotropic. This behaviour is well known for piezoceramics.[22] The cracks were observed to grow during the thermal treatments, though not during the subsequent repoling. An example is shown in Fig. 4a and b, where a crack perpendicular to the poling direction is shown before and after a thermal treatment at 350°C. Extensive chipping was observed around the impression (see Fig. 4c). Fig. 5 shows the increase in crack length as a function of the temperature of the treatment, expressed as% of their initial length. A systematic growth of the cracks with temperature was observed without any dependence on their direction or initial length. The Vicker's hardness of the as-received specimens was ~2.9 GPa and the anisotropic fracture toughness, evaluated as in Ref. 23 ~2 MPa $m^{1/2}$ along the poling direction, and ~1 MPa $m^{1/2}$ perpendicular to it. These values were reproduced for specimens that had been depoled and repoled. New cracks introduced in previously depoled ceramics were also observed to grow when a second treatment at 350°C was accomplished. The driving force for growth of the cracks and the associated chipping during heat treatments is not clear. The mechanism is likely to be associated with the plastic zone produced by the deformation immediately below the indentation impression.[24] It is the mechanical relaxation of this plastic zone as the indenter is unloaded that drives cracks in brittle materials to their equilibrium length. The heat treatments may have the effect of changing the texture and therefore shape of this zone with the consequences that it produces an additional driving force on the cracks.

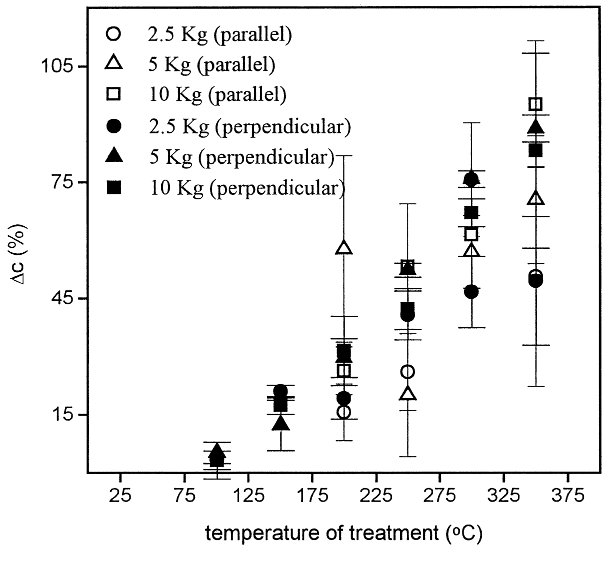

Fig. 5. Growth of Vicker's indentation cracks as a function of the temperature of the thermal treatment for cracks produced with different loads and differently oriented in relation to the poling direction.

4. Conclusions

PZT-4D hard piezoceramics began to depolarise at 150°C, though a high degree of poling remained even after heating at 300°C, only 20°C below the transition temperature ($d_{31} = -83 \times 10^{-12}$ C N^{-1}, $k_{31} = 0.225$). The ceramic progressively depolarised as the temperature of the heat treatment was increased causing ε_{33} and s_{11}^E to increase and d_{31} and k_{31} to decrease.

The ε_{33}, $s^E{}_{11}$, d_{31} and k_{31} properties are smaller for the material in the layer next to the electrodes, and Q_m is higher, compared with the material in the interior (see Tables 1 and 2). This difference in properties can be explained by a decreased mobility of the ferroelastic domain walls in the layer next to the electrodes compared to the interior. This seems to be a consequence of the additional doping of this layer with Ag diffused from the electrodes. Ag^+ is an acceptor dopant that substitutes for Pb^{2+} in the A sites. This substitution produces associated oxygen vacancies, which are well known to increase the electromechanical hardness (decrease domain wall mobility) of piezoelectric ceramics. A significant decrease in the mechanical quality factor of this layer occurs when the ceramics are heated at temperatures as low as 100°C, which is not reversible after cooling. This degradation is probably a consequence of an alteration of the point defect structure leading to greater domain wall mobility.

Acknowledgements

This work was funded through a Marie Curie Fellowship within the Training and Mobility of Researchers Programme of the European Commission (Contract No. ERBFMBICT983359). The support of an EPSRC grant (GR/L90361) is also acknowledged.

References

1. Ochi, A., Takahashi, S. and Tagami, S., Temperature characteristics for multilayer piezoelectric ceramic actuator. *Japanese Journal of Applied Physics*, 1985, **24**(S-3), 209–212.

2. Chang, S. H. and Wang, H. C., A high speed impact actuator using multilayer piezoelectric ceramics. *Sensors and Actuators A*, 1990, **24**, 239–244.
3. Hirose, S., Takahashi, S., Uchino, K., Aoyagi, M. and Tomikawa, Y., Measuring methods for high-power characteristics of piezoelectric materials. *Material Research Society Symposium Proceedings*, 1995, **360**, 15–20.
4. Zheng, J., Takahashi, S., Yoshikawa, S. and Uchino, K., Heat generation in multilayer piezoelectric actuators. *Journal of the American Ceramic Society*, 1996, **79**(12), 3193–3198.
5. White, G. S., Raynes, A. S., Vaudin, M. D. and Freiman, S. W., Fracture behaviour of cyclically loaded PZT. *Journal of the American Ceramic Society*, 1994, **77**(10), 2603–2608.
6. Uchino, K., *Piezoelectric Actuators and Ultrasonic Motors*. Kluwer Academic, Boston, MA, 1997.
7. Takahashi, S. and Hirose, S., Vibration-level characteristics for iron-doped lead zirconate titanate ceramic. *Japanese Journal of Applied Physics*, 1993, **32**, 2422–2445.
8. Alemany, C., Jiménez, B., Mendiola, J. and Maurer, E., Ageing of (Pb,La)(Zr,Ti)O_3 ferroelectric ceramics and the space charge arising on hot poling. *Journal of Materials Science*, 1984, **19**, 2555–2560.
9. Uchino, K., Materials issues in design and performance of piezoelectric actuators: an overview. *Acta Materiala*, 1998, **46**(11), 3745–3753.
10. Morgan Matroc Limited-Unilator Division, Piezoelectric Ceramic Products Catalogue.
11. Carl, K. and Hardtl, K. H., Electrical after effects in Pb(Ti,Zr)O_3 ceramics. *Ferroelectrics*, 1978, **17**, 473–486.
12. Algueró, M., Cheng, B. L., Gibson, I. R., Guiu, F. and Reece, M. J., Crack growth during poling and polarisation reversal in commercial piezoceramics. *Boletín de la Sociedad Española de Cerámica y Vidrio*, 1999. **38**(16), 593–598.
13. Jaffe, B., Cook, W. R. and Jaffe, H., *Piezoelectric Ceramics*. Academic Press, London, UK, 1971.
14. IEEE Standard on Piezoelectricity. ANSI/IEEE Std 176, 1987.
15. Holland, R. and Eernisse, E. P., Accurate measurement of coefficients in a ferroelectric ceramic. *IEEE Transactions on Sonics and Ultrasonics*, 1969, **s-16**(4), 173–181.
16. Robels, U. and Arlt, G., Domain wall clamping by orientation of defects. *Journal of Applied Physics*, 1993, **73**(7), 3454–3460.
17. Uchida, N. and Ikeda, T., Temperature and bias characteristics of Pb(Zr-Ti)O_3 families ceramics. *Japanese Journal of Applied Physics*, 1965, **4**(11), 867–880.
18. Slinkina, M. V., Dontsov, G. I. and Zhukovsky, V. M., Diffusional penetration of silver from electrodes into PZT ceramics. *Journal of Materials Science*, 1993, **28**, 5189–5192.
19. Maher, G. K., Effect of silver doping on the physical and electrical properties of PLZT ceramics. *Journal of the American Ceramic Society*, 1983, **66**(6), 408–413.
20. Sato, Y., Kanai, H. and Yamashita, Y., Effects of silver and palladium doping on the dielectric properties of 0.9Pb(Mg1/3Nb2/3))3-0.1PbTiO3 ceramic. *Journal of the American Ceramic Society*, 1996, **79**(1), 261–265.
21. Zhang, Q. M., Wang, H., Kim, N. and Cross, L. E., Direct evaluation of domain wall and intrinsic contributions to the dielectric and piezoelectric response and their temperature dependence on lead zirconate-titanate ceramics. *Journal of Applied Physics*, 1994, **75**(1), 454–459.
22. Pisarenko, G. G., Chushko, V. M. and Kovalev, S. P., Anisotropy of fracture toughness of piezoelectric ceramics. *Journal of the American Ceramic Society*, 1985, **68**(5), 259–265.
23. Guiu, F., Hahm, B. S., Lee, H. L. and Reece, M. J., Growth of indentation cracks in poled and unpoled PZT. *Journal of the European Ceramic Society*, 1997, **17**, 505–512.
24. Lawn, B. R., Evans, A. G. and Marshall, D. B., Elastic/plastic indentation damage in ceramics: the median/radial crack system. *Journal of the American Ceramic Society*, 1980, **63**(9–10), 574–581.