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High-voltage tunability measurements of the $BaZr_xTi_{1-x}O_3$ ferroelectric ceramics

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One of the most important nonlinear characteristic of ferroelectrics is the tunabilty, i.e. the variation of permittivity with the applied field ε(E). The tunability properties of ceramic are rarely reported since very high voltages are needed for saturation. However, this type of characterization for bulk material is necessary to give reference value for the films characteristics, normally used in applications. A circuit to measure the tunability with a high accuracy was designed and realized. In the present work, the experimental method is described. In addition, tunability data of $BaZr_xTi_{1-x}O_3$ ceramics are shown and discussed.

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1. Introduction

Since the early 1970s, the ferroelectrics applied in the automatic tunable microwave devices has been receiving renewed attention, and a number of practical tunable microwave devices were enameled over the past several decades [1]. It was generally agreed that for such application, ferroelectric should be in the paraelectric phase, since in the polar phase most ferroelectrics show high losses. It was recently demonstrated that such viewpoint is incorrect, and low losses along with substantial tunability of the permittivity were observed in the ferroelectric phase, thus concentrated again the interest on the tunable ferroelectrics [1,2]. $Ba_xSr_{1-x}TiO_3$ (BST) is currently the material of choice for microwave applications due to its low loss and composition dependent Curie temperature, but similar properties show other $BaTiO_3$-based solid solutions like $BaTi_{1-x}Sn_xO_3$ [3]. $BaZr_xTi_{1-x}O_3$ (BZT) was not reported as tunable material, but its properties recommend it as a possible candidate. Recently, this system became attractive from the point of view of its characteristics related to the local polar properties [4], the phase formation mechanism [5, 6] and for the dielectric/tunability properties in the view of microwave applications [7–9].

Tunable circuits are based on capacitors that use a ferroelectric material as the dielectric material. Its dielectric constant and therefore capacitance value, can be adjusted by applying a DC voltage. When the value of a capacitor in a circuit is changed, the impedance and phase relationships in the circuit are affected in predictable ways. These parameter changes can be exploited to yield tunable impedance matching networks, tunable filters, phase shifters, and other functions where a variable capacitor or varactor diode, is used.

The tunability properties of ceramic are rarely reported since very high voltages are needed for saturation. However, this type of characterization for bulk material is necessary to give reference value for the films characteristics. In the present work, tunability data in some BZT ceramics are shown.

2. Experiment

2.1 Sample preparation, structural and microstructural characterisaton

For the preparation by classical solid state reaction method high-purity raw materials as $BaCO_3$ (Flucka), TiO_2 (Merck) and ZrO_2 (Merck) were weighed in appropriate proportions and homogenized with isopropyl alcohol in an agate mortar for 1 hour. The mixture was dried and then granulated using a 4 % PVA (polyvinyl alcohol) solution as binder agent, shaped by

uniaxial pressing at 160 MPa into pellets of 20 mm diameter and ~ 3 mm thickness. The presintering thermal treatment was carried out in air, at 1150°C, with 3 hours plateau. The samples were slowly cooled, then ground, pressed again into pellets of 10 mm diameter and 1 - 2 mm thickness and sintered in air, with a heating rate of 5°C/min, at 1300°C for 4 hours.

X-ray diffraction measurements at room temperature, used to investigate the purity of the perovskite phases were performed 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 $2\theta \in (20 - 80)°$.

A *HITACHI S2600N* scanning electron microscope coupled with EDX was used to analyse the ceramics microstructure and to check the chemical composition of the ceramic samples.

2.2 High voltage measurements cell (HVMC)

For the high measurement voltage measurements, a few precautions have to be taken. A high voltage measurements cell (HVMC) was realized (Fig. 1). The ceramic sample under measurement (S) is usually a plan-parallel ceramic disk with diameter between 10÷20 mm and thickness in the range of (0.6÷3) mm. Ag, Au or Pt electrodes (E) obtained by sputtering or deposited from electrode paste, with thickness below 0.1 mm (E) are commonly used.

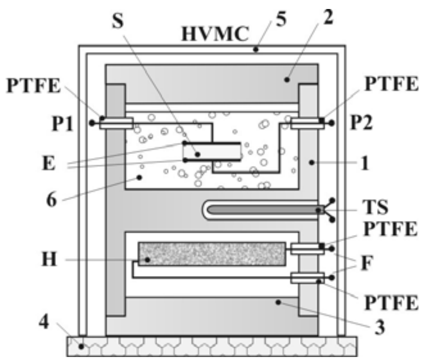

Fig. 1 High-voltage measurement cell: (1) – main body, (2) and (3) – lids, (4) insulating support, (5) insulating cover, (6) transformer or silicon oil, (S) – sample, (E) – electrodes, (H) – heating element, (TS) – temperature transducer, (PTFE) – polytetrafluoretilene, (F) – terminals of the heating element.

The ceramic sample is connected to the circuit by means of thin Cu wires (P1) and (P2) with diameters of around 0.5 mm. To apply a high voltage without breakdown and without causing discharge at the electrodes margins, the sample is embedded into a high-voltage measurement cell (HVMC) containing silicon oil or transformer oil (6). The HVMC is cylindrical and is realized from Al and contains: the main body (1) and two lids, a cover one for manipulating and accessing the sample (2) and a bottom lid (3), ensuring the access on the heating element (H). Inside the main body, a temperature transducer (TS) is introduced. On the top, the HVMC is enclosed by an insulating cover (5) put on the top of the insulating support (4). The connecting cables are insulated out from the HVMC box by using polytetrafluoretilene (PTFE) having a breakdown voltage over 40kV.

2.3 Circuit for the high voltage tunability measurements

A circuit to measure the tunability was designed and realized (Fig. 2). The high voltage source (HVS) is commanded by a function generator (FG), amplified with a TREK 30/20A-H-CE amplifier (PE) is applied by means of a protection resistor (PR) aimed to limit the current through the ceramic sample in case of breakdown of the ceramic sample. A sine wave produced by the generator (G) with stabilized frequency is applied to the sample (P1) by means of a separation capacitor (CS). A current dependent on the ceramic sample capacity is flowing through the resistor (RM) connected to the (P2) contact; the voltage on this resistor is applied through a pass-band filter (PBF) on a selective amplifier (SA). These two blocks, strictly accorded to the frequency of the generator (G) realize such a signal/noise ratio favorable to correctly measure the capacity in the conditions of ripple and noise of the high-voltage generator (HT).

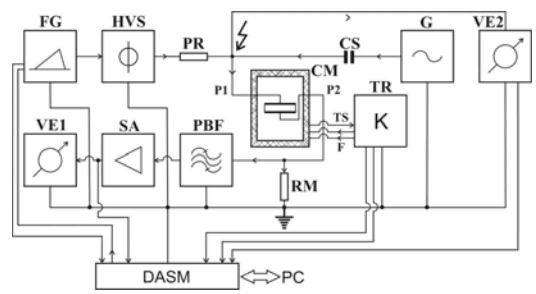

Fig. 2. Block circuit for measuring the high voltage dc-tunability: (FG) – function generator, (HVS) – high voltage source, (FG) – function generator, (PR) – protection resistor,
(G) – generator, (CS) – separation capacitor, (P1), (P2) – ceramic sample contacts, (RM) – resistor, (PBF) – pass-band filter, (SA) – selective amplifier, (VE1), (VE2) – electronic voltmeters, (TR) –temperature regulator (H) – heater, (DASM) – data aquisition system measurements, (PC) – computer.

The voltage measured with the electronic voltmeter (VE1) is in relationship with ceramic capacitance dependent on the high-voltage (tunability), which is measured by the electronic voltmeter (VE2). The temperature control in the sample chamber is ensured by the temperature regulator (TR) commanding a heater (H). A PC – controlled system connected to a data acquisition system of measurements (DASM) is used to command and measure: (a) the generator voltage, (b) the sample capacitance, (c) the temperature and its time-variation. By using this circuit, the high voltage tunability $\varepsilon(E)$ dependences of some $BaTiO_3$ –based ceramics were accurately measured. In the present paper, the data obtained for a $BaZr_xTi_{1-x}O_3$ ceramic are shown.

3. Results and discussions

3.1. Phase composition and microstructure

The room temperature X-ray diffraction pattern of the powder resulted after presintering at 1150°C/3 hours shows the presence of a well crystallized perovskite major phase, with the $BaTiO_3$ structure (Fig. 3(a)). A small amount of $BaZrO_3$ was also identified as secondary phase at the detection limit proving that, in the first stage of the thermal treatment, the two perovskite phases individually form from the raw materials, according to equations (1) and (2).

$$BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2 \uparrow \quad (1)$$

$$BaCO_3 + ZrO_2 \rightarrow BaZrO_3 + CO_2 \uparrow \quad (2)$$

The rise of the thermal treatment temperature leads to the isomorphic integration of the $BaZrO_3$ in the $BaTiO_3$ crystalline lattice (eq. 3), so that after sintering at 1400°C/4 hours, a single phase composition corresponding to the $BaTi_{0.9}Zr_{0.1}O_3$ solid solution was obtained (Fig. 3(b)):

$$0.9\ BaTiO_3 + 0.1\ BaZrO_3 \rightarrow BaTi_{0.9}Zr_{0.1}O_3; \quad (3)$$

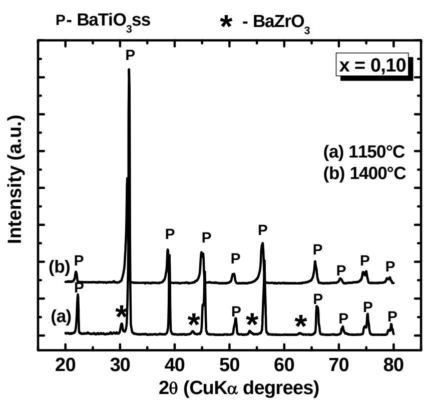

Fig. 3. Room temperature X ray diffraction patterns of: (a) presintered powder; (b) sintered ceramic sample.

The SEM image of the surface of the ceramic sample obtained after sintering at 1450°C/4 hours shows a dense, homogeneous and pore-less microstructure, consisting of large grains (of ~ 50 µm), as a result of the grain growth process induced by the higher thermal treatment temperature. Perfect connections at the triple junctions and well-defined grain boundaries were also pointed out by the micrograph represented in the Fig. 4. For such a dense ceramic, good tunability data have to be obtained.

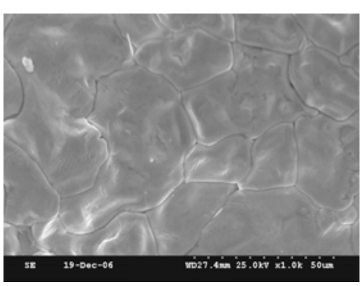

Fig. 4. Surface SEM image of the Ba $Zr_{0.10}Ti_{0.90}O_3$ ceramic sample obtained after sintering at 1450°C/4 hours.

3.2. DC-tunability data at room temperature

Figure 5 shows the capacitance tuning curve for a ceramic capacitor realized with the BZT ceramic described before. By comparison with other literature data [1], a very smooth ε(V) curve was found, proving the reliability of the present system to accurately measure the high voltage tenability of ferroelectric ceramics. For this capacitor, the zero voltage capacitance was about 194 pF but when a voltage of ~11kV is applied, the capacitance decreases by about one half and tends to saturate. Thus, the present ceramic has a rather high tunability, related to its high density and homogeneous microstructure, which might find some important applications.

For example, when used as an element in a resonant circuit, a reduction in capacitance by one half corresponds to a resonant frequency shift of 42% and similarly a 3:1 capacitance change corresponds to a frequency shift of over 70%. An important point to remember is that the ferroelectric capacitor has a very small leakage current, and therefore the power dissipation in the control circuit is virtually negligible. Phase shifters are also a straightforward application of variable capacitance. As pointed out earlier, when capacitance changes, the phase response of the circuit is affected. The critical parameter to be varied in a phase shifter is, of course, the phase. Phase shifters have important applications in base stations and are a critical device in the functioning of phased array antennas. Phased array antennas are expected to increase the efficiency of wireless systems by allowing signals to be radiated only in the direction required, instead of sending it out in all directions as is commonly done now [10].

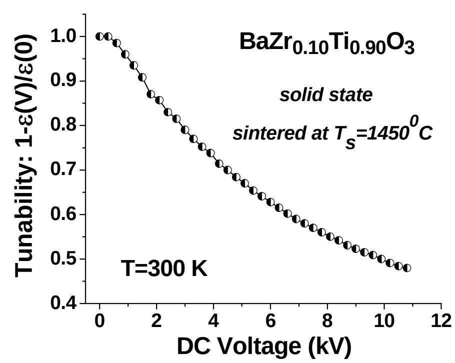

Fig. 5. DC-tunability at room temperature obtained for a $BaZr_{0.10}Ti_{0.90}O_3$ ceramic

Further studies aimed to determine the temperature dependence of tunability in this ceramic and its low-field dielectric characteristics, together with efforts in modeling the tenability data will follow.

4. Conclusions

In the present work, a system to measure the high voltage tenability characteristics of a ferroelectric ceramic was designed and realized. The system was tested by using a BZT ceramic with good microstructural characteristics (homogeneous microstructure, high density, pure phase). Very accurate experimental tunabilities have been obtained. A reduction of the capacitance to around a half when applying a voltage of around 11 kV was observed. Some possible applications of this nonlinear effect were mentioned.

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