Journal of the European Ceramic Society 22 (2002) 1263–1267
www.elsevier.com/locate/jeurceramsoc

# Dielectric relaxation in ceramics with an intragrain concentration gradient

Igor Lubomirsky*, Tzu Yu Wang, Franco DeFlaviis[1], Oscar M. Stafsudd

*Department of Electrical Engineering, University of California at Los Angeles, California, USA*

Received 26 April 2001; received in revised form 5 August 2001; accepted 15 August 2001

## Abstract

We created a material with a composition gradient within each grain. Due to the graded composition the ceramic does not show a sharp change in dielectric constant near the relaxation frequency. Instead, we observe gradual decrease in dielectric constant with frequency, with the loss tangent remaining practically unchanged (below 0.02 everywhere within the frequency range 0.0003–3 GHz). The tunability of the ceramic decreases with increasing frequency but remains in the order of 10% at 3 GHz. Thus we conclude that the dielectric relaxation in high purity (Ba,Sr)$TiO_3$ occurs predominantly by $Ti^{4+}$ ion hopping relaxation. We also expect that the concept of intragrain concentration gradient ceramics may become a useful material for a wide range of electronic devices. PACS: 77.22.Gm, 77.22.Ch, 77.84.Dy © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* (Ba,Sr)$TiO_3$; Dielectric properties; Gradient-composition; Perovskites

## 1. Introduction

The rapid miniaturization of electro-magnetic devices has led to an urgent need for ceramics with tunable dielectric constants and low loss at microwave frequencies (above 1 GHz). The major class of materials that possess significant tunability, i.e change of dielectric constant under applied electric field, is ferroelectrics in the vicinity of the para-electric to ferroelectric phase transition. Variable dielectric constant and high dielectric loss originate from non-harmonic behavior of ions in the lattice and have their maximum values near the ferroelectric transition.[1] As a direct consequence, a sharp drop in dielectric relaxation frequency near the phase transition temperature is observed.[2–5] Ferroelectrics are tunable below the dielectric relaxation frequency, $f_r$, but when the frequency approaches $f_r$, tunability decreases, eventually to unusable values when $f >> f_r$. Even the most promising candidate for a tunable dielectric material, a (Ba,Sr)$TiO_3$ based ceramic, has the dielectric relaxation frequency in the range of 0.5–1 GHz for both ceramics and single crystals.[2,3] This results in the material having limited usefulness in this range, which is important for communications. Because the loss tangent is maximum slightly above the relaxation frequency,[6] ferroelectric based devices have very high insertion loss at microwave frequencies. Far above the relaxation frequency, when the loss tangent is small again, the dielectric constant becomes independent of the applied electric field and the device is no longer tunable. There are two major theories describing dielectric loss in $BaTiO_3$, piezoelectric grain resonance (domain wall resonance)[7–9] and relaxation of hopping $Ti^{4+}$ ions in the crystal lattice.[2–5] Although there is clear evidence that both mechanisms can contribute to loss, the exact role of each is still a matter of investigation. The search for new materials that combine large tunability of dielectric constant and low loss has hitherto focused on the chemical composition of homogeneous materials (i.e. doping)[10] and the use of composites of such materials.[11–13] Attempts to improve chemical composition produced marginal results as no significant increase in relaxation frequency was achieved despite a number of dopants having been investigated.[2] A different approach was suggested by Sengupta et al., who suggested using a

---

* Corresponding author at current address: Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel.

*E-mail address:* cplubomi@wisemale.weizmann.ac.il (I. Lubomirsky).

[1] Current address: Department of Electrical Engineering, University of California at Irvine, California, USA.

PII: S0955-2219(01)00445-9

composite of ferroelectric and non-ferroelectric.[11–13] However, these measurements were performed at fixed frequency and no continuous data of frequency versus dielectric constant were presented.

In this work, we investigate theoretically and experimentally the properties of graded composition ceramics. Due to the graded composition, the ceramics do not show sharp relaxation, and we observe gradual decrease of dielectric constant with frequency, while the loss tangent remains virtually unchanged. We will describe the basic principle behind this idea and the performance of our first devices. The applicability of this concept, which runs counter to the centuries-old struggle of ceramists to fabricate purer and more homogeneous materials, to other areas of ceramics will also be noted.

### 1.1. Influence of relaxation time distribution parameter on loss tangent

Let us consider the relaxation originating from the hopping of $Ti^{4+}$ ions between two equilibrium positions.[2,3] The double-well potential model suggested leads to a Debye type relaxation. The behavior of the complex dielectric constant, $\varepsilon^*$, near the relaxation frequency can be described by Cole–Cole equation:[2–6]

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + (if/f_r)^{1-\alpha}} \tag{1}$$

where $f$ is frequency, $f_r$ is the relaxation frequency, $\varepsilon_\infty$ is dielectric constant at $f >> f_r$, and $\Delta\varepsilon = \varepsilon_{f>>f_r} - \varepsilon_{f<<f_r}$ is a dispersion step, i.e. the parameter that characterizes the relaxation. The parameter $\alpha$ accounts for the fact that in a majority of cases the relaxation frequency is distributed near a certain frequency, $f_r$. This dispersion parameter, $\alpha$, is called the relaxation time distribution. Maglione et al.[2,3] justified the applicability of this approach for $(Ba,Sr)TiO_3$ ferroelectric alloys. According to this theory the dispersion step, $\Delta\varepsilon$, is given as

$$\Delta\varepsilon = \frac{np^2}{3\varepsilon_0 kT} \tag{2}$$

where $n$ is the number of $Ti^{4+}$ ions per $m^3$, p is the local polarization associated with one ion (i.e. dipole moment associated with one $Ti^{4+}$ hopping divided over the volume of the unit cell), $\varepsilon_0$ is the dielectric permittivity of vacuum, $k$ is Boltzmann constant, and $T$ is temperature. Direct application of Eq. (2) produces $\Delta\varepsilon \approx 10^2$,[3] which is a few hundred times below typical observed values. To explain the high experimental values of $\Delta\varepsilon$, Maglione et al. suggested that $Ti^{4+}$ ions undergo collective hopping, i.e. a large cluster comprising a few hundred $Ti^{4+}$ ions hops simultaneously. Ion hopping is understood as non-diffusive individual or collective hopping/displacement of $Ti^{4+}$ ions between symmetry related sites within the original unit cell. The size of the cluster is a material dependent property. $\Delta\varepsilon$ has a maximum at the Curie temperature.[2,3] Assuming that Eq. (2) is true, then the cluster size must be a strong function of temperature.

Since doping of $(Ba,Sr)TiO_3$ by Ca, Sr, Pb (substitute Ba) or by Zr (substitute Ti) changes the relaxation frequency but does not result in significant increase of $\alpha$,[2] the Cole–Cole diagram $\Delta\varepsilon''(f)$ vs. $\Delta\varepsilon'(f)$ remains very close to a semicircle.[2,3] An increase in the relaxation distribution parameter should always result in a significant decrease of the maximum value of loss tangent.[6] Simultaneously it leads to broadening of the relaxation region. Irrespective of a specific type of distribution, (Frönlich, Gaussian or other) broader distributions lead to lower loss tangent maximum and a wider relaxation region.

From the model developed by Maglione and coauthors[2,3] it follows that if the $Ti^{4+}$ ion clusters have a very broad size distribution, the material should exhibit unusual properties. $\alpha$ would become very large and therefore the loss tangent near the relaxation frequency should decrease. Also one could expect that $\varepsilon(f)$ will no longer follow Eq. (1) since it was given for the case, $\alpha << 1$, and the dependence of $\varepsilon''(f) - \varepsilon'(f)$ will be significantly different from an arc. Therefore, it is of fundamental interest to measure materials with very large $\alpha$. We would like to emphasize that as long as the relaxation step remains unchanged, Kroenig–Kramer's theorem[6] requires that any decrease in $\Delta\varepsilon'$ near the relaxation frequency, or other frequency range, results in a corresponding increase of $\Delta\varepsilon''$ in adjacent regions. Therefore, the principle we suggest for tailoring the material properties is loss distribution.

This idea may also have practical applications. The creation of materials with a large distribution of relaxation time will have very low loss tangent, within a range acceptable for practical use, even in the vicinity of the relaxation frequency. One can expect that increasing $\alpha$ extends the region where dielectric constant is a function of applied bias.

To achieve a wide distribution of $Ti^{4+}$ ion cluster size we propose to use a ceramic with a concentration gradient within the grains. The Curie temperature of such a material will be different at every point within each grain. Therefore, the $Ti^{4+}$ clusters will be of different size throughout the sample. Although, polar clusters cannot be directly observed, agreement between predicted behavior and experiment leads to evidence of the existence of $Ti^{4+}$ clusters.

We will show that such a material does possess large relaxation time distribution and low dielectric loss. An important feature is that the dielectric constant remains a function of external bias at higher frequencies than homogeneous materials with the same composition.

## 2. Experimental

We synthesized high purity (Ba,Sr)$TiO_3$ and $SrTiO_3$ powder with an average grain size of 0.2 μm by the sol-gel method.[14] The absence of extra phases was verified by X-ray powder diffraction. The $BaTiO_3$ and $SrTiO_3$ powders were thoroughly mixed in a molar ratio of 4:1. They were then pressed under uni-axial pressure of 2000 atm. into disks of 6.35 mm diameter. Pure $BaTiO_3$ powder was also pressed into disks by the same method. The samples were then sintered in an oxygen flow at one atmosphere. The length of time and temperature of sintering were adjusted in the range of 0.5–4 h at 1300–1400 °C so that different degrees of $BaTiO_3$/$SrTiO_3$ interdiffusion could be obtained. Evidence of (Ba,Sr)-$TiO_3$/$SrTiO_3$ interdiffusion within the grains was obtained by energy dispersive X-ray fluorescence spectroscopy (EDS), performed on polished ceramic surfaces. The samples were milled down to 0.12–0.18 mm thickness and polished with alumina powder (0.05 μm). Evaporated pads of 150 Å of Ti + 2000 Å of Cu in a $0.5\times0.9$ mm$^2$ area served as the top contact. Gold–palladium contacts were also examined and no dependence on contact material was found. The bottom face was completely covered by 150 Å of Ti + 2000 Å of Cu forming plane capacitor. The capacitors were mounted on a setup calibrated by standard microwave capacitors and resistors. Electromagnetic transmission-reflection parameters (S-parameters) were measured with a light wave analyzer, HP4592, in the range of 300 kHz to 3 GHz. Dielectric constant was deduced by modeling S-parameters with microwave simulation software. Because the measurements were contact material independent, contact resistance could be neglected and a parallel resistor and capacitor equivalent circuit was assumed for calculation of the real and imaginary part of the dielectric constant.

## 3. Results and discussion

EDS analysis (Fig. 1) showed that strong interdiffusion between barium and strontium titanate occurs within a few minutes at temperatures above 1300 °C. The interdiffusion is also accompanied by rapid grain growth, such that all the sintered samples had a similar grain size 3–8 μm. Differential scanning calorimetery (Fig. 2) showed that no latent heat associated with phase transition is detectable after short sintering time. This indicates the formation of an intragrain graded composition ceramic. This agrees with EDS data and confirms that the material does not have significantly large regions with the same chemical composition. Low frequency (300 kHz) measurements of dielectric constant vs. temperature revealed very broad paraelectric to ferroelectric transitions for the samples with graded composition (Fig. 3). Measurements of dielectric constant vs. frequency (Fig. 4) for pure Barium Titanate samples showed an almost ideal fit to the Debye semicircle ($\alpha = 0.0$ and $f_r = 0.54$ GHz). This is in complete agreement with Ref. 2. We discovered experimentally that the $BaTiO_3$/$SrTiO_3$ (4:1) mechanically mixed samples fired for 30 min at 1320 °C (sample 2, see figure captions) possess the smallest maximum value of $\varepsilon''$. The dependence of $\Delta\varepsilon'(T)$ shows a smoothed relaxation step that can be fitted to Eq. (1) with $\alpha = 0.24$ and $f_r = 0.51$ GHz (set of curves 2). However the values $\varepsilon'' - \varepsilon'$ (Cole–Cole plot) does not resemble a circular arc. $\varepsilon''$ shows a very small change and the loss tangent is below 0.01 and stays almost unchanged everywhere in the range of 0.0003–3 GHz. One has to point out that at lower frequencies ( $<<$ 100 MHz), $\varepsilon''$ of sample 2 is higher than that of the other samples. Parameter $\alpha$, calculated by fitting the Cole–Cole diagram to an arc, leads to a value of $\alpha \approx 0.4 \pm 0.02$, which indicates inapplicability of the Cole–Cole equation.

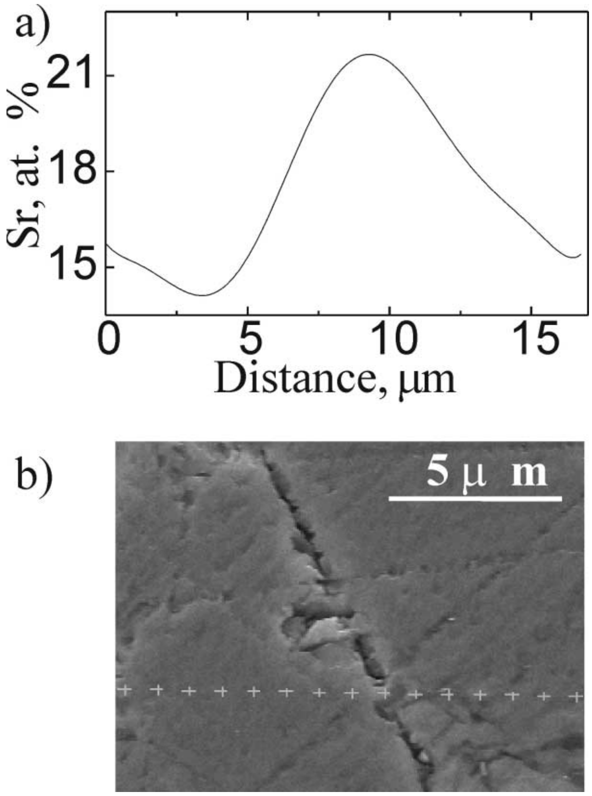

Fig. 1. $BaTiO_3$:$SrTiO_3$ (4:1) interdiffusion for 30 min at 1320 °C observed by EDS. Ceramic sample was polished by 0.05 μm alumina powder: (a) concentration profile; (b) secondary electron image which illustrates the points where measurements were taken. The fissure on the image is a grain boundary. The observed surface is not a cut through the center of both grains and therefore the actual difference in strontium concentration is higher than shown in (a).

To verify that the unusual behavior of sample 2 is due to the intragrain concentration gradient we sintered the sample for additional time to allow further interdiffu-

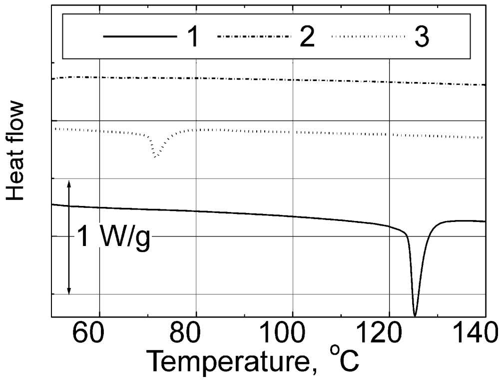

Fig. 2. Differential scanning calorimetery (DSC) measurements illustrating interdiffusion process: (1) high purity $BaTiO_3$ (sample 1); (2) mechanical mixture of $BaTiO_3$:$SrTiO_3$ (4:1) sintered for 30 min at 1320 °C to create intra-grain concentration gradients (sample 2); (3) the same sample after complete interdiffusion (sample 4). The area of the peak on DSC plot is proportional to the latent heat associated with 1st order phase transition. Thus, the large peak on curve 1 indicates that sample 1 undergoes 1st order phase transition from paraelectric to ferroelectric phase at 125 °C. Absence of peaks on DSC for sample 2 shows that no detectable latent heat is associated with the phase transition. Therefore, the sample does not contain any regions with a sharply defined phase transition temperature. The small peak on the DSC plot for sample 4 indicates first order phase transition at 75 °C with the latent heat $\approx 3$ times less than for sample 1, which is expected for a homogeneous $Ba_{0.8}Sr_{0.2}TiO_3$ sample.

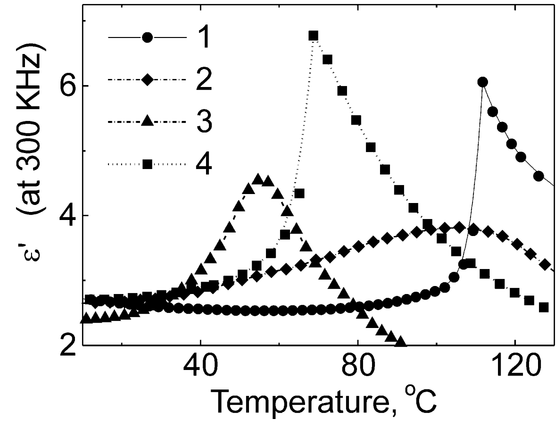

Fig. 3. Real part of dielectric constant as a function of temperature measured at 300 kHz: (1) high purity $BaTiO_3$ (sample 1); (2) interdiffused $BaTiO_3$:$SrTiO_3$ (4:1) for 30 min at 1320 (sample 2); (3) same sample after additional interdiffusion for 2 h at 1380 °C (sample 3); (4) same sample after complete interdiffusion (sample 4).

sion (sample 3, see figure captions). This made the sample more homogeneous and narrowed the distribution of $Ti^{4+}$ cluster size. We clearly observe that after further interdiffusion, the Cole–Cole diagram returns to a circular arc shape and the value of $\alpha$, which fits the $\varepsilon(f)$ dependence, is 0.24, whereas the value, deduced from the Cole–Cole diagram, is 0.97. This indicates that the difference in $\alpha$ calculated by both methods decreases upon decrease in concentration gradient. We also found that after complete interdiffusion, $\varepsilon(f)$ fits Eq. (1) very well, with $\alpha = 0.04$ and $f_r = 0.53$ GHz (not shown), in agreement with Ref. 2.

The measurements of dielectric constant versus applied bias were performed in the 1.8–2.8 GHz frequency range under an applied electric field of 10 kV/cm. The measurements showed that the sample with higher intragrain concentration gradient was less tunable at lower frequencies. However at higher frequencies, in the region where dielectric constant remains a strong function of the applied field, the high intragrain concentration gradient samples exhibited much higher tunability.

The experimental findings can be summarized as follows:

1. The partial interdiffusion of $BaTiO_3$ and $SrTiO_3$ powder forms a ceramic material with intragrain concentration gradient.
2. Graded composition ceramics exhibit a very broad dielectric relaxation region with almost flat Cole–Cole diagram. This indicates an extremely wide distribution of the relaxation time. The relaxation frequency of this ceramic does not significantly differ from a homogeneous material.
3. An unusually flat Cole–Cole diagram appears when an intragrain composition gradient is present. The diagram approaches an arc-like shape when the intragrain composition gradient declines. The $\varepsilon''$-$\varepsilon'$ dependence follows the Debye semicircle when the intragrain composition gradient vanishes completely.

The observed dielectric relaxation cannot be attributed to piezoelectric grain resonance for two reasons. The frequency of the piezoelectric grain resonance for 5 μm $BaTiO_3$ grains is $\approx$150 MHz,[8,9] which is far below the observed relaxation frequency of 500 MHz. Also both samples without concentration gradient, pure $BaTiO_3$ and fully interdiffused $Ba_{0.8}Sr_{0.2}TiO_3$, show $\alpha$ close to zero, which should not be the case for piezoelectric resonance due to the fairly large distribution of grain sizes in the samples.[6]

On the other hand, one can see that the entire observation matches the predictions made on the basis of $Ti^{4+}$ ion clusters relaxation. Therefore, one can consider that low values of $\varepsilon''$ and an almost flat dependence versus frequency is a consequence of a broad distribution of size in $Ti^{4+}$ ion clusters. Although, polar clusters cannot be directly observed, the polar cluster dielectric relaxation theory predicts dielectric properties of graded concentration materials.

Graded materials cannot be treated as a subgroup of relaxors, the dielectric properties of graded materials are equilibrium properties, completely opposite to relaxors.[15]

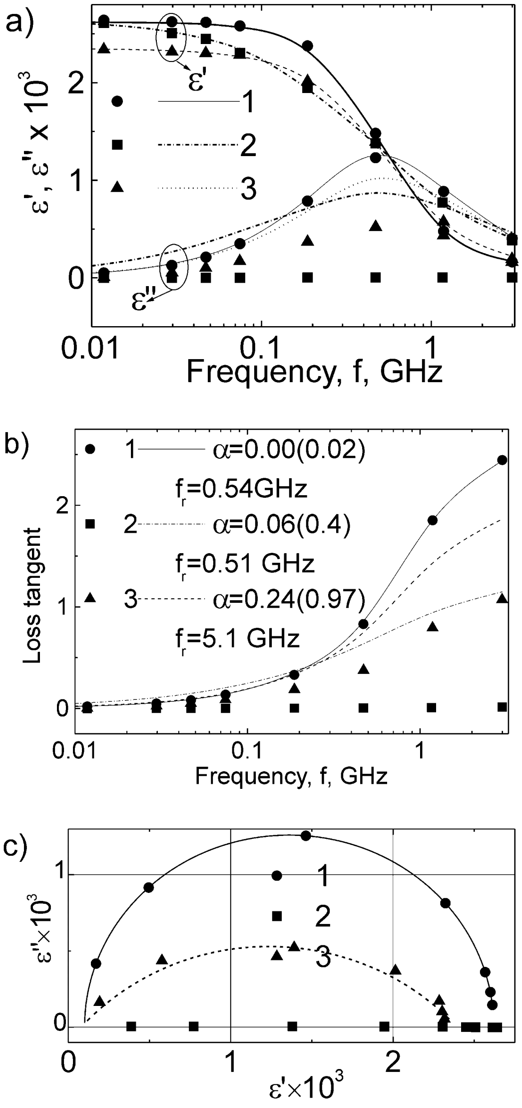

Fig. 4. (a) Real and imaginary part of dielectric constant as a function of frequency; (b) loss tangent as a function of frequency; (c) Cole–Cole diagram: (1) high purity $BaTiO_3$ (sample 1); (2) interdiffused $BaTiO_3$:$SrTiO_3$ (4:1) for 30 min at 1320 (sample 2); (3) same sample after additional interdiffusion for 2 h at 1380 °C (sample 3). After complete interdiffusion, $\varepsilon(f)$ fits Eq. (1) well with $\alpha = 0.04$ and $f_r = 0.53$ GHz (not shown). Points represent experimental data and lines are modeled by Eq. (1). Because $\varepsilon^*(f)$ is a complex function, least square fitting is done separately for the real $\varepsilon'(f)$ and imaginary $\varepsilon''(f)$ components. For the homogeneous samples 1 and 4 (not shown), both fittings result in the same value of $\alpha$, which indicates that the Cole–Cole equation is fully applicable. For samples 2 and 3, there is a large disagreement between values satisfying the real and imaginary parts, which indicates inapplicability of the Cole–Cole equation for samples with intragrain concentration gradients.

## 4. Conclusions

1. $BaTiO_3$:$SrTiO_3$ ceramics with intragrain composition gradient show dispersed dielectric relaxation. The imaginary part of the dielectric constant is almost completely flat with frequency and loss tangent stays below 0.01 over the 0.0003 to 3 GHz frequency range.
2. Dielectric relaxation in $BaTiO_3$ and in the graded composition $BaTiO_3$:$SrTiO_3$ ceramics can be explained on the basis of the $Ti^{4+}$ ion clusters relaxation.
3. Intragrain composition gradients are a promising approach for tailoring dielectric properties of high frequency tunable ceramics.

## Acknowledgements

This material is based upon work supported by, or in part by, the US Army Research Office under contract/grant number DAAH04-96-1-0389. I.L. would like to express his gratitude for the support of the Rueff-Wormster Postdoctoral Fellowship.

## References

1. Mitsui, T., Tatsuzaki, I. and Nakamura, E., *An Introduction to the Physics of Ferroelectrics,* vol. 1, 1st edn.. Gordon and Breach Science, New York, 1976.
2. Kazaoui, S., Ravez, J., Elissalde, C. and Maglione, M., *Ferroelectrics*, 1992, **85**, 135.
3. Maglione, M., Bohmer, R., Loidl, A. and Hochli, U. T., *Phys. Rev. B*, 1989, **40**, 11441.
4. Cheng, B. L., Gabbay, M., Maglione, M., Jorand, Y. and Fantozzi, G., *J. Phys. IV, Colloq*., 1996, **6**, 647.
5. Laabidi, K., Fontana, M. D., Maglione, M., Jannot, B. and Muller, K. A., *Europhys. Lett*., 1994, **26**, 309.
6. Bunget, I. and Popescu, M., *Physics of Solid Dielectrics*, 1st edn. Elsevier, Amsterdam, 1984.
7. Kittel, C., *Phys. Rev*., 1951, **83**, 558.
8. McNeal, M. P., Sei-Joo, J. and Newham, R. E., *IEEE, Transactions Microwave Theory Tech* 837, 1996.
9. McNeal, M. P., Sei-Joo, J. and Newham, R. E., *J. Appl. Phys*., 1998, **83**, 3288.
10. Ghodgaonkar, D. K., Hughes, R., Selmi, S., Varadan, V. V. and Varadan, V. K., *Proceedings of IEEE Antennas and Propagation Society International Symposium*, Vol. 1. Chicago, IL, USA, 18–25 July 1992. IEEE, 1992, p. 272.
11. Sengupta, L. C., Ngo, E., O'Day, M. E., Stowell, S. and Lancto, R., *Proceedings of Proceedings of 1994 IEEE International Symposium on Applications of Ferroelectrics*, University Park, PA, USA, IEEE, 1994, p. 622.
12. Sengupta, L. C., Stowell, S., Ngo, E., O'Day, M. E. and Lancto, R., *Integrated Ferroelectrics*, 1995, **8**, 77.
13. Sengupta, L. C. and Sengupta, S., *IEEE, Transactions Microwave Theory Tech*., 1997, **44**, 792.
14. Lubomirsky, I., Chang, D. T. and Stafsudd, O. M., *J. Appl. Phys*., 1999, **85**, 6690.
15. Vugmeister, B. E. and Rabitz, H., *Physical Review B (Condensed Matter)*, 1998, **57**, 7581.