Temperature dependent tunability data and modelling in the paraelectric $Ba_{0.7}Sr_{0.3}TiO_3$ solid solutions

Lavinia Petronela Curecheriu[1,*], Liliana Mitoseriu[1], Adelina Ianculescu[2]

[1]*Department of Physics, Al. I. Cuza University, Bv. Carol I no. 11, Iasi 700506, Romania*

[2]*Polytechnics University Bucharest 1-7 Gh. Polizu, P.O. Box 12-134, Bucharest 011061, Romania*

Received 1 October 2008; received in revised form 4 March 2009; accepted 1 April 2009

Abstract

The field dependence of the dielectric constant (dc-tunability) as a function of temperature in (Ba,Sr)TiO_3 ceramics was investigated. Dense and homogeneous $Ba_xSr_{1-x}TiO_3$ ceramics prepared by Pechini method show low losses, high dielectric constant of ~4000 and typical ferroelectric properties at room temperature. The dc-tunability at various temperatures, including the Curie range, was obtained. A single polarization mechanism was used in the polar state of the ceramics to describe the tunability data. A good correlation between theory and experiment was found. In the paraelectric phase, a model of random uncorrelated non-interacting dipolar units in a double well potential was considered.

Keywords: *Pechini method, dc-tunability, nanopolar regions*

I. Introduction

(Ba,Sr)TiO_3 (BST) solid solutions are basic ceramic materials for microwave devices in wireless communications (filters, phase shifters, voltage-controlled oscillators, etc.) [1]. Their functional properties have been intensively studied in relationship with their preparation technique and processing parameters, composition and microstructural properties, in single-crystal form, ceramics, epitaxial, polycrystalline films or heterostructures [2–5]. In spite of extensive studies dedicated with the BST solid solutions, the basic physics associated to the functional properties is still of large interest and insufficiently understood. For applications in microelectronics it is necessary to have low losses and a strong variation of permittivity with the applied field ("tunability"). High permittivity and tunability are obtained in the ferroelectric phase, because these properties are related to the ferroelectric non-linearity. The main disadvantage of using the ferroelectric phase is the hysteretic behaviour that is not long-expected in such applications. For this reason, it was suggested to use the paraelectric phase around the phase transition, where permittivity is high, losses are low and tunability is high. The study of a system around its phase transition is also interesting because many non-linear components will contribute to the total polarization.

Taking into account these considerations, $Ba_xSr_{1-x}TiO_3$ ceramics were investigated in this work. An optimum of the desired properties were obtained for the composition $x = 0.30$. For this concentration, the temperature dependence of the dc-tunability was investigated. The experimental data were analysed using a model of random uncorrelated non-interacting dipolar units in a double well potential.

II. Experimental

The ceramic samples were prepared by pressing the pure perovskite powders followed by sintering in air at 1350°C/3h. The powders were prepared by a polymerized complex method based on the Pechini-type reaction route, as described in detail in a previous work [6]. The phase purity of the perovskite powders and sintered ceramics was checked by X-ray diffraction measurements performed with a Shimadzu XRD 6000 diffractometer using Ni-filtered CuKα radiation ($\lambda = 1.5418$ Å) with a scan step increment of 0.02° and with a counting time of 1 s/step, for 2θ ranging between 20–80°.

The electrical measurements were performed on the parallel-plate capacitor configuration. Gold electrodes were applied by rf-sputtering on the polished surfaces of

* Corresponding author:
tel: +40 232 201 175, fax: +40 232 201 205,
e-mail: *lavinia_curecheriu@stoner.phys.uaic.ro*

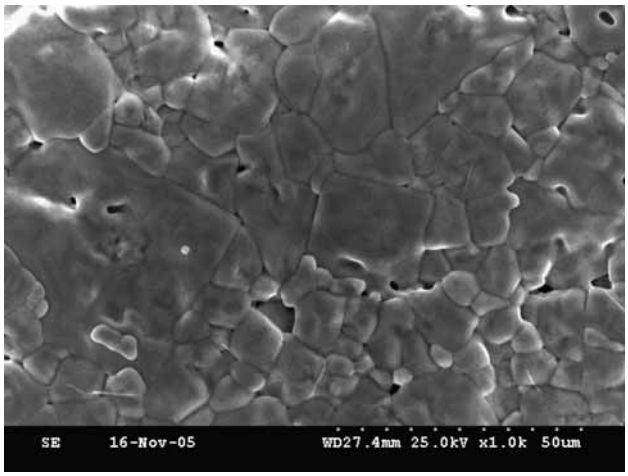

Figure 1. SEM micrographs of the surface of $Ba_{0.7}Sr_{0.3}TiO_3$ ceramic

the sintered ceramic disks. The complex impedance in the frequency domain 1–10^6 Hz and for temperatures below 200°C was determined by using an impedance analyzer (Solartron, SI 1260). For obtaining accurate tunability data, a circuit was designed and realized [7], in which the high voltage was obtained from a dc-function generator coupled with a TREK 30/20A-H-CE amplifier. The ceramic pellets were placed in a cell containing transformer oil to avoid breakdown at high voltages.

III. Results and discussion

X-ray diffraction patterns obtained for the BST ceramics show single-phase composition with the cubic symmetry at room temperature [8]. The SEM image shows a good densification, with a bimodal grain size distribution consisting in exaggerated grown grains with size of ~ 40–50 μm and smaller grains of ~ 3–5 μm (Fig. 1). The temperature dependence of the relative permittivity and the dielectric losses at a few frequencies are presented in the Fig. 2. BST ceramics have excellent dielectric properties, with high values of the permittivity at room temperature (~ 4000) and low losses in the range 25–200°C (*tan* δ < 6%). As expected from the literature data, the ferroelectric BST with the composition x = 0.30 has a Curie temperature around T_C = 20°C and is in its paraelectric state at room temperature [9,10]. The present dielectric data also confirm these properties (Fig. 2).

The dc-tunability was determined at several temperatures around the ferroelectric-paraelectric phase transition and shown in the Fig. 3. A strong nonlinearity of the $\varepsilon(E)$ dependence is observed, with a tendency towards saturation for fields of ~ 20 kV/cm. At room temperature, the sample shows high tunability, $n = \varepsilon(0)/\varepsilon(E)$ of ~ 1.60 for E ~ 20 kV/cm as it can be seen in Fig. 3. For observing the influence of temperature, the dc-tunablity data in range of temperature from 20°C to 70°C were determined (Fig. 4). With increasing temperature, the tunability of BST decreases almost linear from n = 2.6 at 20°C to n = 1.2 at 70°C.

In spite of its paraelectric character, the BST ceramics still show high tunability. One might ask what the origin of this strong non-linear response in the nonpolar state of the BST system is. In the ferroelectric state only one polarization mechanism contribution can be considered, while for the paraelectric state, an overlapping of polarization mechanisms are rather expected, related to: (i) the existence of the dipolar nanodomains (versus individual dipoles or spins) and (ii) the presence of some *degree of correlations* among domains and co-operative freezing of the orientation degrees of freedom below a critical temperature.

For describing the complex polarization process in such system, a simple model considering random non-interacting dipolar units in a double-well potential is considered [11]. It was assumed that $N = N_1+N_2$ is the total number of dipolar units, where N_1 and N_2 are the number of the occupied wells 1 and 2, respectively, and the relative population of the double wells under the field E was calculated. The resulted polarization P of the system of volume V depends on the number of not

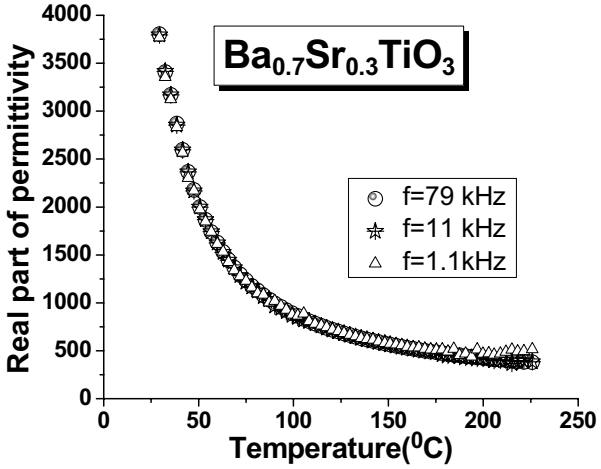

Figure 2. Real part of permittivity vs. temperature for $Ba_{0.7}Sr_{0.3}TiO_3$ ceramic

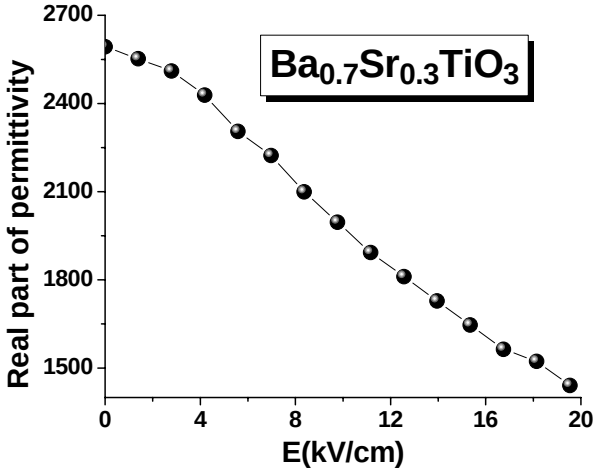

Figure 3. Variation of permittivity with dc-field at room temperature for $Ba_{0.7}Sr_{0.3}TiO_3$ ceramic

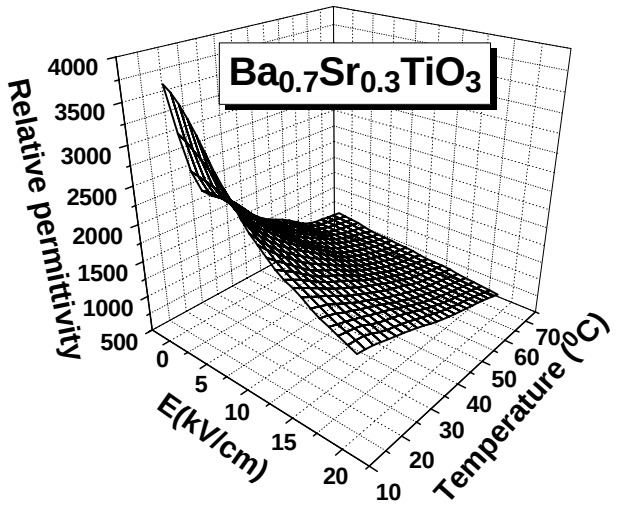

Figure 4. Permittivity vs. dc field at a few temperatures in $Ba_{0.7}Sr_{0.3}TiO_3$ ceramic

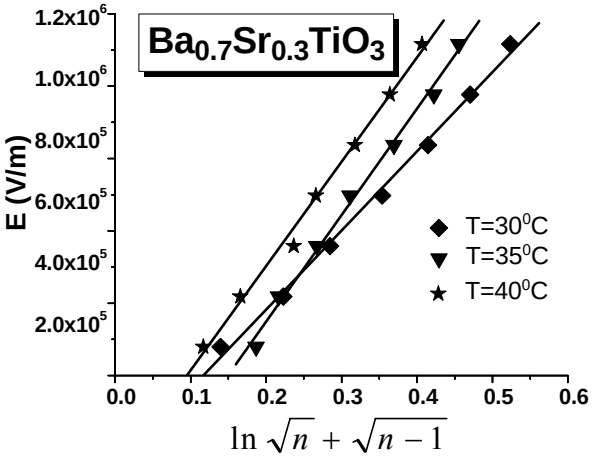

Figure 5. Experimental linear dependence of the applied dc electric field as a function of the logarithm of $\Gamma = \sqrt{n} + \sqrt{n-1}$, according to the equation (3), for a few selected temperatures

compensated dipoles. For a given temperature, it has the expression:

$$P = \frac{p_0 N}{V} \tanh\left(\frac{p_0 E}{kT}\right) \quad (1)$$

Taking into account this polarization-field dependence, the permittivity and tunability at a fixed temperature are calculated as:

$$n = \cosh^2\left(\frac{p_0 E}{kT}\right) \quad (2)$$

from which a logarithmic dependence is obtained:

$$E = \frac{kT}{p_0} \ln\left(\sqrt{n} + \sqrt{n-1}\right) = \frac{kT}{p_0} \ln \Gamma \quad (3)$$

It is worth to mention that this model is valid in the situation when the correlations between the neighbouring dipolar units are negligible. If the model well describes the permittivity-field data for the paraelectric state, a linear dependence of the function $E = f[\ln(\Gamma)]$ should be obtained. The tunability data for the BST ceramics were arranged and represented according to the equation (3). Linear fits according to this function were performed for different temperatures, as shown in the Fig 5. For fields below 20 kV/cm, the agreement between the equation (3) and the experimental data is very good (Fig. 5), allowing to determine the temperature dependence of the average value of the dipole moment p_0 by linear regression. Using this model, the sizes of field-orientable nanopolar regions can be estimated to be in the range of 7.6–8.8 nm for temperatures of 20–70°C. A more detailed study in a large range of temperatures in the paraelectric state is expected to give information on the temperature range of stability of the nanopolar domains in $Ba_{0.7}Sr_{0.3}TiO_3$ ceramic.

IV. Conclusions

The tunability of $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics in the paraelectric state was investigated as a function of temperature. The experimental data were analyzed considering a simple model with field re-orientable non-interacting dipolar units. Using this model, the temperature dependent average dipole moment can be determined and the size of nanopolar regions was estimated in the range of ~7.6–8.8 nm for temperatures of 20–70°C.

Acknowledgements: This work was financial supported by COST 539- ELENA.

References

1. A.K. Tagantsev, V.O. Sherman, K.F. Astafiev, J. Venkatesh, N. Setter, "Ferroelectric materials for microwave tunable applications", *J. Electroceram.*, **11** (2003) 5–66.
2. E.A. Nenasheva, A.D. Kanareykin, N.F. Kartenko, A.I. Dedyk, S.F. Karmanenko, "Ceramics materials based on (Ba,Sr)TiO_3 solid solutions for tunable microwave devices", *J. Electroceram.*, **13** (2004) 235–238.
3. O.G. Vendik, P. Zubko, "Ferroelectric phase transition and maximum dielectric permittivity of displacement type ferroelectrics ($Ba_xSr_{1-x}TiO_3$)", *J. Appl. Phys.*, **88** (2000) 5343–5350.
4. J.F. Scott, S.A.T. Redfern, M. Zhang, M. Dawber, "Polarons, oxygen vacancies, and hydrogen in $Ba_xSr_{1-x}TiO_3$", *J. Eur. Ceram. Soc.*, **21** (2001) 1629–1632.
5. S.U. Adikary, H.L.W. Chan, "Dielectric dispersion and tunability of sol-gel derived $Ba_xSr_{1-x}TiO_3$ thin films", *J. Mater. Sci.*, **39** (2004) 6523–6528.
6. A. Ianculescu, D. Berger, M. Viviani, C.E. Ciomaga, L. Mitoşeriu, V.E. Drăgan, D. Crişan, "Investigation of $Ba_{1-x}Sr_xTiO_3$ ceramics prepared from powders synthesized by the modified Pechini route", *J. Eur. Ceram. Soc.*, **27** (2007) 3655–3658.
7. F.M. Tufescu, L. Curecheriu, A. Ianculescu, C.E. Ciomaga, L. Mitoseriu, "High-voltage tunability measurements of the $BaZr_xTi_{1-x}O_3$ ferroelectric ceramic", *J. Optoelectron. Adv. Mater.*, **10** (2008) 1894–1897.

8. L.P. Curecheriu, F.M. Tufescu, L. Mitoseriu, A. Ianculescu, "Non-linear dielectric properties of ferroelectric ceramics", *J. Optoelectron. Adv. Mater.*, submitted.
9. O.G. Vendik, S.P. Zubko, "Ferroelectric phase transition and maximum dielectric permittivity of displacement type ferroelectrics ($Ba_xSr_{1-x}TiO_3$)", *J. Appl. Phys*., **88** (2000) 5343–5350.
10. G.A. Smolenskii, K.I. Rozgachev, "Dielectric properties of solid solutions in the system of barium titanate-strontium titanate", *Zh. Tekh. Fiz.*, **24** (1954) 1751–1760.
11. A.K. Tagantsev, J.W. Lu, S. Stemmer, "Temperature dependence of the dielectric tunability of pyrochlore bismuth zinc niobate thin films", *Appl. Phys. Lett*., **86** (2005) 03290.