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Tunability characteristics of $BaTiO_3$ – based ceramics: Modeling and experimental study

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The electric field dependence of the dielectric constant in ferroelectrics is described theoretically by means of the Landau-Grinzburg-Devonshire (LGD) theory and by two approximations valid for low polarizations (Johnson's equation and even-power relation). While at low fields, all the approximations are describing well the tunability data, at high fields the LGD and Johnson's equations are only providing realistic approaches for the experimental data. Tunability data in a large range of fields obtained for the $BaTi_{0.9}Zr_{0.1}O_3$ ceramic at room temperature were well fitted by using the Johnson's approximation in the overall range of field amplitudes. This was explained by the low values of the polarization caused by the mixed ferroelectric-relaxor character and by the proximity of the Curie range at room temperature.

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1. Introduction

The polar dielectrics are characterized by a strong nonlinear effect under 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. are 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 material to change its permittivity by the electric field and is defined as:

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

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

The dielectric response of ferroelectrics as a function of the electric field, especially up to high field levels, has been studied less due to difficulties related to the obtaining of data at very high fields ensuring the saturation, and to the lack of a convenient theory like for instance, a simple explicit function to deal with dielectric spectra as a function of electric field in a wide range.

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 behavior in ferroelectrics and other polar dielectrics. In addition, the recent interest in applications as tunable electronic devices make even more interesting a study, from technological point of view.

In the present work, the dc-electric field dependence of the dielectric constant $\varepsilon_r(E)$ in polar dielectrics was theoretically studied and compared with experimental data obtained for a $BaTiO_3$-based solid solution, i.e. for $BaTi_{0.9}Zr_{0.1}O_3$ ceramics. The Landau-Ginzburg-Devonshire (LGD) theory and its approximate treatments (Johnson relation) in case of a single polarization mechanism in dielectrics were firstly used [2]: $\varepsilon_r(E)$ was calculated by using the Johnson's relation the even-power equation, and the LGD theory.

The experimental results for a $BaTi_{0.9}Zr_{0.1}O_3$ 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.

2. Sample preparation and experiment

$BaTi_{0.9}Zr_{0.1}O_3$ ceramics were prepared by mixed oxides method starting with high purity reagents of $BaCO_3$ (Flucka), TiO_2 (Merck) and ZrO_2 (Merck). The powders were weighed, 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. The phase purity was checked by X-ray diffraction measurements with a *SHIMADZU XRD 6000* diffractometer using Ni-filtered CuKα radiation (λ = 1.5418 Å), with a scan step of 0.02° and a counting time of 1 s/step, for $2\theta \in (20 - 80)°$. The microstructures and the local chemical composition of the ceramics were investigated with a *HITACHI S2600N* scanning electron microscope with EDX. For measuring the dc tunability, the electroded ceramic pellets were placed in a cell containing transformer oil. For obtaining accurate tenability data, a circuit was designed and realized, as described in detail elsewhere [3], in which the high voltage was obtained from a function generator coupled with a TREK 30/20A-H-CE amplifier.

3. Theoretical description of the dc-tunability

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

3.1 The LGD approach

For expressing the dependence of the dielectric constant on the external electric field, we start with the LGD expression for the free energy, in a cubic crystal:

$$F(P,T) = F(0,T) + \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{\gamma}{6}P^6 + ... \quad (2)$$

where:

$$\alpha = C(T - T_0) = 1/\varepsilon(0) = 1/[\varepsilon_0 \varepsilon_r(0)] \quad (3)$$

is a temperature-dependent coefficient and β and γ are Landau coefficients independent on temperature, P is the ferroelectric polarization. The relationship between the electric field and polarization can be found from the differential relationship derived from the free energy:

$$E = \frac{\partial F}{\partial P}, \quad (4)$$

Resulting in:

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

The electric susceptibility is:

$$\chi = \frac{\partial E}{\partial P} \approx \frac{1}{\varepsilon_0 \varepsilon_r} = \alpha P + 3\beta P^2 + 5\gamma P^4 ... \quad (6)$$

According to the relationship: $P = \varepsilon_0 \varepsilon_r(E) E$, eq. (6) become:

$$\frac{1}{\varepsilon_0 \varepsilon_r(E)} = \frac{1}{\varepsilon_0 \varepsilon_r(0)} + 3\beta\left(\varepsilon_0 \varepsilon_r(E) E^2\right) \quad (7)$$

Equation (6) can be rewritten as:

$$\frac{\varepsilon_r(E)}{\varepsilon_r(0)} = \frac{\left\{1 - \frac{\varepsilon_r(E)}{\varepsilon_r(0)} + \left[\frac{\varepsilon_r(E)}{\varepsilon_r(0)}\right]^3\right\}^{1/3}}{\left[1 + 3\beta\varepsilon_r(0)^3 \varepsilon_0^3 E^2\right]^{1/3}} \quad (8)$$

Equation (8) represents the dependence of the dielectric constant on the applied field in the LGD approach.

3.2 The Johnson approximation

Johnson's approximation was developed by assuming a small polarization. Johnson gave a semi-empirical relation starting from (8), where considers the numerator equal with 1. This approximation was found as valid, after checking the experimental values of the factor for all the possible $\varepsilon_r(E)/\varepsilon_r(0)$ values in the range (0, 1) [7], when a maximum deviation of 15% was found for $\varepsilon_r / \varepsilon_r(0) \approx 0.6$. Thus, a semiempirical relation is obtained:

$$\varepsilon_r(E) = \frac{\varepsilon_r(0)}{\left[1 + 3\beta\varepsilon_r(0)^3 \varepsilon_0^3 E^2\right]^{1/3}} \quad (9)$$

in 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 (2).

3.3 Even-power relation

Taking into account in the Johnson relation that for low fields: $3\beta\varepsilon_r(0)^3 \varepsilon_0^3 E^2 < 1$, the equation (8) is expanded as a polynomial even-power terms of E:

$$\varepsilon_r(E) = \varepsilon_1 - \varepsilon_2 E^2 + \varepsilon_3 E^4 - \varepsilon_4 E^6 ... \quad (10)$$

where:

$$\varepsilon_1 = \varepsilon_r(0), \varepsilon_2 = \beta\left(\varepsilon_0 \varepsilon_r(0)\right)^4, \varepsilon_3 = 2\beta^2\left(\varepsilon_0 \varepsilon_r(0)\right)^7, \varepsilon_4 = 14\beta^3\left(\varepsilon_0 \varepsilon_r(0)\right)^{10} \quad (11)$$

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

The dependence of the dielectric constant on the electric field was simulated by using the equations (8), (9) and (10). The parameters used in these simulations are:

$\varepsilon_r(0)=978$, $\beta=3x10^{10}$ (Vm^5/C^3), $\varepsilon_2=1.27x10^{-11}$ $(V/m)^{-2}$, $\varepsilon_3=1.38x10^{-25}(V/m)^{-4}$. Further, a set of experimental data was fit with these equations in order to find out the best approximation for our case. Depending on the material and its constants, all the three approaches lead to more or less similar dependences at low fields. The LGD permittivity-field dependence tend to saturate faster than one predicted by the Johnson eq. (Fig. 1). 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 observed. All of these approximations have proved to work mainly for ferroelectrics in their paraelectric state.

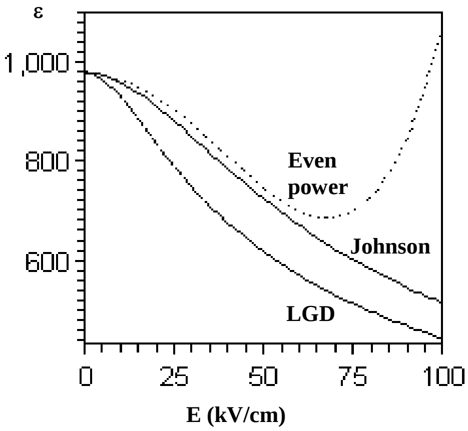

Fig. 1. Simulation of the electric field dependence of the relative dielectric constant by using the LGD, Johnson and even power approximations.

4. Results and discussions

Dc tunability data at room temperatures have been obtained for the $BaTi_{0.9}Zr_{0.1}O_3$ ceramic sample and fits with the three approximations presented before have been performed. This composition is at room temperature in the ferroelectric phase, its Curie temperature is around 85^0C and it was demonstrated to show a mixed ferroelectric-relaxor character [8, 9]. The sample's characteristics and tunability data are presented in the following.

4.1 Microstructure

SEM investigations were performed on the surface of the single-phase $BaTi_{0.9}Zr_{0.1}O_3$ ceramic sample. Despite the lower value of the sintering temperature (of only 1300°C/4h), mainly if we refer to $Ba(Ti,Zr)O_3$ solid solutions processed by the solid state reaction method, an excellent dense and homogeneous microstructure, consisting of well-defined grains of ~ 6 µm was obtained (Fig. 1). The high sinterability of this composition is proved also by the insignificant amount of the intergranular porosity.

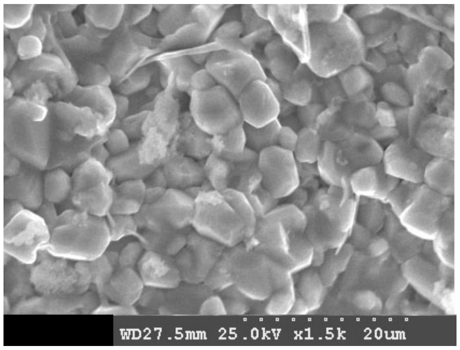

Fig. 2. Surface SEM image of the Ba $Zr_{0.10}Ti_{0.90}O_3$ ceramic sample obtained after sintering at 1300°C/4 hours.

4.2 Tunability data of $BaTi_{0.9}Zr_{0.1}O_3$ ceramics and fits with Johnson model

Accurate tunability data at room temperatures have been obtained for the $BaTi_{0.9}Zr_{0.1}O_3$ ceramic sample in the range of fields (0, 45) kV/cm and they are shown in Fig. 3. The permittivity at zero field is $\varepsilon_r(0)$=983 and reduces to less than 400 at the maximum field, i.e. a reduction of permittivity at 40%. With a dc-field of (25-30)kV/cm, the permittivity diminish at almost half, which means good tunability characteristics of this sample.

These data 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 45kV/cm was in fact obtained by using the Johnson approach, as shown in the Fig. 3. The best fit parameters were: $\varepsilon_r(0)=983, \beta=3.9*10^{21}\left(Vm^5/C^3\right)$ and the correlation parameter was 0.99932, indicating an excellent correlation of the empirical equation Johnson with the experimental data. The LGD theory works well for systems in a full 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, which are superimposed on the dielectric/ferroelectric polarization background of the material. The single polarization mechanism is normally found to be insufficient to describe the whole polarization picture in such a relaxor material. Although the present composition is not in its full relaxor state, but it shows a mixed relaxor-ferroelectric character [8, 9], it probably has a small polarization due both to the mixed ferroelectric-relaxor character and to the proximity of the ferro-para phase transition at around 85^0C. 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. 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.

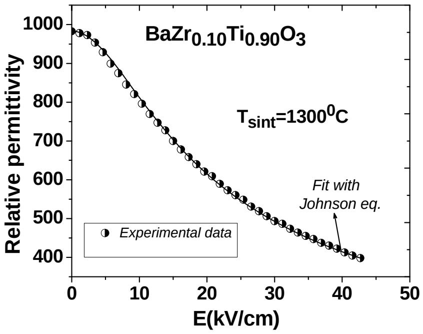

Fig. 3. The dc field dependence of the relative dielectric constant and the fit with Johnson's relation

5. Conclusion

The theoretical approximation treatment based on the Landau-Grinzburg-Devonshire (LGD) theory and two approximations of this theory (Johnson's relation and even-power relations valid for low polarization) for describing the electric field dependence of the dielectric constant are presented. While at low fields, all the approximations are describing well the tunability trend, at high fields the LGD and Johnson's equations are only providing realistic approaches for the experimental data. Accurate tunability data in a large range of fields were determined for the $BaTi_{0.9}Zr_{0.1}O_3$ ceramic samples at room temperature.

These 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.

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