Journal of the European Ceramic Society **19** (1999) 1197–1200
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PII: S0955-2219(98)00403-8
0955-2219/99/$ - see front matter

Peculiarities of Dielectric Properties of Some Compositions of PZT-based Ferroceramics

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Abstract

In PZT-based (Ti/Zr ≈ 0·94) ferroceramics compositions the additional 'low-temperature' anomalies on the temperature dependences of the complex dielectric permittivity ε^*_{ef}(T) *have been found under intermediate and strong ac-fields of low and infralow frequencies. The temperature hysteresis of* ε^*_{ef}(T) *has been found in the region of the 'low-temperature' maximum of* ε^*_{ef}(T). *It is supposed that two phase transitions take place for investigated compositions. The 'low-temperature' phase transition is held with changing of the concentration ratio of two polar phases. So it was analysed the influence of concentrations of some components of ferroceramics on the dielectric properties and on the situation of the morphotropic phase boundary. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: memory effects, hot pressing, composites, dielectric properties, PZT.

1 Introduction

Ferroelectric solid solutions (FSS) have wide application both in technology and as objects of fundamental researches, which properties can essentially vary with introduction of new components or variation of concentration of FSS existing components. For investigation of features of phase transitions (PT) and motion of domain (DB) and interphase boundaries the special interest represents ferroelectrics in the region of the morphotropic phase boundary.[1,2] In this connection we have investigated FSS[3] with perovskits structure[4] based on PZT with the same relation Ti/Zr≅0·94 and insignificant variation of remaining components concentration (including modificator GeO_2: 0·5, 1, 2%). Thus, taking into account, that at similar multicomponent FSS the various types of domain structure (DS) were detected under dc-fields[5] we have put the purpose to define the influence of strong ac-fields on the dielectric response in wide intervals of ac-fields and temperatures to investigate the domain contribution in processes of polarization and repolarization in such materials.

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2 Procedure

Earlier[6,7] we described experimental equipment, samples preparation and common technique of the obtaining of integrated dielectric characteristics (maximum polarization P_{max}, remanent polarization P_r, effective complex dielectric permittivity ε^*_{ef}, etc.) from the experimentally obtained polarization loops.

In this work the temperature measurements were carried out in rates of cooling and heating of samples (the rate of the temperature change was 1°C min^{-1}). The measurements in each temperature point were produced during 1·5–2 min. The investigation on each of ac-field amplitudes has been an independent operation. The previous history of all investigated FSS structures was set similarly described in Refs 3, 7 and 8 Thus all conditions of measurements in heating remained similar to those in cooling.

3 Experimental Results and Discussion

The temperature dependences of $\varepsilon'_{ef}(T)$ and $\varepsilon''_{ef}(T)$ to be obtained under applied ac-fields of $E = 2$, 4 and 6 kV cm^{-1} amplitudes and 1 Hz frequency for three structures (relatively divided on concentration of the modificator GeO_2) are shown in Figs 1 and 2. The following features of this dependences call our attention.

Firstly, at increase of values of the measuring ac-field amplitude for all structures without exception there is an strengthening of the phase transition diffusing and the meanings reduction of temperatures T_m [where T_m = temperature of a maximum of $\varepsilon'_{ef}(T)$] of the dielectric permittivity maximum $\varepsilon'_{ef}(T_m)$. Thus for all investigated structures the 'low-temperature' maxima of $\varepsilon'_{ef}(T)$ and $\varepsilon''_{ef}(T)$ are shown precisely enough (Figs 1 and 2). However, for structures with the contents of the modificator 0·5 and 2% GeO_2 it is near to the basic ('high-temperature') maxima of $\varepsilon'_{ef}(T)$ and $\varepsilon''_{ef}(T)$, but for structure with the contents of the modificator 1% GeO_2 these ('low-temperature') maxima of $\varepsilon'_{ef}(T)$ and $\varepsilon''_{ef}(T)$ are essentially shifted in area of low temperatures (Figs 1 and 2).

For composition with a concentration of modificator 1% GeO_2 the values of $\varepsilon'_{ef}(T)$ in T_m is less than for structures 0.5 and 2% GeO_2, whereas the situation was inverse under ultraweak fields.[9]

Earlier[3,7,8] for structure with 1% GeO_2 we already made the assumption of presence of an additional PT at $T \approx 120°C$. The PL-s evolution on Fig. 3 shows, that this PT is not induced by the ac-field (there is no double PL-s), but, most likely, it is the diffused structural PT (SPT). That is a consequence of a composition being on the MFB. One can mark that the evolution of PL-s is similar for structures with 0·5 and 2% GeO_2.

Taking into account that the differences of chemical structure of FSS investigated by us are insignificant, it is possible to expect presence of SPT also for 0·5 and 2% GeO_2 compositions. However the temperature of such SPT, most likely, lays close to T_m. In view of outcomes of researches in Refs 1 and 5 one may assume that the SPT represents

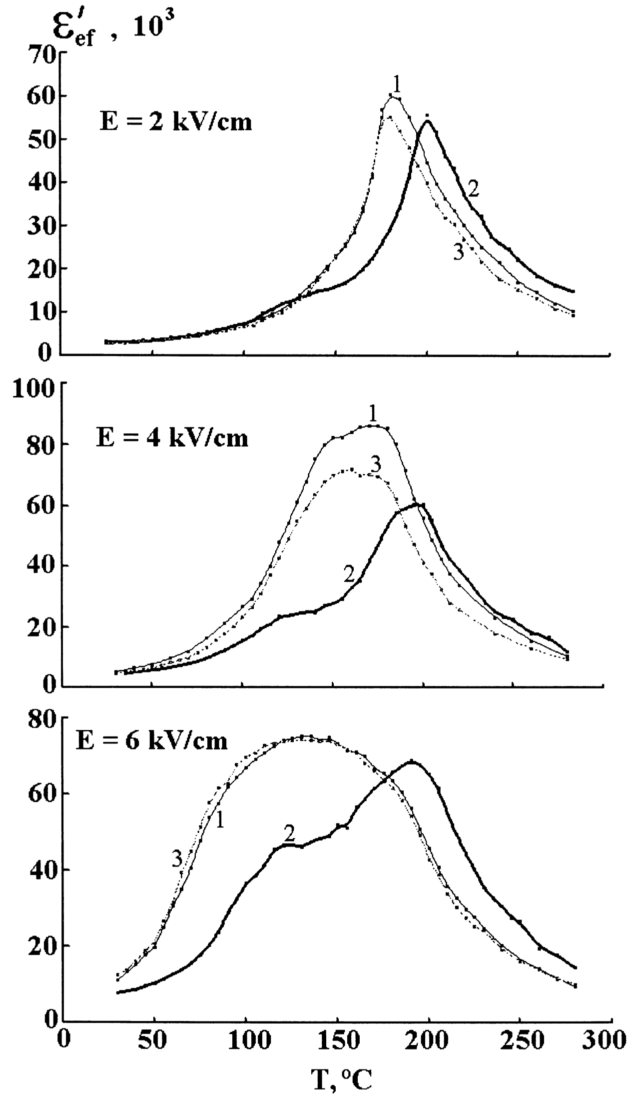

Fig. 1. Temperature dependences of the effective dielectric permittivity $\varepsilon'_{ef}(T)$ for the compositions with (1) 0·5%, (2) 1%, (3) 2% GeO_2 in the cooling mode under ac-fields of 1 Hz frequency.

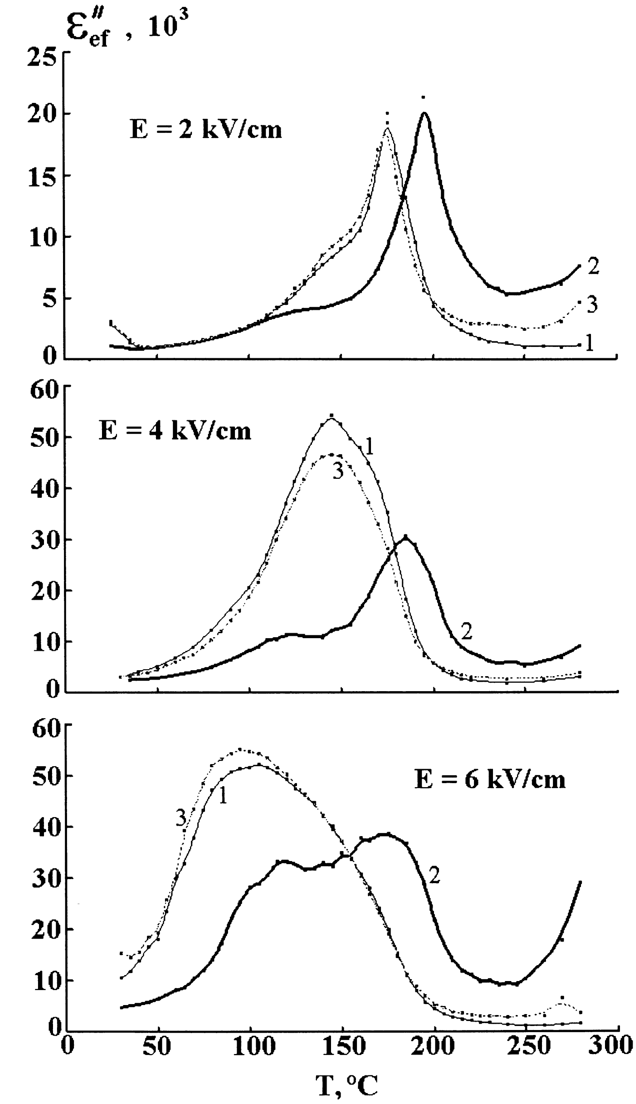

Fig. 2. Temperature dependences of effective dielectric losses $\varepsilon'_{ef}(T)$ for the compositions with (1) 0·5%, (2) 1%, (3) 2% GeO_2 in the cooling mode under ac-fields of 1 Hz frequency

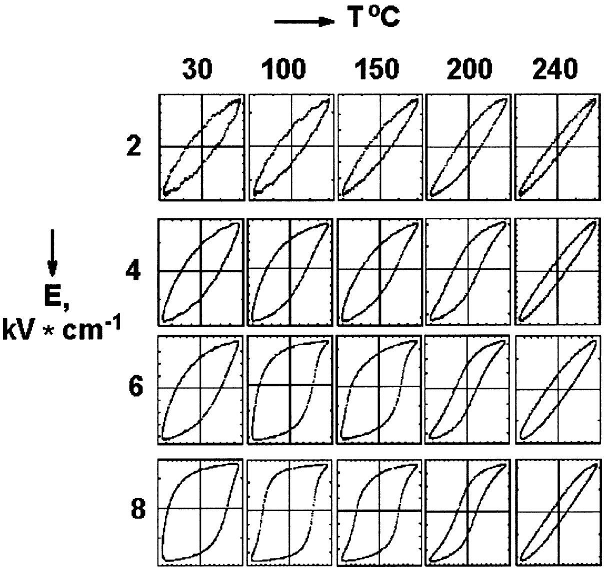

Fig. 3. PL-s evolution for a composition with 1% GeO_2 under ac-fields of 1 Hz frequency.

the transition from tetragonal phase (T) to rhombohedral (R) one and on the contrary. If to assume (as it is made above) that the temperatures of SPT is close to T_m for 0·5 and 2% GeO_2 compositions the evolution and the reorganization of the DS in this SPT intensifies by lability of the cristalline lattice and by the modification of DS stipulated by PT from polar phase to unpolar one. So the high values of $\varepsilon'_{ef}(T)$ and $\varepsilon''_{ef}(T)$ at T_m (Figs 1 and 2) in rather strong fields ($E=4\,kV\ cm^{-1}$) at these compositions are understandable.

Such (close in temperature) coexistence of PT-s is reflected in some features of polarization and repolarization processes which were studied in heating and cooling rates. So for the FSS with 1% GeO_2 the influence of measurement modes to behaviour of $\varepsilon'_{ef}(T)$ and $\varepsilon''_{ef}(T)$ near to the temperatures of the assumed SPT (120–140°C) was exhibited, at first, in significant temperature hysteresis and, secondly, in wide difference of values of ε'_{ef} and ε''_{ef} for heating and cooling rates (Fig. 4).

One can mark that in conditions of our experiment ($E=4000\,V\ cm^{-1}$) values of $\varepsilon'_{ef}(T)$ and $\varepsilon''_{ef}(T)$ in the heating mode for temperatures of the SPT (120–140°C) are much above the same values in the cooling mode. On the contrary it is observed in classical $BaTiO_3$ ceramics (in very weak fields),[10] where the reversible motion of DB determine the contribution to dielectric permittivity. In our case the influence of strong ac-fields in range of low and especially infralow frequencies causes that the irreversible motion of DB gives the main contribution in the $\varepsilon^*_{ef}(T)$. Thus the value of the contribution in $\varepsilon^*_{ef}(T)$ of irreversible motion of DB depends on the direction of SPT passing (i.e. mode of measurement). So peculiarities of polarization and repolarization processes are connected with coexistence of

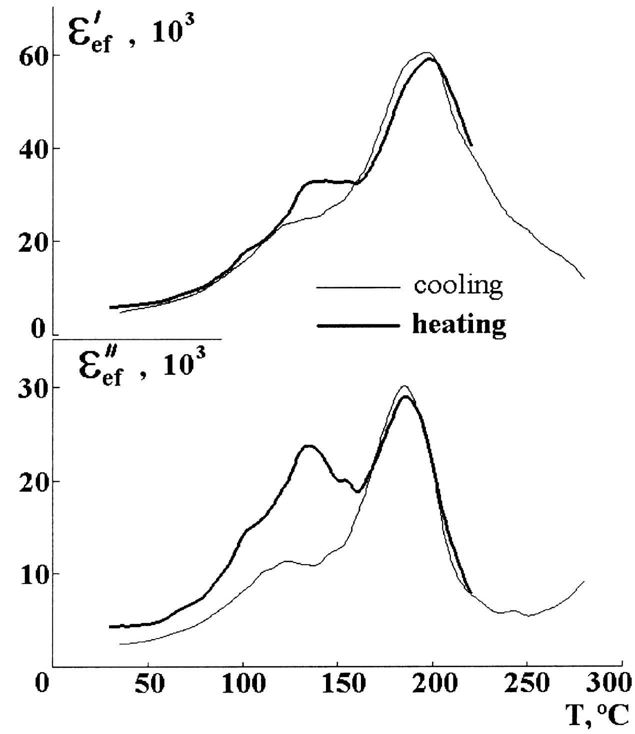

Fig. 4. Temperature dependences of the effective dielectric permittivity $\varepsilon'_{ef}(T)$ and effective dielectric losses $\varepsilon''_{ef}(T)$ for a composition with 1% GeO_2 under ac-fields of $E=4\,kV\ cm^{-1}$ amplitude and 1 Hz frequency in heating and cooling modes.

two phases (R and T) which defines the DS of a sample depending on the direction of the SPT passing.

4 Conclusions

From the analysis of dielectric response of investigated samples it was found that:

1. All investigated structures are on the morphotropic phase boundary, and the coexistence of rhombohedral and tetragonal phases is in a rather wide temperature range. Thus the concentration of rhombohedral phase increase with the decreasing of the temperature.
2. The dielectric properties of the investigated compositions are defined by the fact that the irreversible motion of domain and interphase boundaries gives the main contribution in ε^*_{ef}. So it is reflected in values of $\varepsilon^*_{ef}(T)$ at different passing directions of the phase transition (heating or cooling modes).

Acknowledgements

The work is carried out with support of RFBR (grant 98-02-16146) and of the Contest Center of the Russian Ministry of Education.

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