Tunability modelling and experiments for BaTiO$_3$-based solid solutions

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Abstract

In this paper, the electric field dependence of the dielectric constant in some BaTiO$_3$-based ferroelectrics is theoretically described by means of the Landau-Ginzburg-Devonshire (LGD) theory and its' approximations valid for low polarizations (Johnson's equation and even-power relation) when the sample is in its ferroelectric state and by a model considering random non-interacting dipolar units in a double well potential for the paraelectric state. High-voltage tunability data were obtained at room temperature for BaZr$_{0.10}$Ti$_{0.90}$O$_3$ and Ba$_{0.70}$Sr$_{0.30}$TiO$_3$ ceramics. The data were well fitted by using the Johnson's approximation for the ferroelectric-relaxor BaZr$_{0.10}$Ti$_{0.90}$O$_3$ and satisfactory for the Ba$_{0.70}$Sr$_{0.30}$TiO$_3$ ceramics, close to its ferro-para phase transition. For the last one, the non-interacting dipolar units model allows to determine the average dipolar moment.

Keywords: ferroelectric, tunability, Landau-Ginzburg-Devonshire (LGD) model, non-interacting dipolar units

I. Introduction

The polar dielectrics are characterized by a strong nonlinear effect under the electric field. In the last few years, electric field-tunable dielectrics have attracted much interest for their potential applications as variable capacitors, phase shifters, tunable filters and voltage-controlled oscillators [1], particularly in circuits and devices needed by the wireless communications industry, for scientific, space, commercial and military use. Among them, SrTiO$_3$- and BaTiO$_3$-based solid solutions like (Ba,Sr) TiO$_3$, (Pb,Sr) TiO$_3$, Ba (Zr,Ti) O$_3$, (Ba,Sn) TiO$_3$, etc. were the most reported materials, due to their high dielectric constant, low losses and high tunability, but also for their low cost, high integrability and potential for device miniaturisation.

The electric field-induced tunability describes the ability of a dielectric material to change its permittivity by the electric field and is defined as:

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

where $\varepsilon_r(0)$ and $\varepsilon_r(E)$ are the permittivities in the absence/presence of the electric field, respectively.

The dielectric response of the ferroelectrics as a function of the electric field has been less studied, due to the difficulties to obtain data at very high fields ensuring the saturation, and to the lack of a convenient theory like a simple explicit function to deal with dielectric spectra as a function of the electric field in a wide range of frequencies, amplitudes and temperatures.

The electric-field dependence of the dielectric response can provide very useful information on the basic physics of dielectric polarization. In some cases, such information is critical in understanding the dielectric/ferroelectric behaviour in ferroelectrics and other polar dielectrics. In addition, the recent interest in applications as tunable electronic devices make even more interesting such a study, from technological point of view.

In the present work, the dc-electric field dependence of the dielectric constant ε_r (E) in polar dielectrics was theoretically studied and compared with experimental data obtained for some BaTiO$_3$-based solid solution, i.e. for: (i) BaZr$_{0.10}$Ti$_{0.90}$O$_3$ ceramics with relaxor-ferroelectric mixed character, which at room temperature is in its polar phase (T_C~85°C), and (ii) Ba$_{0.70}$Sr$_{0.30}$TiO$_3$ ceramics, for which T_C~20°C and is fully ferroelectric below the room temperature. For the theoretical description

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two different models have been used: (i) for the polar phase, the Landau-Ginzburg-Devonshire (LGD) theory and its approximate treatments (Johnson relation) in case of a single polarization mechanism [2] and (ii) model of random non-interacting dipolar units in a double well potential, mainly valid in ferroelectrics in their paraelectric state [3]. First of all ε_r (E) was calculated by using the Johnson's relation the even-power equation, and the LGD theory, and after that some experimental data for a $BaZr_{0.10}Ti_{0.90}O_3$ ceramic were fitted with these models. An excellent agreement was obtained with the Johnson equation in the overall range of fields. The limits of these models are also discussed.

In the case of $Ba_{0.70}Sr_{0.30}TiO_3$ ceramics, which at room temperature is in its Curie range, in addition to the Johnson approximation, the model of non-interacting dipolar units was employed and the average dipolar moment was calculated. The results were compared with data from the literature and a good agreement was obtained.

II. Theoretical descriptions of the dc tunability

Landau-Ginzburg-Devonshire (LGD) model

The dielectric constant has a non-linear behaviour under the applied external fields. The dc-electric field dependence of the dielectric constant in ferroelectrics can be calculated in the framework of the Landau-Ginzburg-Devonshire (LGD) thermodynamic approach [4–6], in a similar manner as used in the paper of Ang and Yu [7].

Starting with the LGD expression for the free energy, the dependence of the dielectric constant on the electric field is derived from the polarization-field P (E) dependence given by the implicit equation:

$$E = \alpha P + \beta P^3 + \gamma P^5 \dots \quad (2)$$

According to the relationship: $P = \varepsilon_0 \cdot \varepsilon_r (E) \cdot E$ and the definition of the electric susceptibility, a relation between permittivity and the applied field is derived:

$$\frac{\varepsilon_r(E)}{\varepsilon_r(0)} = \frac{\left\{ 1 - \frac{\varepsilon_r(E)}{\varepsilon_r(0)} + \left[\frac{\varepsilon_r(E)}{\varepsilon_r(0)} \right]^3 \right\}^{1/3}}{\left[1 + 3\beta \varepsilon_r(0)^3 \varepsilon_0^3 E^2 \right]^{1/3}} \quad (3)$$

In this complicated form the relation is not useful for fitting the experimental data. Some of the terms can be simplified to give a more adequate and easy working relation, as described in the following.

A. The Johnson approximation

The Johnson's approximation was developed by assuming small polarization values. Johnson gave a semi-empirical relation starting from the equation (3), where the numerator was approximated to 1. Thus, a semi-empirical relation is obtained:

$$\varepsilon_r(E) = \frac{\varepsilon_r(0)}{\left[1 + 3\beta \varepsilon_r(0)^3 \varepsilon_0^3 E^2 \right]^{1/3}} \quad (4)$$

which is called the Johnson's approximation. This relation can be used only when $\beta > 0$, because in the other case it is necessary to include at least the fourth-order terms in the free energy development. Another limit is given by the approximation of small polarization, meaning that the equation (4) is useful for polar systems with small polarization (e.g. relaxors) or at such temperatures or fields ensuring not very high polarization values (e.g. temperatures in the Curie range, fields far from saturation).

B. Even-power relation

Taking into account in the Johnson relation that for low fields: $3\beta \cdot \varepsilon_r (0)^3 \cdot \varepsilon_0 \cdot E^2 < 1$, the equation (4) is expanded as a polynomial even-power terms of E:

$$\varepsilon_r(E) = \varepsilon_1 - \varepsilon_2 E^2 + \varepsilon_3 E^4 - \varepsilon_4 E^6 \quad (5)$$

where:

$$\begin{aligned} \varepsilon_1 &= \varepsilon_r(0) \\ \varepsilon_2 &= \beta [\varepsilon_0 \cdot \varepsilon_r(0)]^4 \\ \varepsilon_3 &= 2\beta^2 [\varepsilon_0 \cdot \varepsilon_r(0)]^7 \\ \varepsilon_4 &= 14\beta^3 [\varepsilon_0 \cdot \varepsilon_r(0)]^{10} \end{aligned} \quad (6)$$
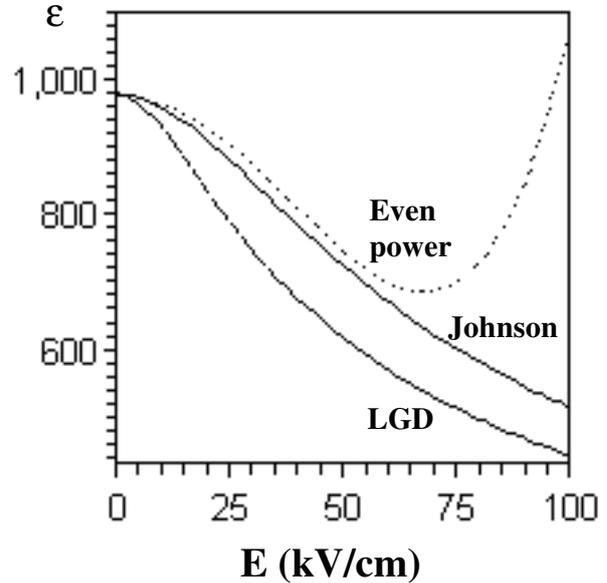
Figure 1. Simulation of the electric field dependence of the relative dielectric constant by using the LGD, Johnson and even power approximations

This equation is valid only for small fields and in case of small polarizations. Again, small polarization is normally obtained either close to the paraelectric state or in the solid solutions with relaxor character for which the spontaneous polarization is almost zero. Thus, for such systems the approximation might be valid even in the ferroelectric state.

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The dependence of the dielectric constant on the electric field was simulated by using the equations (3), (4) and (5). The parameters used in these simulations are: $\varepsilon_r\ (0)\ =978$, $\beta=3\times10^{10}\ [Vm^5/C^3]$, $\varepsilon_2=1.27\times10^{-11}\ [V/m]^{-2}$, $\varepsilon_3=1.38\times10^{-25}\ [V/m]^{-4}$. Depending on the material constants, all the three approaches lead to more or less similar dependences at low fields. At high fields, the LGD permittivity-field dependence tends to saturate faster than one predicted by the Johnson eq. (Fig. 1). As expected, serious deviations are found at high fields, mainly in the case of the even-power approximation, for which a minimum at intermediated fields followed by an increasing permittivity with the applied field without saturation at very high fields are predicted. Such a behavior was not observed experimentally.

Dipolar model

For describing the polarization process of a system with uncorrelated dipolar moments (ferroelectric in the paraelectric state or other non-ferroelectric polar systems), another simple model considering random non-interacting dipolar units in a double well potential will be considered. A similar approach gave good results in modelling the tunability of the non-ferroelectric pyroclore bismuth zinc niobate thin films [3].

The application of a dc-field favours the hopping of such dipoles towards the energetically favourable minimum. By assuming that $N=N_1+N_2$ is the total number of dipolar units, where N_1, N_2 are the number of the occupied wells 1 and 2, respectively, the relative population of the double wells under the field E is given by:

$$\frac{N_1}{N_2} = \exp\left(\frac{-2p_0E}{kT}\right) \qquad (7)$$

where p_0 is the individual dipole moment, E is the applied field, k – the Boltzmann constant and T – temperature. The resulted polarization P of the system of volume V depends on the number of not compensated dipoles. Using equation (7) the field-induced polarization of the dipolar system at a fixed temperature is found as:

$$P = \frac{p_0N}{V}\tanh\left(\frac{p_0E}{kT}\right) \qquad (8)$$

Thus, the field-dependent dielectric constant ε at a given temperature is:

$$\varepsilon = \frac{\partial P}{\partial E} = \frac{Np_0^2}{kTV}\sec h^2\left(\frac{p_0E}{kT}\right) \qquad (9)$$

Taking into account for the equation (9), the tunability n can be written by using hyperbolic function:

$$n = \cosh^2\left(\frac{p_0E}{kT}\right) \qquad (10)$$

It results that the relationship between the field E necessary to achieve a given tunability n is obtained by the equation:

$$E = \frac{kT}{p_0}\ln\left(\sqrt{n}+\sqrt{n-1}\right) \qquad (11)$$

If the model is well describing the permittivity-field data for paraelectric state, a linear dependence of the function $E = f\left[\ln\left(\sqrt{n}+\sqrt{n-1}\right)\right]$ should be obtained. It is worth to mention that this model is valid in the situation when the correlations between the neighborring dipolar units are negligible. Thus, deviations from the predicted equation (11) will appear when the hypothesis of uncorrelated identical dipoles is not anymore valid. This situation is expected for very high fields causing both increasing of the individual dipolar moments and also the increase of the correlation degree between the neighboring dipolar units. Of course such a model is not valid in the ferroelectric state, for which strong dipolar correlations (interactions) within the ferroelectric domains are present.

III. Experimental Results

Sample preparation

$BaZr_{0.10}Ti_{0.90}O_3$ ceramics were prepared by mixed oxides method starting with high purity reagents of $BaCO_3$ (Fluka), TiO_2 (Merck) and ZrO_2 (Merck) [8]. The powders were weighted, homogenized, dried and then granulated. The samples were shaped by uniaxial pressing at 160 MPa and pre-sintered in air, at 1150°C/ 3h. After cooling they were ground, pressed again into pellets and sintered in air at 1300°C/4h.

$Ba_{0.70}Sr_{0.30}TiO_3$ ceramics have been obtained by using nanopowders prepared by Pechini method from titanium isopropoxide, barium and strontium carbonates, using citric acid as a chelating agent and ethylene glycol as an esterification agent [9]. Dense (85–93% relative density) and homogeneous microstructures, free of secondary phases have been obtained when the polymeric precursors were calcined in air at 850°C/2h and the powder sintered at 1350°C/3h.

Tunability data

Accurate tunability data at room temperatures have been obtained for $BaTiO_3$– based solid solutions by using a circuit for high voltage tunability measurements as described in the ref. [8].

For the ferroelectric $BaZr_{0.10}Ti_{0.90}O_3$ ceramic sample in the range of fields of (0, 45) kV/cm the tunability results are shown in Fig. 2. The permittivity at zero field is $\varepsilon_r\ (0)$ =983 and reduces to less than 400 at the maximum available field. With a dc-field of (25–30) kV/cm, the permittivity diminish at almost a half, which means good tunability characteristics of this ceramic sample.

For the $Ba_{0.70}Sr_{0.30}TiO_3$ ceramic which is paraelectric but close to the Curie temperature T_C, in the range

of fields of (0–14) kV/cm the results are shown in the Fig. 3. The permittivity at zero field is $\varepsilon_r (0)$ =3334 and reduces to less than 2040 at the maximum field, i.e. a reduction of permittivity at 60% is obtained. When the field is decreasing to zero, the permitivity increased with a hysteretic behaviour: at zero field the permitivity is 3000 that means with almost 10% less than the initial one. The history effects on the tunability data will be further investigated. Here the analysis is performed for the first cycle of increasing field, starting from the depolarized state.

IV. Discussion

First of all, the data for BZT, at room temperature in its ferroelectric state [9] were fitted with the three approximations. Since the available field amplitude is rather high, the even power law is expected to work only at low field amplitudes. For the high range of field amplitudes, the LGD and Johnson approach were expected to give a better approximation of the experimental data. An excellent fit in overall range of fields from 0 to 45 kV/cm was in fact obtained by using the Johnson approach, as it is shown in the Fig. 2. The best fit parameters were: $\varepsilon_r (0)$ =983, β=3.9×10¹¹ [Vm⁵/C³] and the correlation parameter was 0.9993, indicating an excellent correlation of the experimental data with the empirical equation Johnson. Thus, the LGD theory works well for our systems in the ferroelectric state.

The efforts on applying this approach for ferroelectric relaxors seem rather difficult [10–12]. This might be mainly due to the existence of some nanopolar clusters in the ferroelectric relaxor state, which are superimposed on the dielectric/ferroelectric polarization background of the material. The fact that in our case, the Johnson approach fits better the permittivity-field dependence is thus related to the small values of the polarization of this BZT sample at room temperature. The small polarization is due both to the mixed ferroelectric-relaxor character and to the proximity of the ferro-para phase transition at around 85°C in this ceramic. Further investigations aimed to determine the polarization-field $P (E)$ dependences and the temperature dependence of the tunability are expected to clarify the multiple polarization mechanisms and the limits of the LGD and Johnson approximations in describing ceramics with mixed relaxor-ferroelectric character.

The Johnson approximation was also used to describe the tunability data of BST ceramic (Fig. 3) for which the fit parameters are: $\varepsilon_r (0)$ =3334, β=1.96×10¹º [Vm⁵/C³] and the correlation parameter was 0.9957, indicating also a satisfactory agreement for this sample. However, the BST composition being close to its paraelectric state, a more valid physical approach seems to be the use of the non-interacting dipolar model.
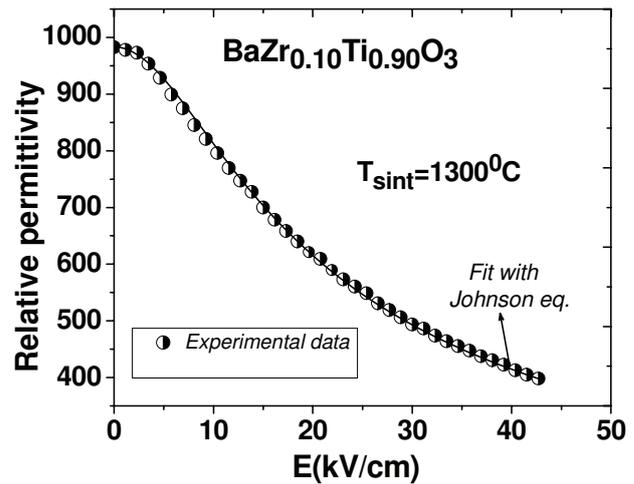
Figure 2. The experimental dc-tunability data for BZT for increasing field and fit with Johnson equation
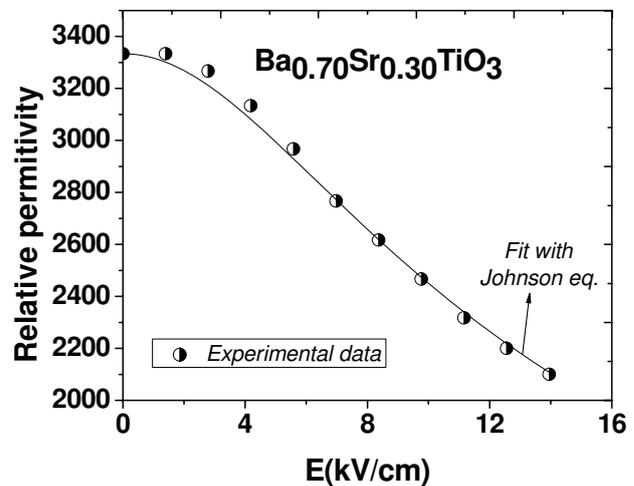
Figure 3. The experimental dc-tunability data for BST and fit with Johnson equations
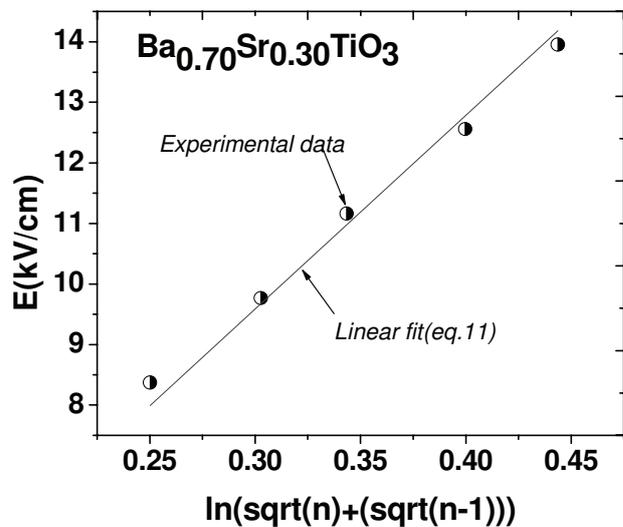
Figure 4. Linear fit of the experimental data for the BST ceramic at low fields with dipolar approach, for computing the average dipolar moment of the system

The tunability data for the BZT and BST ceramics were arranged and represented according to the equation (11) and a linear fit of the function $E = f\left[\ln\left(\sqrt{n} + \sqrt{n-1}\right)\right]$ was performed. While for the BZT ceramic, a nonlinear dependence was found (not shown here), a good linearity is present in the case of the BST sample (Fig. 4). This was expected as a limit of the dipolar model for ferroelectric systems where the model of uncorrelated (non-interacting) dipoles fails in describing ferroelectric and relaxor systems. In the case of BST sample, it was observed a good agreement between the equation (11) and the experimental data, but only for not very high fields where the dipoles remain uncorrelated. The linear regression allowed determine the average value of the individual dipole moment as being: $p_0 = 2.76 \times 10^{-27}$ *Cm*. This is a reasonable value for the average dipolar moment which is ~3 times higher than the dipolar moment associated to the tetragonal distortion of the unit cell in ferroelectric $BaTiO_3$ of *~0.38×10⁻²⁷ Cm* at room temperature. This value is not an individual unit cell dipolar moment, but an effective dipolar moment of the BST system in this case. This value can rather give information on the spatial extension of the nanopolar uncorrelated regions (to around 3 unit cells), still existing in the paraelectric state of the BST ceramic. The temperature and field-dependence of the effective dipolar moment is expected to give information on the changes in the dipolar correlation length induced by temperature and field in the present systems.

V. Conclusions

The theoretical approximation based on the Landau-Ginzburg-Devonshire (LGD) theory and non-interacting dipolar moment models for describing the electric field dependence of the dielectric constant are presented. For the $BaZr_{0.10}Ti_{0.90}O_3$ ceramic samples at room temperature, the tunability data were better fitted by using the Johnson's approximation in the overall range of field amplitudes, most probably due to the low values for the polarization caused by the mixed ferroelectric-relaxor character and by the proximity of the Curie range at room temperature. For the $Ba_{0.70}Sr_{0.30}TiO_3$ ran-

dom non-interacting dipolar units (nanopolar clusters existing also in the paraelectric state) in a double well potential was considered for describing the dc-tunability. By linear regression, it was estimated the average dipolar moment of the dipolar units and the obtained results were in a good agreement with the literature data.

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