Journal of the European Ceramic Society 21 (2001) 1377–1381

www.elsevier.com/locate/jeurceramsoc

Properties of nanocrystalline ferroelectric PZT ceramics

Z. Surowiak [a,*], M.F. Kupriyanov [b], D. Czekaj [a]

[a] *University of Silesia, Department of Materials Science, 2, Sniezna St., Sosnowiec, PL-41-200, Poland*
[b] *Rostov State University, Faculty of Physics, 5, Zorge St., Rostov-on-Don, SU-344-104, Russia*

Received 4 September 2000; received in revised form 2 November 2000; accepted 15 November 2000

Abstract

Amorphous nanopowders of $Pb(Zr_{0.5}Ti_{0.5})O_3$ (PZT) solid solution were obtained by sol-gel processing. As-obtained nanopowders ($\bar{r}\approx 30\times10^{-9}$ m) underwent consolidation by conventional ceramic sintering, hot pressing, and rapid thermal annealing. As result of such technological methods PZT ferroelectric ceramic samples were obtained. They exhibited lack of voids, density close to the theoretical X-ray density, homogeneity from both chemical and physical point of view and stoichiometric chemical composition. It was found that each ceramic sample was a conglomerate of grains exhibiting mean dimension $\bar{r}=0.3\text{–}3\times10^{-6}$ m depending on sintering conditions. The nanocrystalline structure of the ceramics grains has been revealed. Dimension of the crystallites ($\bar{D}=20\text{–}75\times10^{-9}$ m) were found to depend on temperature (T_S) and the rate of sintering (ν_T) of the amorphous nanopowders. Dielectric and piezoelectric properties of nanocrystalline PZT ceramics depended on both sol–gel processing conditions and sintering conditions.

Keywords: Ferroelectric properties; Grain size; PZT; Sintering; Sol–gel processes

1. Introduction

Poled ferroelectric materials have gained widespread application in practice due to their piezoelectric properties. In principle, one can speak about common and dynamic applications of piezoelectric materials in electronic technology since the piezoelectric ceramic materials have been developed. Ferroelectric ceramics are used in piezoelectronics mainly as a source of ultrasonic waves. Among other common applications of ferroelectric ceramics we can mention filters of electric signals, functional elements used in many devices like, e.g. stabilisers, piezoelectric transformers, modulators, parametric amplifiers, frequency multipliers, logic circuits, sensors, etc.[1]

Some limitations in replacing piezoelectric crystals (quartz, $LiNbO_3$, etc.) with piezoceramics are due to difficulties in obtaining piezoceramics exhibiting repeatability of parameters, small temperature and time stability of these parameters, strong non-linear phenomena, strong damping of ultrasonic waves, etc. Most of the mentioned shortcomings follow from the nature of piezoceramics, which is connected with the technology of their fabrication.[2,3] It is now considered that possibilities of improving properties of piezoceramics by means of proper selection of parameters of the sintering process of mixed oxide powders have been used up.[4] Therefore, new technological approaches have been developed for a few last years.[5] One of them is the wider and wider utilisation of the sol–gel process in technology of piezoceramics.[6–8]

In the present paper, the sol–gel process was exploited to obtain fine-grained ($\bar{r}\approx30\times10^{-9}$ m) amorphous nanopowders of the solid solution $Pb(Zr_{0.5}Ti_{0.5})O_3$. As result of consolidation and crystallisation of such nanopowders during sintering, ferroelectric PZT ceramic material has been obtained. The ceramic grains exhibited average dimension within the range $\bar{r}=0.3\text{–}3\times10^{-6}$ m and they consisted of crystallites (or, in other words, areas of coherent X-ray scattering) which displayed mean dimension $\bar{D}=20\text{–}75\times10^{-9}$ m and relatively large degree of structural perfection.

The objective of the present paper is to investigate the influence of conditions of the sol–gel process as well as conditions of consolidation and sintering on microstructure, structure and ferroelectric properties of piezoceramics. As an example sol–gel-derived ceramic

* Corresponding author. Tel.: +48-32-291-8243; fax: +48-32-291-8243.
E-mail address: surowiak@us.edu.pl (Z. Surowiak).

0955-2219/01/$ - see front matter
PII: S0955-2219(01)00022-X

material with chemical composition $Pb(Zr_{0.5}Ti_{0.5})O_3$ was taken into consideration.

2. Technology and experimental

The technological process of fabrication of PZT ceramics included two basic stages. First, preparation of amorphous nanopowders of solid solution $Pb(Zr_{0.5}Ti_{0.5})O_3$ by the sol–gel method, second, consolidation of nanopowders and preparation of fine-grained PZT ceramics by conventional ceramic sintering (CCS), hot pressing method (HP) and rapid thermal annealing (RTA).

In the sol–gel process for the preparation of PZT nanopowders, the best results were obtained by introducing lead in a form of trihydrate lead acetate $[Pb(COOCH_3)_2 \times 3H_2O]$ into the environment of the chemical reaction. Lead acetate was added in excess of 5 mole %. Titanium and zirconium were introduced in form of alkoxides, namely $Ti(CH_3(CH_2)_3O)_4$–titanium (IV) butoxide, and $Zr(CH_3(CH_2)_3O)_4$–zirconium (IV) butoxide. In case of the precursors used, the most suitable solvent was found to be an organic solvent — butyl alcohol $CH_3(CH_2)_3OH$.

The reaction of synthesis was carried out in an argon atmosphere by heating the solution for $t = 1$–2 h below the boiling temperature. The waste product of the reaction — ester (butyl acetate) — was removed by simple distillation. After cooling the solution to room temperature the additional amount of solvent was added to obtain (0.8–1)-mol solution and acetylacetone was added as a stabilising agent.

The colloidal solution was then dried at $T = 300°C$. The so-obtained sol–gel derived powder was ground in a mortar with addition of a softening agent for $t = 2$ h. After that the compacts were prepared by pressing in a hydraulic press at pressure $p = 10^8$ Pa. Later on they were annealed at $T = 600°C$ for $t = 2$ h. The powder obtained after disintegrating the annealed pellets was mixed with liquid paraffin (in amount of 5 wt.%) for $t = 2$ h and it was finally used for preparing the ceramic samples. It is worth noting that irrespective on the method of sintering, the powder was pressed at pressure $p = 2 \times 10^8$ Pa to form disk-shaped compacts of $d = 10^{-2}$ m in diameter and $h = 3$–5×10^{-3} m thick. Finally, the compacts were sintered by one of the three methods mentioned above, namely CCS method, HP method or RTA method.

Conventional ceramic sintering was carried out in a KS1350-type furnace in an air atmosphere for $t = 3$ h at temperature T_S^I. The accuracy of the temperature stabilisation was $\Delta T = \pm 2°C$. The heating and cooling rate was $V_T = 300°C/h$. After cooling the samples to room temperature they were powdered and the compacts were formed and sintered a second time at temperature T_S^{II}. Finally, a procedure of fabrication of the ceramic samples was repeated once again so every batch of pellets was sintered a third time at temperature T_S^{III}.

However, it was found that the CCS method carried out at temperature range $T_S^{III} = 827$–$1227°C$ made it possible to obtain PZT ceramic samples exhibiting the average grain dimensions $\bar{r} = 1.2$–4.6×10^{-6} m and density $\rho = 0.82$–$0.92\ \rho_{theor}$. In this connection, the method of rapid sintering was applied. The RTA method made it possible to decrease the time of sintering, provided better stoichiometric composition of PZT ceramics (due to decreased possibility of lead volatilising from the sample) and favoured greater density of the final ceramic pellets ($\rho = 0.96$–$0.97\ \rho_{theor}$). For this purpose the Heat Pulse 300 rapid thermal processor was used. So, the sintering process was carried out at $T_S^{MAX} = 727$–$1227°C$ with the heating rate $v_T = 100$–$300°C/min$.

To obtain greater density of ceramic samples, decrease temperature of sintering (T_S) and decrease average grain size ($\bar{r}$) the hot pressing method was employed. The customised USSK-1-type hot pressing unit was used to produce disk-shaped PZT ceramic pellets of $d = 10^{-2}$ m in diameter and $h = 2 \times 10^{-3}$ m thick. Maximal pressure applied to the samples during sintering worked out at $p_S \approx 60$ MPa. Maximal sintering temperature $T_S = 1327°C$ and maximal heating rate was $v_T = 100°C/min$. Pressure p_S was applied to the sample at room temperature and released after sintering the sample at temperature T_S for a time t_S.

The structure of the ceramic samples was studied by X-ray diffraction (CuK_α radiation; nickel filter) whereas the microstructure was investigated by scanning electron microscopy (SEM).

The mean dimensions $\bar{D}$ of coherent X-ray scattering regions and mean microdeformations $< \Delta d_{hkl}/d_{hkl} >$ were determined from X-ray patterns by an approximation method.[9] The concept of areas of coherent X-ray scattering is taken to mean crystallites mutually oriented at a considerable angle $\alpha > \lambda/\bar{D}$, where λ is the X-ray radiation wavelength. The mean microdeformation $< \Delta d_{hkl}/d_{hkl} >$ is the mean of the relative changes in interplanar distance d_{hkl} inside crystallites.

The density of fired samples was determined by the Archimedes method in water (measuring error $\Delta\rho = \pm 0.02 \times 10^3\ kg/m^3$).

For electrical measurements silver electrodes were deposited on the ceramic surfaces. Capacitance (C) and dielectric loss tangent ($tg\delta$) was measured by a capacitance bridge ($\nu = 1$ kHz) and the dielectric permittivity (ε) was calculated. Remanent polarisation was calculated from the ferroelectric hysteresis loop measured by the Sawyer–Tower method.

Poling treatment of the obtained ceramic samples was carried out in silicone oil at $T = 120°C$ by applying a DC field of $E = 4 \times 10^6$ V/m for $t = 1$ h. The samples were then cooled to room temperature under the influence of the electric field in $t = 30$ min.

The piezoelectric coefficient d_{33} and the electromechanical coupling factor k_p were measured by the

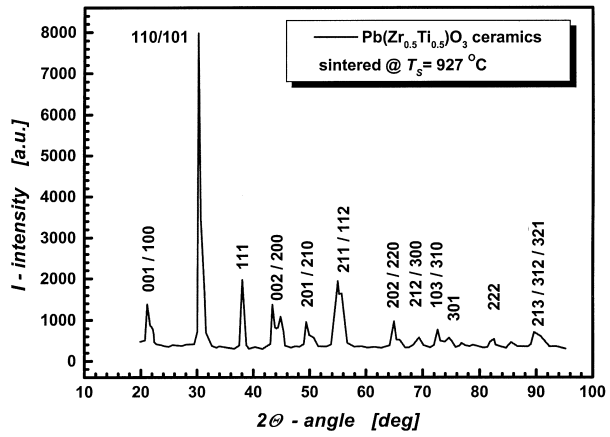

Fig. 1. Typical X-ray pattern of nanocrystalline $Pb(Zr_{0.5}Ti_{0.5})O_3$ ceramics obtained by conventional ceramic sintering at $T_S = 927°C$. Ceramics exhibited: tetragonal structure, $\rho/\rho_{theor} = 85\%$, $\bar{r} = 1.8$ μm, $\bar{D} = 48$ nm, $< \Delta d_{hkl}/d_{hkl} > = 2.5 \times 10^{-3}$.

modified resonance–antiresonance method at room temperature.

3. Results and discussion

It was found that the tetragonal structure was formed irrespective on the method of sintering of amorphous nanopowders $Pb(Zr_{0.5}Ti_{0.5})O_3$ at temperature $T_S > 927°C$ (Fig. 1). It is worth noting that such parameters like: density of ceramics (ρ), the average grain dimension ($\bar{r}$), the mean dimension of areas of coherent scattering ($\bar{D}$), and value of mean microdeformation $< \Delta d_{hkl}/d_{hkl} >$ depend on conditions of sintering at $T_S > 927°C$.

By means of the CCS-method we have obtained ceramics, which exhibited density $\rho = 0.93\ \rho_{theor}$. On the other hand, rapid sintering made possible to obtain ceramic samples with $\rho/\rho_{theor} = 97\%$. Exploiting the hot pressing method made it possible for us to obtain PZT ceramics with density close to the theoretical X-ray density $\rho/\rho_{theor} = 99\%$, which is typical for non-void ceramics.

A positive influence of pressure applied during sintering process on density of ceramics has been confirmed both theoretically and experimentally in previous papers.[10] However, there are no unambiguous explanations of results obtained by the rapid thermal annealing. Especially the reasons of paradoxically small porosity and large density are not clear enough. In this connection, the Refs. 11 and 12 should be mentioned.

Under the conditions of sintering of amorphous nanopowders used in the present work fine-grained PZT ceramics has been obtained. The range of grain dimensions exhibited by ceramic samples were as follows: $\bar{r} = 1.2$–4.6×10^{-6} m in case of CCS-method, $\bar{r} = 0.3$–2.5×10^{-6} m in the case of RTA-method and $\bar{r} = 0.5$–3.0×10^{-6} m in the case of HP (Fig. 2).

It was shown in the present studies that in the case of polycrystalline ferroelectric ceramics there are two factors governing its dielectric and piezoelectric properties. First, we can mention mean dimensions $\bar{D}$ of the areas of coherent X-ray scattering and, second, mean values of the lattice strains, or in other words, microdeformations $< d_{hkl}/d_{hkl} >$ in the direction perpendicular to the surface of the disks. In practice, a decrease in $\bar{D}$ and an increase in $< d_{hkl}/d_{hkl} >$ may be taken as a total measure of the divergence from structural perfection of the crystallites. These divergences are revealed as a broadening of the diffraction peaks in an X-ray diffraction spectrum. One can see in Fig. 3 the dependence of the mean dimension of the crystallite $\bar{D}$ and the mean microdeformation $< \Delta d_{hkl}/d_{hkl} >$ on sintering temperature T_S of $Pb(Zr_{0.5}Ti_{0.5})O_3$ ceramics.

Irrespective on the sintering method the mean dimension of crystallite $\bar{D}$ is seen to increase with increasing in sintering temperature T_S. On the other hand, microdeformation $< \Delta d_{hkl}/d_{hkl} >$ decreases with an increase in the temperature T_S. In other words, the degree of perfection of the crystalline structure improves. It was found that smaller crystallites exhibited more structural defects, but such dependence was quantitatively different for different sintering method. The smallest amount of structural defects exhibited small crystallites, which had grown during hot pressing method (e.g. for $T_S = 1127°C$, $p_S = 60$ MPa, $t_S = 30$ min and $v_T = 100°C/min$ ceramics exhibited $\bar{D} = 36 \times 10^{-9}$ m, $< \Delta d_{hkl}/d_{hkl} > = 0.8 \times 10^{-3}$). The RTA method made possible to grow crystallites with larger microdeformations (e.g. for $T_S^{MAX} = 1227°C$, $v_T = 100°C/min$ ceramics exhibited $\bar{D} = 36 \times 10^{-9}$ m,

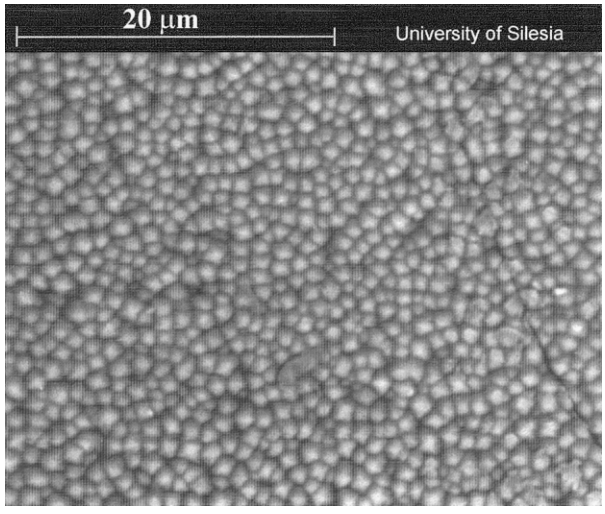

Fig. 2. Microphotography (×25,000) of the etched surface of $Pb(Zr_{0.5}Ti_{0.5})O_3$ ceramics sintered by HP method under the following conditions: $T_S = 927°C$, $p_S = 60$ MPa, $t_S = 30$ min, $v_T = 100°C/min$. Ceramics exhibited: tetragonal structure, $\rho/\rho_{theor} = 95\%$, $\bar{r} = 1.0$ μm, $\bar{D} = 28$ nm, $< \Delta d_{hkl}/d_{hkl} > = 2.0 \times 10^{-3}$.

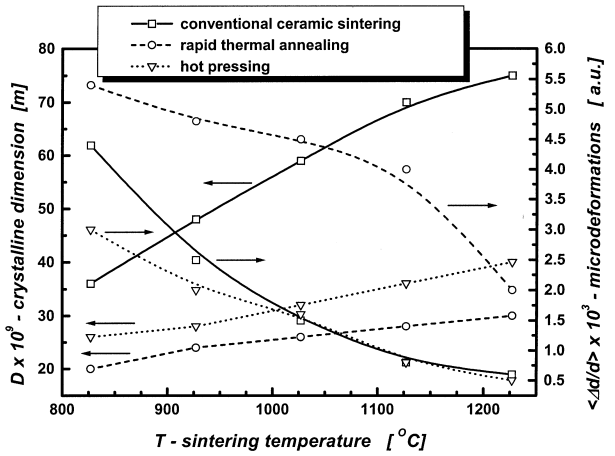

Fig. 3. Dependence of degree of perfection of the nanocrystallites which constitute the grains of $Pb(Zr_{0.5}Ti_{0.5})O_3$ ceramics on temperature of sintering T_S: mean dimensions of areas of coherent X-ray scattering ($\bar{D}$) (mean dimensions of crystallites) and mean microdeformations $< \Delta d_{hkl}/d_{hkl} >$ are shown.

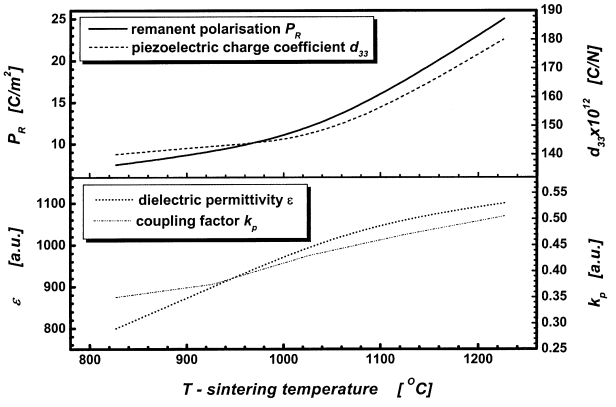

Fig. 5. Dependence of dielectric permittivity (ε), remanent polarisation (P_R), electromechanical coupling coefficient (k_p) and piezoelectric charge coefficient (d_{33}) on sintering temperature (T_S) for $Pb(Zr_{0.5}Ti_{0.5})O_3$ ceramics obtained by CCS method (the smaller T_S the larger $< \Delta d_{hkl}/d_{hkl} >$).

$< \Delta d_{hkl}/d_{hkl} > = 3.5 \times 10^{-3}$). The CCS method, however, caused the largest microdeformations in small grains (e.g. for $T_S^{III} = 927°C$ and $t_S = 3$ h ceramics exhibited $\bar{D} = 36 \times 10^{-9}$ m, $< \Delta d_{hkl}/d_{hkl} > = 4.4 \times 10^{-3}$). In this connection, it should be noted that the degree of structural perfection of nanocrystallites influences strongly dielectric and piezoelectric properties of PZT ceramics (Fig. 4 and 5).

With an increase in the mean microdeformation the maximal value of permittivity ε_m at temperature T_m decreases. The characteristic peak on $\varepsilon(T)$ curve broadens what is typical for the diffuse phase transition[6] (Fig. 4). Value of the basic piezoelectric parameters of poled ferroelectric ceramics, namely piezoelectric charge coefficient d_{33} and electromechanical coupling coefficient

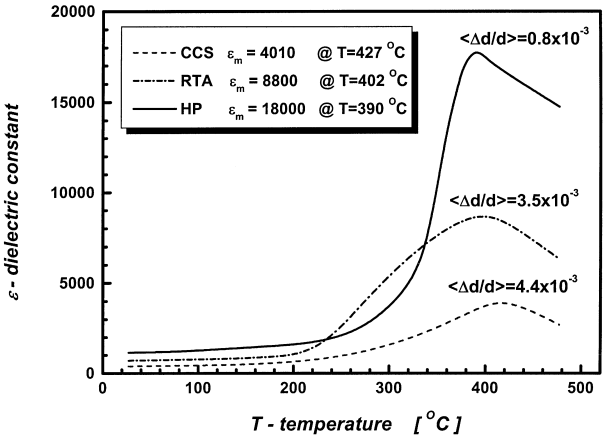

Fig. 4. Dependence of dielectric permittivity (ε) on temperature T for $Pb(Zr_{0.5}Ti_{0.5})O_3$ ceramic samples exhibiting similar grain dimensions ($\bar{r}$) and mean dimensions of crystallites ($\bar{D} \approx 36$ nm), but different microdeformations $< \Delta d_{hkl}/d_{hkl} >$. The samples prepared by: CCS method (at $T_S^{III} = 927°C$ and $t_S = 3$ h) $-\bar{r} = 1.2$ μm, $< \Delta d_{hkl}/d_{hkl} > = 4.4 \times 10^{-3}$; RTA method (at $T_S^{MAX} = 1227°C$ and $v_T = 100°C/min$) $-\bar{r} = 2.5$ μm, $< \Delta d_{hkl}/d_{hkl} > = 3.5 \times 10^{-3}$ and HP method ($at T_S = 1127°C$, $p_S = 60$ MPa, $t_S = 30$ min and $v_T = 100°C/min$) $—\bar{r} = 2.0$ μm, $< \Delta d_{hkl}/d_{hkl} > = 0.8 \times 10^{-3}$, are shown.

k_p is seen to increase with increasing sintering temperature T_S (decreasing microdeformations) (Fig. 5).

While analysing the obtained data we found the close relation between the average grain dimension ($\bar{r}$) and mean dimension of crystallites ($\bar{D}$). The parameter $\bar{D}$increases with an increase in $\bar{r}$ but in a different way for a particular sintering method. In the case of sintering of sol–gel derived amorphous nanopowders, the mean dimension of crystallites ($\bar{D}$) which constituted $Pb(Zr_{0.5}Ti_{0.5})O_3$ ceramics did not exceed $\bar{D} \leqslant 100$ nm what is a typical dimension for nanostructures.

4. Conclusions

By means of sol–gel method, amorphous nanopowders ($\bar{r} \approx 30 \times 10^{-9}$ m) of the solid solution $Pb(Zr_{0.5}Ti_{0.5})O_3$ were obtained and they were used as initial material for ceramic technology.

The technological conditions that restricted the grain growth process, favoured an increase in density and decrease in porosity as well as provided perfection of the crystalline structure of the crystallites constituting the ceramic grains were selected. The best results were obtained in case of sintering of amorphous powders by rapid, high-pressure hot pressing method. The fine-grained ($\bar{r} \geqslant 0.5$ μm) and non-void ($\rho = 99\%$ ρ_{theor}) ceramics has been obtained. The ceramic grains were constituted from nanocrystallites of $\bar{D} \geqslant 20 \times 10^{-9}$ m exhibiting high structural perfection ($< \Delta d_{hkl}/d_{hkl} > = 10^{-4}$–$3 \times 10^{-3}$).

Fine-grained ceramics exhibited good ferroelectric properties. For HP-method ($T_s = 1127°C$) the basic parameters were as follows: $\varepsilon(300\ K) = 1100$, $\varepsilon_m = 18000$, $P_R = 0.25\ C/m^2$, $k_p = 0.5$, $d_{33} = 180 \times 10^{-12}\ C/N$. Such results were obtained at smaller sintering temperature as compared with temperature of synthesis and sintering of mixed oxide powders.

Acknowledgements

This work was supported by the Committee for Scientific Research (KBN), Poland, under the research grant No. 7 T08D 005 17.

References

1. Xu, Y., *Ferroelectric Materials and Their Applications*. North-Holland, New York, 1991 pp. 72–100.
2. Rahaman, M. N., *Ceramic Processing and Sintering*. Marcel Dekker, New York, 1995 pp. 1–37.
3. Ring, T. A., *Fundamentals of Ceramic Powder Processing and Synthesis*. Academic Press, New York, 1996 pp. 7–41.
4. Murray, G. T., *Introduction to Engineering Materials*. Marcel Dekker, New York, 1993 pp. 479–534.
5. De Araujo, C. P., Scott, J. F. and Taylor, G. W. (eds.), *Ferro-Electric Thin Films: Synthesis and Basic Properties*. Gordon and Breach, Amsterdam, 1996, pp. 1–10.
6. Malič, B., Kosec, M., Smolej, K. and Stavber, S., Effect of precursor type on the microstructure of $PbTiO_3$ thin films. *Journal of the European Ceramic Society*, 1999, **19**, 1345–1348.
7. Colla, E. L., Kholkin, A. L., Taylor, D., Tagantsev, A. K., Brooks, K. G. and Setter, N., Characterisation of the fatigued state of ferroelectric PZT thin-film capacitors. *Microelectronic Engineering*, 1995, **29**, 145–148.
8. Scott, J. F., The physical of ferroelectric ceramic thin films for memory applications. *Ferroelectric Review*, 1998, **1**, 1–129.
9. Surowiak, Z., Czekaj, D., Bakirov, A. A. and Dudkevich, V. P., Influence of conditions of r.f. sputtering on chemical constitution and structure of PZT-type thin films. *Integrated Ferroelectrics*, 1999, **23**, 229–257.
10. Cross, L. E., Ferroelectric materials for electromechanical transducers applications. *Jpn. J. Appl. Phys.*, 1995, **34**, 2325–2532.
11. Griswold, E. M., Weaver, L., McIntyre, D. S., Sayer, M. and Calder, I. D., Crystallization of rapid thermal processed PZT. *Integrated Ferroelectrics*, 1995, **10**, 123–130.
12. Daush, D. E. and Haertling, G. H., Comparison of properties between rapid thermally processed and conventional furnace pyrolyzed PLZT thin films. *Integrated Ferroelectrics*, 1994, **5**, 311–320.