Characterization of $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$ ceramic by dielectric spectroscopy

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ABSTRACT

Purpose: The purpose of this paper was characterization of electric properties of polycrystalline nanograin solid solution of $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$, x = 0.65 (BNTN65) within the temperature range 153 K-573 K.

Design/methodology/approach: The dielectric spectroscopy method (DSM) has been applied to measure dielectric and electric parameters within frequency range from 20 Hz to 1 MHz and within the temperature range of diffused ferroelectric – paraelectric transition and above within paraelectric state.

Findings: Analysis of temperature and frequency dependences of real (ε') and imaginary (ε") parts of dielectric permittivity and electric modulus provided the new details about specific features of paraelectric properties of ceramic BNTN65 sample. They involve weak relaxational diffused processes as well as dielectric losses. Specific two steps increase of ε' values turned out to be frequency dependent and of thermal activated character.

Research limitations/implications: Above specified new details of polarizability of paraelectric phase for ceramic sample should be treated as a base for new modelling approach and quantitative description of polar clusters dependence on temperature and frequency.

Originality/value: For the first time, details of polarizability of paraelectric phase, which are temperature and frequency dependent in such specific manner were described.

Keywords: Ceramics; Electrical properties; Dielectric spectroscopy method

MATERIALS

1. Introduction

A method of dielectric spectroscopy, known also as impedance spectroscopy method (IS) or admittance spectroscopy (AS) as well, rely on current response collection in frequency domain. It is defined as current – voltage (I–V) technique applied within frequency range from mHz up to 1 MHz [1, 2]. According to macroscopic polarization theory is in common to describe dielectrics by means of notions of electric equivalent RC circuits (ERC) [3, 4]. Equivalency of both: material under test (MUT) and its ERC are only formal analogues from mathematical point of view. Electric response of MUT can be modelled by more than one equivalent circuit [5–7]. Thus additional information of MUT have to be known to select appropriate equivalent ERC. Formally, physical properties of dielectrics are being described by complex functions: dielectric permittivity (ε*), electric modulus (M*;

M* = 1/ε*) as well as electric impedance (Z*) and admittance (Y*; Y* = 1/Z*). To full MUT characterization, one have to vary temperature (T) and frequency (f) in order to establish ε*, M*, Z*, Y* dependences on these variables. In case of ferroelectrics, all above specified complex functions can reflect selectively the transition of MUT from ferroelectric to non–ferroelectric phase. Additionally, the temperature dependence of electric conductivity of MUT can be also taken into consideration.

In this work the MUT was polycrystalline solid solution of $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$ with x = 0.65 [8, 9]. BNTN65 was prepared by means of classical system of two nonrelaxors mixture of $BaTiO_3 - NaNbO_3$ [10, 11]. It is known from literature [12–14], that in the case of $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$, one can expect different ferroelectric behavior dependently on x value: within the range of x: $0 \leq x \leq 0.075$ – classical ferroelectric behaviour, for $0.075 \leq x \leq 0.55$ – relaxor type of behavior. For $0.55 \leq x \leq 1$ –

range of x both types: classical ferroelectric or antiferroelectric properties can be observed.

The purpose of this work was to establish in what extent, the application of two components: $BaTiO_3$ and $NaNbO_3$ in the form of nanopowders influence the dielectric and electric properties of find ceramic material BNTN65.

2. Experimental

Ceramic sample BNTN65 was prepared by means of conventional method [15] but $BaTiO_3$ and $NaNbO_3$ reagents were applied in the form of nanopowders. The sintering temperature equal to 1573 K. The sample in cylinder form with 7 mm diameter and 1 mm thick was covered by silver conducting point.

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 gas was nitrogen.

The data were taken at stabilized temperature points within the range from 573 K to 153 K with 5 K step. Measurements of permittivity, impedance, admittance, and electric modulus values of the BNTN65 sample were performed by using dielectric spectroscopy method in the frequency range between 20 Hz and 1 MHz. Amplitude of measuring voltage was 1 V.

3. Results and discussion

Dielectric and electric properties of ceramic BNTN65 sample were measured and represented in the form of temperature (T) and frequency (f) dependences of dielectric permittivity ($\varepsilon*$) and electric modulus ($M*$). Above specified complex functions are demonstrated by means of their real and imaginary parts.

The real part of dielectric permittivity (ε') and imaginary one (ε'') as functions of T are shown in the Fig. 1. Both parts (ε', ε'') are almost frequency independent for temperature region of ~200 K (ferroelectric phase) (Fig. 1). Temperature increase up from ~200 K for ε'' induces strong frequency dependence. The same takes place in the case of ε' but up above ~280 K. According to literature [8], above 200 K and for x > 0.55 one should expect classical phase transition of paraelectric – ferroelectric type.

Generally, T increase induces ε' and ε'' rising up but with slightly visible thermally activated process manifesting themselves as transient peaks presence with their maxima positions approximately reversely proportional to the frequency (Fig. 1). One can notice, that transient maxima of dielectric losses (ε'') occur for lower temperatures than those of ε' for all frequencies applied. These peaks are slightly overlapped on the thermally activated two steps increase of $\log\varepsilon'$ (and $\log\varepsilon''$ also).

Approach to better understanding of this behaviour, should involve the following structural aspects of ceramic BNTN65: every nano–grain contains two ionic subnetwork (cationic) and the surface. In case of ceramic, grain boundaries (surfaces) creates energetically instable states for ions of both types present in the structure. The temperature increase can activate changes of intergrain polarization giving effective polarization even higher than those in ferroelectric state. Especially for low frequencies.
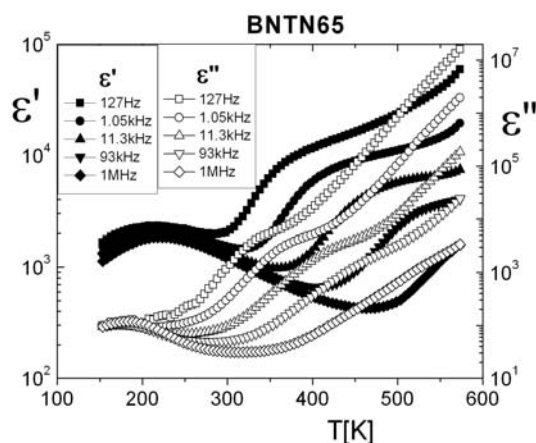

Fig. 1. Temperature dependence of real (ε') and imaginary (ε'') part of dielectric permittivity for ceramic BNTN65 sample

It can explain low frequency effective ε' values higher than those for ferroelectric phase (below ~220 K). Process of ions movements and fluctuation on the nanograins surfaces can alter the conditions of charge transport along nanograins boundaries. This can postulate mechanism of rapid increase of $\log\varepsilon''$ values with temperature increase.
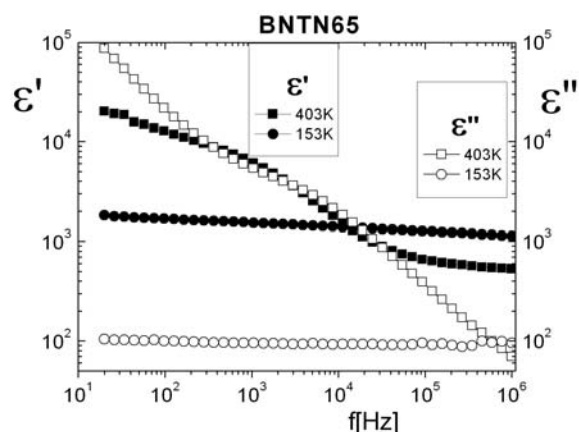

Fig. 2. Frequency dependence of real (ε') and imaginary (ε'') part of effective dielectric permittivity for ceramic BNTN65 sample

Thus, inhomogeneities of electric microstructure on inter – nanograin boundaries can be postulated as a source of new past phase transition features described in our sample. One can also mention the literature information [9] about paraelectric phase properties of BNTN65 involving "rich structure polymorphism".

The frequency dependence of real (ε') and imaginary (ε'') parts of effective dielectric permittivity for nanoceramic BNTN65 sample, are demonstrated in the Fig. 2.

At the 153 K (ferroelectric phase), electric polarization and dielectric losses are practically frequency independent and ε' is of one order of magnitude higher than ε''. In the paraelectric phase (403 K), weak relaxational process is visible (Fig. 2) but is strongly covered by losses of conductivity at low frequencies.

This process has its maximum between 10^3 Hz and 10^4 Hz. As it is seen in the Fig.2, values of ε' and ε" in paraelectric phase (403 K) are almost identical within about 2 decades of frequency at 403 K. This process may be of classical dispersion character, diffused one or can involve a wide distribution of relaxational times. It originates probably from thermally driven process of ferroelectric domains destruction initiated on the surface of nanograins. Further T increase initiates changes of effective polarization dependence on frequency. This can be followed as two step rising up of ε' value (Fig. 1). For example, at 127 Hz, starting at about 280 K up to about 357 K, the first step of ε' increase occurs. The second stage with slower increase takes place above 357 K. The temperature of transition from fast to slower rising up of ε' depends on frequency of measuring field applied. It reflects the simultaneous change of numbers of polarizable species (clusters) and is followed by stronger thermal oscilation of the whole cluster (and/or their) fragments. Cluster can undergo a dynamic quasi equilibrium fragmentation process originating from weaker dipolic interaction at high T.

Characteristic transition points can be defined as ε'$_{min}$ (T$_{mint}$): transient minimum values of ε' (for 127 Hz ε'$_{min}$ (~280 K)). They can be treated as starting T points at which the rapid increase of ε' are initiated. At these T points, the falling contribution to polarization of ferrodomains become compensated by rising the number of more polarizable smallerr fragments and clusters.
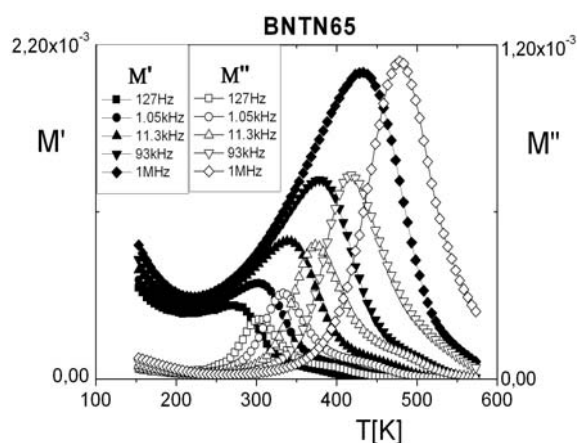

Fig. 3. Temperature dependence of real (M') and imaginary (M") part of electric modulus for BNTN65

The effective polarization changes, thermally induced and described as ε' fast increase can be also described by means of dielectric complex modulus $M^* = M' + jM''$ dependence on T (Fig. 3) and frequency (Fig. 4). Transient peaks of ε' and ε" (Fig. 1 and Fig. 2) are correlated with peaks positions and their slopes of M' and M" dependence on T (Fig. 3). Representation of dielectric properties of the sample in such form (M', M") turned out to be useful in case of strong local fields and internal polarization dependence and coupling between locally interacting dipoles and charges (ions). Modulus representation is sensitive on small changes of local polarization (capacity) as well as resistance (charge density). Peaks position on M'(T) and M"(T) graphs can be interpreted as temperature points representing transitions from one to second form of polarization and losses behaviour.
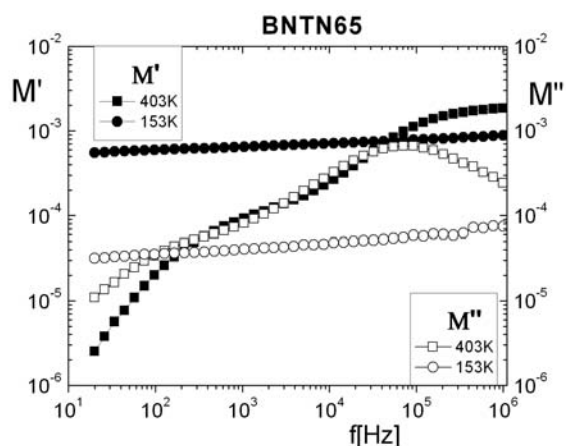

Fig. 4. Frequency dependence of real (M') and imaginary (M") part of electric modulus for BNTN65

In the Fig. 4, the frequency dependence of M' and M" for two phases (temperatures): ferroelectric (153 K) and paraelectric one (403 K) are demonstrated. Again, the ferroelectric phase of ceramic BNTN65 sample are represented by small M' and M" values which are practically frequency independent. For paraelectric phase, two weak processes are visible: one at about 100 Hz and the second at ~7·10^4 Hz. One can postulate that they originate from two kind of ions present at the interface between nanograins.

4. Conclusions

Dielectric spectroscopy method was applied within the frequency range 20 Hz-1 MHz, and within the temperature range 153 K-573 K, to nanoceramic sample BNTN type. The new details of dielectric behavior were observed during ferroelectric – paraelectric transition and new specific features of paraelectric properties were monitored. It involves frequency and T dependence of ε', ε", M', M" of post ferroelectric – paraelectric transition. The enhanced conductivity losses, covering a weak relaxational process is visible on ε"(T) dependence in paraelectric phase. The two stages of polarizability increase and dielectric losses in paraelectric phase consist of specific frequency dependence manifesting itself also in dielectric complex modulus components. New features of paraelectric polarizability are postulated as originating from interface of nanograins states of electrons and two kind of ions present in sample structure.

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