

Study of some perovskite solid solutions with ferroelectric-relaxor crossover

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I. Ferroelectricity

I.1 Ferroelectric materials. General properties of ferroelectrics

Ferroelectrics are dielectrics for which the relationship between polarization and electric field is nonlinear and with hysteresis effects, i.e. the polarization values on increase/decrease the applied field may be different.

Ferroelectric materials are characterized by the following specific properties:

- 1) It has a spontaneous polarization domain structure under a certain temperature. Spontaneous polarization can be reversed by the action of an external field between values $\pm P_S$, a phenomenon accompanied by the polarization hysteresis and remanence.
- 2) During the transition from the polar state (ferroelectric) to the non-polar one, (paraelectric) ferroelectrics shows a transition phase that can be of order I or II. The paraelectric phase always has a higher symmetry than the ferroelectric one.
- 3) Temperature dependence of electrical, mechanical, optical, caloric quantities and structural parameters present abnormalities on the phase transition.

I.2 Ferroelectric relaxors

Generally, ferroelectric materials can be classified according to the behavior of the dielectric polarization and the phase transitions [1] into three categories: normal ferroelectrics, which have a well-defined ferroelectric transition at a well defined temperature (sharp transition); ferroelectrics with diffuse phase transition, which have a large flat ferroelectric transition and the ferroelectric relaxors.

Ferroelectric relaxors are solid crystalline materials, characterized by the following properties:

1. Diffuse phase transition (DPT);
2. In the paraelectric phase ($T > T_m$) dielectric constant varies with temperature according to a different law from the Curie-Weiss law;
3. Complex dielectric permittivity shows a frequency dispersion;
4. The values of the induced dipole moment depend on the applied field E, they are high and they strongly respond to external actions: electrical, piezoelectrical (?) and pyroelectrical(?);
5. Macroscopic spontaneous polarization is zero in the absence of the field. However, there is locally a polarization associated with the nanopolar regions. Only the electric field can produce a nonzero macroscopic polarization, even if local polarization is nonzero in nanoscale regions.
6. Crystalline anisotropy is very small. This structure is called a pseudocubic structure.
7. In relaxors there exists a polar order with a short-range, which extends on nanometric distances in nanopolar areas.

I.3 Polarisation mechanisms, hysteresis, polarisation curves of the first order „First order Reversal Curves (FORC)

The polarization reversibility, i.e. the ability to switch between $\pm P$, is the main feature of ferroelectric systems. This process is accompanied by hysteresis, which is a typical irreversible phenomenon. The shape of ferroelectric hysteresis curve (saturation, rectangularity) and the main characteristics: residual polarization (P_r), polarization saturation (P_S) and coercive field (E_C) are characteristic of each material,

being dependent on composition, material impurities, defects, local inhomogeneities, etc..

A new method inspired by the Preisach model calculation is FORC distribution ("First-order Reversal Curves"). In last years this method has been frequently used to describe the reversible characteristics of the ferroelectrics' polarization. The FORC diagram is an outline of the FORC distribution wich is defined as the mixed second order derivative of polarization with respect to E and E_r [2,3].

1.4 Field dependence of dielectric constants („dc-tunability”). Theoretical models

An important property of ferroelectrics is dielectric permittivity dependence by the externally applied electric field (nonlinear behavior of $\epsilon(E)$). This property is used in applications in microwave and is conventionally called "tunability". It is described by a quantity that is defined as the ratio of the permittivity of the material in the absence of the field and the dielectric permittivity at a nonzero field. Applying an external electric field induces changes in the structure at all scales, which is reflected in the macroscopic dielectric properties of the material. Furthermore, nonlinear dependence of permittivity with the field in ferroelectrics is strongly influenced by temperature and frequency.

II. BaTiO₃ and its solid solutions

II.1 General properties of BaTiO₃

Barium titanate ($BaTiO_3$) belongs to the perovskite class. To summarize, $BaTiO_3$ undergoes the following structural transitions on cooling from high temperatures: 120°C temperature: *cubic* ($Pm3m$) \rightarrow *tetragonal* ($P4mm$), 5°C temperature: *tetragonal* ($P4mm$) \rightarrow *orthorhombic* ($Bmm2$), -90°C temperature: *orthorhombic* ($Bmm2$) \rightarrow *rhombohedral* ($R3m$).

It is important to note that the properties of $BaTiO_3$ are dependent on the system form: powder, films, polycrystalline ceramics, crystal, etc.. In addition, the permittivity values are dependent on the preparation route (wet methods or solid state reactions), which determines the degree of purity, density, size of grains, structural defects, impurity density, etc. [4]. Grain has a significant effect on all dielectric and ferroelectric properties of $BaTiO_3$, as was shown in ref. [5].

II.2 Solid solutions with homovalent substitutions $BaM_xTi_{1-x}O_3$: state-of-the-art

In this section we give a brief overview of some solid solutions with isovalent substitution in the B position of the perovskite cell (position of Ti^{+4}), focusing on the studied system in the present work.

$Ba(Ti_{1-x}Zr_x)O_3$ is a mainly compound of multilayer ceramic capacitors MLCC, being considered an attractive alternative in the manufacturing of high capacity capacitors instead of the $Ba_xSr_{1-x}TiO_3$ system. At low concentrations of isovalent substitute Zr^{+4} the sequence of structural transitions remains the same as the one for $BaTiO_3$, the transitions remain sharp (ferroelectric), increasing the amount of Zr ($x > 0.20$), the system undergoes a transition to relaxor.

Another system which has a diffuse phase transition is the solid solution composed by the ferroelectric $BaTiO_3$ and the non-ferroelectric $BaSnO_3$ on high Sn additions [6]. The substitution of Sn^{+4} on the B position of the perovskite cell produces changes to the Curie temperature and maximum dielectric values similar to those characteristic to other solid solutions based on $BaTiO_3$. The $Ba(Sn_xTi_{1-x})O_3$

(briefly noted BSnT) has drawn the attention due to the different abnormalities of the dielectric properties and the presented strong dielectric nonlinearity [7].

X. Wei [8] and other authors [9,10] have studied different aspects of a number of functional properties of this system. However, most of those articles do not present structural data dependent on the composition. A phase diagram for this system was proposed by X. Wei and X. Yao [8], designed by the abnormalities detected in the temperature dependencies of the dielectric constants. In that diagram, the compositions between (0.10, 0.15) at temperatures around room temperature, there seems to be a superposition of several structural phases (rhombohedral, tetragonal and cubic). In contrast, S. Markovic [11] found a continuous reduction of the tetragonality degree with increasing Sn concentration, reaching a value of 1 (specific cubic structure) for Sn concentration $x = 0.12$. Although there are various scientific articles that have as topic the BSnT ceramic system, the phase transitions sequence induced by the addition of Sn is not yet fully understood and there is still missing a detailed analysis of the functional properties in connection with the composition, the microstructure and the phase symmetry.

II.3 The study of solid solutions of $Ba(Sn,Ti)O_3$: justification for the choice of the system

The present study focuses on the investigation of ferroelectric ceramic systems with the composition BSnT, the identifying superpositions of phases, the relaxor state description and how these characteristics are reflected in the dielectric properties under weak field and intense field (dielectric nonlinearity), and the detection by combined experiments of multiple polar contributions to macroscopic properties. In literature there is no agreement regarding the types of symmetries and superpositions of crystalline phases for Sn concentrations ranging between (0.05-0.15). Therefore, it appears necessary to further investigate this area of composition and understand how to control at the micro level the system characteristics and therefore macroscopic properties by adjusting preparation conditions.

III. The research methodology and experiment details

In the third chapter there are described the preparation methods for ceramics and the main experimental techniques used in the investigation of micro- and macroscopic properties of the systems studied. They were prepared using the solid state reaction method, four sets of samples with the composition BSnT: $x = 0, 0.05, 0.10, 0.15$ and 0.20 , the aim being to investigate the influence of the composition and the sintering treatment on the functional properties of the system. Also there are presented various devices and measuring systems used throughout the present study.

IV. THE STUDY OF THE SOLID SOLUTIONS OF $BaTiO_3$ - $BaSnO_3$

IV.1 The preparation by solid state reaction of ceramic series samples

$BaSn_xTi_{1-x}O_3$

The preparation of studied ceramics materials BSnT with different concentrations ($x = 0, 0.05, 0.1, 0.15, 0.2$) was achieved by solid state reaction in collaboration with Prof. Adelina Ianculescu's group from the Polytechnic University of Bucharest, in a research grant [15].

Following the preparation steps [15] there were obtained 4 series (A-D) of BSnT

samples with the compositions mentioned above and the diameter of ~ 10mm and the thickness of ~ 1.5mm.

IV.2 Microstructural and phase characterization (XRD, SEM for all series)

1) Phase characterization by X-ray diffraction of powders and ceramic samples: verification of the forming, the perovskite phase purity and the degree of crystallization of different types of heat treatment [15]. Diffractometry noted the formation of the pure perovskite phase for all ceramic samples of BSnT without notice other secondary phases (the detection limit of XRD analysis).

2) The microstructural characterization performed by SEM analysis on the surface.

Changing the composition, temperature and time of sintering, leads to the obtaining of different microstructures, which will be reflected in different macroscopic properties.

IV.3 Analysis of ceramic samples series A (solid solutions $BaSn_xTi_{1-x}O_3$ sintered at 1300°C/4 hours)

We performed a detailed study of ferroelectric and dielectric properties for the series of samples A. The dielectric data obtained from impedance spectroscopy showed a reduction of ferroelectric - paraelectric transition temperature with increasing Sn concentration, resulting for the composition $x = 0.20$ negative values of Curie temperature [15]. Interesting dielectric characteristics were found for the composition $x = 0.05$ and were explained by the coexistence of different structural phases that generate multiple components in response to the action of the electric field polarization. While some authors [9,10] reported only relaxor state for concentrations higher than 0.25, in the present study, the concentrations $x \geq 0.15$ of series sintered at 1300°C temperature, relaxor state is already prevalent. This shows that compositional limits delimiting the relaxor character to the ferroelectric ones is strongly dependent on the preparation method and the sintering temperatures. Relaxor character presence was highlighted by several different methods (analysis based on the modified Curie-Weiss law Raman analysis, "tunability" and the FORC method). Hysteresis cycles P(E) and the FORC analysis [16,17] showed a clear reduction of the irreversible part of the polarization (with coercivity nonzero), in favor of the reversible contribution on the ferroelectric polarization with increasing Sn concentration. An important conclusion of this study is the demonstration that the relaxor and ferroelectric characteristics coexists in solid solutions of BaTiO₃ with Sn, the relaxor state being initiated even at lower Sn concentrations than those reported in the literature.

To support the results of the previous analysis there was also performed detailed thermo-Raman analysis on a wide range of temperatures. It was confirmed the existence of structural phase overlaps in wide range of temperatures and the presence of stable nanopolar regions to temperatures well above the Curie temperature, favored gradual increase in the concentration of Sn. Another complementary method of study was to investigate the nonlinear dielectric properties at room temperature and at different temperatures above the Curie temperature. Permittivity dependencies in large fields were analyzed using the Johnson model and the multipolar mechanisms model in order to highlight the mechanisms that contribute to the permittivity of the system under different field values. It monitored the evolution of tunability values with ferroelectric-relaxor transition [16,17]. Tunability high values obtained for ceramics in paraelectric phase were explained by other nonhysteretic extrinsic mechanisms

polarization, which can be described by Langevin-type contributions.

In conclusion, the most important results of the complex investigations performed on the BSnT system described in this paragraph:

- 1) allowed completing the phase diagram proposed by other authors in the literature, with complete data for compositions $x \leq 0.20$,
- 2) gave a full description and a deeper understanding of polarization mechanisms that operate at different scales (nano, meso, micro and macroscale).

IV.4 Analysis of ceramic samples series A (solid solutions of $BaSn_xTi_{1-x}O_3$ sintered at $1400^\circ\text{C}/4$ hours) (D series)

In this chapter there are presented in detail the results for D ceramic samples series, in order to identify the differences from series A, to identify structural changes, microstructural and functional properties induced by increasing sintering temperature. From the SEM microstructural analysis, this series stands for a significant increase in grain size compared to the ceramic samples of series A. For the ceramic samples of the D series there is still a bimodal structure but with large granules sized between 40-60 μm . The densification of the samples was improved with increasing sintering temperature, resulting values of relative density above 90%.

From the structural data at room temperature there were carried out calculations of structural parameters, the results are presented in [18]. As the proportion of Sn increases, also the elementary cell parameters grow, due to larger ionic radius of Sn^{+4} than that Ti^{+4} , which it substituted. Correspondingly, the elementary cell volume increases, while tetragonality level decreases, so that for $x = 0.20$ the structure is 100% cubic. For the sample with $x = 0.15$, the concentration we have now is a purely tetragonal, unlike the sample with the same composition, sintered at $1300^\circ\text{C}/4$ hours, for which at room temperature (20°C) there was identified a mixture of phases (C/T). This finding suggests that an increase in grain size induced by higher temperature heat treatment favors a polar tetragonal structure and the morfo-trope composition causes a shift to higher Sn concentrations.

The Raman vibrational spectroscopic study of this series is the first one for the samples sintered at a temperature of 1400°C , complements the few existing data in the literature for this system. As in the case of the A series, the Raman analysis for this series confirms the transition from the ferroelectric to the paraelectric stage and the possibility of obtaining relaxed behavior with increasing Sn concentration. The obtained difference compared to the series sintered at a lower temperature is given by the fact that the substitution of Sn starts to affect the long-distance order, but without degrading it dramatically as it happens in the A series.

The dielectric study of the D series has shown that there are differences dielectric relaxation processes compared to the A series, due to microstructural differences caused by high temperature sintering [18,19]. In addition, the analysis of the complex dielectric frequency module allowed the obtaining of activation energies corresponding to these processes for each composition separately.

V. The comparative study of solid solutions of $BaTiO_3$ - $BaSnO_3$

Chapter V is dedicated to the comparative analysis performed on all series of samples sintered under different conditions, analysis which allowed highlighting the influence of the microstructure on the relaxor ferroelectric properties and the material constants.

VI. General conclusions

- 1) In the present study it was demonstrated that both the relaxor character and the ferroelectric one can coexist in BaTiO₃ solid solutions of Sn, the relaxor state being initiated even at low concentrations of Sn.
- 2) All compositions have significant variation of permittivity with the applied field at the room temperature, $\epsilon(E)$ dependences tending to reduce its hysteresis with the addition of Sn. One exception is the composition $x = 0.15$ that shows superposition of phases at the room temperature.
- 3) The mechanisms which contribute to the permittivity of the system in the field were analyzed using the Johnson model and model of the mechanisms. The evolution of the tunability values was monitored at the same time with the ferroelectric-relaxor transition. The high values of permittivity obtained for ceramics being in paraelectric phase can be explained by other extrinsic mechanisms of polarization that can be described by Langevin contributions.
- 4) The detailed thermo-Raman analysis on a wide range of temperatures revealed overlapping phases over wide temperature ranges and the presence of nanopolar regions favored by gradual increase of the Sn concentration.
- 5) The hysteresis cycles P(E) and FORC analysis have clearly showed the reduction of the irreversible part in favor of the reversible contribution to the ferroelectric polarization with the increasing of the Sn concentration.
- 6) The preparation and the sintering conditions have a major influence on the macroscopic properties, enabling the possibility of their control by adjusting the preparation parameters.

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The original results were materialized by publishing of 7 ISI articles (with 3 citations) and a number of 36 presentations on national and international conferences (in which 5 oral presentations at international conferences), a third prize at National Physics Conference and Educational Technologies modern "Science (2010) and participation as a member of various grants. Detailed list of scientific activity is contained in the Annexes attached to the end of the sentence.

Total scor of influence 3.129

Published or accepted articles in ISI journals

1. N. Horchidan, A. C. Ianculescu, L. P. Curecheriu, F. Tudorache, V. Musteata, S. Stoleriu, N. Dragan , D. Crisan, S. Tascu and L. Mitoseriu, "Preparation and characterization of barium titanate stannate solid solutions", Journal of Alloys and Compounds 509, 4731-4737 (2011)

Impact factor: 2.289

Influence factor: 0.507

2. L. P. Curecheriu, A.C. Ianculescu, N. Horchidan, S. Stoleriu, F. Tudorache, S. Tascu, L. Mitoseriu "Temperature dependence of tunability of Ba(Sn(x)Ti(1-x))O(3) ceramics", Journal of Applied Physics 109, 084103 (2011)

Impact factor: 2.168

Influence factor: 0.834

3. M. Deluca, L. Stoleriu, L.P. Curecheriu, N. Horchidan, A.C. Ianculescu, C. Galassi, L. Mitoseriu, „High-field dielectric properties and Raman spectroscopic investigation of the ferroelectric-to-relaxor crossover in BaSn_xTi_{1-x}O₃ ceramics”, Journal of Applied Physics 111, 084102 (2012)

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Impact factor: 0.304

Factor de influență: 0.052

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Impact factor: 1.006

Influence factor: 0.396

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Influence factor: 0.396

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N. Horchidan, A. Ianculescu, L. Curecheriu, M. Deluca, V. Musteață, L. Mitoșeriu, trimis spre publicare la Journal of Applied Physics).