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# Thick film capacitors with relaxor dielectrics

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**Abstract**

Thick film pastes destined for class II capacitors were developed, based on four relaxor ferroelectrics: $Pb(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Fe_{1/2}Nb_{1/2})O_3$, $Pb(Fe_{2/3}W_{1/3})O_3$ and $Pb(Zn_{1/3}Nb_{2/3})O_3$, and two normal ferroelectrics: $PbTiO_3$ and $BaTiO_3$. The layers made of these pastes, without any addition of nonferroelectric fluxes, can be fired according to the conventional thick film procedure at 880–950 °C. The dielectric constant and dissipation factor of the layers were determined in the temperature range −55 to +125 °C and in the frequency range 10 Hz to 1 MHz. A model of the equivalent circuit was proposed on the basis of impedance spectroscopy studies. Resistivities of the thick films were measured in the temperature range 20–500 °C. Relaxor thick film capacitors manufactured in this work are characterised by: low firing temperature, high dielectric constant (200–4000), low changes in capacitance after dc bias ageing and good resistance to moisture.

*Keywords:* $BaTiO_3$; Capacitors; Dielectric properties; $Pb(Fe,Nb)O_3$; $Pb(Fe,W)O_3$; $Pb(Mg,Nb)O_3$; $PbTiO_3$; $Pb(Zn,Nb)O_3$; Thick-films

## 1. Introduction

Relaxor ferroelectric materials of general formula $Pb(B'B'')O_3$, owing to their high dielectric constant, broad maxima of dielectric characteristics, relatively low sintering temperature and low electrical field dependence, are widely used in multilayer ceramic chip capacitors (MLCC). In spite of the great interest paid to relaxor ferroelectrics for several years, little published information is available on thick film capacitors based on these materials.[1–4]

Thick film technology has successfully been applied in microelectronics for a few decades. This simple and inexpensive technique, consisting in deposition of special pastes on insulating substrate by screen printing, offers good miniaturisation and reliability for such elements as: conductors, resistors, capacitors, inductors, sensors, etc.

In this work, pastes containing four relaxors: $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN), $Pb(Fe_{2/3}W_{1/3})O_3$ (PFW) and $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN), and two normal ferroelectrics: $PbTiO_3$ (PT) and $BaTiO_3$ (BT) were developed. The essential component of most pastes was PFW. Because of the low sintering temperature of this compound the developed compositions, in spite of lack of any glass frit or other nonferroelectric fluxes, can be fired at temperatures lower than 900 °C. Typically, a significant amount of fluxing agents (even 20%) is used to sinter ferroelectric layers at temperatures corresponding to the conventional thick film technology. Generally, the presence of nonferroelectric phases causes a significant decrease in dielectric constant (relative permittivity) values of layers as compared with bulk ceramics.

PMN, PZN, PFN and PFW relaxors have a disordered perovskite-type structure and exhibit the so-called diffuse or broadened paraelectric–ferroelectric transition. Relaxor behaviour has been attributed to local inhomogeneity in the distribution of the B-site cations which leads to formation of microregions characterised by slightly different Curie temperatures.

The temperatures of phase transition for pure compounds, used in this work as components in thick film pastes, are approximately: −10, 140, 110, −90, 490 and 120 °C for PMN, PZN, PFN, PFW, PT and BT, respectively. Combination of various mentioned above materials can provide ceramic compositions whose parameters, like Curie temperature, permittivity, temperature coefficient of capacitance, are tailored to the expected values.

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## 2. Experimental

Relaxor ferroelectrics PMN, PFN, PFW and PZN were synthesised by the two-step "columbite" or "wolframite" methods described by Swartz and Shrout.[5,6] According to this procedure the oxides of B-site cations prereact prior to the reaction with PbO in order to achieve the perovskite structure and to prevent the formation of detrimental phases with pyrochlore structure. In the case of PZN synthesis the addition of 10 mol% of $BaTiO_3$ was used to enhance stability of the perovskite structure. Small amounts of $MnO_2$ and $Co_3O_4$ (0.05–0.5 mol%) were introduced to the batches in order to increase resistivity and decrease dissipation factor. The constituent oxides were mixed in appropriate proportions, ball-milled in alcohol, dried, palletised and calcined. The calcination temperatures were 950–1000 °C for the first synthesis step and 800–900 °C for the second one. During the second reaction step pellets were placed in closed crucibles and covered with $PbZrO_3$ powder enriched with PbO in order to control lead volatilisation. Phase compositions of the powders after the syntheses were determined by X-ray diffraction analysis.

The preliminary choice of compositions destined for thick film capacitors was carried out in a simple and fast manner and with a minimal material consumption by means of a Leitz heating microscope. Basing on the registration of changes in sample dimensions in the temperature range 20–1250 °C the optimal sintering range, the softening temperature and the melting temperature can be determined.

The synthesised relaxor materials were used to manufacture thick film pastes. They were prepared by mixing nonorganic powders, previously ball milled, with an organic binder—ethyl cellulose solution in terpineol, without any addition of glass frit.

Thick film capacitors were screen printed on 96% $Al_2O_3$ substrates. The bottom and top electrodes were made of Ag, Au and Pt pastes. The dielectric layers based on relaxor compositions were deposited using a 260-mesh screen, dried and fired in a VI-zone BTU belt furnace at peak temperature 880–950 °C for 10 min. The printing–drying–firing cycle was carried out two or three times. The thicknesses of layers, examined by means of a Hobson–Taylor profilograph, were 20 and 30 μm for double and triple dielectric layers, respectively.

Resistivity of the layers was measured in the temperature range 20–500 °C by means of a 6517A Keithley electrometer and a Philips resistance meter. Dielectric constant and dissipation factor were determined in the temperature range $-55$ to $+140$ °C at frequencies 10 Hz to 1 MHz using a LCR QuadTech bridge model 7600 B. Preliminary impedance spectroscopy studies of relaxor thick films in the frequency range $10^{-2}$–$10^{7}$ Hz were carried out at room temperature by means of a Solartron frequency response analyser, model 1260 A. The effect of the direct current bias of 2 kV/mm on dielectric characteristics was investigated in the temperature range $-25$ to $+100$ °C. Changes in capacitance after the moisture test (100 h, relative humidity- 95%, 40 °C) and after ageing under the dc field of 1 kV/mm at 70 °C for 1–500 h were determined.

Scanning electron microscope and microprobe were applied to examine the microstructure and the chemical composition of thick film dielectrics as well as the interaction between ceramic layers and electrodes made of various conductive pastes.

## 3. Results and discussion

X-ray diffraction analysis confirmed that single perovskite phases were formed as a result of the syntheses of the examined materials. Little or no pyrochlore phases were detected.

On the basis of the data obtained by means of the heating microscope the compositions with a too high sintering temperature were eliminated and those with the temperature of the ultimate shrinkage not exceeding 900 °C, were chosen. Thus, the attainment of compactness of the chosen dielectric compositions after the conventional thick film firing procedure was guaranteed. Fig. 1 presents behaviour of a sample with composition 0.75PFW–0.25PT during heating in the temperature range 700–1110 °C. It can be seen that up to 800 °C the initial dimensions (the initial height of the sample at 20 °C was six units at the scale) did not change, at 850 °C the shrinkage started, in the temperature range 870–1060 °C the dimensions of the pellet were stable (five units at the scale), at 1100 °C softening of the sample took place and at 1110 °C—its violent melting and flow.

It was found that the developed layers containing 10–80 mol% of PFW could be densified during the conventional thick film firing process at peak temperature 880 °C. In the case of compositions with PFN serving as a component lowering the sintering temperature, the maximum temperature was higher (900–950 °C). It was very important that the firing process of dielectric layers could be carried out without any glass addition, which would dramatically degrade permittivity of a capacitor material.

In Fig. 2 scanning electron micrograph of a fracture of the thick film capacitor with 0.75PFW–0.25PT dielectric is presented. The relaxor layer is dense, with small porosity, looking like a fine grained bulk ceramic.

The dielectric properties of thick films based on relaxors PMN, PZN, PFN and PFW are given in Table 1. The highest values of dielectric constant was achieved for 0.8PFW–0.2PT and 0.75PFW–0.25PT layers.

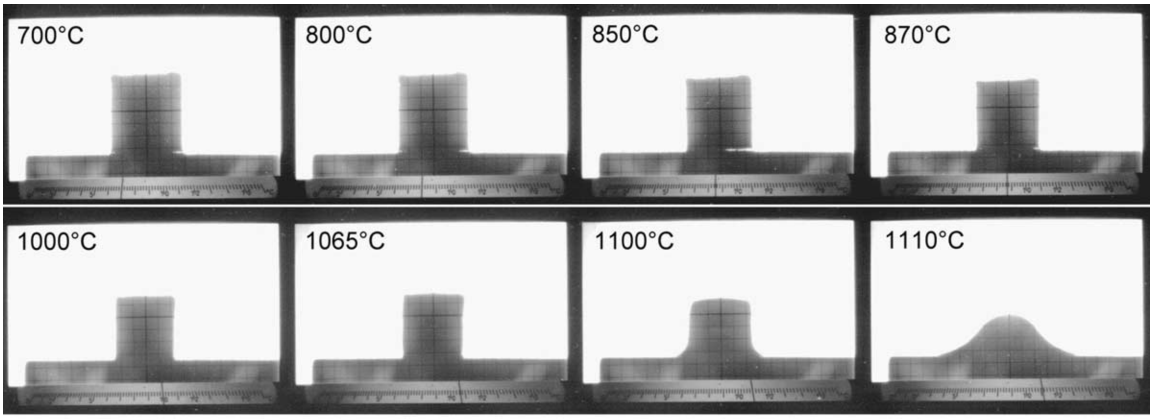

Fig. 1. Change in dimensions of 0.75PFW–0.25PT sample during testing in the heating microscope in the temperature range 700–1100 °C.

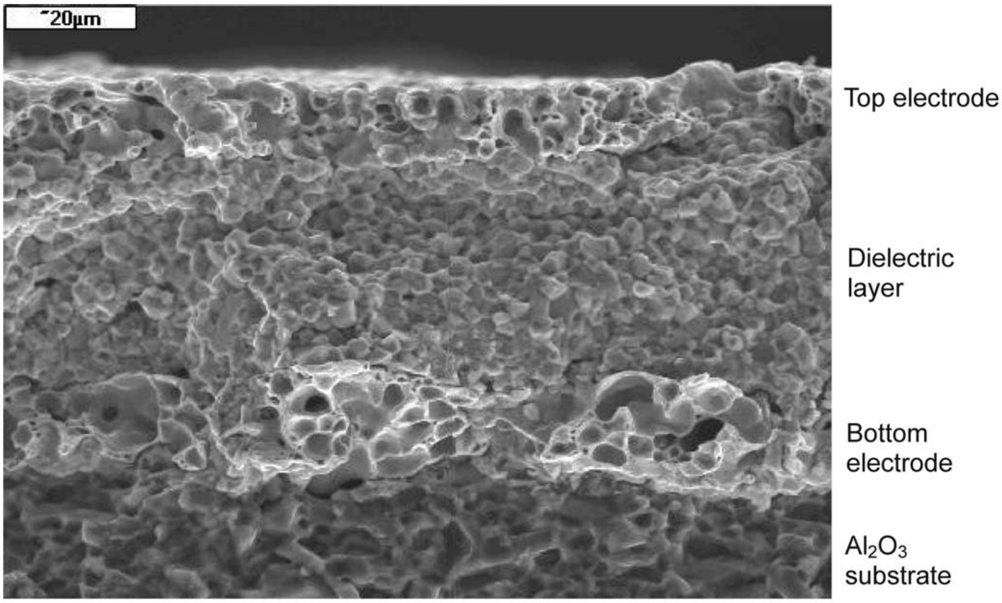

Fig. 2. SEM micrograph of fractured cross-section of thick film capacitor with 0.75PFW–0.25PT dielectric.

Fig. 3 illustrates temperature dependence of relative permittivity ($\varepsilon_r$) for the 0.8PFW–0.2PT thick film fired at 880 °C, measured in the frequency range 10 Hz to 1 MHz. The $\varepsilon_r$ maximum was 3000–3200 and occurred at 20 °C. The dissipation factor was 0.005–0.025 at room temperature. The influence of frequency on location and magnitude of the maximum on $\varepsilon_r = f(T)$ curves for thick films developed in this work was not so significant as in the case of bulk relaxor ceramics. Curie temperatures seemed to be almost independent of frequency. However, in the case of samples with a high PFW content, dielectric constant and dissipation factor values dramatically increased at frequencies below 100 Hz and at higher temperatures (Fig. 3). This indicates that the contribution of conductivity in such conditions became significant. At higher frequencies (100 kHz and 1 MHz) $tg\delta$ was low ($<0.01$).

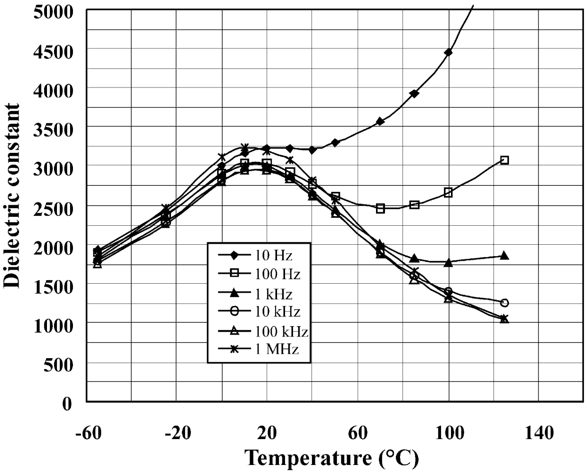

Fig. 3. Temperature dependence of dielectric constant of 0.8PFW–0.2PT thick film fired at 880 °C.

Table 1
Dielectric properties of thick films based on relaxor materials

| Composition, mol fraction | 0.8PFW–0.2PT (0.5 mol% $MnO_2$) | 0.75PFW–0.25PT (0.5 mol% $MnO_2$) | 0.3PMN–0.3PZN–0.3PFW –0.1BT(0.2 mol% $MnO_2$) | 0.5PMN–0.3PFN–0.1PFW –0.1BT(0.2 mol% $MnO_2$) | 0.6PZN–0.3PFW–0.1BT (0.4 mol% $MnO_2$) | 0.5PMN–0.3PFN–0.15BT –0.05PT(0.05 mol% $MnO_2$) |
|---|---|---|---|---|---|---|
| Firing conditions | 3×880 °C, 10 min | 3×880 °C, 10 min | 3×880 °C, 10 min | 3×880 °C, 10 min | 3×880 °C, 10 min | 3×950 °C, 10 min |
| Curie temperature, °C | 20 | 50 | 30 | 30 | 120–140 | 20–30 |
| Dielectric constant at $T_C$(100 Hz to 1 MHz) | 3000–3200 | 3300–4100 | 1400–1500 | 500 | 850–1400 | 230 |
| Dielectric constant at 20 °C (100 Hz to 1 MHz) | 3000–3200 | 2700–3400 | 1400–1500 | 500 | 560–620 | 230 |
| $tg\delta$ at 20 °C (100 Hz to 1 MHz) | 0.005–0.025 | 0.005–0.02 | 0.015–0.03 | 0.01 | 0.015–0.025 | 0.002–0.006 |
| Resistivity at 20 °C, Ωcm | $10^{10}$ | $10^{11}$ | $10^{12}$ | $10^{13}$ | $8\times10^{12}$ | $2\times10^{14}$ |
| TCC (1 kHz),% +10 to 85 °C | −46 to 0 | −14 to +18 | −17 to +1 | −10 to +1 | −4 to +33 | −7 to 0 |
| −25 to 85 °C | −46 to 0 | −40 to +18 | −20 to +1 | −10 to +1 | −19 to +33 | −7 to 0 |
| −55 to 125 °C | −58 to 0 | −50 to +18 | −33 to +1 | −22 to +1 | −29 to +52 | −15 to 0 |
| EIA specifications | X7U | X7U, Z5S | X7T, Y5S | X7S, Y5R | Y5U | X7R |

In Fig. 4 and 5 the comparison of temperature dependencies of $\varepsilon_r$ and $tg\delta$ measured at 1 MHz are given for some of the examined layers. Fig. 6 presents differences in the values of the temperature change of capacitance ($\mathrm{TCC} = 100\%(C_T - C_{20°})/C_{20°})$) at 1 kHz.

The maximum dielectric constant for the 0.75PFW–0.25PT layers fired at 880 °C was 3300–4100 in the frequency range 10 Hz to 1 MHz and was observed at 50 °C. The TCC values were rather high, fulfilling according to EIA standards X7U (−55 to +125 °C, $-56\% < \mathrm{TCC} < +33\%$) and Z5S specifications (10–85 °C, $-22\% < \mathrm{TCC} < +22\%$). The samples fired at 900 °C exhibited a higher value of $\varepsilon_r$ at the level of 3700–4700, a higher temperature change of capacitance and a higher Curie temperature (70 °C).

The influence of $PbTiO_3$ as a shifter of Curie point of the compositions based on $Pb(Fe_{2/3}W_{1/3})O_3$ toward higher temperatures was evident. The values of $T_c$ were

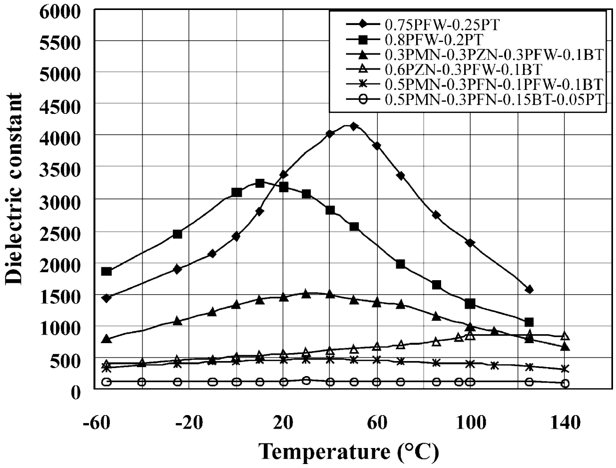

Fig. 4. Temperature dependence of dielectric constant for various relaxor thick film capacitors at 1 MHz.

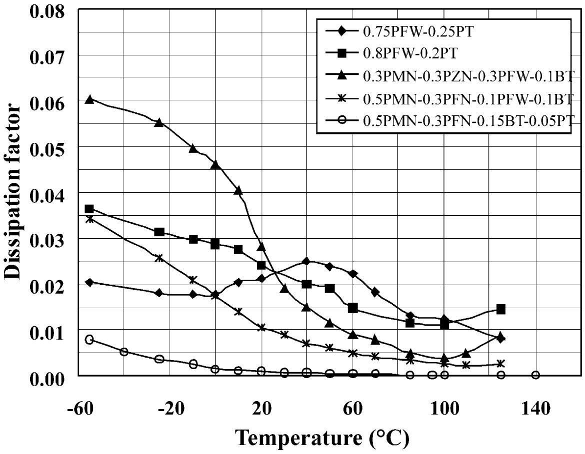

Fig. 5. Temperature dependence of dissipation factor for various relaxor thick film capacitors at 1 MHz.

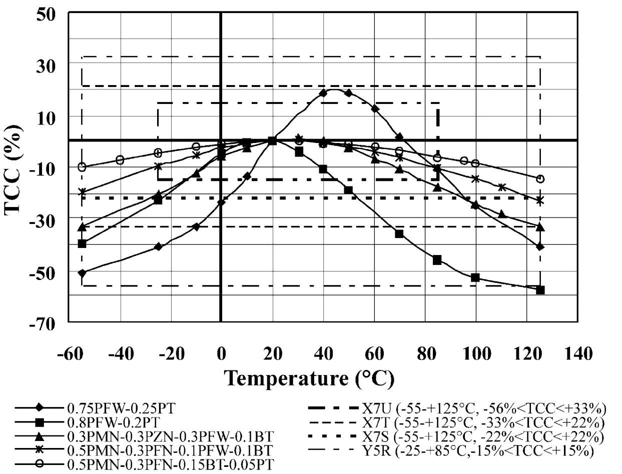

Fig. 6. Temperature change of capacitance for various relaxor thick film capacitors at 1 kHz.

−25, 20 and 50 °C for 10, 20 and 25 mol% of this compound, respectively.

The serious disadvantages of undoped $Pb(Fe_{2/3}W_{1/3})O_3$ ceramics are a rather poor resistivity and a high dissipation factor. It is known that these parameters can be significantly improved by the addition of small amounts of $MnO_2$.[7] The resistivities of the obtained PFW–PT layers with the addition of this oxide were rather good—$10^{10}$–$10^{11}$ Ωcm at room temperature. The layers 30 μm thick withstood 250 V load.

Thick films with the composition 0.3PMN–0.3PZN–0.3PFW–0.1BT were characterised by: maximum dielectric constant—1500, Curie temperature—about 30 °C, *tgδ*—0.015–0.03 in the frequency range 100 Hz to 1 MHz and high resistivity at 20 °C—about $10^{12}$ Ωcm.

The 0.6PZN–0.3PFW–0.1BT layers showed the maximum dielectric constant of 850–1400, a rather high Curie temperature (about 130 °C) and high resistivity at 20 °C (about $10^{13}$ Ωcm).

Thick films with the composition 0.5PMN–0.3PFN–0.1PFW–0.1BT exhibited a lower dielectric constant (about 500). The advantageous features of this composition are the following: the Curie temperature—about 30 °C, relatively low dissipation factor—below 0.03 in the temperature range −25 to +85 °C (0.01 at 20 °C) and a low temperature change of capacitance. The TCC values were −10% to +1% in the temperature range −25 to +85 °C and −22% to +1% in the temperature range −55 to +125 °C. Thus, EIA specifications Y5R (−25 to 85 °C, $-15\% < \text{TCC} < +15\%$) and X7S (−55 to +125 °C, $-22\% < \text{TCC} < +22\%$) were fulfilled. Resistivity of these layers at 20 °C was high—about $10^{13}$ Ωcm.

The 0.5PMN–0.3PFN–0.15BT–0.05PT layers exhibited a very low temperature change of capacitance (−15% to 0%) meeting X7R requirements (−55 to +125 °C, $-15\% < \text{TCC} < +15\%$), low dissipation factor ($< 0.006$ at 20 °C) and high resistivity ($> 10^{14}$ Ωcm). However, the values of dielectric values were small (about 200) and the firing temperature 950 °C was much higher than that of the layers containing PFW.

The values of electrical permittivity presented above for relaxor thick films were, of course, lower than those of the bulk ceramics with the same compositions. However, these differences did not exceed one order of magnitude. The $\varepsilon_r$ values for thick films with a high PFW content, given in Table 1 (3000–3200 and 3300–4100 for 0.8PFW–0.2PT and 0.75PFW–0.25PT, respectively), were lower only less than two times than those for the bulk ceramics (5400–5800 and 5400–6200 for 0.8PFW–0.2PT and 0.75PFW–0.25PT, respectively). The dielectric constants for multicomponent sintered materials with a lower PFW content, reported in another work,[8] were: 6400–7100 for 0.3PMN–0.3PZN–0.3PFW–0.1BT, 4400–5200 for 0.3PMN–0.3PZN–0.3PFN–0.1BT and 3600–4100 for 0.5PMN–0.3PFN–0.15BT–0.05PT ceramics, respectively. These values were a few times higher than those for the analogous thick film compositions presented in Table 1.

It was found that the short time (1 min) effect of the dc bias of 2 kV/mm caused a small decrease in capacitance of the developed thick films (0.1–0.8%). No significant influence of the measurement temperature in the range −25 to +85 °C was observed. Ageing under the direct field of 1 kV/mm during 1–500 h led to a small capacitance change up to about 2%. There occurred stabilisation of capacitance after approximately 100 h under applied voltage. This behaviour, advantageous for capacitors, is illustrated in Fig. 7.

After moisture tests the changes in capacitance of the relaxor thick film capacitors without encapsulation were rather small, at the level of 1–1.4% and the increase in dissipation factor was also small—about 0.0001–0.006. The good resistance to moisture was the consequence of the excellent compactness of the dielectric layers and

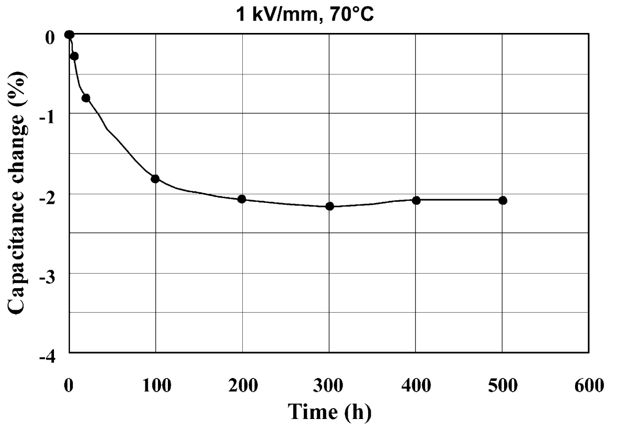

Fig. 7. Changes in capacitance of a thick film relaxor capacitor after testing under dc bias of 1 kV/mm at 70 °C.

indicated that these capacitors could be applied without additional encapsulation by a resin or a glaze.

In Fig. 8 the results of conductivity measurements carried out in the temperature range 20–500 °C are shown for an exemplary relaxor thick film. Temperature dependence of conductivity followed well the Arrhenius law:

$$\sigma = \sigma_o \exp\frac{-E}{k_{\mathrm{B}}T}$$

where $E$ is activation energy of electrical conductivity, $k_{\mathrm{B}}$—Boltzmann constant, $T$—temperature.

The slope of the plots in the considered temperature range has changed, indicating that a change in the conduction mechanism took place. In the temperature range from 20 to 240-280 °C the slope of $\ln \sigma = f(1/T)$ was lower, with the activation energy of 0.7–0.8 eV. At higher temperatures (above 280–350 °C) the slope was higher and the activation energy increased to 1.1–1.2 eV. Such a course of the relationship between conductivity and temperature suggested that a transition from dominating dopant mechanism at lower temperatures to intrinsic one at higher temperatures occurred.

In Figs. 9 and 10 some results of impedance spectroscopy measurements were given for relaxor thick film capacitors. On the basis of these data the model of equivalent circuit was determined by the use of a special computer program, described by Boukamp.[9] This model presented in Fig. 11 and in Table 2 is composed of:

- resistance R 1—assigned to the electrodes
- inductance L 1 in series with R 1—corresponding to the inductance of the leads; and
- parallel combination of the constant phase element CPE 1 and the second constant phase element CPE 2 connected in series with the resistance R 2—representing the dielectric layer.

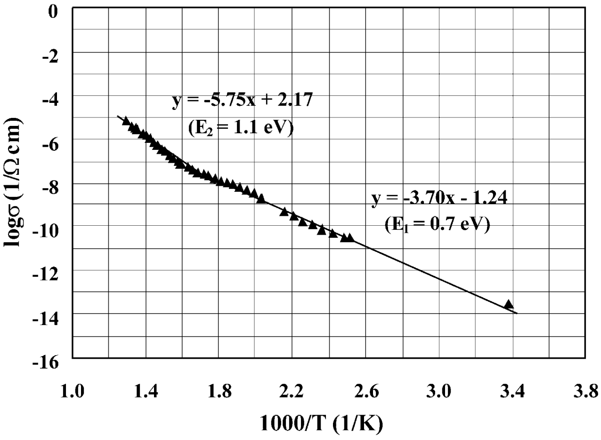

Fig. 8. Temperature dependence of electrical conductivity in the temperature range 20–500 °C for 0.5PMN–0.3PFN–0.1PFW–0.1BT thick film (+0.2 mol% $MnO_2$).

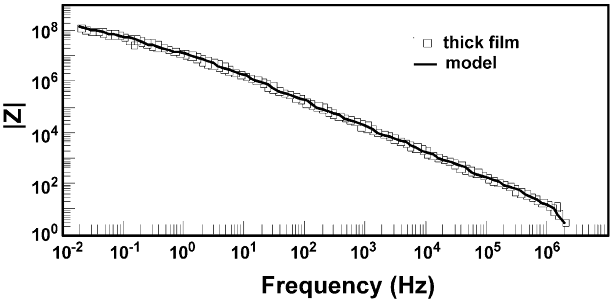

Fig. 9. Dependence of impedance modulus $|Z|$ on frequency for a thick film capacitor with 0.8PFW–0.2PT dielectric.

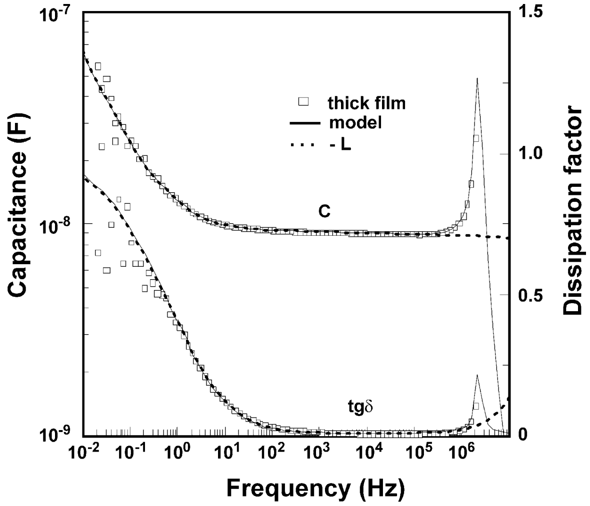

Fig. 10. Dependence of capacitance ($C$) and dissipation factor ($tg\delta$) on frequency for a thick film capacitor with 0.8PFW–0.2PT dielectric.

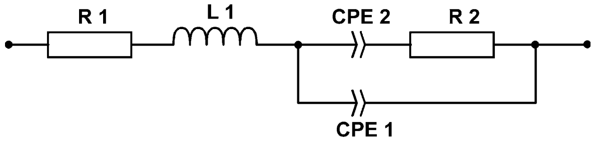

Fig. 11. Model of equivalent circuit for thick film capacitors with relaxor dielectric.

Table 2
Parameters of model equivalent circuit for thick film relaxor capacitors

| Element | Value | Error (%) |
|---|---|---|
| R 1 | 0.2 Ω | 35.6 |
| L 1 | $4.80\times10^{-7}$ H | 2.0 |
| CPE 1—$Q$ | $9.67\times10^{-9}$ F | 1.3 |
| CPE 1—$n$ | 0.99 | 0.12 |
| CPE 2—$Q$ | $1.99\times10^{-8}$ F | 2.0 |
| CPE 2—$n$ | 0.49 | 1.9 |
| R 2 | $7.8\times10^{6}$ Ω | 14.5 |

The constant phase element is a circuit element with impedance Z given by:

$$1/Z = Y = Q_0(j\omega)^n, \quad 0 < n < 1$$

where $Y$ is admittance, $\omega$—angular frequency, $Q_0$—the admittance at $\omega = 1$/rad/s.

CPE is a useful modelling element, its behaviour often fitting very well the experimental data.[9–12] The Nyquist plot ($Z' = f(Z'')$) of a CPE is a straight line making an angle of $n$ 90° with $x$-axis. Physical explanations for CPE behaviour are related to: electrode roughness and heterogeneity, inhomogeneous reaction rates at polycrystalline surfaces, varying composition of coating.[10] In the case when $n$ is close to 1 the CPE resembles a capacitor with admittance $Y = 1/Z = j\omega C$.[11] When $n$ value for a constant phase element is equal to 0.5, that is the phase angle is 45°, one should consider diffusion controlled, the so called Warburg impedance.[13] This element can be utilised to model unrestricted diffusion to a large planar electrode. In the range of lower frequencies, where the Warburg impedance dominates, the slope of the Bode plot ($\log|Z| = \log\omega$) is $-1/2$. The value of the Warburg impedance is inversely proportional to the square root of the frequency.

From Table 2, presenting the parameters of the equivalent circuit for the thick film relaxor capacitors, it can be seen that the exponent $n$ for the CPE 2 was 0.49. This value, very close to 0.5, showed that this element can be considered a Warburg impedance, most likely associated with a diffusion process at the electrode/thick film interface. This element is connected in series with $R$ 2, representing the resistance of the dielectric layer (about $10^7$ Ω). For the CPE 1 the value of $Q_o$ parameter was about $10^{-8}$ F and the exponent $n$ was 0.99, indicating that this constant phase element was in fact a capacitor with capacitance of 10 nF.

In Fig. 9, the experimental relationship between the modulus of impedance $|Z|$ and frequency for the capacitor with 0.8PFW–0.2PT thick film dielectric was compared with the theoretical curve calculated from the model. A similar comparison was given in Fig. 10 for the frequency dependencies of capacitance and dissipation factor. From the plots of capacitance and dissipation factor as a function of frequency it could be predicted that maxima on these curves would occur at low frequencies (below $10^{-2}$ Hz) (Fig. 10). This indicated that in the examined material slow relaxation processes have taken place, like Maxwell Wagner relaxation. It can be seen from Figs. 9 and 10 that fitting of the model to the experimental data is excellent. The strong increase in capacitance and dissipation factor observed beginning from 1 MHz resulted from the inductance of the leads. It is evident from Fig. 10 that subtraction of the inductance results in flattening of the theoretical curve.

## 4. Conclusions

Low firing temperature (880–950 °C), lack of any nonferroelectric fluxes, dense microstructure, high dielectric constant, low electrical field dependence and resistance to moisture without encapsulation are the advantages of the relaxor ferroelectric layers developed in this work for thick film capacitors. The presented model of equivalent circuit, consisting of: the resistance of the electrodes, the inductance of the leads, two constant phase elements and the resistance of the dielectric layer describes very well the behaviour of the investigated thick films.

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