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Influence of external electric field on relaxor behaviour of $(Pb_{0.75}Ba_{0.25})(Zr_{0.70}Ti_{0.30})O_3$ ceramics

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Abstract

The effects of the external d.c. and a.c. electric field on the dielectric response and relaxor behaviour of lead–barium–zirconate–titanate (PBZT) ceramics of the composition Ba/Zr/Ti 25/70/30 have been studied. The significant influence of the strength of the d.c. bias field and the amplitude of the a.c. field on the dielectric constant maximum and frequency dispersion was determined. The magnitude of the dielectric response strongly decreases under the bias field and increases with the increase of the a.c. field amplitude. All parameters describing the relaxor behaviour of the studied ceramics changed under the external d.c. and a.c. electric field. The experimental results can be explained in terms of existing models of relaxors.

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1. Introduction

Dielectric properties of $(Pb_{0.75}Ba_{0.25})(Zr_{0.70}Ti_{0.30})O_3$ (PBZT 25/70/30) ceramics have been broadly investigated and the behaviour of these ceramics typical for the relaxor ferroelectrics was confirmed [1–4]. Relaxor ferroelectrics (RF) are characterized by the existence of a strong non-Debye frequency dispersion of the dielectric constant (ε'). The dielectric dispersion occurs in a broad temperature region of the diffuse dielectric constant maximum ($\varepsilon'_{\max}$). The peak of $\varepsilon'(T)$ and the corresponding temperature $T_{\rm m}$ move towards higher temperatures with the increasing frequency of the measuring field. The dielectric behaviour of Pb-containing relaxors is generally explained in the literature in terms of small regions of local spontaneous polarisation (so-called polar regions) with a nanometre scale size [5,6] which appear on cooling at the temperature $T_{\rm B}$ much higher than $T_{\rm m}$.

Recently published results indicate that the experimental investigations of the RF under high external field conditions could provide a basis for better understanding of the processes and mechanisms responsible for their particular macroscopic behaviour [7–10]. In the present paper, the effects of the external d.c. and a.c. fields on the dielectric response and relaxor behaviour in the vicinity of the diffuse ferroelectric–paraelectric phase transitions in PBZT 25/70/30 are studied. The weak field dielectric constant depends on measurement procedures reflecting different electrical and thermal history of the studied samples [7]. Therefore, the investigations were carried out for the different electrical states of the ceramic samples (field-heated after zero-field-cooled; zero-field-heated after field-cooled).

2. Ceramics preparation and experimental procedure

The $(Pb_{0.75}Ba_{0.25})(Zr_{0.70}Ti_{0.30})O_3$ ceramics were prepared using a conventional method of sintering. Thermal synthesis of the mixed and pressed PbO, $BaCO_3$, ZrO_2 and TiO_2 oxides was carried out at 925 °C for 2 h. The crushed,

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milled, and sieved material was pressed into cylindrical pellets and sintered again at 1250 °C for 4 h. This procedure was repeated before the final sintering at 1300 °C for 7 h. During sintering, the ceramics were placed inside a double crucible with some amount of PbO and ZrO_2 in order to preserve the predetermined composition, and especially to avoid the loss of PbO caused by its sublimation. The weight losses were smaller than 1%. Archimedes displacement method with distilled water was employed to evaluate sample density. Sample bulk density was 6.8 g/cm^3 (92% of the theoretical density). The grain structure and the atomic composition of the obtained ceramics were examined by a scanning electron microscope JSM-5410 equipped with an energy dispersive X-ray spectrometer. The average grain size was ca. 15 μm. The EDS analysis indicated a homogenous distribution of all the elements throughout the grains.

Samples 0.2–0.6 mm thick coated with sliver electrodes were used for measurements of the dielectric constant as a function of temperature. The weak field dielectric constant, ε', was measured using an HP4192A impedance analyzer in the frequency range 0.1–100 kHz, on heating from 50 to 300 °C, at bias levels of 0, 0.5, 1, 1.5, and 2 kV/cm. The effect of external a.c. field was investigated in the same temperature and frequency range using an HP4284A LCR meter. The amplitude of the a.c. measurement field was varied from 0.01 kV/cm (the field level normally used in the measurements of the weak field dielectric constant) up to 1 kV/cm. Before the measurements, the samples were rejuvenated by annealing for 30 min at 300 °C and then cooled down to 50 °C without applying the external electric field (zero-field-cooled state, ZFC). The weak field dielectric constant was also measured for the samples after initial polarisation in the d.c. field of strengths 1, 2, and 4 kV/cm, applied for 30 min at 250 °C and then cooled in the field to 50 °C (field-cooled state, FC). All the measurements were carried out on heating with constant rate 0.5 °C/min.

3. Results and discussion

The temperature dependencies of the weak a.c. measurement field ($E_m = 0.01$ kV/cm) dielectric constant and the loss factor measured at various frequencies are shown in Fig. 1. They demonstrate the typical relaxor behaviour with the magnitude of the dielectric constant decreasing with increasing frequency and the maximum shifting to higher temperatures.

The dependence of the 1 kHz dielectric response on various bias levels from 0.5 to 2 kV/cm (bias field-heated state, BFH) is illustrated in Fig. 2. It can be seen that the electric field very strongly reduces the dielectric constant and decreases the temperature T_m of its maximum (see the inserted plot in Fig. 2). The similar results were obtained for the other frequencies. The dependencies of $\Delta\varepsilon'_{max}$, defined as the difference between ε'_{max} measured at 0.1 and 100 kHz, and ΔT_m, defined in similar manner on the bias field are listed in Table 1. The increase of these parameters means that the mechanism responsible for the relaxor behaviour of the investigated ceramics strongly depends on the bias field.

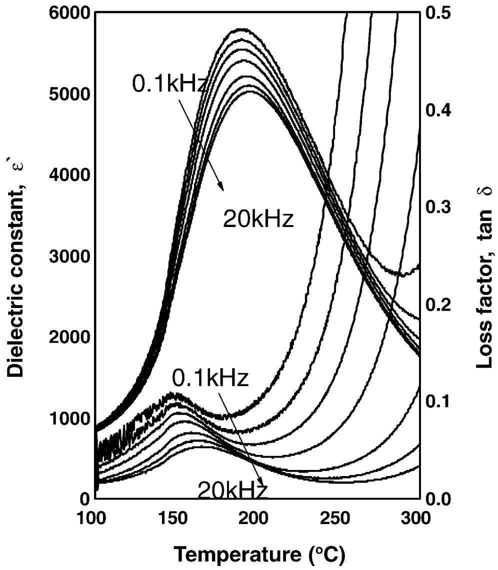

Fig. 1. Dielectric constant (ε') and loss factor (tan δ) as a function of temperature at frequencies of 0.1, 0.2, 0.4, 1, 4, 10, and 20 kHz for PBZT 25/70/30 ceramics. The amplitude of the a.c. measurement field, $E_m = 0.01$ kV/cm.

The influence of an initial polarisation (field-cooled state, FC) on the dielectric response measured at 1 kHz is shown in Fig. 3. The polarising electric field strength effect on ε'_{max} is

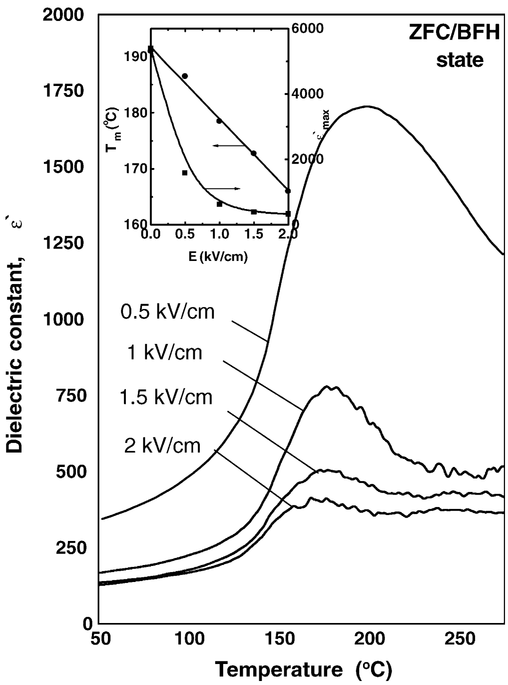

Fig. 2. Dielectric constant as a function of temperature, measured at 1 kHz for various the d.c. bias field.

Table 1
Characteristic parameters T_m, ε'_{max}, γ determined from $\varepsilon'(T)$ measurements at 1 kHz and $\Delta T_m = T_m\ (100\ \text{kHz}) - T_m\ (0.1\ \text{kHz})$ and $\Delta\varepsilon'_{max} = \varepsilon'_{max}\ (0.1\ \text{kHz}) - \varepsilon'_{max}\ (100\ \text{kHz})$ for the different d.c. and a.c. external fields

	State	E (kV/cm)	T_m (°C)	ε'_{max}	γ	ΔT_m (°C)	$\Delta\varepsilon'_{max}$
Without field	ZFC/ZFH state	0	191.4	5390	1.94	7.4	1594
d.c. field	FC/ZBFH state	1	197.1	3993	1.96	13	1574
		2	202.1	3512	1.98	9.5	1421
		4	210.8	2369	2.00	6	1307
	ZFC/BFH state	0.5	186.5	1583	1.91	5	312
		1	178.5	624	1.38	8	768
		1.5	172.7	389	1.29	12	886
		2	166	332	1.21	14	978
a.c. field	ZFC/FH state	0.01	191	5325	1.84	5	1261
		0.1	187	5561	1.76	7	1430
		0.5	184	6023	1.68	20	1625
		1	176	7002	1.53	29	2015

similar to the bias influence but this time the corresponding temperature T_m shifts to higher values (see the inserted plot in Fig. 3). In this case, the values of $\Delta\varepsilon'_{max}$ and ΔT_m describing the degree of frequency dispersion are decreasing with the increase of the d.c. field strength (Table 1).

Fig. 4 shows changes in the 1 kHz dielectric constant with the increase in the amplitude of the a.c. field. The opposite effect, in comparison with the influence of the initial polarisation, can be seen in the case of increasing a.c. field—the temperature T_m shifts to lower values and the dielectric constant maximum increases with increasing of the a.c. amplitude (see the inserted plot in Fig. 4). The parameters describing the degree of frequency dispersion, $\Delta\varepsilon'_{max}$ and ΔT_m exhibit an opposite behaviour with the increase of field in comparison to these determined for samples in the FC-state (Table 1).

In order to estimate the effects of d.c. and a.c. field on the FE–PE phase transition in PBZT 25/70/30 ceramics, the expression describing its diffuseness was used

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

where γ and δ are assumed to be constant and $1 \leq \gamma \leq 2$. The critical exponent γ insignificantly increases for the FC state and strongly decreases under the d.c. bias and a.c. electric field (Table 1). The Curie–Weiss law ($\gamma = 1$) was observed only at temperatures much higher than T_m.

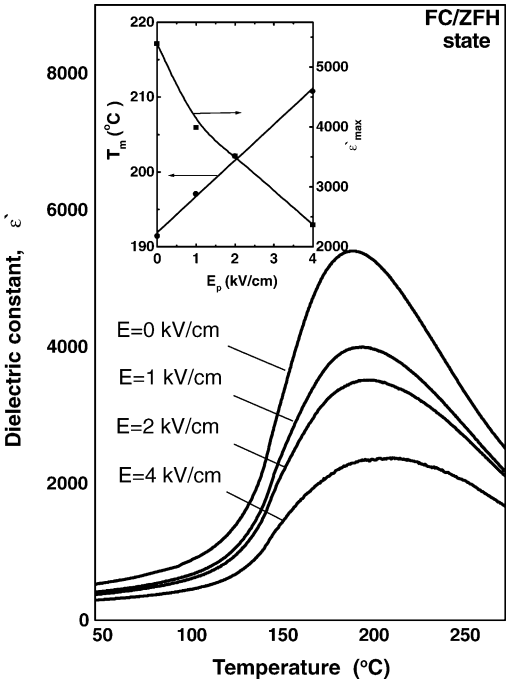

Fig. 3. Dielectric constant as a function of temperature, measured at 1 kHz for the samples pre-polarised by d.c. field of various strength.

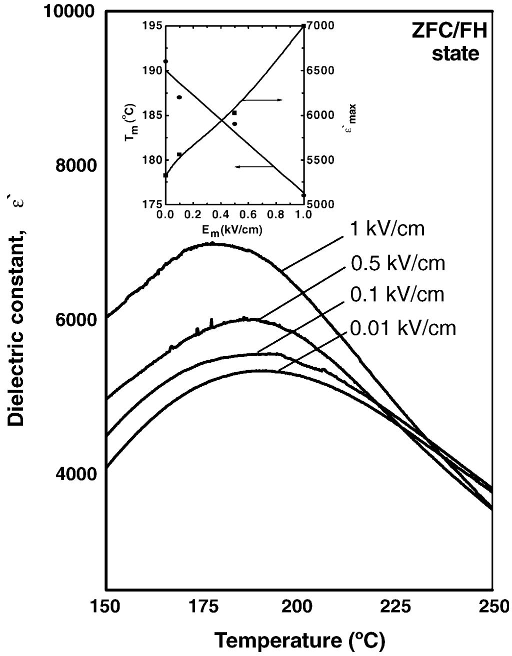

Fig. 4. Dielectric constant as a function of temperature, measured at 1 kHz at various amplitudes of the a.c. field.

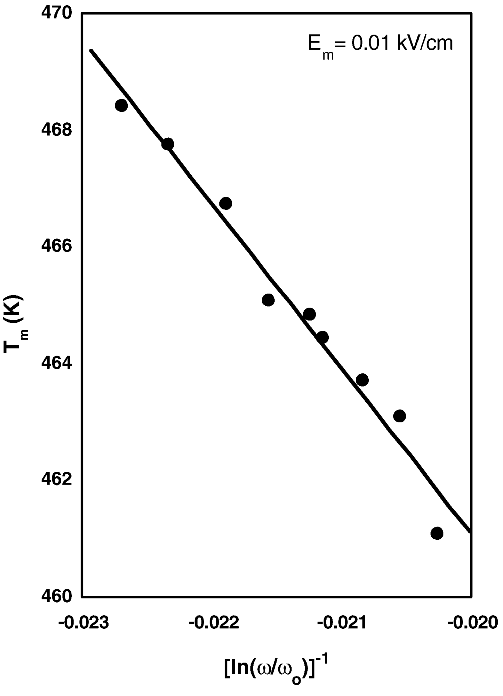

Fig. 5. Temperature T_m, corresponding to the position of the maximum in $\varepsilon'(T)$, as a function of the frequency of the measurement field. The amplitude of the a.c. measurement field, $E_m = 0.01$ kV/cm.

The frequency dependence of the temperature T_m corresponding to the position of $\varepsilon'(T)$ maximum is usually described for the RF with Vogel–Fulcher relationship

$$\omega = \omega_0 \exp\left[\frac{-E_a}{k(T_m - T_f)}\right] \qquad (2)$$

where T_f is the freezing temperature of polarisation fluctuations, E_a is the activation energy, k is the Boltzmann constant and ω_0 is the pre-exponential factor. We found that the frequency dependencies of the dielectric constant maximum temperature were consistent with the Eq. (2). The temperature T_m was a linear function of $[\ln(\omega/\omega_0)]^{-1}$ for all obtained experimental results (Fig. 5). The values of T_f and E_a for the pre-polarised samples (FC-state) and for samples investigated with applied a.c. electric field are listed in Table 2. The value of the activation energy insignificantly decreases under the d.c. and a.c. field, whereas the freezing temperature increases for the pre-polarised samples and decreases for ceramics measured under the high-level a.c. field.

Table 2

Freezing temperature T_f and activation energy E_a determined from Vogel–Fulcher relationship for the different d.c. and a.c. external fields

	State	E (kV/cm)	E_a (eV)	T_f (°C)
Without field	ZFC/ZFH state	0	0.2	143
d.c. field	FC/ZBFH state	1	0.19	148
		2	0.18	153
a.c. field	ZFC/FH state	0.01	0.2	143
		0.1	0.19	142
		0.5	0.19	140
		1	0.18	137

The obtained results can be understood in terms of existing models of relaxors. Several various concepts have been proposed to explain the polarisation mechanism and dielectric response of relaxors [6,7,9,11,12]. It is widely accepted by many authors that the polar regions appearing in relaxors at temperatures much higher than T_m are the key to understand their dielectric behaviour [5,6]. The polar regions are defined as separate regions of the crystal, which have nanometre scale size and possess spontaneous polarisation. The dielectric properties of relaxors can be described as a result of the response of an ensemble of the polar regions to the applied field. Each polar region can be treated as a single dipole moment with several energy minima corresponding to different orientations of the dipole moment. In the absence of the external field, the dipoles are in the equilibrium state and distribution of the dipoles over the minima is controlled by Boltzmann statistics. The d.c. electric field significantly changes the depth of the potential wells and the effect of d.c. bias on the frequency dispersion of the small-signal dielectric constant can be explained this concept. The potential barrier that must be overcome by the dipoles with their directions parallel to the external field becomes deeper and the relaxation time longer. The frozen dipoles or frozen regions occur. They do not contribute to the orientation dielectric response and the dielectric constant decreases.

With the increasing of d.c. field, the order degree of polar regions increases due to the development of longer correlations. Additionally, the electric field, which produced by dipoles can pole the non-polar regions and the volume of polar regions increase. In this way, external d.c. field can induce the ferroelectric state. Therefore, the freezing temperature T_f increases under the d.c. field such as it was observed in the present paper.

We also observed that the dielectric constant is strongly dependent on the amplitude of the measuring signal (a.c. field) at temperatures around and lower than T_m. It was shown that increasing amplitude of a.c. field has the same effect as decreasing frequency on the maximum in the temperature dependence of the real part of the dielectric constant. This behaviour could not be explained with the orientation polarisation of the polar regions. In order to understand the experimental results, another possible mechanism of the dielectric response is considered [8,9,11,12]. The direction of the spontaneous polarisation in polar regions is reversed not by means of a thermally activated flip but by a dissipate motion of the P_S. This is a process close to the domain wall motion in ordinary ferroelectrics. When the relaxor ferroelectrics are considered as multidomain type systems, the increase in the dielectric constant maximum with increasing amplitude of applied field and relationship between the effects of the amplitude and frequency on ε' can be explained [8,9]. The effect of increasing amplitude on dielectric constant has already been observed in the RF [8–10].

4. Conclusions

1. The strong changes of dielectric response under the d.c. and a.c. external electric field have been revealed.
2. All parameters describing relaxor behaviour of the studied ceramics are changed under the d.c. and a.c. fields.
3. The experimental results can be partially understood in terms of existing models of relaxors.

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