I. Introduction in ferroelectricity

I.1. Short history

Ferroelectricity as a field of study appeared in 1920, when Joseph Valasek informed the scientific community that Rochelle salt (double sodium potassium tartrate) have permanent polarization in its natural state, also publishing the first image of the ferroelectric hysteresis cycle. In 1922 he published the first graphic of temperature dependent piezoelectric response of Rochelle salt that indicates the existence of two structural phase transitions in this material. Similar ferroelectric properties were discovered in 1935 in potassium dihydrogen phosphate. Georg Busch and Paul Scherrer found that below - 150 °C this substance is ferroelectric.

Studies looking for materials with high dielectric constant ($\varepsilon_r \geq 100$) have established the usefulness of barium titanate ($BaTiO_3$) in the manufacture of capacitors with $BaTiO_3$ having $\varepsilon_r > 1100$. The main qualities are simple structure, cubic symmetry in polar phase, mechanically and chemically stable ferroelectric phase at room temperature, Curie point of 120 °C, non-piezoelectric and thus non-polar in paraelectric phase having high permittivity (>1000) at room temperature. It was later discovered similar substances like: $KNbO_3$, $KTaO_3$, $LiNbO_3$, $LiTaO_3$, $PbTiO_3$.

Modern theories of feroelectricităţii occurred in 1960 - 1970, in which it is considered that the phase transitions from ferroelectric or antiferroelectric phase in paraelectric state are particular cases of structural phase transitions that occur with changes in the crystal symmetry.

I.2. Specific notions on ferroelectric materials study

The ratio of a dielectric capacitor's capacity and capacity of the same capacitor having air as dielectric is a specific measure and was called by Faraday specific inductive capacity - later called the relative dielectric constant and dielectric permittivity. A system of spatially separated positive and negative electric charges is characterized by the physical quantity called electric dipole moment. The polarization $\vec{P}$ of a macroscopic volume is given by the macroscopic dipole moment per unit volume having the IS unit [C/m^2]. Materials may be polar, having permanent dipoles or non-polar having no electric dipole in the absence of any external electric field. When applying an external electric field materials polarizeby means of mechanisms of polarization: electronic polarization, ionic polarization, orientation polarization, space charge polarization and ferroelectric polarization.

Permittivity ε is the proportionality between $\vec{D}$ and $\vec{E}$, ε_r is called relative electric permittivity or dielectric constant of the environment, and ε_0 is the permittivity of vacuum (8.854×10^{-12} F/m). Each polarisation mechanism is characterized by a finite speed, which causes a specific maximum frequency (resonance), and the dielectric relaxation phenomenon which is the delay of polarization of a dielectric medium to the action of an external electric field. Thus, the dielectric permittivity becomes a complex quantity and the ratio between the imaginary part and the real part causes the dielectric loss tangent δ. The real part of the dielectric permittivity ε' 'is associated with the electricity stored in the dielectric and the imaginary part $\varepsilon''$with the energy dissipation (loss).

I.3. Ferroelectric materials

There are nonlinear dielectric mediums whose permittivity is not constant but depends on $\vec{E}$. These materials are characterized by a Curie point - T_C at which the transition from ferroelectric state to paraelectric state occurs with increasing temperature. In the vicinity of T_C, the dielectric permittivity has a maximum value. When switching from paraelectric state having a cubic electrically neutral crystal lattice, into ferroelectric state, network irregularities are leading to the emergence of electric dipole in the rhombohedral and tetragonal type of crystal lattices, exhibiting high practical interest. A ferroelectric sample is spontaneously polarized. In general, the direction of the spontaneous polarization is not the same in the entire sample, which can be divided into regions of space (volumes) within which there is only one polarization direction, but the direction varies from region to region (ferroelectric domains separated by walls). Applying a strong field can lead to the reversal of polarization (polarization switching) by nucleation and growth processes.

Hysteretic *P(E)* dependence is a characteristic of ferroelectrics. Extrapolation towards P axis of saturation area of the *P(E)* graphic determines the polarization saturation - P_s. Diminishing E, at zero external electric field a remanent polarization persists - P_r. To cancel the remanent polarization an external electric field must be applied in the opposite direction E_C - coercive field.

Ferroelectrics class is composed of several subcategories, the most important economically and technologically being the perovskite class. They present a cubic structure with the chemical formula ABO_3, where A cations occupy the corners of the cube, B cations occupy the central position of the cube and anions O (oxygen ions) are seated in the middle of the cube faces.

I.4. The properties of ferroelectrics

Ferroelectric substances are characterized by a structure of the spontaneously polarisased domains under T_C, polarization switching accompanied by hysteresis under an external applied electric field, ferro – para phase transition of order I or II, abnormal physical properties near the phase transition and ε_r that dependent nonlinearly on E, property described by the term tunability.

The behavior of ferroelectrics in electric circuits is mainly due to the properties of ferroelectric switching and hysteresis and to permittivity dependence of the applied electric field.

I.5. Applications of ferroelectric materials

Referring only to the electrical properties, the types of applications can be divided by the exploitation mode of the dielectric permittivity and spontaneous polarization. The category of high dielectric constant capacitors or uses none of the dielectric permittivity nonlinearity with applied field and the polarization switching. The category of tunable devices devices refers to those ferroelectric devices which exploit the dependence $\varepsilon(E)$ - ferroelectric varactors. The remanence devices category refers to devices whose operation is based on the remanence of polarization that enables the development of new types of binary electronic memories. The category of nonlinear devices involves using ferroelectric devices in alternating electric fields comparable with the saturation field of said ferroelectric. Thus, the state of polarization is switched every half-alternation and dielectric permittivity is not constant.

II. Nonlinear dielectric properties in ferroelectric ceramics

II.1. Dielectric properties characterisation methods

Electrical characterization of dielectrics means getting the electric response $\vec{D}$ to the application of an electric stimulus $\vec{E}$. Experiments are simplified cases, generally single-dimension, in which E is determined by an applied voltage $U(t)$ and D is derived from the determined electrical response of the material. They involve the use of samples in a convenient geometric known configuration, according to the theoretical model underlying the experiment. Ferroelectrics characterization methods can be divided by E into weak field methods, without switching ferroelectric domains (finding ε_r, $\mathrm{tg}\,\delta$, $\varepsilon(T)$, $\varepsilon(f)$, etc.) and strong field methods, with domains switching (finding a $P(E)$, $\varepsilon(E)$, $\mathrm{tg}\,\delta\,(E)$). Nonlinear behavior of ferroelectrics can be studied quantitatively by Fourier analysis of the sample's electric response to the stimulation with a sinusoidal signal having an amplitude comparable to the saturation value of the field.

II.2. Electric response measurement

Typically, bulk ferroelectric samples have thicknesses of the order of 1 mm, thus to study the non-linear regime (the achievement of E values in the order of kV/mm) one needs high voltages of the order of kilovolts to be applied on the electrodes of the samples.

Seen as an electric circuit element, a ferroelectric sample is a real, non- linear parallel-plate capacitor, whose capacitance varies with the applied voltage. For normal sizes and working frequencies (in the order of Hertz), ferroelectric samples insert a Megaohm range or higher impedance into the measuring circuit. For signal/noise ratio improvement it is necessary to establish a measuring current intensity I_{mas} in the milliamps range, much higher than the noise currents. The electrical response of the studied ferroelectric sample is obtained by measuring/recording the electric current I_{mas} when applying an alternating electric voltage $U(t)$. The lower limit of the electric current is determined by the minimum acceptable signal/noise ratio and the upper limit is given by the maximum power that the sample can dissipate. By measuring the current passing through an I-V conversion circuit a voltage V_o proportional to I_{mas} is obtained at the outlet circuit. A XY graphical representation of $V_o(t)$ ($V_o^{-sat} < V_o < V_o^{+sat}$) and $U(t)$, which provide positive and negative saturation of the sample has a current hysteresis form. Replacing the I-V converter with an integration circuit, the output voltage depends linearly on the electric charge developed on the samples' electrodes. Thus, the XY graphical representation of $V_o(t)$ ($V_o^{-sat} < V_o < V_o^{+sat}$) and $U(t)$ is proportional to the $P(E)$ hysteresis, referred to as the voltage hysteresis.

II.3. High voltage interface for measuring dielectric properties

To study the nonlinear switching properties of ferroelectric ceramics an electronic device with multiple role was designed and built. It comprises a measuring circuit, an attenuator circuit, galvanic isolation amplifiers (for the measurement signals), and protection against the effects of dielectric breakdown of the sample. The measuring circuit can perform either as integrator (modified Sawyer-Tower circuit) or as I-V converter. The attenuator enables the measurement of the high voltage applied on the sample.

The high voltage signal is generated by a function generator connected to the input of a high-voltage amplifier. High voltage thus obtained is applied to the studied sample and attenuated by the measuring interface for recording purposes. At the same time, the electric response of the sample is processed for recording. The signals proportional to the applied voltage and to the electric response of the experiment are galvanically decoupled inside the measuring interface and then applied to a digital oscilloscope for recording. The measurement system synchronizes the data aquisition beginning by means of a trigger signal from the function generator to the oscilloscope. Operation of the measurement system was checked with linear circuit elements.

II.4. Ferroelectric ceramics based on $BaTiO_3$

The ceramic materials considered for the experimental study are compositions of $BaCe_xTi_{1-x}O_3$ (BCT) with concentrations x = 0.06; 0.10 and 0.20, and $BaSn_xTi_{1-x}O_3$ (BSnT) with concentrations x = 0; 0.05; 0.10; 0.15; 0.20. The apparent density of the samples was determined using the method of immersion in water. Dielectric properties at both weak and strong electric fields were investigated for both sets of materials. The maximum dielectric permittivity of $\varepsilon(T)$, which indicates the transition from paraelectric phase to ferroelectric phase (with decreasing temperature) is moved with increasing addition of Ce and Sn from high temperatures to lower temperatures. Also, increasing additions determines a transition towards a relaxor type of character with a frequency dispersion permittivity and diffuse phase transitions.

The results of tunability experiments $\varepsilon(E_{DC})$ reveal that only one of the two series of material is suitable for the experimental study of nonlinear dielectric properties in alternating electric field, which is the subject of this work. The series of materials chosen for the experimental study of nonlinear dielectric properties in alternating electric field is the BSnT type. It contains several compositions, some in ferroelectric phase, others in paraelectric phase, thus increasing the chances of identifying a material suitable for applications of dielectric nonlinearity. Also, compared with BCT series, compositions of the BSnT series present higher tunability factors at less intense electric fields.

III. Study on the aplicative potential of the nonlinear character in ceramic $BaSnTiO_3$

Experimental study of the present work aims to expand research in ferroelectric ceramic dielectric nonlinearity applications. The context is largely defined by studies on tunability properties of capacitive devices (varactors) based on solid solutions of BST type with various concentrations of Sr. In general it is about tunable devices exploiting the dependence $\varepsilon(E_{DC})$, with great potential for use in various radio frequency and microwave circuits. But the applicative possibilities of $\varepsilon(E_{AC})$ dependence were less investigated so far, the latest studies demonstrating the possibility of generating harmonics with BST based thin film varactors in the role of frequency multipliers. In this context, the subject of the investigation is focused on nonlinear dielectric properties of less investigated materials compared with BST, including proposing and implementing a suitable device for these properties.

III.1. Nonlinear dielectric response spectral perspective

For sufficiently high values of the field, the polarization tends to saturate, which means that it does not respond linearly to the applied electric field. When applying a sinusoidal electric field the variation over time of the polarization will not be harmonic but will also highlight the phenomenon of saturation. Nonlinear behavior depends on the amplitude of the electric field, with increasing of the latter also increasing the deviation of the response signal from a sinusoidal shape. This deviation is called nonlinear distortion and it manifests by the appearance in the electric response of spectral components called harmonics. To analyze harmonics and thus the degree of distortion of the electric response it is necessary to translate the signal from the time domain to the frequency domain using Fourier analysis. The degree of distortion is directly reflected in the amount of generated harmonics and different amplitudes of the applied electric field cause various degrees of distortion.

In the case of non-biased, non-textured ferroelectric ceramics, with grains oriented randomly, an alternating electric field (with no DC component) will generate a symmetrical response to horizontal axis of the polarization (half-wave symmetry), which means that the even harmonics that appear, and the DC component (at 0 Hz) will have zero amplitude.

Using the spectral perspective one can quantitatively assess the degree of deformation of the response signal by calculating the distortion factor - the ratio of harmonics power output and fundamental harmonic power output. For a given signal the distortion factor (DF - Distortion Factor or THD - Total Harmonic Distortion) is expressed by the square root of the ratio of the effective values of superior harmonics and effective value of the fundamental harmonic.

III.2. Evaluation of nonlinear dielectric response in ceramic BSnT

The experimental study was focused on the spectral analysis of non-linear dielectric response of the $BaSn_xTi_{1-x}O_3$ (x = 0; 0,05; 0,1; 0,15 and 0,2) series of samples in order to obtain a sorting of the studied ferroelectric systems by harmonic generation capacity. In this purpose the evolution of the distortion factor depending on the amplitude of the applied electric field was obtained for all samples of the BSnT series.

The measurement of a sample resulted in the obtaining of the pair of signals proportional to E and P acquired synchronously which describe the dynamics of the hysteresis loop at different values of the applied electric field. After that the signals were translated from the time domain to the frequency domain. For each E amplitude *P(t), E(t), P(E), P(f), E(f),* the amplitudes and phases of E, P_1 ... P_{19} were obtained with which ε_{r1}, tg δ_1 and THD were calculated, so it was possible to represen then $\varepsilon_{r1}(E_{AC})$, $tg\delta_1(E_{AC})$, $THD(E_{AC})$, $P_1(E_{AC})$... $P_7(E_{AC})$ şi $phaseP_1(E_{AC})$ ... $phaseP_7(E_{AC})$.

Criteriului de comparație este gradul de distorsiuni armonice al răspunsului electric în funcție de amplitudinea câmpului electric aplicat. În cazul de față, materialul cel mai potrivit pentru exploatarea proprietăților dielectrice neliniare este $BaSn_{0,05}Ti_{0,95}O_3$.

The comparison criteria is the level of harmonic distortion of the electric response depending on the amplitude of the applied electric field. In this case, the most suitable material for exploiting nonlinear dielectric properties is $BaSn_{0,05}Ti_{0,95}O_3$.

III.3. Making a ferroelectric based RF mixer

Previous study's results have been obtained by applying a sinusoidal electrical signal with a frequency of 10 Hz. To make a RF device the existence of nonlinear dielectric properties in this domain must first be confirm. Checking nonlinear dielectric properties at a frequency relevant for RF field can be done by means of a *I(V)* type comparative experiment, in which the electric response is evaluated by the amount of harmonics. This check was performed at a frequency of 1 MHz. The values of total harmonic distortion calculated for each sample confirm the existence of nonlinear dielectric properties: different materials determine different values of total harmonic distortion factor. BSnT composition with x = 0.05 was selected to carry a radio frequency applications that exploit the nonlinearity of the dependence $\varepsilon(E_{AC})$.

The main effect of a nonlinear system is the generation of harmonics by distorting an input signal. $BaSn_{0,05}Ti_{0,95}O_3$ composition is such a system when the input signal is strong enough, thus the use of nonlinear dielectric properties it possess is suitable in applications such as harmonics generators. Having in mind the total dielectric losses (in nonlinear mode), applications that require high efficiency are not suitable in this case (ie. frequency multipliers). Instead, a more suitable application relies more on the dielectric nonlinearity than on energy efficiency, therefore the chosen composition was used to make a frequency mixer, a fundamental electronic device in RF domain. An ideal RF mixer multiplies two periodic input signals, resulting another two periodic signals whose frequency is given by the difference and sum of the initial signals' frequencies.

The prototype of the ferroelectric based mixer developed in this study replaces the resistive non-linearity of semiconductor (currently the main technology) with the dielectric nonlinearity (reactive) ot the ferroelectric material. The selected configuration contains four capacitors connected in a Wheatstone bridge like electric circuit in which the LO signal (which stimulates the non-linearity of the device) is applied to two diagonally opposed circuit nodes. Given that the four capacitors are identical, the voltage present between the othe two circuit nodes of the other diagonal is zero. Thus, the presence of LO signal and its harmonics at the other two ports is avoided, by connecting the latter to circuit nodes with identical potential. The ferroelectric capacitors were constructed in planar configuration, by metallization of the surface of the chosen ceramic sample and microstructuring of the deposited metallic layer (Ag).

The construction differences between the co-planar capacitors determine different non-linearity thresholds (voltage) from one capacitor to another. Thus the electrical behavior of the mixer loses symmetry, resulting the appearance of low rank harmonics (RF ± LO) in the mixer's output, non-existent in the symmetric case simulated in this study. The first two most important intermodulation harmonic (by amplitude) are (2LO - RF) and (2LO + RF), like in the simulation.

The functional properties of the ferroelectric mixer differ fundamentally from those of the semiconductor type in that the intermodulation generated harmonics are fewer and more dispersed, spectrally described by (± 2nLO RF).

A key consequence of using the dielectric non-linearity in a RF mixer is that the LO signal may be added a DC offset component with the aim to exploit only portions of the bipolar non-linear transfer characteristic, which makes the mixer a reconfigurable one.

IV. Conclusions

This work presents a staged way from studying the dielectric properties of ferroelectric materials to exploiting these properties in a ferroelectric mixer. A new concept of RF mixer was demonstrated – in situ reconfigurable RF mixer, which seems to have a high applicative potential, given the trend in the multistandard wireless devices. The proposed concept has several advantages (simplicity, cost, functional features), but brings with it the significant disadvantage of dielectric loss which causes thermal dissipation of energy, capable of altering the temperature of the material and therefore its dielectric properties.

Any dielectric non-linearity may be exploited in a mixer type application, and this type of non-linearity has the advantage that is not based on electronic conduction, which theoretically means lower generated noise levels, a feature that impact directly functional performance as the minimum threshold of signals that can be processed (sensitivity in radio reception equipment)

The research in this thesis resulted in several original contributions that have been published or presented at international and national conferences, and the high voltage interface for measuring dielectric properties was proposed for certification:

Patent application:

1. M. V. Pop, L. Mitoşeriu, „Interfață de tensiune înaltă pentru măsurarea proprietăților electrice ale materialelor dielectrice si feroelectrice", OSIM registration No: A/00861/04.03.2014 (in evaluation)

Indexed papers (Thomson Reuters, former ISI):

1. L. P. Curecheriu, M. Deluca, Z. V. Mocanu, M. V. Pop, V. Nica, N. Horchidan, M. T. Buscaglia, V. Buscaglia, M. van Bael, A. Hardy, L. Mitoseriu, „Investigation of the ferroelectric-relaxor crossover in Ce-doped $BaTiO_3$ ceramics by impedance spectroscopy and Raman study", Phase Trans., Vol. 86, Nr. 7, pg. 703–714, 2013; (Special edition: The Third COST MP0904 WG Workshop, 23-24 April 2012)

2. C. E. Ciomaga, A. M. Neagu, M. V. Pop, M. Airimioaei, S. Taşcu et al, „Ferroelectric and dielectric properties of ferrite-ferroelectric ceramic composites", J. Appl. Phys., Vol. 113, Nr. 7, pp. 074103, 2013

Send to publication:

1. M. V. Pop, L. Mitoşeriu, „Ferroelectric mixer – a simple, reconfigurable frequency conversion device”, spre publicare la IEEE Transaction on Electron Devices