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On Resonance Charts of Piezoelectric Ceramics of Perovskite -Type in Microwave Range

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Abstract — Determination of the electrical resonance positions on frequency scale for the multicomponent materials is a necessity for the a correct exploitation of the material in the HF range, where multiple resonances are present. We have used for resonances determination a microwave simulation method, applied for a class of piezoelectric ceramics of perovskite-type: the KxNa1−xNbO3 and (1 − y)K0.5Na0.5NbO3–ySrTiO3 crystals. Results were obtained in the frequency domain of 0.3–30 GHz. Structural interpretations and conclusions about geometrical and physical resonances determined for the material samples are available. The links between the resonances of the electrical displacement and the internal structure of the material samples were illustrated by resonance charts and commented as well. Geometrical parameters of the constituents (ionic radii, ion relative distances, average grains dimensions, etc.) and also the physical parameters (ions nature, concentration factors, phase transitions, polarization mechanisms, etc.) influence the resonance charts and can be also coordinated for resonances modification.

***Index Terms* — electrical resonances, finite element method, microwave range, piezoelectric ceramics, structural simulation**

I. INTRODUCTION

Discontinuities of the electric properties for a class of piezoelectric ceramics have been analyzed in this paper. Strongly dependent on the internal structure and components nature, the resonances of electrical permittivity give us information about the material response in high frequency fields. A precise localization of these resonances on the frequency scale is necessary for a correct exploitation of the composed material in the domain of interest. An exact determination of these resonances can be experimentally done in AF and even RF range. At higher frequencies (in the microwave range), theoretical models are incomplete, the analysis being complicated by the wavelength decreasing down to the macroscopic components dimensions, inside the samples [1]. Simulations results, verified by measurements at punctual frequencies, come to complete the information about the composed material resonances, in these frequency domains.

We have used a microwave simulation method for electrical resonances determination, applied in the case of the considered piezoelectric ceramics of perovskite-type [2], [3]. The computing program was High Frequency Structure Simulator, HFSS 12.0 by Ansoft. The geometrical resonances, depending exclusively on geometrical parameters of the constituents (ionic radii, ion relative distances, average grains dimensions, etc.), have been descerned by the physical resonances, depending on sample ions nature, concentration factors, phase transitions, polarization mechanisms [4]. Conclusions were formulated, considering the links between resonances magnitude and position on frequency scale, samples structure (geometrical and physical configuration) and material response to the external field. Results are available for the design optimization of different optoelectronic devices like spatial light modulators or electro-optic switches.

II. STRUCTURAL SIMULATION OF THE PIEZOELECTRIC CERAMICS

The perovskite ceramics analyzed in this paper are the piezoelectric $K_xNa_{1-x}NbO_3$ ($x = 0.00 \div 0.65$) (PSN) crystals and the relaxor lead-free solid solution $(1 - y)K_{0.5}Na_{0.5}NbO_3$–$y$SrTiO$_3$ (KNN–STO 80/20) with $y = 0.15 \div 0.25$. A study of the electrical resonances for the composite materials function of sample configuration has been performed, by structural simulation of the internal structure and setting the exposure level. The working frequencies were in the domain of 0.3–30 GHz. The eigenmode module of the HFFS solver has been set for resonances determinations for each material sample. Electrical resonances depend of the geometrical and physical parameters of the structures, which can be easily modified with help of the simulation method. A pure PTFE samples was also considered, as comparison basis.

Geometrical, respectively physical parameters have been modified successively, in order to determine their influence on different resonances of the analyzed structures.

The structure of the piezoelectric ceramics $K_xNa_{1-x}NbO_3$ evolves with temperature, the material presenting a succession of phases. The crystalline structure is typical perovskite, ABO_3 (figure 1), with the Nb atoms positioned in B sites, on the surfaces of spheres of constant radii surrounding centers of NbO_6 octahedrons. The octahedrons geometry does not depend on the x value, only the octahedron rotation angles do [5], [6]. The temperature and implicit the phase transitions determine modification of the Nb atom distribution on the sphere surfaces. At usual temperature (300K ÷ 423 K), the local structure of the NbO_6 octahedrons is described by the 12-site model [5]. The following internal parameters have been used: r_0, the radius of the small sphere surrounding the immediate center of a NbO_6 octahedron = 0.195 Å; R_0, the average Nb-O distance = 2.02 Å.

The lead-free ceramic $(1 - y)K_{0.5}Na_{0.5}NbO_3$–$y$SrTiO$_3$ (KNN–STO 80/20) is a solid solution having pseudo-cubic perovskite structure [7], [8]. The material is a typical relaxor for $y = 0.15 \div 0.25$, with nonlinear optic properties and large quadratic electro-optic Kerr effect. It is also characterized by a high density (4760 kg/m^3) and an uniform distribution of the micrograins [9]. The considered average grain size was of 50 - 100 µm at room temperature.

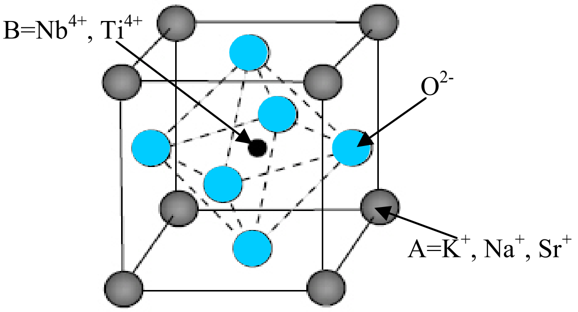


Fig. 1. The perovskite basic cell, ABO$_3$, for the K$_x$Na$_{1-x}$NbO$_3$, respectively K$_{0.5}$Na$_{0.5}$NbO$_3$ and SrTiO$_3$ ceramics; one observes the NbO$_6$ octahedral subnetwork (dash lined). The represented cell is ideal cubic; octahedral-site rotations in the orthorhombic phase have to be considered (for K$_{0.5}$Na$_{0.5}$NbO$_3$) and also the imperfections in the pseudo-cubic case (for the solid solution).

Details of the structures were also presented in figure 2.

Resonances of the electrical displacement $\left|\vec{D}\right|$ have been determined by structural simulation, considering this vector dependence on the exposure electrical field and internal polarization:

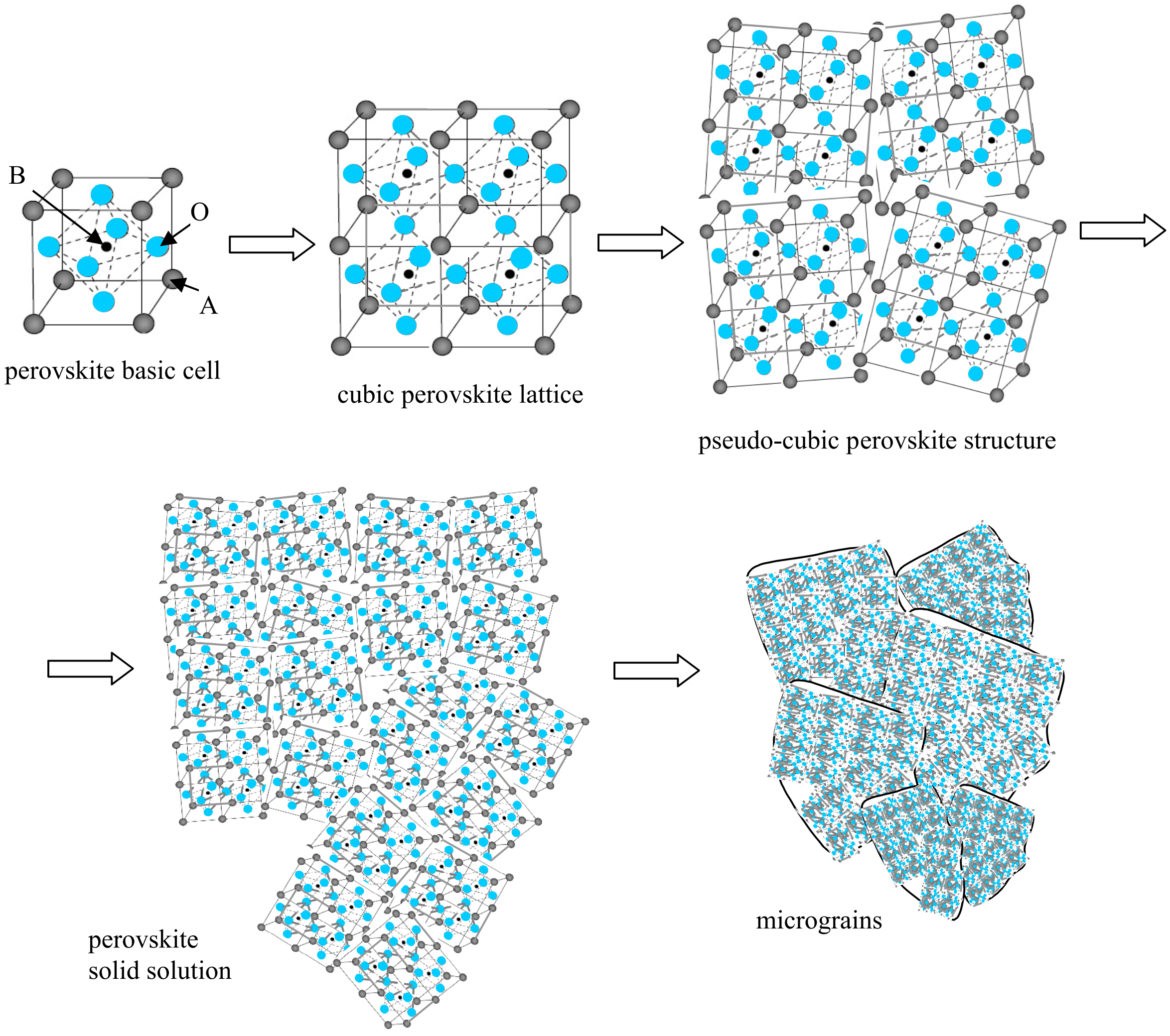
$$\nabla \times \vec{D} = \varepsilon_0 \left(\nabla \times \vec{E} \right) + \nabla \times \vec{P} \qquad (1)$$

Fundamental resonance and the first ten resonances in microwave range were determined for different values of the concentration factor, x, respectively y.

The calculation of resonance frequencies was done using the HFSS program and a proper algorithm. In order to find the resonances of the structure, the eigenmode solver sets the source field $\boldsymbol{b}$ to zero and solves the matrix equation:

$$\boldsymbol{Sx} + k_0^{\,2} \boldsymbol{Tx} = \boldsymbol{b} \qquad (2)$$

where $\boldsymbol{S}$ and $\boldsymbol{T}$ are matrices that depend on the geometry and the mesh defined for the finite element method (FEM); $\boldsymbol{x}$ is the electric field solution; k_0 is the free-space wave number corresponding to that $\boldsymbol{x}$ mode and $\boldsymbol{b}$ is the value of the source (testing field) defined for the problem. Equation is solved for sets of (k_0, $\boldsymbol{x}$), one for every $\boldsymbol{x}$.



perovskite basic cell

cubic perovskite lattice

pseudo-cubic perovskite structure

perovskite solid solution

micrograins

Fig. 2. Models for the structural simulation of the considered perovskite ceramics - evolution of the structure from microscopic to macroscopic parameters of the material samples.

The finite element method applied by the eigenmode solver is characterized by the following steps:

- Formulate a weak or variational form of the partial differential equations for the material response at the field.
- Choose a macroscopic finite element inside the structure (at least 10^3 times larger than the molecular dimensions and

comparable with the dimensions of the micrograins).

- Create a mesh for the continuous domain (a group of micrograins, here) using the reference shape of chosen finite element.

- Assemble a set of linear equations by applying the weak form on each element in the mesh.

The ***S*** and ***T*** matrices are frequency dependent. The wave number k_0 is related to the frequency of the resonant modes:

$$f_i = \frac{k_0 c}{2\pi}, \qquad (3)$$

where c is the light speed in the free space.

III. RESULTS FOR THE ELECTRIC RESONANCES IN MICROWAVE RANGE

The interaction field - substance is characterized by the resonances amplitude and position on frequency scale. Electrical displacement resonances indicate the maxima of polarization of each structure.

The obtained results are illustrated in Table 1 for the frequency domain of 0.3 - 10 GHz and are represented on charts similar with these given in figures 2 - 5 for the frequency domain above 10 GHz. On resonance charts we have represented the relative electrical displacement $\vec{D}$ reported to the displacement far from a resonance $\vec{D}_{1\,GHz}$, or $\left|\vec{D}\right| / \left|\vec{D}_{1\,GHz}\right|$ versus frequency. At exploitation temperatures around the room temperature and below TC corresponding to the piezoelectric phase transition, the structures are thermally stable and the frequency dependence of the material response to the external field can be studied.

Internal geometrical and physical parameters of the samples have been varied gradually and successive, in order to obtain each resonances dependence of these parameters.

Ionic radii of the constituent atoms, their relative spacing and the grain size are the main parameters which impose the first resonance value. Rotation angles, pseudo-cubic decrement, non-repetitive orientation coefficient in the solid solution and other secondary geometrical parameters have a low influence on the first resonance and its multiples (e.g. low differences from cubic to orthorhombic), but determine additional resonances of low magnitude at higher frequencies and influence superior order resonances on chart.

The simulation method allows a very easy modification of the structural parameters for the considered perovskite ceramics in comparison with the experimental cases. These modifications reverberate directly on each resonance position on chart.

At macroscopic level, the average grain size, the vacuum content in the ceramic material and the boundary conditions on the grain walls are responsible of a bunch of high amplitude resonances which appear in the vicinity of the first resonance in the microwave range. These resonances are marked with a superscript cross in Table 1.

Resonances magnitude depends on the physical parameters of the materials. Ions nature influence is the most important (between 20 and 80 %). The concentration of phases is the second important element for resonances magnitude determination. Resonance charts were obtained in the temperature domain from the room temperature to the T_{Curie} of the piezoelectric phase transition, which is around 420 - 460 K for the considered materials. The phase diagrams were used in this temperature domain for the correct description of the structures [5], [6]. We have to mention that at phase transitions the resonance chart modifies substantially, but the phenomenon doesn't make the subject of our analysis.

Atomic and electronic polarization mechanisms are preponderant at the considered perovskite ceramics, responsible of first resonance in the considered frequency domain. Local electric charge accumulations occur, due to the pseudo-cubic lattice, in the case of the solid solution. A bunch of resonances are generated in this way (inside the dashed ellipsoid on figures), whose position on frequency scale is almost un-reproducible from a simulation to another.

A resonances pattern displacement to sensible higher frequencies observes then the concentration factors x increases, respectively y increases. Displacement occurs especially in the frequency domain up to the first multiple of the resonant frequency, f_0. This appears to be caused by replacement of the Na^+ ions with more K^+ ions in the A position of the perovskite basic cell, in the case of the $K_xNa_{1-x}NbO_3$. In the case of the solid solution, even the $K_{0.5}Na_{0.5}NbO_3$ (the perovskite with K) concentration increases, the resonances are not shifting to higher frequencies. This is an example of a physical element influence on resonance pattern.

One observes that, in despite of resonances displacement to higher frequencies when the K content increases for a single perovskite, the fundamental resonance frequencies are decreasing in the case of a solid solution. This fact demonstrates that the K content is not the most influent parameter in this case.

If we superimpose the resonance charts of the separate perovskites included by the solid solution ($K_{0.5}Na_{0.5}NbO_3$ and $SrTiO_3$), and then compare with the solid solution resonance chart, one can observe that the perovskite with an increased symmetry ($SrTiO_3$, with all A position occupied only by Sr) and stronger inter-atomic forces imposes its resonances. Resonances corresponding to the other perovskite in the solution have lower magnitude and will be taken into account at higher frequencies (over 30 GHz), when the all the molecular dipoles follows harder the time evolution of the external field.

TABLE I. THE FUNDAMENTAL RESONANCE AND THE FIRST TEN RESONANCES IN MICROWAVE RANGE FOR THE PEROVSKITE CERAMICS $K_xNa_{1-x}NbO_3$ AND $(1-y)K_{0.5}Na_{0.5}NbO_3$–$ySrTiO_3$.

No.	Material	f_0 [GHz]	f_1 [GHz]	f_2 [GHz]	f_3 [GHz]	f_4 [GHz]	f_5 [GHz]	f_6 [GHz]	f_7 [GHz]	f_8 [GHz]	f_9 [GHz]	f_{10} [GHz]
a	$NaNbO_3$	2.23	2.95	3.54	4.43*	4.75$^+$	4.92$^+$	5.14	6.23	6.64*	6.93	7.15
b	$K_{0.05}Na_{0.95}NbO_3$	2.46	3.02	3.85$^+$	4.24$^+$	4.96*	5.29	6.83	7.37*	7.64	7.95	8.24
c	$K_{0.3}Na_{0.7}NbO_3$	2.15	2.87	3.62$^+$	4.11$^+$	4.33*	4.76	5.56	6.21	6.44*	6.87	6.92
d	$K_{0.4}Na_{0.6}NbO_3$	2.79	3.12	3.94$^+$	4.65$^+$	5.52*	6.62	7.14	7.84	8.34*	8.68	8.93
e	$K_{0.5}Na_{0.5}NbO_3$	2.88	3.14	4.07$^+$	4.68$^+$	5.77*	6.84	7.25	8.09	8.62*	8.97	9.16
f	$K_{0.65}Na_{0.35}NbO_3$	2.96	3.25	4.19$^+$	4.75$^+$	5.90*	6.97	7.58	8.29	8.84*	9.07	9.52
g	$0.75K_{0.5}Na_{0.5}NbO_3$–$0.25SrTiO_3$	1.83	2.06	2.58$^+$	3.14$^+$	3.26$^+$	3.62*	4.16	4.53	4.87	5.13	5.45*
h	$0.8K_{0.5}Na_{0.5}NbO_3$–$0.2SrTiO_3$	1.62	1.89	2.38	2.57$^+$	2.83$^+$	3.21*	3.64	3.85	4.18	4.65	4.83*
i	$0.85K_{0.5}Na_{0.5}NbO_3$–$0.15SrTiO_3$	1.47	1.82	2.26$^+$	2.54$^+$	2.75$^+$	2.92*	3.14	3.46	3.78	4.08	4.40*

* Resonances marked are multiples of f_0.

$^+$Resonances due to the macroscopic geometrical parameters of the samples.

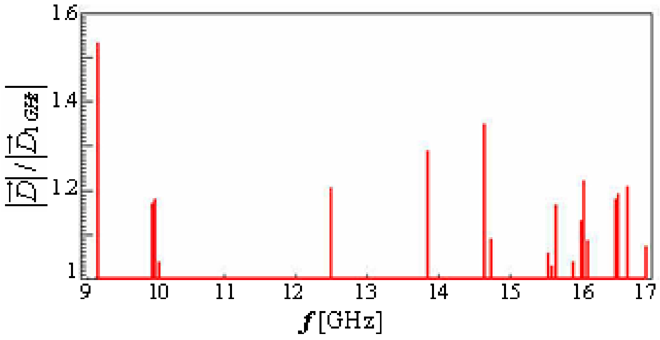


Fig. 3. Resonances chart for sample ***b)***: $K_xNa_{1-x}NbO_3$, with $x = 0.05$.

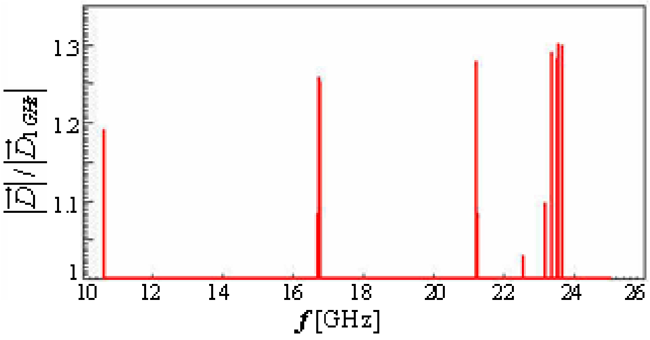


Fig. 4. Resonances chart for sample ***e)***: $K_xNa_{1-x}NbO_3$, with $x = 0.50$.

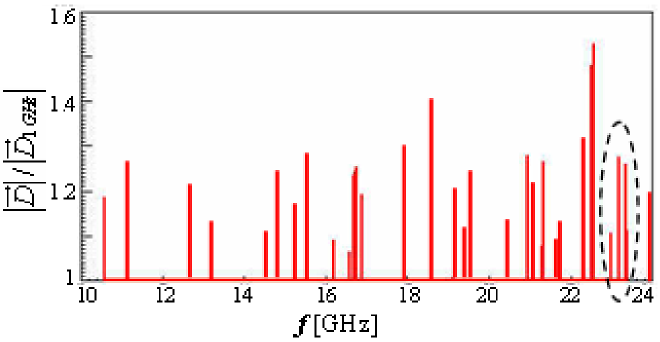


Fig. 5. Resonances chart for sample ***g)***: $(1-y)K_{0.5}Na_{0.5}NbO_3$–$ySrTiO_3$, with $y = 0.25$.

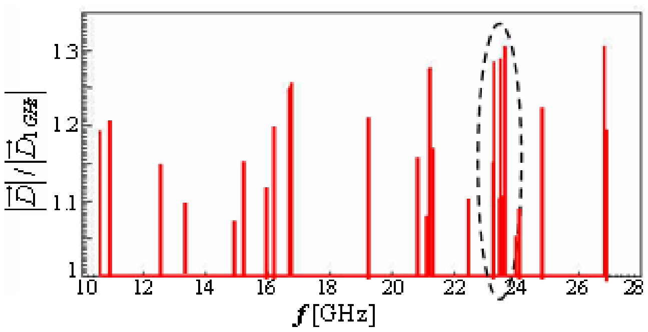


Fig. 6 Resonances chart for sample ***i)***: $(1-y)K_{0.5}Na_{0.5}NbO_3$–$ySrTiO_3$, with $y = 0.15$.

IV. CONCLUSIONS

Electrical resonances for a class of piezoelectric ceramics of perovskite-type were calculated in the frequency domain of 0.3 – 30 GHz. Structural interpretations and conclusions about geometrical and physical resonances determined for the material samples are available.

- Ionic radii, ions relative spacing are the main parameters which impose the first resonance value. Other geometrical parameters (orientation angles, pseudo-cubic decrement, non-repetitive orientation coefficient in the solid solution, etc.) have a lower influence on the first resonance but are responsible of the position on frequency scale of a few superior order characteristic resonances.
- Average grain size, the vacuum content in the ceramic material and the boundary conditions on the grain walls are responsible of a bunch of high amplitude resonances which appear in the vicinity of the first resonance in the microwave range.

- Ions nature influence is the most important (between 20 and 80 %). The concentration of phases given by the phase diagrams is the second important element for resonances magnitude determination.
- Polarization mechanisms are preponderant atomic and electronic, but local electric charge accumulations due to the pseudo-cubic lattice in the case of the solid solution determine a bunch of resonances with higher frequencies in the considered domain.
- Concentration factors, symmetry degree, etc. are cumulative factors which influence the resonance magnitude or resonance shifting on frequency scale for every structure.

The simulation method is a flexible one, the main advantage consisting in the structural re-construction of the material samples at microscopic level. The internal parameters variation is facile in comparison with the experimental cases, allowing the parametrical analysis on a complete variation domain of the considered parameter.

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