University „Alexandru Ioan Cuza”of Iaşi
Faculty of Physics

Summary of PhD thesis

„Study of dielectric and conduction properties in oxide ceramic systems with applications in electronics”

Scientific advisor
Professor Phd. Liliana Mitoșeriu
Phd Student
Zîna-Violeta Chiochiu (married Mocanu)

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CONTENTS

I. Introduction

After long time ceramics were used only for domestic purposes, today they are studied due to their multifunctional properties (dielectric, ferro/piezoelectric, magnetic or superconducting) useful in applications.

Main polarization mechanisms in dielectrics are [1,2,3]: electronic polarization, ionic polarization, orientation polarization, space charge polarization, ferroelectric polarization.

There are two types of dielectrics: linear and nonlinear (dependence P (E) is nonlinear).

The main characteristics of ferroelectric materials are:

- Spontaneous polarization that depends on the temperature and can be switched by applying an external field, a hysteretic phenomenon
- The transition from the polar to the non-polar state for ferroelectrics have a phase transition that can be first order or second order. The paraelectric phase has a higher simetry than ferroelectric state.

The relaxor behaviour (G.A. Smolensky [4]) is characterized by:

- A diffuse phase transition
- The complex permittivitz has a frequencz dispersion
- In paraelectric state, the temperature dependence of permittivity follow the modified Curie-Weiss law
- The P(E) dependence in polar state is nonlinear and non-hystertic.

An important property of ferroelectrics is the field dependent permittivity (nonlinear dependence of $\varepsilon(E)$) [5]). This property can be explain using Landau-Ginzburg-Devonshire (LGD) theory and its approach: Johnson aproximation and multipolar model.

II. Barium titanate ceramic

Barium titanate is the most used ferroelectric material in the electronics industry. It has a perovskite structure and is found in four crystalline phases: cubic (paraelectric), tetragonal, orthorhombic and rhombohedral (ferroelectric).

The most stable states in terms of minimum free energy are the states for which the ions are replaced by ions with similar atomic radius. The solid solutions of $BaTiO_3$, izovalente substitutions on position A (eg Sr, Ca) lead to electrical compensation and a shift of Curie temperature [9]. The Izovalente substitutions in position B, Zr or Sn [10], determines the transition to the relaxor state. Heterovalente substitutions at positions A and B, leading to changes in both the Curie temperature and the electrical behaviour.

III. Magnetic materials. Ferrite

Ferrites are metal oxides with chemical formula AB_2O_4 and ferrimagnetic character. Their elementary cell are spinel and containing 96 occupied interstices: 32 anions O, 16 cations A, 8 cations B and 40 vacations [11].

Mg ferrite has a normal spinel cubic structure with soft magnetic properties and an intrinsic semiconductor character. Ni ferrite has an inverse spinel structure, in which half of the Fe^{3+} ions occupy the tetrahedral positions A and the rest occupy octahedral positions B of the structure of spinel. To improve the electrical and magnetic properties was attempted substitution of Ni ions with Mg ions [12].

The study of ferrites is important due to applications in radio frequency, microwave, biomedicine, as gas sensors [13] and the high-frequency.

IV. Experimental methods

In chapter three the preparation methods of ceramics and experimental techniques used for ceramics characterisation were detailed. Also, the impedance spectroscopy method (IS) was presented and the methods was validated for ceramics systems [14,15,16].

V. Contributions to the study of ferroelectric-relaxor transition in $BaCe_xTi_{1-x}O_3$

V.1 Preparation of $BaTiO_3$-$BaCeO_3$ system by solid state reaction

The $BaCe_xTi_{1-x}O_3$ (BCT) ceramics with x = 0.06, 0.10 and 0.20 were prepared by solid state reaction. The ceramics were sintered at 1500 ° C / 4 hours (Series I) and 1540 ° C / 6 hours (Series II). relative densities greater than 95% for all compositions.

V.2 Microstructural and phase characterization

XRD patterns obtained for the two series of ceramic indicates the formation of pure perovskite phase, without secondary phases, for all investigated ceramics.

SEM images taken on the surface shows that the addition of Ce favors grain growth and better densification [17].

V.3 Comparative study of dielectric properties depending on the frequency and temperature. Discussions

It was accomplished a detailed study of low field dielectric properties of both ceramics series. A reduction of transition temperature and Curie-Weiss temperature was obtained for ceramics sintered at higher temperature. The variation is more evident for the ceramics with high Ce content.

Also, a ferroelectric-relaxor crossover with ceriu addition was observed. The η parameter incresed to 1.95 for x = 0.20. The relaxor behaviour is more pronunced for ceramics sintered at higher temperature.

V.4 Dielectric nonlinearity ε(E) - a comparative study. Discussions

The high field properties investigation shows a strong nonliner character of delectric constant for x = 0.10 and 0.20 without a tendency to saturation, even for very large fields (~ 30 kV / cm). The electric field dependence has a nonhysterectic behaviour due to their relaxor character.

V.5 Raman study

The Raman spectra recorded at room temperature (in collaboration with Univ. Leoben, Dr. Marco Deluca) indicates that the composition x = 0.06 has ferroelectric order and in this case the Ce was integrated in both positions B and A. For x = 0.10 and x = 0.20 the Ce substitutions were only in positions B, leading to relaxor behavior [17].

V.6 Piezoelectric characterization

Piezoelectric characteristics of ceramics for series I were studied in collaboration with CSIC-ICMM Madrid, Spain [18] and showed that at low concentrations of cerium piezoelectric activity is comparable to $BaTiO_3$.

VI. Contributions to the study of dielectric properties of $M_xBa_{1-x}TiO_3$ (M=La, Ce)

VI.1 Contributions to the study of $La_xBa_{1-x}TiO_3$ system

VI.1.2 Preparation and microstructural characterization

The La-BT solid solutions with different La content were prepared by solid state reaction in collaboration with Politehnica University of Bucarest, prof. Adelina Ianculescu. Ceramics with low dopant content (x = 0.001, 0.0025, 0.005) have $Ba_{1-x}La_xTiO_3$ formula, and those with high proportion of La and Ti vacancies: $Ba_{1-x}La_xTi_{1-x/4}O_3$ were ($0.005 \leq x \leq 0.05$).

The X-ray diffraction and SEM investigations indicate the formarea of pure perovskite phase and absence of any secondary phases rich in Ba, Ti or La.

VI.1.3 Dielectric properties. Discussion

By increasing the La addition, the Curie temperature decreases from ~ 125 ° C for x = 0.001 to ~ 60 ° C for x = 0.025, togheter with a tendency to relaxor. For ceramics with Ti vacancies were obtained high permittivity values for all investigated temperatures, suggesting that the donor dopant is more easily accommodate in solid solution with Ti vacancies than the stoichiometric.

Dielectric losses are below 12% and decrease for samples with higher content of La and Ti vacancies. Ferroelectric-paraelectric transition is sharp for ceramics with small La content and extends in a wide temperature range by increasing La content, indicate a diffuse transition. The evolution towards relaxor state appears with increasing x is highlighted by increasing empirical parameter η (from 0.98 for x = 0.0025 to 1.52 for x = 0.025) [19].

VI.1.4 Nonlinear dielectric and ferroelectric properties. Discussions

The dependence ε (E) at room temperature indicating non-linearity for all compositions, with a tendency toward saturation only for very large fields (~ 20 kV / cm), particularly for samples of titanium vacancies. For a given value of the applied field E = 15 kV / cm, most tunability was obtained for the composition of x = 0.005 with V(Ti) (n = 1.51).

The nonlinearity is small in low ow field (<5 x 10^5 kV / cm) for ceramics with low La contents and increases with La addition. This behavior is given by the formation of 90° domains that are easier oriented in weak fields and lead to a strong variation in permittivity [20].

The nonlinear contributions are: at small fields, extrinsic contribution is significant and can be correlated with the degree of orientation of the polar nanoregions, while at moderate and high fields non-linear nehaviour is mainly related to field-induced ferroelectric polarization.

VI.2 Contributions to the study of dielectric properties of $Ba_{1-x}Ce_xTiO_3$ ceramics

The Ce-BT solid solution with composition x = 0.05, stoichiometric (samples A and B) and with titanium vacancies (C and D) sintered at 1200^0C and 1300^0C were prepared by the Pechini method at University Politehnica Bucharest, the group of prof . Dr. Adelina Ianculescu and PhD. Student Catalina Vasilescu.

VI.2.1 Investigation of low field dielectric properties. Discussions

All the investigated ceramics have good dielectric properties, and losses below 5% in the whole temperature range.

Ferroelectric-paraelectric phase transition is clearly evidenced by a maximum in the permittivity for ceramics sintered at 1300^0C and a diffuse maximum for ceramics sintered at the temperature 1200^0C. Curie temperature is in the range of $25\text{-}35^0$C, with the exception of sample B, which has $T_C \sim 102^0$C.

VI.2.2 Nonlinear dielectric properties. Discussions

There is a strong nonlinearity for all samples, with a tendency to saturation for large fields (~ 30 kV / cm). Tunability values are in the range 1.64 (B) and 4.04 (D), at E = 20 kV / cm.

At small fields, all the samples have a hysteretic character of the dependence ε (E), which is more pronounced in the case of the sample B (the most ferroelectric at room temperature). Increasing the sintering temperature causes an increase in both permittivity and the nonlinearity of the stoichiometric composition as a result of a better densifications and closer Tc room temperature.

Using the multipolar model for samples (A and C) shows that: the low fields (≤ 10 kV / cm), extrinsic contribution is important and can be correlated with nanoregiunilor polar reorientation, at moderate and high fields, the nonlinearity can be described again the law Johnson and ferroelectric polarization under applied field.

VII. Contributions to the study of electrical, conduction and magnetic properties of $Mg_xNi_{1-x}Fe_2O_4$ ferrites

VII.1 Preparation and microstructural and phase characterization

Ceramic ferrites with compositions x = 0, 0.17, 0.34, 0.50, 0.66, and 1 obtained by sol-gel self combustion after sintering at 1200 ^{0}C/8h have relative densities of 90-92%. Structural analysis by X-ray diffraction showed the spinel phase purity of all compositions. SEM images show that the average grain size of ceramics increases systematically when the Mg concentration increases and becomes more homogeneous microstructure.

VII.2 Electrical and conduction properties investigated by the Impedance Spectroscopy method

Investigated ceramics was modelated in impedance diagram by two parallel RC circuits connected in series corresponding to the grain boundary respective grains. Measurements show an increase in resistance grains and the grain boundaries, indicating a tendency to shift from predominant semiconductor character to better dielectric properties with increase the addition of Mg.

Activation energy of the samples was determined using the maximum imaginary part of the complex impedance and the temperatura dependency of imaginary part of the dielectric modulus. Activation energies obtained are typical for complex oxides. Frequency dependence of the electrical conductivity indicates partial compensation n-p type[21].

VII.3 Testing ferrites as humidity sensor

For small values of the frequency investigated sample have a small variation in resistivity with increasing humidity (due to the porosity of less than 10%) [22].

VII.4 Magnetic properties of ferrites

All samples show a typical ferrimagnetic character with a strong nonlinearity, and low values for coercive and saturation field. Substitution of Mg ions decreases Curie temperature.

General conclusions

The main objectives of this study were to investigate and describe properties of oxide ceramics with perovskite or spinel structure, in order to understand the properties related to microstructure, composition and preparation conditions, the identification of new or enhanced properties useful in electronics applications .

Oxide ceramic systems investigated are interesting due to their multiple properties that can be controlled and used in applications.

The properties control can be achieved by: the method of preparation, thermal treatment and the type and concentration of dopant. Also, the extern parameter of the material such as the temperature, the frequency of the applied field, electric or magnetic field, the level of humidity can influenced functional characteristics of materials.

Original contributions obtained in this study are:

I. Application and validation of the impedance spectroscopy method IS

- Realization and investigation by impedance spectroscopy of a circuit with known elements using the model proposed by JE Randels and validation of measurement method. Complex impedance analysis of experimental data made using equivalent circuit models confirmed the values of the circuit elements with a maximum error of 0.05%. Impedance spectroscopy method was applied to the study of polycrystalline $BaTiO_3$ ceramic doped with 0.5% La at the different temperatures and (Ni, Zn) ferrites prepared under different conditions.

II. Study of ferroelectric-relaxor tcrossover in $BaCe_xTi_{1-x}O_3$ (effect of Ce substitution on the Ti position in $BaTiO_3$)

- Increasing the particle size of the powder and ceramic grains with increased sintering temperature and with increased Ce content.
- High permittivity ($\varepsilon > 1000$ at room temperature) and low losses ($tg\delta \leq 5\%$) for all the investigated compositions
- Decrease of Curie temperature decrease and a transition from ferroelectric to relaxor with increasing amount of Ce;
- Decreases of maximum permittivity and dielectric losses for all compositions with increasing sintering temperature;
- At low content of Ce substituent tends to occupy both positions (of Ba and Ti) in the perovskite network, which was confirmed by Raman investigations. Raman study confirmed also the transition to the relaxor state with increasing the addition of Ce;
- All samples show a nonlinear and nonhisteretic dependence of the dielectric constant with applied electric field, making them useful for tunable microwave applications;
- All ceramics investigated have piezoelectric characteristics comparable to $BaTiO_3$, but the addition of Ce progressively reducing piezoelectric and coupling constants values.

III. Study of dielectric properties of $Ba_{1-x}M_xTiO_3$, M = La, Ce (effect of doping on Ba position in BaTiO3)

The study of $Ba_{1-x}La_xTiO_3$ system demonstrated that:

- All compositions obtained using conventional ceramic method have insulator character;
- Ceramic systems presented a small PTCR effect to the Curie temperature;
- Increasing the La content Curie temperature decreases to values close to room temperature and the phase transition becomes a diffuse character;
- All ceramics shows a strong nonlinear and nehysteretic character in electric field. Using the multipolar model were explained the different contributions to the dielectric permittivity;
- The dielectric constant of ~ 2000, small losses (tgδ <6%) and tunability ~1,5 makes from La-BT ceramics a promising candidate for tunable applications.

The most interesting results of the investigation $Ba_{1-x}Ce_xTiO_3$ system are:

- An insulating behaviour for all samples (stoichiometric and with Ti vacancies) prepared by the Pechini method;
- The Ce content (5%) shifts the Curie temperature near the room temperature (35^0C), except for sample B, which presents an anomaly;
- The dielectric anomalies were interpreted considering substitutions in both positions A and B of perovskite cell and the presence of secondary phases;
- All samples are strongly nonlinear at room temperature in electric field and hysteretic at low fields, due to the ferroelectric character;
- By increasing temperature to the nonlinear dependence ε(E) appear extrinsic contributions

IV. Study of the electrical, conduction and magnetic properties of *$Mg_xNi_{1-x}Fe_2O_4$* ferrites

The most interesting results of the investigation of the system are:

- Ferrites obtained by the sol-gel self combustion have a spinel structure with a lattice parameter increase with increasing degree of substitution;
- Microstructural analysis showed homogeneity and high density ceramics, with an increase in the size of ferrite grains from 1-2 μm (for x = 0) to 3-4μm (for x = 1).
- Complex impedance data indicate two distinct relaxation phenomena confirmed by the evolution with temperature of the imaginary part of the impedance. Activation energy calculated by several methods has typical values for complex oxides (0.33eV-0.43eV) and increase with increasing Mg concentration.
- By increasing humidity there is a change in resistivity at low frequencies (more pronounced for samples with finer grains).
- It was obtained a decrease of magnetization at room temperature and a reduction of Curie temperature with increasing Mg content. This behavior can be attributed to the ocupancy of metal cations of both A and B positions in the spinel structure.

The important properties identified and possible relevant applications

- High permittivity, low losses and low dispersion in frequency can be applied in multilayer ceramic capacitors;
- The PTCR effect of the La-BT system can be used for temperature sensors and thermal controller;

- Change in resistivity with humidity levels can be applied for the humidity sensor;
- The electric field dependence of all the systems can be used to achieve tunable circuits (varicap) in radiofrequency and microwave;
- Piezoelectric properties are interesting for the development of pressure sensors, for biomedical applications or energy recovery.

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The original results have been materialized by the publication of three articles ISI (one has two citations), the reference to the evaluation of other 3 and a number of 34 papers presented at national and international conferences (including four oral presentations at international conferences) . Detailed list is contained in the Annexes attached to the end of the thesis.

Published articles

1. **Z.V. Mocanu**, G. Apachiţei, L. Padurariu, L.P. Curecheriu, L.Mitoşeriu, “Impedance spectroscopy method for investigation of polycrystalline inhomogeneous ceramics”, European Physical Journal of Applied Physics 56, 10102 (2011)
Impact Factor: 0.77, *Influence score: 0,265*

2. A. C. Ianculescu, **Z.V.Mocanu**, L. P. Curecheriu, L. Mitoseriu, L. Padurariu, R. Truşcă, “Dielectric and tunability properties of La-doped BaTiO3 ceramics ”, Journal of Alloys and Compounds 509,10040– 10049 (2011)(with two citations)
Impact Factor: 2.289, *influence score: 0,507*

3. L. P. Curecheriu, M. Deluca, **Z. V. Mocanu**, M. V. Pop, V. Nica, N. Horchidan, M. T. Buscaglia, V. Buscaglia, M. Van Bael Bael, A. Hardy, Liliana Mitoseriu
„Investigation of the ferroelectric-relaxor crossover in Ce doped BaTiO3 ceramics by

impedance spectroscopy and Raman study”, Phase Transitions, 86, 7, 703(2013)
Impact Factor: 1.006, *influence score: 0,396*

Articles sent to

1.C. Vasilescu, A.C. Ianculescu, D. Berger, C. Matei, M. Olariu, L.P. Curecheriu, A. Gajović , **Z.V. Mocanu**, „Preparation of Ce doped-BaTiO3 ceramics by modified-Pechini route and its functional properties”, J. Eur. Ceram. Soc. (sent to).

2.**Z.V. Mocanu**, M. Airimioaei, C.E. Ciomaga, L. Curecheriu, F. Tudorache, S. Tascu, A.R. Iordan, N.M. Palamaru and L. Mitoseriu „Investigation of the functional properties of MgxNi1-xFe2O4 ceramics”, Journal of Materials Science (JMSC) (send to and accepted) 2013.

3. L.P. Curecheriu, **Z.V. Mocanu**, M. Olariu, C. Vasilescu, A.C. Ianculescu, L. Mitoseriu ”Non-linear properties of 5% Ce-doped $BaTiO_3$: the role of Ti stoichiometry”, Current Applied Physics (sent to).