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Fabrication and dielectric properties of modified calcium $(Pb_{0.75}Ba_{0.25})(Zr_{0.7}Ti_{0.3})O_3$ ceramics[*]

Zbigniew Machnik, Dariusz Bochenek, Beata Wodecka-Dus[a], Małgorzata Adamczyk, and Katarzyna Osińska

University of Silesia, Institute of Technology and Mechatronics, 12, Zytnia St., 41-200 Sosnowiec, Poland

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Abstract. The aim of the present work is to report investigations concerning the influence of homovalent modificators on relaxor properties of PBZT 25/70/30 ceramics. The selection of the proper homovalent additive was very important. Literature reports as well as data taken from the periodic table indicated, that calcium ions substitute themselves for lead ions with high likelihood of occurrence. The investigations showed that the substitution significantly changed the microstructure of ceramics – with grains of calcium modified ceramics decreasing and density increasing. The XRD measurements indicate that the pure PBZT ceramics as well as calcium dopant were characterised by tetragonal structure with space group $I4/mmm$. Addition of calcium leads to a slight decrease in the lattice constant and crystal structure. The calcium modification also changes the dielectric properties. The temperature characteristic of the dielectric constant achieved a broadened maximum at temperature T_m, which decreases with increasing Ca content. The properties typical for ferroelectric relaxors weaken with increasing calcium dopant.

1 Introduction

Among the ceramic materials exists a certain special group, which is characterised by an extremely quick response to an external electrical impulse. The materials are called ferroelectric relaxors (RF) or relaxors. They are a class of disordered materials possessing peculiar structure and properties. At high temperature they exist on a non-polar paraelectric (PE) phase, which is similar in many respects to the PE phase of normal ferroelectrics. Upon cooling, at the so-called Burn's temperature (T_B), they transform into the ergodic relaxor (ER) state, which characterised by the presence of a polar region of nanometer scale with randomly distributed direction of dipole moments [1]. The beginning of investigations on this type of material is attributed to Cross [2]. Over the last thirty years, a number of models have attempted to explain the extraordinary behaviour of these materials, but a fully consistent model describing the behaviour of relaxors has not existed up to now. The intriguing features of RF makes them very attractive from the viewpoint of basic research. The RF are also very original materials with potential applications in electronic, optical and precision mechanical systems [3–6], mainly on the grounds of their physical properties revealed upon application of the electric field [7,8]. The relaxor behaviour was first observed in the perovskites with disorder non-isovalent ions, including the stoichiometric complex perovskite compounds (e.g. $Pb(Mg_{1/3}Nb_{2/3})O_3$ or $Pb(Sc_{1/2}Ta_{1/2})O_3$) and non-stoichiometric solid solutions, which originate from the PZT system. It is commonly known that the properties of PZT are enhanced or by the addition of different dopants in "A" or "B" sites [1]. The proper additives cause the appearance of relaxor behaviour [2,3]. One example of such additives is the barium ion. The modification of the PZT system by barium was connected with the creation of the $(Pb, Ba)(Zr, Ti)O_3$ (PBZT) system. The investigations into the PBZT system were initiated by Smolenskii et al. [8]. Structural studies of the discussed ceramic materials were performed by Ikeda [9] who worked out the phase diagram on this base. The investigations were continued by Li and Haertling [7]. The authors found that the ceramics for the range of compositions near the boundaries between the ferroelectric (FE) rhombohedral, tetragonal and paraelectric (PE) cubic phases show behaviour typical of a ferroelectric relaxor. The example of such compositions are PBZT 25/70/30 ceramics. Further investigations revealed that heterovalent additives intensified the behaviour considerably [5,7,10].

Investigations described in this paper are focused on PBZT ceramics with Zr/Ti ratios of 70/30 and Ba content of 25 [11]. The influence on relaxor properties of heterovalent additives substituted Pb or Ba in the A-site of the crystal lattice as well as Nb in the B-site were described in detail in the series of papers published previously [12–15]. The additives improved relaxor properties and extended the temperature range along with their presence.

[a] e-mail: beata.wodecka-dus@us.edu.pl
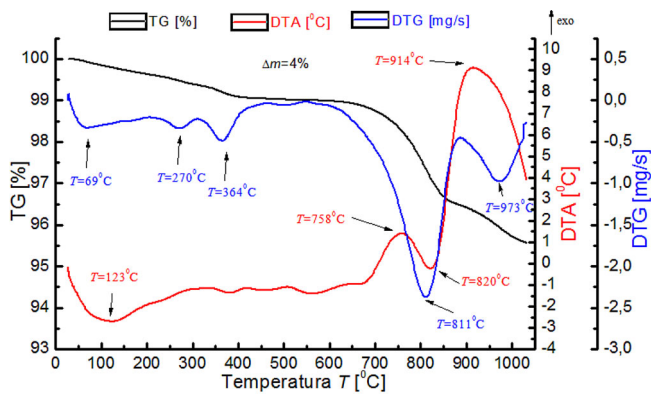
Fig. 1. Thermal analysis data of PBZT 25/70/30 ceramics modified by 1 at.% of calcium.

The thorough analysis of the results allows the author of this publication to suggest that the influence of homovalent additives would have the opposite effect. Very important for verification of the hypothesis was the selection of the proper homovalent additive. Data taken from the periodic table indicated that calcium ions would be suitable. However, despite of fact that the literature around the subject includes a lot of work describing the influence of homovalent as well as heterovalent modificators on the ferroelectric relaxor behaviour [16,17], the influence of calcium ions has not been reported up to now. The literature describes the influence of calcium ions on the physical properties of PZT system, and shows that the calcium ions meaningfully improved the physical properties of ceramics (among other piezoelectric and dielectric properties) [18–20]. The aim of this paper is to present the influence of calcium ions on the dielectric and ferroelectric relaxor properties.

2 Sample preparation

Powders of the selected compositions were prepared from stoichiometric mixtures of the constituent oxides or carbonates, PbO; $BaCO_3$, ZrO_2, TiO_2 and $CaCO_3$, which were mixed for 12 h, and pressed into cylindrical pellets. Before the synthesis process the small amount of obtained powder had been tested using the thermal analysis. Exemplary results of PBZT ceramics modified by 1 at.% of calcium are presented in Figure 1.

The precise analysis of obtained results of TG, DTA and DTG measurements point towards the slight loss of the total of weight $\Delta m \approx 4\%$. The TG curve shows three temperature ranges connected with this loss. The first one takes place at the RT−400 °C range of temperature and is connected to the three small local minimums which are visible on the DTG curve at $T = 69$ °C, $T = 270$ °C and $T = 364$ °C. The moisture evaporation is responsible for the first local minimum appearing on the DTG curve. The second notable weight loss occurs within the temperature range in of 700 °C−825 °C and is connected with the large local minimum observed on DTG curve at

temperature 811 °C. The weight loss in this range is most significant and equals $\Delta m \approx 2.5\%$. The loss is probably a result of barium carbonate and calcium carbonate decomposition and emission of carbon dioxide. The last temperature range, within which the loss of weight takes place, is between 750 °C−1000 °C. Moreover, at this temperature range on the DTA curve two relatively broad exothermic peaks are visible, evidently due to the crystallisation process of oxides and the transformation of amorphous phase into the perovskite phase. Based on the thermal analysis results, the following conditions of the thermal synthesis were set: 2 h at a temperature of 970 °C. The crumbled, milled and sieved materials were once more pressed into cylindrical pellets and sintered at 1250 °C for 4 h. This procedure was repeated before final sintering at 1300 °C for 12 h. Those sintering processes were carried out in a double crucible with some amount of PbO and ZrO_2 in order to preserve the established composition and in particular, to avoid the loss of PbO caused by its sublimation. The Archimedes displacement method with distilled water was employed to evaluate sample density. The density changed very slightly from 6.8 g/cm³ when undoped, to 7.0 g/cm³ when doped with 4 at.% Ca. The microstructure of the discussed samples was analysed by a scanning electron microscope equipped with an energy dispersive X-ray spectrometer (EDS) with Si(Li) X-ray detector.

The obtained ceramics exhibit perovskite structure, which was confirmed by XRD measurements. The measurements were carried out on the ceramic samples at room temperature, using a Huber diffractometer. The diffraction diagram was measured from 19° to 100° in 2θ with a 0.05° step and analysed using a set of programs i.e. the DHN powder diffraction system ver. 2.3.

The computerised automatic system based on precision LCR meter Agilent E4980A was used to measure the temperature dependencies of permittivity at several frequencies in the range 0.1−1000 kHz of the measuring field. The samples were deaged by thermal treatment at 400 °C prior to measurements. Consequently some of the frozen defects, formed during the sintering process, recombined and the tensions caused by mechanical treatment relaxed.

3 Results and discussion

The microstructure of pure PBZT ceramics was described in the previous paper [11]. The material had a good developed microstructure consisting of polyhedral-shaped grains with an average size in the order of 15 μm. The grain structure of calcium modified ceramics are illustrated in Figure 2. Generally the addition of calcium resulted in decreasing of average grain size. However there are no apparent differences in microstructure between undoped PBZT 25/70/30 and 1% calcium doped samples. The average grain size of these ceramics is equal to 15 μm and 13.5 μm, for pure ceramic and 1 at.% of calcium modified ceramic, respectively. The additional increase in modifier content is connected to the significant changes in average grains size. For samples with the 4 at.% of calcium dopant the average grain size (>6.2 μm) was approx.
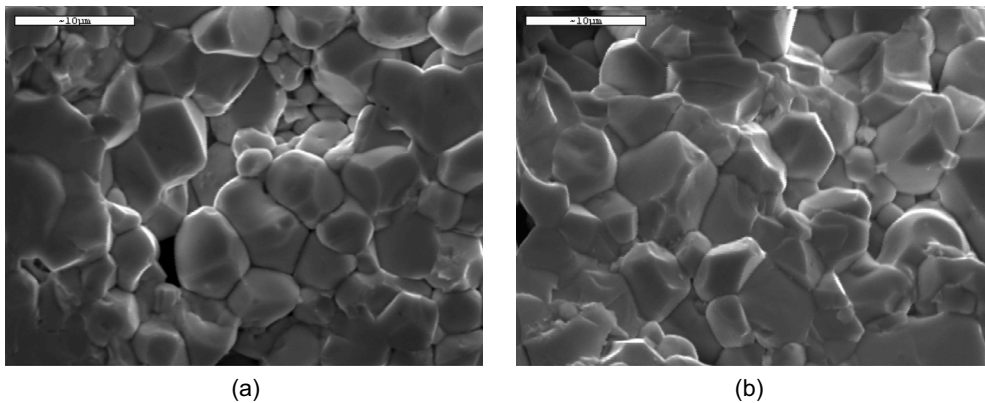
Fig. 2. Scanning electron micrograph of fracture surface of PBZT ceramics modified by (a) 1 at.% and (b) 4 at.% of Ca.
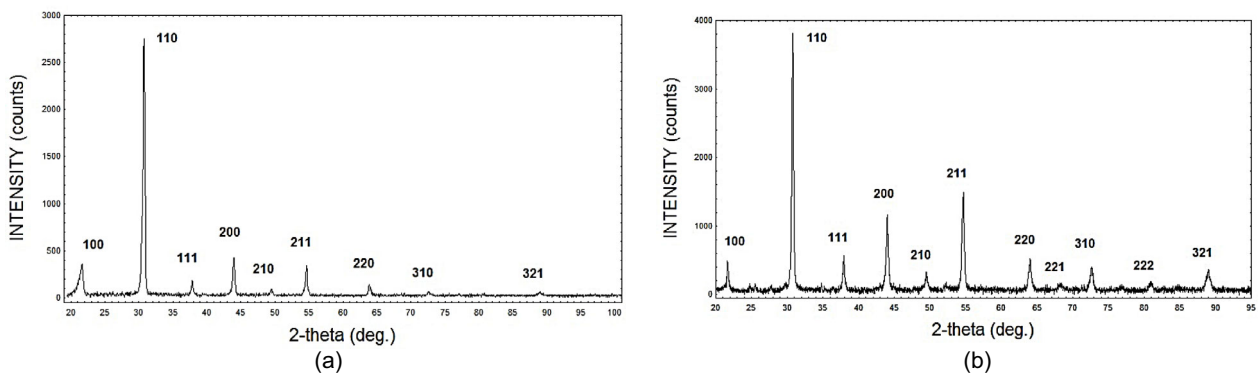
Fig. 3. XRD pattern of (a) pure 25/70/30 PBZT ceramics and (b) 25/70/30 PBZT ceramics modified by 1 at.% of Ca.

Table 1. Structural parameters for the PBZT 25/70/30 + x at.% Ca samples.

x at.% Ca	a [Å]	α [deg]
0	4.1136 (1)	89.928
1	4.1140 (4)	89.969
2	4.1115 (1)	89.968
3	4.1123 (3)	89.965
4	4.1075 (5)	89.968

2.5 times smaller when compared to undoped ceramics. The participation of smaller grains increased.

As mentioned, above the crystallographic structure of the ceramics was examined by XRD. The X-ray diffraction pattern (XRD) of pure and calcium doped PBZT ceramics obtained at room temperature is shown in Figure 3.

The results of those measurements revealed that the single perovskite structure was formed without any detectable secondary phase. The pure PBZT ceramics as well as calcium dopant ceramics were characterised by tetragonal structure with space group $I4/mmm$. Addition of calcium leads to a slight decrease in lattice constant a (see Tab. 1), what is obvious takes under consideration the ionic radius of lead, barium and calcium.

The temperature characteristic of real (ε') and imaginary (ε'') part of dielectric permittivity measured on heating at 100 kHz frequency, for undoped and Ca-modified PBZT 25/70/30 is shown in Figure 4.
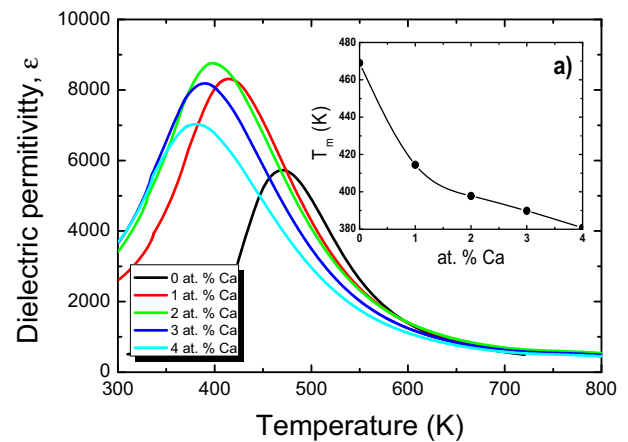
Fig. 4. Temperature dependencies of dielectric permittivity, measured at frequency 100 kHz, for PBZT 25/70/30 ceramics with various Ca contents; the insert (a) shows dependence of temperature T_m, corresponding to ε_{max} on calcium concentration.

The diffuse maximum can be seen on Figure 4, showing the temperature dependencies of dielectric permittivity. The value of this maximum initially increases with increasing calcium content but for the content equal to 3% at. the trend changes. The increasing participation of calcium ions is connected also with the movement of maximum permittivity temperature (T_m) to low value, however
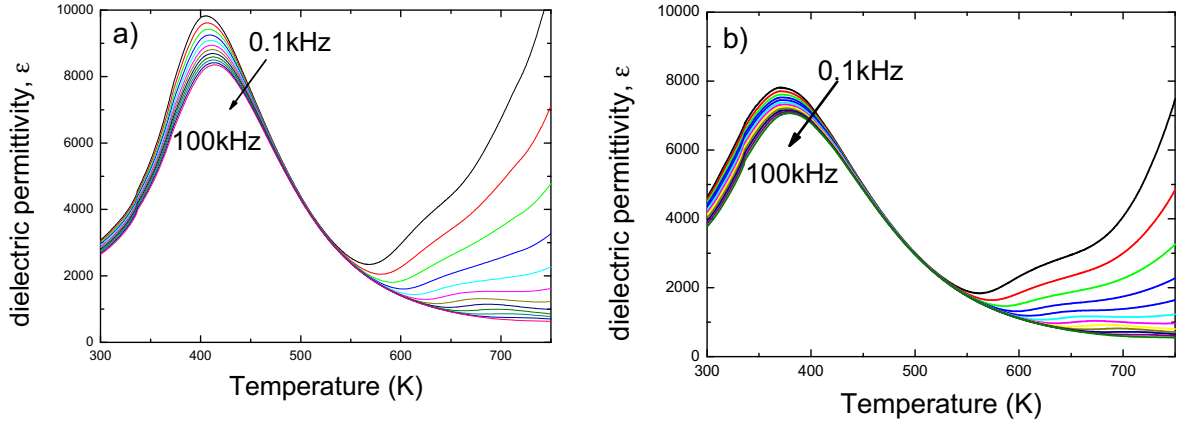
Fig. 5. Temperature dependencies of the dielectric constant measured on heating at various frequencies of measuring field, for calcium modified ceramics (a) $x = 1$ at.%, (b) 4 at.%.

Table 2. The diffuse parameter γ, activation energy E_a and freezing temperature T_f for the PBZT 25/70/30 + x at.% Ca samples.

| x at.% Ca	γ	T_f (K)	E_a (eV)
0	1.94	425	0.2
1	1.85	375	0.1
2	1.84	355	0.1
3	1.83	–	–
4	1.8	–	–

the displacement is not as marked as it was in the case of heterovalent additives [12–15].

As mentioned above, the maximum of dielectric permittivity is significantly broadened. In literature the occurrence of such diffuseness is generally argued in terms of variation in local composition and local internal field causing the appearance of micro-regions, each of which has slightly different temperature T_m [1,2]. The diffusion decreased with an increase in calcium content. The quantitative assessment of diffusion (γ) in the paraelectric phase was evaluated using the expression given by Martirena and Burfoot [21]:

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_{max}} = \frac{(T - T_m)^\gamma}{2\delta^2},\qquad(1)$$

where γ and δ are constants. It is known that the value of γ ($1 \leqslant \gamma \leqslant 2$) is the expression of the degree of dielectric relaxation in the ferroelectric relaxors. The γ value for different compositions of PBZT 25/70/30 + Ca ceramics is given in Table 2.

Temperature changes of the real part of dielectric permittivity were obtained for 20 frequencies of the measuring field ranging from 0.1 kHz to 1 MHz, in logarithmic steps. The example of obtained characteristics are presented in Figures 5a and 5b, for PBZT 25/70/30 modified by 1 and 4 at.% of calcium. All the investigated ceramics show two types of frequency dispersion. The first one is observable in the vicinity of temperature T_m and is connected with the reduction of maximum value of ε and shift in the corresponding temperature T_m with frequency increase – it is
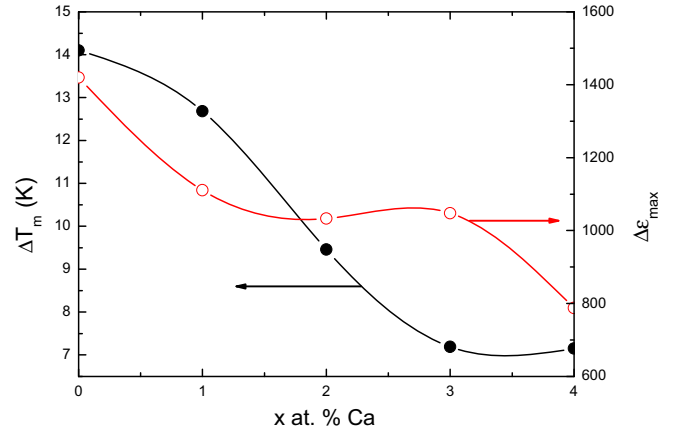
Fig. 6. Degree of frequency dispersion $T_m = T_m$ (0.1 kHz)$-T_m$ (100 kHz) and $\varepsilon_{max} = \varepsilon_{max}$ (0.1 kHz)$-\varepsilon_{max}$ (100 kHz).

a typical feature of ferroelectric relaxors. The dispersion is present in all investigated ceramics, however the behaviour stays less pronounced with the increase in participation of calcium ions.

The degree of frequency dispersion ΔT_m (is defined here as the difference between the T_m measured at 0.1 kHz and that measured at the 100 kHz) and $\Delta \varepsilon'_{max}$ (defined in a similar manner) decreased with calcium concentration (Fig. 6), which shows that the Ca ions are the first among the dopants that we have previously investigated [12–15].

The frequency dispersion of T_m temperature can not be described by the Arrhenius law and hence, as with many other ferroelectric relaxors, another formula should be applied. Two different formulas exist in the literature [22,23]. However the most popular is the Vogel-Fulcher relationship:

$$f = f_0 \exp \left[\frac{-E_a}{k(T_m - T_f)} \right],\qquad(2)$$

where E_a is an activation energy associated with the mechanism of re-orientation of the dipole moments polar nanoregions; T_f is the freezing temperature of polarisation fluctuation and f_0 is the pre-exponential factor.
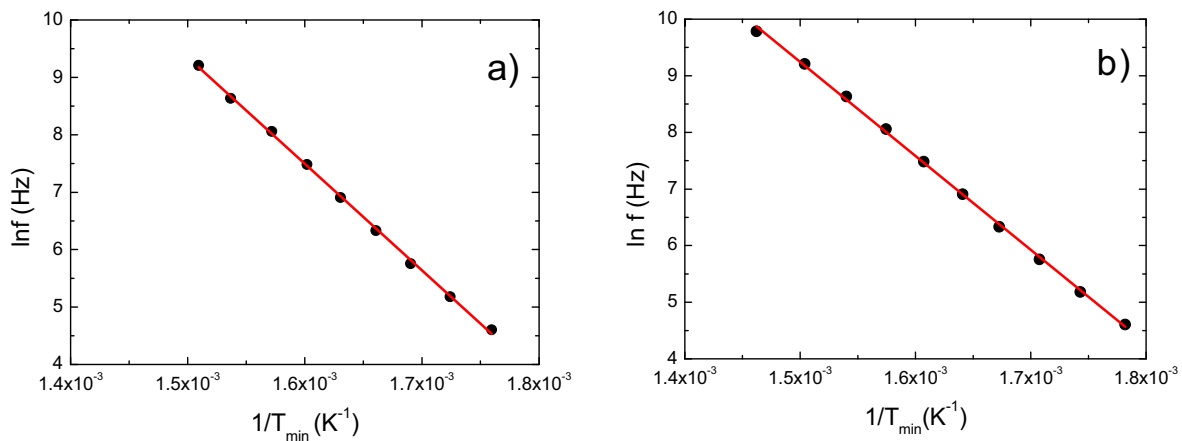
Fig. 7. The Arrhenius plot for calcium modified PBZT-25/70/30 ceramics (a) $x = 1$ at.%, (b) 4 at.%.

Tagantsev [24] has suggested that the formula can be obtained as a direct consequence of the gradual broadening of the relaxation time spectrum with decreasing temperature [25]. This formula was used with success to fit the $T_m(f)$ dependence for undoped 25/70/30 PBZT material as well as the ones modified by 1 and 2 at.% calcium. The obtained values of E_a, T_f and f_0 are collected in Table 2. For ceramics containing 3 and 4 at.% of calcium the fitting procedure did not work – the obtained results were beyond the upper limit of their physical meaning.

The second type of frequency dispersion is observed on the temperature characteristic of dielectric permittivity obtained for frequency of measuring field of range 100 Hz−10 kHz, in a temperatures considerably higher than T_m. The plot of natural logarithm of the measuring frequency versus the reciprocal absolute temperature, corresponding to the local minima in the $\varepsilon'(T)$ curves (Figs. 5a and 5b), is shown in Figure 7 for PBZT 25/70/30 ceramics containing 1 and 4 at.% of calcium. The linear dependency shown proves that they obey the Arrhenius formula $f = f_0 \exp(-E_a/kT)$. Based on the formula the value of activation energy was calculated the for all discussed ceramics. The value were equal to 1.5; 1.59; 1.6; 1.57; 1.43 eV for ceramics modified by 1, 2, 3 and 4 at.% of calcium.

The discussed type of frequency dispersion has been observed for pure PBZT-25/70/30 ceramics as well as other perovskite materials, for example PLZT ceramics [25]. What is more interesting is that PBZT 25/70/30 ceramics the effect completely disappears in the case of modification by heterovalent additives. The origin of the effect was widely discussed in the paper [11]. Some remaining FE domains (clusters) can be surrounded by the PE phase in the temperature range $T_f < T < T_m$ and in a certain range of $T > T_m$ due to the mentioned differentiation in the local Curie temperatures. The depolarisation field associated with polarisation of such domains tends to the compensated state in two possible ways. One of the ways is connected with the screening of the domains by electron and ion space charges from the surrounding medium. Even after the disappearance of screening domains at a high enough temperature, the non-randomly distributed space charges (previously participating in the screening process) remain in the PE matrix because of the relatively low mobility of ion defects and the long relaxation time and contribute to the low frequency dispersion observed in PBZT 25/70/30 ceramics.

4 Conclusions

The experimental results presented above show that the calcium modification introduces significant changes to the properties of PBZT 25/70/30 ceramics. The investigations indicate that the substitution significantly changed the microstructure of ceramics – size of grains of calcium modified ceramics decreased, whereas the density increased. Moreover, addition of calcium leads to a slight decrease in the lattice constant and crystal structure. The calcium modification also changes the dielectric properties. Temperature characteristics of the dielectric constant achieve broadened maximum at T_m temperature, which decreases with increasing Ca content.

The most important achievement of this paper is confirmation of the negative influence of homovalent calcium additive on relaxor behaviour of PBZT 25/70/30 ceramics. Namely the calcium ions caused a decrease of diffuse parameters; values of degree of frequency dispersion ΔT_m and $\Delta\varepsilon'_{max}$. The Vogel-Fulcher relationship above is successfully used only for a small amount of calcium dopant. Moreover the calcium ions do not change the second type of dispersion.

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