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Peculiarities of temperature and field dependence of tunability in $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics with differing grain sizes

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ABSTRACT

Study of the dielectric tunability and susceptibility, in a wide temperature range and at different bias fields, in $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) sol–gel derived ceramics of different crystallite sizes (between 1 and 6 μm), establishes two new regularities. The first one concerns the relative temperature of the maxima positions of the tunability and susceptibility. We show that the maximum in tunability is always at lower temperatures compared to the maximum in susceptibility. The second regularity tells that the electric field dependence of the susceptibility maximum temperature is always stronger than the one for the tunability maximum temperature. In small-size crystallite BST ceramics the temperature of susceptibility maximum starts changing only above a certain threshold field. Additionally, we discuss the nature of an extrinsic contribution to tunability in small-size crystallite BST ceramics.

1. Introduction

Tunability is one of the main characteristics of microwave phase shifters and provides information about the degree of the nonlinearity of dielectric permittivity ε [1–4]. From the early sixties up to now, (Ba,Sr)TiO_3 (BST), which shows a large ε value combined with a low dissipation factor, serves as a model material for such applications [3]. Much attention has been paid in the past to the mechanisms of tunability in ferroelectrics and, in particular, in BST [1–4]. However, we will show that the modern understanding of the nature of tunability is insufficient to fully explain our experimental results. We carefully study the dependency of tunability on the electric field, temperature, and crystallite size in BST and, on this basis, we established two new regularities. This study, thus, is important for both fundamental physics of tunable dielectrics as well as for applications.

2. Experimental results

$Ba_{0.6}Sr_{0.4}TiO_3$ ceramic samples were prepared by a sol–gel method. The BST powder was obtained from precursor solutions of barium and strontium acetates, tetrabutyl titanate and acetic acid glacial [5]. The powder was then pressed into disc-shaped pellets at the isostatic pressure of 200 MPa. Sintering was performed in an Al_2O_3 covered crucible at a temperature of 1340 °C for different time intervals. After sintering, X-ray diffraction (Rigaku Co. Model D/max 2000) confirmed the formation of a single phase perovskite structure. Microstructures of cross sections of the sintered samples were examined using a Shimadzu EPMA-8750 microscope. It was found out that the mean grain size D of the samples increased with increasing sintering time t_S from 1.2 μm (at t_S = 5 min) to 5.8 μm (at t_S = 240 min). Dielectric permittivity ε of the 0.3 mm-thick disc samples with Ag electrodes fired on both large surfaces at 750 °C was measured under differing bias field E values using a HP4284A LCR meter at a frequency of 10 kHz in the course of continuous heating at a rate of 2 K/min. The tunability was calculated then by the following formula [1]

$$n = \frac{\varepsilon(E=0)-\varepsilon(E)}{\varepsilon(E=0)} = 1 - \frac{\varepsilon(E)}{\varepsilon(E=0)} \qquad (1)$$

We found out that the properties of the BST ceramics with the grain size larger than 3 μm are very similar. This is why, we shall present the data only for the samples with D = 1.2 μm and 5.8 μm, which are good representatives for the large- and low- size crystallites. The temperature dependencies of the dielectric permittivity and tunability for these samples at differing bias field E values are shown in Fig. 1. The density of these samples measured by Archimedes's method was 90 and 92% of the theoretical density, correspondingly. Thus the measured ε values are apparent ones and correspond to the mixture of ceramic matrix and pores. Though the relative density of both samples is not very high, it falls within the range where the true ε values of ceramics matrix can be calculated with high accuracy using the well-known mixing rules [6]. In the following we will use the ε values corrected for porosity using the Maxwell–Wagner formula [6]. It is worth noting that tunability values are also known to be insensitive to porosity up to the pores content of 20–30 vol.% [7]. On the other hand, pores play a role of a stress buffer and are known to reduce greatly the internal stress in ferroelectric ceramics [6]. The value of dielectric losses ($\tan\delta \sim 0.04 - 0.06$ at +30 °C and E = 0) were typical of the BST ceramics of this composition. This fact implies that the defect (e.g. oxygen vacancies) concentration is rather low and very similar in all the samples studied.

Though the maximal tunability values for the specimen with $D \approx 1.2$ μm are somewhat lower than for the sample with $D \approx 5.8$ μm, the temperature stability of n is much better for the small-grained ceramics. We show in Fig. 2 the dependency

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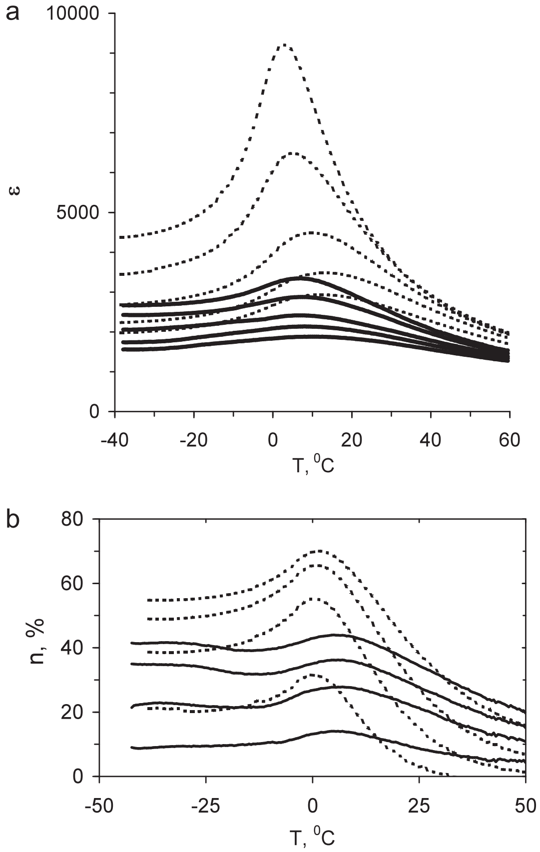

Fig. 1. Temperature dependency of permittivity ε (a) and tunability n (b) for the $Ba_{0.6}Sr_{0.4}TiO_3$ samples with the mean grain size $D \approx 1.2\,\mu m$ (solid lines) and $D \approx 5.8\,\mu m$ (broken lines) at differing bias field E values, kV/cm: 0; 4; 8; 12; 16 (a) and 4; 8; 12; 16 (b). The bias field grows from the uppermost curve to the lowermost one in panel (a) and in the inverse order in panel (b). The ε values are corrected for porosity using the Maxwell–Wagner formula.

of the temperature of the maximum of n (T_{mn}) and of the maximum of ε ($T_{m\varepsilon}$) on the bias field. One can see that the field dependence of T_{mn} differs drastically from the dependence of $T_{m\varepsilon}$. First of all, T_{mn} is lower than the temperature of the maximum of ε at $E = 0$, but, at large fields, asymptotically converges to this temperature. We will call this finding as Regularity #1.

Additionally to this fact, one can see from Fig. 1 that the inclination of the field dependence of $T_{m\varepsilon}$ largely exceeds the one for T_{mn}. Indeed, as one can see from Fig. 1, T_{mn} changes under the bias field only slightly, and, for small crystallites, T_{mn} is almost constant. Whereas $T_{m\varepsilon}$, for crystallites of small enough sizes ($D \approx 3.2\,\mu m$ and less), is constant below some threshold field, but then, at larger fields, starts rapidly increasing. It is remarkable that this threshold field correlates strongly with the crystallite size, the larger the size, the smaller is the threshold field. Altogether, this is our Regularity #2. In Section 3, we will argue that both regularities are fulfilled in other tunable materials.

According to formula (1), $\varepsilon(E) = (1 - n)\varepsilon(E = 0)$. Thus, at a fixed T, $\varepsilon(E)$ is proportional to 1–n. According to Landau theory [1], the inverse dielectric susceptibility is universally proportional to a polynomial of P^2, where P is the polarization. In the ferroelectric phase, in which P is finite, the dependence of P^2 on the field is linear, while in a paraelectric phase, it is quadratic. Thus, the inverse ε (or, equally, 1–n) is an important characteristic of P^2. Fig. 3 presents the dependence of inverse 1–n on the bias field at three different temperatures: −30 °C (well below T_m), 0 °C (near T_m), and +30 °C (well above T_m). One can see that some of these dependencies are quasilinear, while some are quadratic. For example, the large-grain ceramics has a quasilinear field dependence of the inverse 1–n at $T = -30\,°C$, while, at +30 °C, this dependence is rather quadratic. Surprisingly, the behavior of the small-grain ceramics is just opposite, at $T = -30\,°C$, the field dependence of the inverse 1–n is quadratic, but at $T = +30\,°C$ it is quasilinear. It is important to note that the magnitude of tunability in the low-crystallite-size ceramics is comparable with the one for the large-size crystallites, and, above the room temperature, even exceeds the value inherent to the large-grain ceramics that is rather important for applications, because, for example, of the problem of miniaturization of tunable devices. Below, we will discuss the nature of these interesting properties and we will argue that this uncommon behavior of the small-size BST ceramics manifests hydrodynamic fluctuations of the atomic displacements.

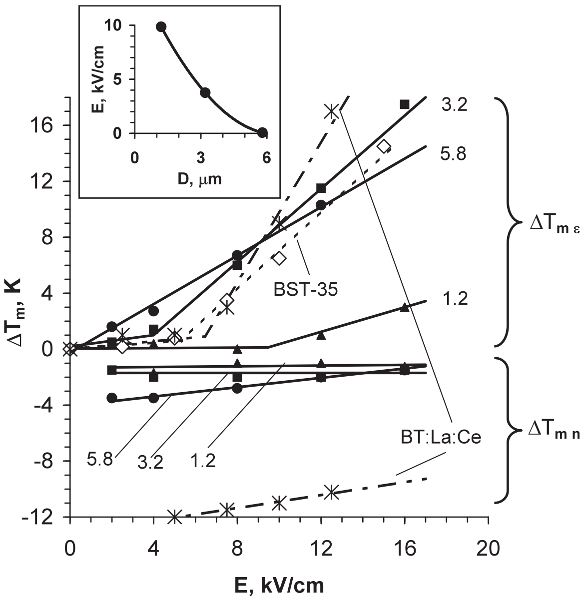

Fig. 2. The dependence of the reduced temperature of the permittivity and tunability maxima $\Delta T = T_{m\varepsilon}(E) - T_{m\varepsilon}(E = 0)$ and $\Delta T = T_{mn}(E) - T_{m\varepsilon}(E = 0)$ on dc bias E for $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics with differing mean grain size, μm: 1.2; 3.2; 5.8. The lines are guides for the eye. The numbers at the lines correspond to the mean grain size (in μm) of the given sample. Diamonds show the $T_{m\varepsilon}(E)$ dependence for $Ba_{0.65}Sr_{0.35}TiO_3$ (BST-35) [12]. Asterisks show the $T_{mn}(E)$ and $T_{m\varepsilon}(E)$ dependences for $Ba_{0.97}La_{0.03}Ti_{0.94}Ce_{0.06}O_3$ (BT:La:Ce) [19]. The inset shows the dependence of the threshold bias corresponding to the bend of the $T_{m\varepsilon}(E)$ curve, on the mean grain size D.

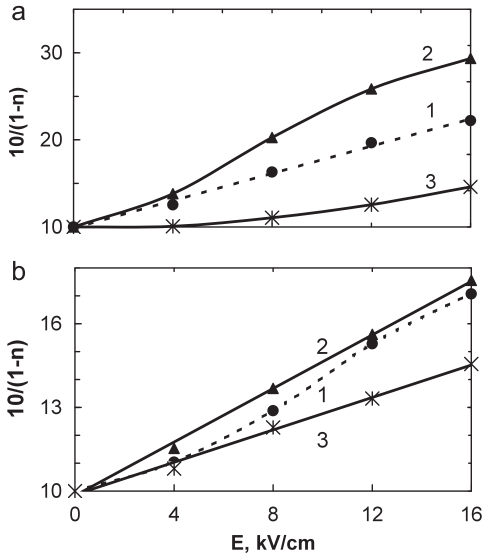

Fig. 3. Field dependency of the reciprocals $(1 - n)$ for the $Ba_{0.6}Sr_{0.4}TiO_3$ samples with the mean grain size $D \approx 5.8\,\mu m$ (a) and $D \approx 1.2\,\mu m$ (b) at three temperatures: −30 °C (1), 0 °C (2), and 30 °C (3).

3. Discussion

We searched for literature data concerning the temperature and field dependency of n. Unfortunately, in the majority of works only the room-temperature dependency of permittivity versus the bias field E were usually studied. In some rare cases, when the authors show the temperature dependency of n or give the corresponding data in tables, they use to do this only for one value of E. However, we succeeded to find some data supporting Regularity # 1 (see Table 1). One can see that, in all the cited data, the position of

Table 1
Correlation of $T_{m\varepsilon}(E=0)$, $T_{m\varepsilon}(E)$ and $T_{mn}(E)$ in various ferroelectric ceramic compositions.

Ceramics composition	$T_{m\varepsilon}(E=0)$ (°C)	E (kV/cm)	$T_{m\varepsilon}(E)$ (°C)	T_{mn} (°C)	Reference
$Ba(Sn_{0.1}Ti_{0.9})O_3$	53	10	66	30	[15]
$Ba(Zr_yTi_{1-y})O_3$ ($y=0.2$)	24	20		22	[16]
$Ba(Zr_yTi_{1-y})O_3$ ($y=0.35$)	−88	20	−37	−91	[17]
$Ba_{0.8}Sr_{0.2}TiO_3$	55	5	56	53	[18]
$Ba_{0.65}Sr_{0.35}TiO_3$	17	20		13	[19]
$(Ba_{0.97}La_{0.03})(Ti_{0.94}Ce_{0.06})O_3$	38	10	46	27	[13]
$0.9PbMg_{1/3}Nb_{2/3}O_3–0.1PbTiO_3$	44	3.1	41	40	[20]
$0.9Pb(Fe_{1/2}Nb_{1/2})O_3–0.1CaTiO_3$	10.5	1.4	11.5	−2	[21]
$0.98Pb(Fe_{1/2})O_3–0.02PbTiO_3$	111	2.5	117	108	[22]

the temperature maximum of tunability is lower than the position of the temperature maximum of ε at $E=0$. Thus, these data confirm the found regularity of tunability. This finding has also a mathematical reason. Indeed, in the definition of tunability, formula (1), both the numerator and denominator depend on temperature and both have a temperature maximum. Tunability increases, when $\varepsilon(E=0)$ increases, but it decreases, when $\varepsilon(E)$ increases. This is why, mostly $\varepsilon(E=0)$ defines the position of the temperature maximum of n, and this implies that this maximum hardly depends on E, in contrast to the temperature maximum of ε at $E \neq 0$.

We continue with the discussion of the anomalous (from the point of view of ordinary ferroelectrics) low-field portion of the $T_{m\varepsilon}(E)$ dependence shown in Fig. 2. One can see that this dependence is constant, at low fields, but then, at larger fields, $T_m(E)$ strongly increases. Such a ‘threshold-kind’ behavior has never been reported for BST compositions. However it was recently observed in relaxor $(1-x)PbMg_{1/3}Nb_{2/3}O_3-(x)PbTiO_3$ [see Ref. [8] and references therein]. According to Dorogovtsev model [9], the increase of T_m with E begins after the external field overcomes the action of the random fields. Below this field, the dependence of T_m on E is constant or weak. This fact gives one an opportunity to obtain the value of the random field magnitude from experiment. Such a turning point is well seen in our plots shown in Fig. 2 presenting the dependence of $T_{m\varepsilon}$ on the electric field. The data given in the inset in Fig. 2 show that the mean deviation of the random field increases as the crystallite size D decreases. One can see that this field is the largest for the smallest studied sizes of the grains. We relate this evidence to the fact that the source of the random field is in the inter-crystallite media, and the part of the crystallite embedded into this field is larger for the small crystallites, even under the condition of the same magnitude of the random field. Usually, the surface effect in ferroelectric ceramics is related to the dead-layer [1,10], but, it follows from our observation that, in reality, the dead layer is a result of the action of the random fields with the source in the inter-crystallite interface. Thus, indirectly, our data are supported by the theories of tunability of small-crystallite-size ceramics employing the idea of the dead layer [10,11].

Our analysis of the literature data has shown that the threshold-type $T_{m\varepsilon}(E)$ dependency can be found in some other experimental works. For example, similar shape has the $T_{m\varepsilon}(E)$ dependence for $Ba_{0.65}Sr_{0.35}TiO_3$ and $(Ba_{0.97}La_{0.03})(Ti_{0.94}Ce_{0.06})O_3$ ceramics plotted using the data of Refs. [12,13], respectively (Fig. 2). Such threshold character of $T_{m\varepsilon}(E)$ usually is not even mentioned in the papers. Notice that, in contrast to $T_{m\varepsilon}$, this effect is absent in T_{mn}, because T_{mn} is more or less constant with the increase of E, as we stated above.

Let us now turn to the electric field dependency of the magnitude of n and ε in the small- and large-grain size ceramics. According to Landau theory [1], dielectric permittivity in the ferroelectric phase is so that the inverse dielectric permittivity (which is proportional to inverse 1–n) is proportional to the electric field, while, in the paraelectric phase, this dependence is quadratic [1,11]. The existence of the quasilinear dependence of inverse 1–n in small-grain ceramics deserves a special consideration. We cannot relate this effect to the presence of a spontaneous polarization, because it happens at high temperatures, but one can assume the presence in the small-grain crystallites of super-dipole moments with fluctuating directions. It was shown earlier that such super-moments can result in an extrinsic contribution to dielectric permittivity stemming from the hydrodynamic fluctuations of the atomic displacements [11] (see also Ref. [14] describing extrinsic contributions to ε of different nature). Such fluctuations were shown to result in a linear behavior of inverse ε though this linear dependence has nothing to do with ferroelectricity, but rather mirrors frustration of the atomic displacements with respect to the direction in the space. Very probably, at low T's, the super-dipole moments freeze up and no further contribute to the linear dependence, in agreement with our experiment. An alternative description of the quasilinear electric field dependence follows from a rather recent work performed in the framework of the effective media approximation [10]. However the field magnitudes necessary for the latter effect are an order of magnitude larger than ours.

4. Conclusions

From the data observed we established two new regularities for the field dependence of the temperature maximum and magnitude of tunability and ε. We prove that the behavior of n drastically differs from the behavior of ε. We also showed that the effect of the size of the crystallites on tunability presents a large extrinsic effect. Generally, the established regularities together with the found dependency of tunability on the crystallite size provide a new fundamental knowledge, which is the basis for further applications.

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