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Characteristics of phase transitions in $Ba_{0.995}Na_{0.005}Ti_{0.995}Nb_{0.005}O_3$ ceramic

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ABSTRACT

Purpose: The purpose of this work was to prepare ceramic material $BaTiO_3$ (BT) as well as solid solution of $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$ (for x = 0.005) (BNTN05) type and correlate their structural (polycrystalline) properties with phase transitions within the temperature range from 153 K to 473 K.

Design/methodology/approach: The dielectric spectroscopy method has been applied to measure dielectric and electric parameters within the frequency from 20 Hz to 1 MHz.

Findings: The measured dependences of: complex dielectric permittivity and its phase angle (between measuring voltage and current response) points out on complex phase transition character for both investigated materials. Experimental outcomes for BT are consistent with those already published. Achieved results in the case of BNTN05 are published here for the first time. They were correlated with those of BT as unmodified one. Phase transitions parameters of both materials were described by means of generalised Curie-Weiss rule including step of phase transition diffusivity. Small amount (x = 0.005) of $NaNbO_3$ (NN) admixture makes sharp, classical transition of first order kind occurring in the case of BT, to be a diffusive one and shifted by about 20 K towards lower temperatures.

Research limitations/implications: Further investigations should be carried out in a broaden frequency range (up to 1.8 GHz) in order to establish the influence of network dynamics on ferroelectric-paraelectric phase transition as well as others low–temperature phase transitions. In order to complete structural data of new BNTN05 material additional X-ray and calorimetric measurements will be performed.

Originality/value: The same method and components were used for preparation of BT and new BNTN05 material. Thermally induced phase transitions, mutually related in both materials were measured and described.

Keywords: Ceramics; Phase transitions; Ferroelectrics; Dielectric spectroscopy

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MATERIALS

1. Introduction

Among materials of perovskite type structure, the ABO_3 oxides with their ferroelectric properties plays important role because of technical and technological reasons. Long lasting investigations of the origin and nature of ferroelectricity in case of these materials did not get clear answer. Despite of their structural similarity, these oxides posses a wide range of different ferroelectric behaviours. It involves substantial differences in temperatures of ferroelectric - paraelectric (FE - PE) phase transitions as well as widespread values of spontaneous polarisation [1]. The chemical composition /structure determines the equilibrium between short and long-range interactions [2]. Dynamic local and wider-range of coupling between electromagnetic

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and phonon interactions which is temperature dependent, creates conditions for ferroelectric phase stability (polar one) and also for paraelectric phase (non polar, or with smaller polarity) inside of cubic physical geometry [3]. Physical properties of composed oxides of $(A_1A_2)(B_1B_2)0_3$ type, depends on the step of spatial order of given ions arrangement [4]. Thus, the way of cations (with different valency) spatial arrangement in a given subnet determines final properties as diffuse character of phase transition or relaxor ones [5]. Such properties can be described as a result of translational symmetry breaking and polar regions creation [6, 7].

The two ferroelectrics, selected for dielectric investigations are of perovskite type [8]. The advantage of this choice is that their structures do not contain lead. Thus they are easy to prepare and environment friendly. It is known from the literature that solid solution $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$, demonstrates three types of ferroelectric behaviours [9-11]. For compositions with $0 \le x \le 0.075$, the classical ferroelectric one dominates. Within the range $0.075 \le x \le 0.55$ this solid solution creates relaxor behaviour. And within the range $0.55 \le x \le 1$ of admixture the phase transition character is classified as ferroelectric or antiferroelectric ones. At room temperature, BT structure is determined as tetragonal characteristic for space group P4*mm* [12]. The temperature lowering one can observe two structural phase transitions: at 268 K to orthorhombic and at 183 K to rhombohedral one. Above 393 K the paraelectric phase occurs classified as cubic and space group P*m*3*m*. The NN, at room temperature is antiferroelectric with space group P*mmm* [13]. Additionally, for this material two more structural phase transitions occur: at 400 K to tetragonal and at 600 K to cubic phase. The measurement of complex dielectric permittivity as a function of temperature is a common way to record and characterise sharp phase transitions of first order kind, of second order as well as diffuse and relaxor type of transitions [14, 15]. The purpose of this work was to measure and analyse such characteristics for ceramic samples: BT and BNTN05.

2. Experimental

Ceramic samples of BT and BNTN05 composition were prepared by means of conventional method and BaC_2O_4, $Na_2C_2O_4$, TiO_2, Nb_2O_5 reagents of 99.99% purity. Reagents mixed with ethanol were grained in ball mill for 2 h. Next mixtures were dried, pressed and synthesis was thermally initiated. Temperature and time of synthesis duration was 1370 K and 15 h. Then, samples were grained again, pressed and sintered for 2 h at 1570 K for BT and 1430 K for BNTN05. The real density of final ceramics equals 5.16 g/cm^3 (BT) and 5.39 g/cm^3 (BNTN05). Samples in the shape of disc-pellets sized 8.80 mm (diameter) and 1.60 mm thick (BT) and 1.67 mm thick (BNTN05) were painted with silver electrodes.

All measurements were performed by means of QUATRO KRIO 4.0 temperature system together with precise LCR Agilent 4284A meter, BDS 1100 cryostat and WINData 5.62 Novocontrol software. The heating and cooling agent used was nitrogen. The data were taken at stabilized temperature points within the range from 473 K to 153 K with 5 K step. Measurements of dielectric permittivity, admittance and electric modulus were performed using standard dielectric spectroscopy in the frequency range 20 Hz-1 MHz. Amplitude of measuring voltage was 1V.

3. Results and discussion

The real part of complex dielectric permittivity (ε') dependence on temperature and frequency for BT and BNTN05 samples are presented in the Fig.1. For BT sample temperature points for all maximum permittivity values are the same for all frequencies applied. At 403 K, cubic structure, one can see the classical (sharp) phase transition of FE - PE type with simultaneous structure change to tetragonal one. With further lowering the temperature, at 288 K one can identify another maximum of ε'(T).

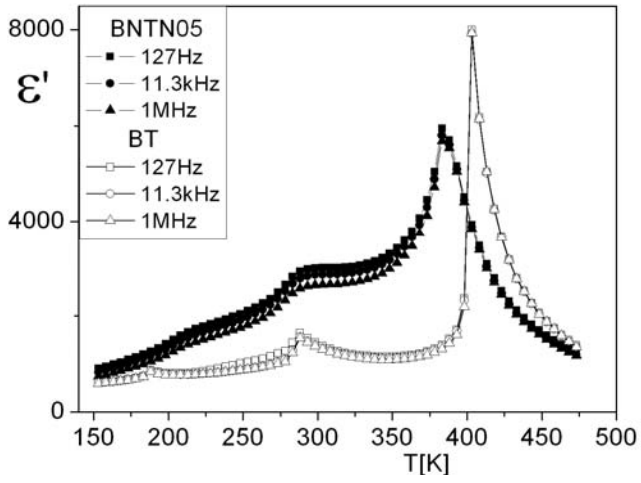

Fig. 1. The dependence of real part of complex dielectric permittivity (ε') for BT and BNTN05 samples on temperature

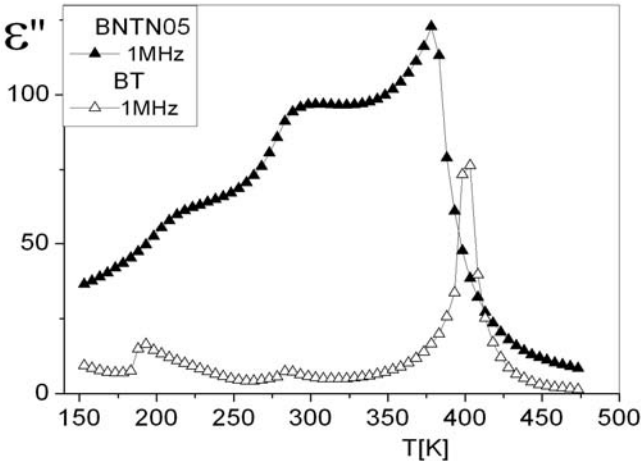

Fig. 2. The dependence of imaginary part of complex dielectric permittivity (ε'') for BT and BNTN05 samples on temperature

The value of this maximum equals 1/4 of the former one. The values of phase transitions temperatures found in this work are shifted about 5 K - 20 K as compared to those mentioned in the literature. Nevertheless, one can assume that transition observed at 288 K is connected with structural transition to orthorhombic one. Lowering further the temperature leads to very weak maximum at 188 K, which is connected with the structural transition of even lower symmetry of rhombohedral type. The dispersion observed within the whole temperature range applied for BT sample and in the vicinity of permittivity maximums is low. For BNTN05 sample at 383 K the FE – PE phase transition occurs. This transition is diffused and dispersive one. The further temperature lowering implies such strong dispersion that no sharp maximums are visible. One can postulate then, that diffusive character of these transitions in BNTN05 sample is a result of different valency of substituted ions in both cationic subnets.

The imaginary part of complex dielectric permittivity ε''(T) for both investigated samples as a function of temperature and frequency is presented in the Fig. 2. The ε''(T) values represent a measure of electric field energy loss taking place during one field cycle. Data for only 1 MHz are presented. For BT sample, energy losses are connected with phase transitions: they are correlated with maximums ε'(T) in the Fig. 1. Energy losses for BNTN05 sample are substantially higher as compared to BT.

The measurements results presented in Fig.1 and Fig.2 are mutually connected by phase angle Φ(T) as a function of temperature and frequency (Fig. 3). It is measured as a phase shift between measuring voltage and current response for a given frequency (I-V method). Generally, within the whole temperature range values of Φ for both materials remains in the range characteristic for dielectrics (Fig. 3).

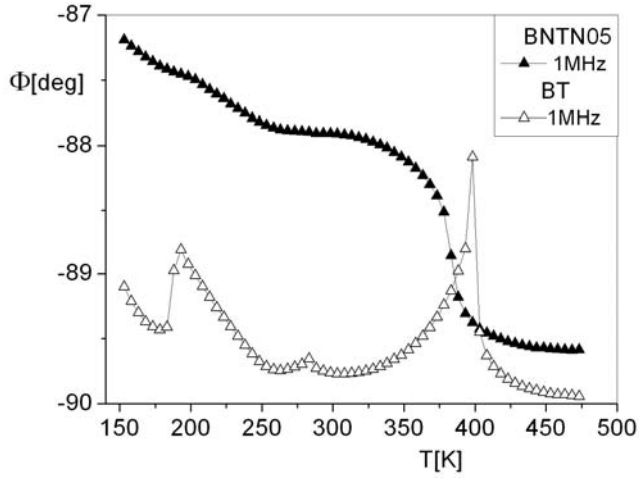

Fig. 3. The dependence of phase angle Φ(T) for BT and BNTN05 samples on temperature

The Φ(T) function for BT is also phase transition sensitive. It is not the case of BNTN05 sample at low temperature transitions. The strongest Φ change for this sample appears at ~383 K transition and the whole temperature dependence is monotonic. This turned out to be the main difference between both materials.

In order to analyze other differences characters, one have to compare reciprocals of ε'(T) functions to electric modulus M'(T) calculated and shown for both materials in Fig.4 and Fig.5. Scales of 1/ε'(T) and M'(T) were chosen identical in both Figures. Looking from the side of higher temperatures, down to about 390 K one can see dielectric permittivity and electric modulus linear and identity of both reciprocals for both materials. Within this range of temperatures there is no dependence on frequency.

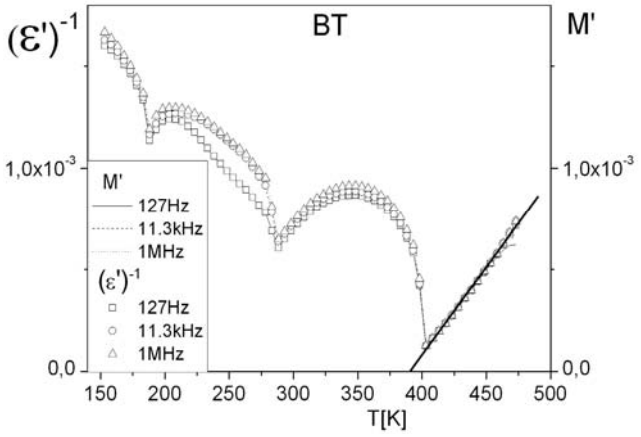

Fig. 4. The inverse of real part of complex dielectric permittivity (1/ε') and real part of electric modulus (M') as a function of temperature at chosen frequencies for BT sample

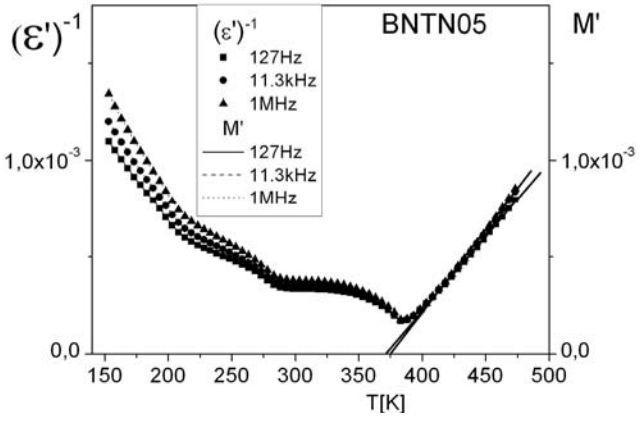

Fig. 5. The inverse of real part of complex dielectric permittivity (1/ε') and real part of electric modulus (M') as a function of temperature at chosen frequencies for BNTN05 sample

Linear form originates from reciprocal of hyperbolic permittivity and modulus dependencies on temperature. For both materials temperatures of phase transitions are more or less visible as a change of graphs forms (discontinuity of first or second kind) but there are also very interesting differences reflecting individual character of each material composition and structure. Down from about 390 K for BT (Fig.4) three temperature ranges are visible. For first and third values of 1/ε'(T) and M'(T) they are almost identical and frequency independent. The nature of this effect will be a subject of separate work. Within the second range of temperature (~280 K - ~160 K) one can see the difference: compared quantities are not identical and / or frequency dependent. The possible reason can be a relaxation and

local range dispersion in this phase. For BNTN05 (Fig.5), along the temperature decrease the dispersion for both values undergoes weak but permanent increase with higher frequencies supremacy. The origin of this temperature activated almost monotonic dispersion increase will be investigated separately.

For paraelectric phase ranges of temperature: BT (T > 403 K) and BNTN05 (T > 383 K), 1/ε'(T) functions obeys the rule of Curie-Weiss in the form:

$$\varepsilon = \frac{C}{T - T_0} \tag{1}$$

where: C - Curie-Weiss constant, T_0 - Curie-Weiss temperature. Values determined by means of linear regression for BT equals: $C = 1.15 \cdot 10^5$ K and $T_0 = 390$ K. Calculation for the BNTN05 sample showed that both constants are frequency dependent. For 1 MHz they got values: $C = 1.17 \cdot 10^5$ K and $T_0 = 375$ K. For low frequency (127Hz) they equal: $C = 1.30 \cdot 10^5$ K and $T_0 = 372$ K.

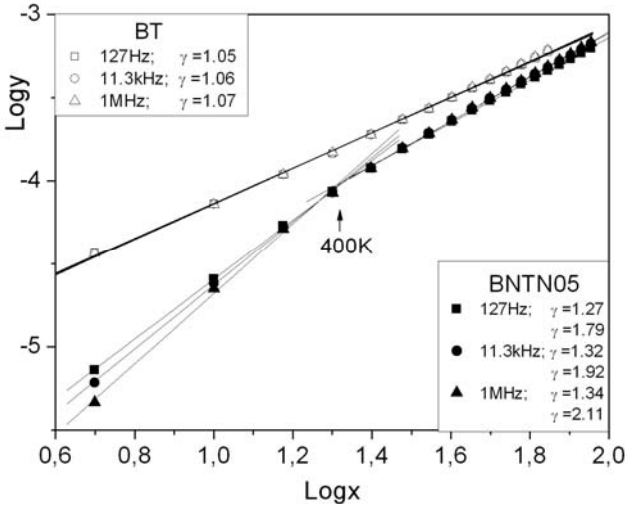

Fig. 6. The dependence of log(y) on log(x) for BT and BNTN05 samples (for abbreviations see text).

The geometric interpretation of equation (1) cannot be a source of other phase transition features extraction. Thus, the following relation was introduced [3] in order to describe dielectric permittivity dependence on temperature:

$$\varepsilon^{-1} = \varepsilon_m^{-1} + A(T - T_m)^{\gamma} \tag{2}$$

where: ε_m - maximum value of dielectric permittivity, T_m - the temperature value at ε_m, A, γ - constants for chosen frequency.

In the case of classical phase transitions γ = 1 and for diffusive transitions it approaches about 2. Linearization of equation (2) was performed by applying following abbreviations:

$$y = \varepsilon^{-1} - \varepsilon_m^{-1} \tag{3}$$

$$x = T - T_m \tag{4}$$

The result is seen in the Fig.6. The equation (2) is presented here in the form: logy=f(log(x)) for chosen frequencies. The value of γ about 1 in the case of BT sample points out on classical type of phase transition. In the case of BNTN05 one can separate two ranges of linear character in the Fig.6. The point T = 400 K separates both ranges. Fitted slopes of straight lines in the Fig.6 of γ values: 1.79, 1.92, 2.11 are connected with the temperature range from 383 K to 400 K. These values are close to 2 pointing on diffused character of phase transition. Slopes of straight lines in temperature range 400 K to 473 K (1.27, 1.32, 1.34) are not so close to 2, thus phase transition in this temperature range is to be identified as one of less diffusivity. The rapid change of γ parameter value at ~400 K in the case of BNTN05 ceramic reflects the fact that we have to do with phase transition of FE-PE type.

4. Conclusions

The conventional method of calcination was used to prepare two materials: the first one, BT with well known properties as reference sample and the second: BNTN05 not described yet in the literature. Thermally induced phase transitions in these materials were measured by means of dielectric spectroscopy method in a frequency range 20 Hz - 1 MHz and temperature range 473 K - 153 K. Measurement outcomes for both materials were analyzed and mutually correlated. Analysis of data from the literature and our own outcomes have shown that method of preparation as well as method of measurements influences reported values of phase transitions temperatures. The measurement of dielectric properties of BT ceramic convinced the occurrence of three phase transitions as well as classical character of first order type transition of FE - PE one at 403 K. The observed character of phase transitions for BNTN05 ceramic and frequency dependent deviations from the Curie-Weiss rule pointed out on diffused type of these transitions. The step of this diffusivity falls down above 400 K at which structural transitions takes place in BT (tetragonal to cubic one) and in NN where it is from orthorhombic to tetragonal one.

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